Growth of Ge, Ag and Multilayered Si/Ge Nanostructures by Ion Beam Sputter Glancing Angle Deposition

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DISSERTATION

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This thesis deals with the growth of ion beam sputter glancing angle deposited Ge, Ag and multilayered Si/Ge nanostructures. Under oblique angle deposition conditions, due purely geometrical shadowing effects, the growth of columnar nanostructures can be achieved. Moreover, with the aid of appropriate substrate rotation nanostructures of different shapes can be sculpted. The aim of the present work is to understand the basic morphological evolution of the nanostructures under different growth conditions (e.g.: influence of substrate temperature, deposition geometry, pre-patterned substrates etc).

The properties of dense films deposited with normal particle incidence (where the deposition angle is measured with respect to the substrate normal) differ from those of the glancing angle deposited films due to differences in porosity, growth mechanism, surface-to-volume ratio etc.

Among several variables that influence the growth of a film, the substrate temperature plays a key role that can lead to enhanced surface diffusion effects. Hence at the beginning, influence deposition geometry on the growth of Ag films at elevated substrate temperature is presented in detail. On native oxide covered Si(100) substrates ion beam sputter deposition of epitaxial Ag films at elevated substrate temperature under normal angle incidence is described. On the other hand, under glancing angle conditions the growth of atypical ‘whisker-like’ and ‘mountain-like’ nanostructures is discussed in the later subsection. Particularly, in this case the influence particle flux collimation is examined thoroughly with the use of the proposed growth model.

In the later part, the influence of various deposition conditions on the glancing angle deposited Ge nanostructures on planar and pre-patterned substrates is presented. Initially, substrate temperature induced morphological alterations on Ge nanocolumns are carefully studies. Besides, the shadowing effects on rotationally asymmetric honeycomb-like templates and symmetric planar-hcp templates are comprehensively explained on the basis of seed dimensions, showing lengths and template geometries. Furthermore, post-deposition annealing of Ge nanostructures grown planar and pre-patterned Si substrate is also presented.

Finally, the growth of multilayered Si/Ge nanostructures realized by alternate sputtering of Si and Ge targets on planar substrates is described. Moreover, the feasibility of Ag capping layer on the top of such multilayered structures on planar and pre-patterned substrates is verified. Such multi-component nanostructures could offer promising future prospects in for e.g: multilayered Si/Ge thermoelectric devices.
Dedicated to my parents…
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Chapter 1

Introduction

The object and device component miniaturization down to sub-micron and nano-scale regime in order to fulfill the rapidly growing technological requirements is one of the major challenges addressed during last few decades. Indeed, precisely controlled deposition and structuring techniques including physical vapor deposition (PVD) and chemical vapor deposition (CVD) have gained a massive importance in the quest to realize low-dimensional structures. A physical vapor deposition technique, ‘Glancing Angle Deposition’ (GLAD) developed in mid-1990s by Robbie et al. [1-3], has promised a great deal of relevance in the fabrication strategies for regular nanostructure arrangements.

The capability of GLAD to form manifold nanostructures by “sculpting” makes it an unique PVD process. The substrate rotation during the growth provides an additional degree of freedom to deposit complex nanostructures of various shapes (such as, e.g.: spirals, vertical columns, n-fold-spirals, chevrons etc). As a result GLAD films are often termed as ‘Sculptured Thin Films’ (STFs). Nanostructures of all commonly used materials in PVD processes can be deposited with this technique due to a purely geometrical phenomenon of self-shadowing process. GLAD on planar surfaces results in randomly arranged isolated nanostructures of non-specific diameters [4]. Malac and co-workers [5] pioneered the utilization of artificially patterned substrates to grow periodic nanostructure arrays. Later on, several pre-patterning approaches have been developed and adapted to realize nanostructures of precisely controlled dimensions. These sculptured thin films offer multiple applications, namely in photonic crystals [6], polarization filters [7], anti-reflection coatings [8], bio-sensing [9, 10], pressure sensing [11], and humidity sensing [12].

Most of the GLAD research done so far concentrates on single element material systems. However, only few studies [13-18] focused on the fabrication of hetero-structures by combining different material elements. In fact, multi-component GLAD nanostructures with high porosity (thus increased surface-to-volume ratio) and manifold shapes could find a wide range of applications, for instance wear resistant surface coatings, anti-reflection coatings etc. Indeed, this encourages the study of the growth behavior of glancing angle deposited multi-component nanostructures.
1.1 Scope and outline of the thesis

This work concentrates on the growth of Ge, Ag and multilayered Si/Ge nanostructures by ion beam sputter deposition (IBSD) under glancing angle conditions. The aim is to understand the basic morphological evolution of the nanostructures under different growth conditions (e.g.: influence of substrate temperature, deposition geometry, pre-patterned substrates etc). Further subsections in this chapter outline the motivational background of the work presented here and the organization of this thesis. A brief introduction on the fundamentals of the GLAD technique is presented in Chapter 2, followed by a detailed description about the experimental setup and characterization techniques in Chapter 3.

Subsection 1.1.1 elaborates the motivation behind the investigation of growth characteristics of dense Ag and under dense GLAD Ag films deposited on Si substrates at elevated deposition temperatures by ion beam sputter deposition. The later subsection 1.1.2 focuses on the requirements to study the growth properties of Ge and multilayered Si/Ge GLAD nanostructures for the potential application in a thermoelectric power generation device.

1.1.1 Ag nanostructures on Si substrate

Metal films on silicon substrates have been the focus of extensive study since past decades, as they offer unique applications in electronic, optical and magnetic devices [19-22] such as Schottky barrier contact [23], optical filters [24], multilayered giant magnetoresistance materials [25] etc. Particularly, Ag film on Si substrate presents an exemplary system that offers a metal/semiconductor interface required for the ideal metal contact and Schottky barrier applications. Likewise, a Ag layer can also be used as a promising conductive capping layer on the top of GLAD nanostructures. Such capping layers necessarily need to be defect free to ensure the protection of GLAD nanostructures beneath. Different capping layers on GLAD films have been studied by a few groups [26-30]. But before investigating the capping layer properties of Ag films, it is required to examine the growth of Ag films with the ion beam sputter deposition method. The properties of dense films deposited with normal particle incidence ($\beta = 0^\circ$, where $\beta$ is the deposition angle as measured with respect to the substrate normal) differ from those of the GLAD films ($\beta = 86^\circ$) due to differences in porosity, growth mechanism, surface-to-volume ratio etc. Among several variables that influence the growth of a film, the substrate temperature $T_s$
plays a key role that can lead to enhanced surface diffusion effects. The specific interest to investigate the ion beam sputter deposition of dense Ag films grown with normal particle incidence ($\beta = 0^\circ$) and Ag nanostructures grown under GLAD conditions ($\beta = 86^\circ$) is presented as follows:

- **Ag dense thin film deposition:**

Growth of Ag films on oxide free Si substrates in an ultra-high-vacuum (UHV) environment presents an example of Stranski-Krastanov (SK) growth mode, where the growth of a two-dimensional wetting layer is followed by subsequent growth of three-dimensional islands. Most of the previous investigations carried out concerning the epitaxial growth of Ag films are devoted towards molecular beam epitaxial (MBE) growth of Ag on oxide layer free Si substrates under ultra-high vacuum conditions [31-33]. Additionally, with the MBE process it was shown that the Ag films do not exhibit an epitaxial relationship with Si(100) substrates having a thin SiO$_2$ layer [34].

However, some studies concerning the growth of hetero-epitaxial layers on native oxide covered Si surfaces highlight a vital role of the native oxide [35-39]. Recently, Hur et al. reported growth of radio-frequency magnetron sputter deposited Ag films on Si substrates covered with native oxide layer that exhibited an epitaxial relationship with the underlying Si(100) substrate at elevated deposition temperature (550 °C) [37, 38]. The proposed mechanism suggests that the combination of high energetic sputtered particles impinging the substrate surface and elevated deposition temperatures can activate the desorption process of the native oxide from the Si surface and thus allowing Ag adatoms to reach the Si surface [37, 38]. With impinging metal adatoms, the oxide layer is locally desorbed allowing high energetic metal atoms to diffuse through a thin layer at high substrate temperature. In this case, the significant difference in the lattice constants of Si and Ag is compensated by a “3-to-4” matching condition [19, 40-43], where epitaxial growth of a Ag film on a Si(100) substrate is realized by cube-on-cube domain epitaxy.

Although, these Ag film growth investigations present a valuable insight and prospect to grow Ag hetero-epitaxial layers by sputter deposition technique, a precise growth mechanism is yet to be comprehended. Hence, the growth of ion beam sputter deposited dense Ag films and the
substrate temperature influence on the growth process becomes an encouraging subject to examine.

- **Ag GLAD nanostructures:**

For metals, the substrate temperature $T_S$ during growth is known to alter the morphology of GLAD films to a considerable extent [44, 45] and high temperature induced diffusion effects are observed to be responsible for whisker-like growth and loss of the GLAD-intrinsic columnar structures [46, 47]. Besides, a precise mechanism of such whisker-like growth still remains unexplained. A thorough report by Mukherjee et al. demonstrated a variation of the scaling exponent $p$ value during the growth of metal nanostructures (for a fixed deposition angle $\beta = 84^\circ$) at different temperatures [48-50]. They observed a discontinuity in the $p$ value with respect to the homologous temperature at a critical value $T_S / T_M = 0.24\pm0.02$ (where $T_M$ is the melting temperature), which was attributed to a transition from two-dimensional to three-dimensional island growth [48, 49]. Although this growth exponent variation against the homologous temperature provides a significant insight regarding the important nanocolumn characteristics, the reports do not state the effects of deposition angle variation. However, in fact under a negligible surface diffusion scenario, $p$ values fluctuate with respect to the deposition angle $\beta$ as pointed out by Buzea et al.[51]. Hence, the deposition angle variation ($\Delta\beta$) can certainly get important in the case of ion beam sputter deposition (due to relatively broad angular distribution of the particle flux), which can influence the resulting morphology in the presence of surface diffusion. Therefore, it is indeed intriguing to examine the particle flux collimation effects on the morphology of GLAD films grown at elevated temperatures.

*Chapter 4* describes deposition angle dependent morphological aspects of ion beam sputter deposition of Ag films at high substrate temperatures. In the first subsection, for dense Ag films the role of the native oxide layer prior to the growth of an epitaxial film is studied in detail. In the later subsection, the effects of particle flux collimation and substrate pre-patterning on Ag-GLAD nanostructures grown at elevated substrate temperatures are examined thoroughly.

**1.1.2 Ge GLAD nanostructure arrays**

Thin films comprising of complex nanostructures can be deposited by applying the GLAD approach. Moreover, STFs exhibit a highly porous microstructure with a remarkably high
surface-to-volume ratio that can be controlled precisely [52-54]. The exceptional possibility to directly control the structure shape by coupling with an appropriate substrate rotation scheme offers the possibility to ‘sculpt’ specific structures that influence several properties of the formed structure [4]. Substrate pre-patterning, elevated substrate temperature deposition or post-deposition thermal annealing also provide additional preferences to attain desired structural properties.

With the increasing interest in Ge in the semiconductor industry [55] and the potential application of SiGe modules in thermoelectric devices [56, 57], the structural and morphological characteristics of both Si and Ge STFs need to be investigated. In the case of GLAD-grown semiconductor films, a large number of studies are devoted to Si films [58-61]. Therefore, it is essential to study Ge GLAD nanostructures deposited on planar as well as pre-patterned substrates in order to obtain the desired multilayered Si/Ge GLAD nanostructures.

Several materials have been investigated for the feasibility to scale up three-dimensional nanostructures to avail size limited confinement effects. More often, numerous applications require crystalline nanostructures that can be obtained by depositing films at a high substrate temperature. But while obtaining crystalline GLAD-grown nanostructures at elevated deposition temperatures, the control over the inherent columnar morphology is often strongly altered due to thermally driven surface diffusion effects [44-48, 50, 61, 62]. Therefore, post-deposition annealing could possibly serve as an alternative to realize crystalline Ge nanostructures with columnar morphologies. Previously, in order to obtain crystalline GLAD-grown nanostructures, post-deposition annealing methods have been used for a variety of materials [63-67]. The melting of such low-dimensional structures is reported to be significantly different than bulk materials [68-70]. The enhanced surface diffusion at elevated annealing temperatures is known to influence the melting and recrystallization processes [67-70]. In such a condition, reduced particle sizes cause the atoms at the surface to more likely sever and to diffuse on the surface as adatoms resulting in a change in shape [67, 68, 71].

The growth of periodically arranged nanostructures can be realized by utilizing pre-patterned substrates with a pre-defined pattern geometry prepared by methods including electron-beam (E-beam) lithography [72-75] or nanosphere lithography (NSL) [76-81]. Instead, as is demonstrated in this thesis, that it is possible to grow GLAD nanostructures at room temperature, and then
alternatively retain the distinct GLAD morphologies upon post-deposition annealing processes. For that purpose, it is required to attain self-elevated hillocks on a Si substrate for a large area periodic growth of GLAD nanostructures.

For thermoelectric device applications, the required multilayered Si/Ge heterojunction nanostructures can be fabricated with alternate material supply under glancing angle deposition conditions. The morphology of such multilayered-GLAD nanostructures has been the interest of study in recent years [13-15] to provide the capability of fabricating complex nanostructures. In this thesis, first the morphology of Ge nanostructures is presented. Making a further step towards complexity, the morphology of multilayered Si/Ge nanostructures deposited with alternate material supply on planar and pre-patterned substrates is investigated.

In the beginning of Chapter 5, the basic morphology of ion beam sputter glancing angle deposition of Ge nanostructures is examined. In the following subsection the substrate temperature altered morphology of Ge nanocolumns is investigated. Later, two substrate patterning approaches to attain Si seeds on the substrate surface and the subsequent fabrication of Ge-GLAD nanorod arrays thereon will be presented. The final subsection describes thermal annealing of Ge nanocolumns grown on planar and pre-patterned substrates.

Finally Chapter 6 describes the fabrication of multilayer Si/Ge nanostructures using the GLAD approach on planar and Si patterned substrates.
Chapter 2

Columnar nanostructure growth by using the shadowing mechanism

2.1 Thin film growth under oblique angle incidence

Various PVD methods including electron beam or thermal evaporation, magnetron or ion beam sputter deposition and pulsed laser deposition have been adapted to obtain thin films with desired properties. The angle of the incoming particle flux is one of the several variables that influences the growth of the film to a large extent. The deposition angle ($\beta$) measured between the direction of the incoming particle flux and the substrate normal governs the film morphology due to the intrinsic shadowing principle [6].

The growth of a compact dense film is attained by the particle flux that reaches the substrate under normal angle incidence as illustrated in Fig. 2.1(a). On the contrary, under oblique angle deposition (OAD) conditions columnar structures evolve due to the self-shadowing mechanism. Thus, under extreme shadowing conditions (usually, $\beta \geq 80^\circ$) the formation of randomly arranged mounds subsequently serve as growth seeds for the growing columnar structures (Fig. 2.1(b)).

2.1.1 Oblique angle incidence

The growth of a thin film under negligible surface diffusion, favoring growth in Zone 1 of the structure zone model (SZM) [82, 83] and the growth process governed by the Volmer-Weber or the Stranski-Krastanov growth mode, leads to the formation of structures of distinct heights $h_S$. 

Figure 2.1: The mechanism and examples of thin film growth under different deposition angles: (a) normal angle incidence ($\beta = 0^\circ$) leading to the growth of a compact thin film (b) oblique angle incidence ($\beta \geq 80^\circ$) attributing the growth of columnar structures due to self-shadowing mechanism.
2.1 Thin film growth under oblique angle incidence

[84]. Thus, with geometric considerations subsequent self-shadowing of early stage seeds affirm the fundamental relation of shadowing length \( l \) to be:

\[
l = h_s \cdot \tan \beta
\]

(2.1)

where \( h_s \) is the seed height and \( \beta \) is the deposition angle. During thin film growth, the geometrical influence restricts the particle flux arriving at the substrate surface to the tops of the growing seeds [6, 85]. As a consequence, columnar, needle-like nanostructures are formed, with columns inclined roughly in the direction of the particle flux [26], as sketched in Fig. 2.2. The primary empirical evidence of the deposition angle influenced microstructure of sputtered metallic films illustrating an optical anisotropic behavior was reported by Kundt in 1886 [86]. Later, in 1950 by König and Helwig [87] and in 1967 by van de Waterbeemd and van Oosterhout [88] the important role of shadowing was deduced for the thin film under oblique angle deposition.

![Figure 2.2: Schematic diagram of the shadowing mechanism: (a) The particle flux arrives at an angle \( \beta \) and seeds of height \( h_s \) are formed at the substrate surface resulting in the corresponding shadowing length \( l \), (b) Columns evolve on the seeds with a tilt angle \( \delta \).](image)

**2.1.2 Influence of deposition angle**

The inclination of the columnar nanostructures under OAD conditions demonstrate that the column growth direction angle \( \delta \) differs from the deposition angle \( \beta \) (both measured with respect to the substrate normal) as depicted in Fig. 2.2 (a) and (b). The tangent rule is the foremost empirical rule proposed in 1966 by Nieuwenhuizen and Haanstra [89] based upon experimental observations that relates both, \( \delta \) and \( \beta \):

\[
tan \beta = 2 \cdot tan \delta
\]

(2.2)
But, this empirical rule was found to be consistent only for low deposition angles, while inadequate to explain the column growth direction for large deposition angles ($\beta \geq 60^\circ$) [4, 90, 91].

Later, a ballistic model that attempted to improve this deficiency was proposed by Tait et al. [90]. This model focuses on the fact that the exposed surface of the column is not symmetric about the deposition axis, but it is shadowed by the adjacent column [90]. Therefore, the column orientation tilts towards the substrate normal leading to a relation:

$$\delta = \beta - \arcsin\left(\frac{1-\cos \beta}{2}\right)$$  \hspace{1cm} (2.3)

Equation (2.3) limits the columnar growth direction to $\delta_{\text{max}} \approx 60^\circ$, while the drawback remains as it is a purely geometrical relation and disregards certain effects like surface mobility of the adatoms, conservation of parallel momentum of the adatoms and residual gas pressure\(^1\). In fact, recently it was demonstrated that the column tilt depends upon the variable deposition background pressure (varied by Ar-partial pressure during sputter deposition method) [92].

Out of several models Hara et al. [93] pointed out the distinction between the directional and the random surface diffusion, which needs to be taken into account. Inclusion of conservation of angular momentum accounts for the directional surface diffusion that leads to a deviation of the column growth tilt away from the direction of the incoming particle flux towards the substrate normal. However, the model argues that thermally activated surface diffusion induces contrary effects by tilting the column growth direction away from the substrate normal. Therefore, increasing diffusion lengths of the adatoms leads to an increase of the column tilt angle ($\delta$) under oblique angle deposition for constant deposition conditions [85]. In other words, an increase of the substrate temperature $T_S$ for a given $\beta$ would lead to an increase of $\delta$ for a constant deposition condition.

A continuum model put forward by Lichter and Chen [94] includes the influence of surface diffusion. The derived relation incorporated a variable $\eta$ which depends upon the height of the

\(^1\)This can influence the growth during the sputter deposition method.
initial surface perturbation, surface diffusion and the beam flux magnitude (volume per unit beam area per time).

The proposed relation is expressed as:

\[ \tan \delta = \frac{2 \tan(\beta)}{3 - \left(1 + \eta \tan(\beta) \sin(\beta)\right)} \]  

(2.4)

The model predicts an increase of \( \delta \) corresponding to a decrease in \( \beta \) value, however, a drawback arises as it does not take into account the shadowing effect. Due to the sensitive reliance of the columnar structure on deposition conditions and material dependent parameters precise predictions are certainly difficult. Even though different models explain acceptable trends based on experimental evidences, the qualitative predictions of \( \delta \) values are found to be insufficient. Therefore, usually the tangent rule is adapted for low \( \beta \) values, while the cosine rule is used for large \( \beta \) values for the prediction of the growth direction angle \( \delta \).

**Glancing Angle Deposition: origin of the term**

The first effort of combining OAD with azimuthal substrate rotation (for deposition angles: \( 30^\circ < \beta < 60^\circ \)) was made in 1959 by Young and Kowal [95] to realize a polarization filter for visible light on glass. Apart from this attempt, a combined use of OAD and substrate rotation to obtain porous film morphology remained unexplored until the mid-1990s. With the availability of a powerful analytical technique such as scanning electron microscopy (SEM), Robbie et al. established the “sculpting” of columnar structures by combining OAD with an appropriate substrate rotation to form structures of arbitrary shapes [1-3]. Since then, by exploiting an even larger deposition angle \( \beta \) (typically \( \beta \geq 80^\circ \)) namely “glancing angle” thin porous films comprising of complex manifold structures are sculpted by the glancing angle deposition (GLAD) technique (Fig. 2.3 (a)). An extra degree of freedom provided by the substrate rotation enables manifold structures. Thus, these GLAD films with a variety of columnar shapes are widely recognized as sculptured thin films (STFs) [3, 6, 26, 96].

In general, different substrate rotation schemes [6] allow the formation of various types of isolated, free-standing nanostructures under glancing angle deposition conditions. A drastic
increase in the shadowing length $l$ for $\beta \geq 80^\circ$ ensures columnar nanostructures with a considerably decreased film density.

![Diagram of glancing angle deposition and substrate rotation](image)

Figure 2.3: Principle of glancing angle deposition: (a) Oblique particle incidence (typically $\beta \geq 80^\circ$) is coupled with azimuthal substrate rotation. $\Phi$ represents the azimuthal angle. (b) The elementary structures that can be fabricated with substrate rotation schemes. With *continuous* rotation either vertical (fast $\omega$) or helical (slow $\omega$) structures can be grown. Alternatively, with *stepwise* substrate rotation n-fold structures (e.g.: 4-arm chevron) can be deposited.

An additional choice can be integrated by changing the deposition angle during film deposition to alter the density of STFs with film thickness [12, 97].

### 2.1.3 Substrate rotation

Generally, two different types of substrate rotation schemes are used to deposit isolated nanostructures:

- **Continuous substrate rotation**: This scheme affirms the growth of three fundamental nanostructure shapes, namely spirals, screws and vertical columns, by rotating the substrate continuously with a defined rotational velocity $\omega$ [6]. The ratio $\rho = r / \omega$ of deposition rate $r$ and substrate rotational velocity $\omega$ decides the type of shape. For a slow substrate rotational velocity (large $\rho$ values) the growing surface tops “follow” the slow rotational change resulting in a spiral-like shape. A rapid substrate rotation (small $\rho$ values) yields vertical column-like structures due to even particle flux from all directions, while intermediate substrate rotational velocity (intermediate $\rho$ values) forms screw-like structures, as schematically shown in Fig 2.3(b). For helical
structures the height \( c \), known as pitch, of the spiral attained during a complete rotation is lesser than the structure diameter.

- **Stepwise substrate rotation:** This scheme constitutes of rapid rotation about a predefined azimuthal angle \( \Phi \) succeeded by a pause to grow an “arm” of desired shape. This enables sculpting of \( n \)-fold nanostructures (where \( n \) is the number of repetitions in one full turn of the substrate) with inclined needle-like columnar arms. For example, with stepwise substrate rotation two-arm-chevron structures or \( n \)-fold spiral structures can be deposited.

GLAD is a versatile bottom-up technique with which a variety of free-standing isolated nanostructures can be fabricated with an appropriate substrate rotation. Fig. 2.3(b) shows a schematic of elementary types of nanostructures possible by *continuous* and *stepwise* substrate rotation.

At the early stages of growth, the columns are generally symmetric about the growth axis. But under continued deposition conditions, the symmetry vanishes and the columns are prone to fan out in a direction perpendicular to the particle flux direction [4]. This column broadening effect is a result of the anisotropic nature of shadowing, while broadening is continued until the columns become large enough to chain-together [98]. Therefore, during column evolution several growth trends occur, which influence the overall morphology of STFs.

**Column evolution during continuous substrate rotation**

For GLAD on planar substrates, the growth process is governed by an initial random arrangement of mounds of non-specific sizes. As subsequent growth proceeds, single columnar nanostructures evolve out of non-uniform seeds that are distributed statistically on the substrate surface during the early stages of the growth [97, 99]. This leads to the extinction of some of the structures, while predominant adjacent structures overgrow due to a temporarily existing local non-uniform particle flux. The temporal evolution of these nanostructures with increasing structure height causes ‘*competitive growth*’ [100]. Consequently, the diameters of surviving columns increase with increasing film height in order to keep the planar density constant [4]. With increasing height \( h \), structure diameter \( w \) also increases. For vertical column-like structures deposited with rapid substrate rotation the width \( w \) follows a power scaling relation:
\[ w \propto h^p \]  

where \( p \) is the growth exponent and it varies between \( 0.3 < p < 0.5 \) depending upon the strength of surface diffusion [101, 102]. Besides, a variation in the deposition angle can attribute to a variation of the \( p \) value, especially an increase above \( p = 0.5 \) was reported for \( \beta < 80^\circ \) by Buzea et al. [51]. Moreover, a variety of values are reported for different materials. Evidently, the growth exponent also depends upon deposition conditions, substrate rotation, and even the method of measurement techniques [51, 58].
2.2 Periodic nanostructure arrays on pre-patterned substrates

The control over the morphology of GLAD nanostructures can be attained by introducing artificial seed patterns onto the substrate surface prior to the deposition. The nanostructure regularity can be controlled by optimizing the seed pattern placement on the substrate surface and subsequent random nucleation can be avoided. Therefore, different seed pattern design considerations have to be taken into account within the perspective of geometrical shadowing [103, 104].

- **Depletion of inter-seed condensation**: To deplete the inter-seed condensation, the inter-seed spacing $d_S$ should satisfy the following relation:

$$d_S \leq h_S \cdot \tan(\beta)$$  \hspace{1cm} (2.6)

where $h_S$ is the seed height and $\beta$ is the deposition angle [72]. A highly directional collimated particle flux with minimum deviation ($\Delta \beta$) should prevent the inter-seed condensation for a negligible surface diffusion condition. However, with azimuthal substrate rotation, the direction of incoming particle flux is altered and for rotationally non-symmetric patterns void spaces are often exposed to the particle flux. This generally results in an undesired inter-seed growth despite adequate shadowing lengths.

- **Planar density**: In order to avert the changes in the columnar morphology, the pattern design should suffice the following condition:

$$w_S \geq R_S - h_S \cdot \tan(\beta)$$  \hspace{1cm} (2.7)

This condition arises from the planar density of seeds, which is defined as the ratio of planar seed area to the total substrate area. Thus, the seed layer planar density should be congruent with the volume density (the ratio of a unit volume containing column material) [4]. Otherwise, if the pattern period $R_S$ becomes too large and even though the seed height $h_S$ is adequate to deplete inter-seed condensation, the growing structures tend to broaden and bifurcate as an attempt to fill the inter-seed void spaces.
**Seed dimensions:** In order to prevent a multiple-column growth on an individual seed pattern, the seed width \( w_S \) needs to be smaller than the equilibrium structure diameter [104]. But generally with azimuthal substrate rotation, the direction of incoming particle flux is altered and for rotational non-symmetric patterns seed walls and void spaces are often in line-of-sight to the arriving particle flux. Additionally, if \( R_S < l \), the growth on side walls of pattern seeds is expected [105]. The ratio \( a_S \approx R_S / l \) describes the ‘exposure height’ of the corresponding seed (as sketched in Fig 2.4).

So far, various seed pattern designs have been used to optimize GLAD morphology. Among reported patterns, the **rectangular array** [5, 72, 106, 107] has been used most widely. In 2001 Toader and John [108] proposed a square spiral architecture for three-dimensional photonic band gap crystals which encouraged the GLAD-based realization of such three-dimensional periodic nanostructures [73, 109-111]. Since then, various template patterns including **triangular arrays** [107], **quasi-one dimensional line arrays** [105], **planar hexagonal-closed-packed** [44, 45, 59, 78, 79, 81, 112, 113] and **honeycomb-like arrays** [76-80] have been used for the growth of periodic nanostructures.

To obtain artificial seeds according to the specific design considerations, various substrate pre-patterning techniques have been used until today. These schemes comprise of substrate patterning with polystyrene nanospheres (PS) [59, 112, 114] or SiO\(_2\) nanospheres [14, 15, 44, 45, 113], electron beam lithography (EBL) [72-75, 115], nanosphere lithography (NSL) [76-79] and optical lithography [105-107].

With the aid of a continuum model approach, Main et al. demonstrated that for GLAD nanostructures deposited with continuous substrate rotation on pre-patterned substrates with distinct inter-seed distance \( d_S \) column saturation radius \( R_{Sat} \) follows a scaling relation [116]:

\[
R_{Sat} \propto d^g
\]

(2.8)
where $q$ is the growth exponent. However, these consistent experimental results were observed for quadratic seed templates, which are higher symmetric templates as compared to for example honeycomb-like seed arrays. Therefore, for complex seed patterns, such as honeycomb-like templates, shadowing from different neighbors needs to be considered.

Computational simulation of GLAD nanostructures

So far, Monte Carlo simulations with ballistic deposition models are often used algorithms for the study of growth dynamics of OAD and GLAD by computational simulation. Few studies also report the use of molecular dynamics models [117] or continuum models [94, 116] to simulate thin films deposition under OAD conditions. But most of the simulations are based on either two- or three-dimensional ballistic deposition [1, 72, 101, 118-123]. A three-dimensional MC simulation that included an oblique deposition angle $\beta$, substrate rotation (with a possibility to alter the azimuthal angle) and surface diffusion was introduced by Karabacak et al. [99, 101, 102]. These simulation results, when compared to the experimental observations, illustrated a good agreement with GLAD grown films. Further reports [60, 80] concentrate on the comparison of MC simulation results and experimental findings of the growth of Si nanostructures on the pre-patterned honeycomb-like substrates.
2.3 Substrate temperature influence on GLAD nanostructures

As the GLAD technique is fundamentally based upon the inherent shadowing mechanism, so far extensive research has been focused on the deposition performed at low substrate temperature ($T_S$). The substrate temperature-induced surface diffusion is believed to be counterproductive as against the self-shadowing mechanism [104]. According to the Structure Zone Model (SZM) [82, 83, 124], surface diffusion becomes prominent once $T_S / T_M \geq 0.3$, where $T_M$ is the melting temperature of the material to be deposited. However, in recent years researchers have paid considerable attention towards GLAD nanostructures deposited at elevated substrate temperatures in a zest to explore new morphological varieties.

The morphological alterations induced by the diffusion-driven mass transport during the growth of metal and semiconductor GLAD nanostructures have been studied only recently. Magnetron sputtered Ta structures at elevated temperatures (melting temperature $T_M = 3017 ^\circ C$, experiments performed for the homologous temperature $0.10 \leq T_S / T_M \leq 0.40$) deposited on the substrate patterned with silica nanospheres were reported by Zhou et al. [44, 45, 113]. The branching behavior of a single column into sub-columns and a degradation, as well as a loss of periodic arrangement of single columns were reported for the temperature range $200 ^\circ C \leq T_S \leq 700 ^\circ C$ [44, 113] and $T_S \geq 900 ^\circ C$ [45], respectively. The modifications were attributed to the increased adatom mobility with increasing substrate temperature that enhances competitive growth mechanism between adjacent columns.

Vapor phase growth of Al whiskers was reported by Suzuki et al. for oblique angle electron beam evaporation conditions [46, 47, 125]. They reported that the GLAD-inherent columnar morphology disappears and extremely long whiskers of sub-$\mu$m length grow on the substrate surface. The critical temperature of the formation of such GLAD-grown Al-whiskers was observed to be between $180 ^\circ C \leq T_S \leq 290 ^\circ C$ [46]. However, the precise mechanism of such whisker-like growth is not yet well-understood.

Choi et al. reported growth of single crystalline Ge nanowires (width ~ 50 nm) by electron beam evaporation at a substrate temperature $T_S = 330 ^\circ C$ and the thermal stability was examined by annealing these nanowires at higher temperatures [65]. The report illustrated that e-beam
evaporation grown Ge nanowires withstand annealing temperatures up to $T_A = 500 \, ^\circ\text{C}$, whereas nanowires disintegrate at $T_A = 600 \, ^\circ\text{C}$ due to the elevated temperature annealing process.

The substrate temperature influence on GLAD-grown Si nanostructures was reported by Schubert et al. [64, 126] and Patzig et al. [59-61]. For the Si nanostructures on continuously rotating substrates, a critical height of adjacent column merging was found to be dependent on the *pitch c* of the nanostructures [61], while on silica nanospheres patterned substrates a moderate broadening was reported [59].
2.4 Applications of glancing angle deposited nanostructure arrays

Complex and miniaturized nanostructures are often required to fulfill the rapidly growing technological demands of many device objects. High porosity [52] (and increased surface-to-volume ratio) and an exceptional ability to form nanostructures of manifold shapes with a suitable substrate rotation makes GLAD a versatile technique that can be used to fabricate desired nanostructures.

A promising approach to use a Si square spiral photonic crystal structure proposed by Taoder and John [108] encouraged extensive research on the realization and optimization of GLAD-grown STFs photonic crystals [73, 109, 110, 127, 128]. Moreover, helical STFs have been used to build polarization filters [7] or polarized light emitters [129]. By altering the porosity of STFs by adjusting the deposition angle [130], narrow bandpass optical filters [131], highly reflecting films [132] as well as anti-reflection coatings [8] have been fabricated in the past.

Several GLAD nanostructures have been used in sensing applications. External pressure sensing Cr nanostructure arrays were developed by Kesapragada et al [11], wherein the pressure sensing was calibrated during external loading, when the initially isolated nanostructures touched each other changing the cross-film resistivity. In another sensing application, the changes in the transmittance spectrum were identified for GLAD-grown TiO$_2$ nanostructures for humidity sensing [12]. In recent years, one of the rapidly growing fields of application is bio-sensing using GLAD nanostructures. Several reports highlight the use of noble metal STFs (like Ag and Au) with extremely sensitive surface-enhanced raman spectroscopy (SERS) for potential bio-sensing applications [9, 10, 133-136]. Additionally, biomimetization of systems such as butterfly wings and fly eyes were achieved by oblique angle deposited nanostructures [137].

Other important applications exploit the increased surface area of GLAD-grown nanostructures as against compact thin films. Karabacak et al. reported increased photoluminescence of a polymeric film on GLAD-grown W nanocolumns [138]. The increased effective surface area is responsible for the observed enhancement. In a similar approach, Si nanocolumns showed higher enzyme immobilization in comparison to the reference compact film [139].

Recently, due the commendable porosity, GLAD nanostructures have also been utilized in Li-ion batteries, photovoltaic cells, and fuel cells. Teki et al. reported use of GLAD-grown nano-
structured silicon anodes for a new generation of Li-ion batteries [140]. Here, a high charge capacity of Si and capability of accommodating volume changes encouraged growth of Si nanorod arrays for Li-ion batteries. Similarly, CuPc and TiO$_2$ thin films deposited by glancing angle deposition exhibited promising potential for organic photovoltaic architectures [141, 142]. Magnetron sputtered GLAD porous platinum films [143] and carbon films coated with platinum [144, 145] were utilized as proton exchange membrane (PEM) fuel cell electrodes by Ghasda et al. They report that the precise porosity control provided by GLAD helps to attain efficient reactant flow for high-current-density processes.

**Multilayered Si/Ge nanostructures using GLAD technique**

Thermoelectric devices are able to convert the thermal gradient directly to electricity. They have been extensively used for power generation from waste heat recovery. A dimensionless quantity figure-of-merit ($ZT$) describes the performance of such thermoelectric device. Recent reports [146-148] suggest that an appropriate selection of materials and processing steps to attain desired microstructure properties (including particle size distribution, material densification, grain boundaries etc) must be optimized in order to enhance the figure of merit. Among several thermoelectric materials investigated so far, it has been suggested that the nanostructured SiGe alloys could offer enhanced figure of merit [56, 147, 149]. Hence, it is indeed intriguing to investigate the growth characteristics of GLAD multilayered Si/Ge nanostructures that could potentially find application in the fabrication of thermoelectric devices.
3 Experimental setup, deposition method and analysis

3.1 Ion beam sputter glancing angle deposition

3.1.1 Sputter deposition process

In the present study, the ion beam sputter deposition method is used to deposit Ge, Ag, Si and multilayered Si/Ge GLAD nanostructures. Typically, when accelerated high energetic ions (generally, positive noble gas ions extracted from a glow discharge plasma) are bombarded on the surface of a target, surface erosion occurs due to energy transfer from ions to target atoms in the cascades of atomic collisions [150]. This erosion process is termed as ‘sputtering’. If the ion energy is sufficient to overcome the surface binding energy, the surface atoms can be knocked out with the ion beam bombardment. This momentum-transfer process can generate a particle flux from the target surface, which can be utilized to deposit a thin film on a substrate surface [6].

At high ion energies (300-2000 eV), the sputtering process can generate an adequate amount of vapor flux to deposit a thin film. Particularly, there are three sputtering regimes defined according to the kinetic energy of the incident ion and the mass ratio of target atom and bombarding ion [151]. The sputtering yield \( Y \) (average number of extracted atoms per incident particle) depends upon parameters including ratio of masses \( M_T / M_I \) (mass of target atom/incident ion mass), ion energy \( E \) and incidence angle of ions \( \alpha_{ST} \) with respect to the target normal [150]. Thus, yield \( Y \) can be estimated from the relation:

\[
Y(E, \alpha_{ST}) \approx \frac{4.2 \cdot F_D(E, \alpha_{ST})}{N U_0} \quad (3.1)
\]

where \( N \) and \( U_0 \) are target density and the average surface binding energy of the target element respectively, and \( F_D(E, \alpha_{ST}) \) is the depth distribution of deposited energy. The sputtering yield \( (Y) \) can vary between \( 10^{-5} < Y < 10^3 \) [151].

\footnote{In this case, electronic excitation is left out of consideration. The three sputtering regimes are as following: single knock out regime \( (E: \text{medium eV region}) \), linear cascade regime \( (E: \text{few hundred keV}) \), spike regime \( (E: \text{in the MeV range}) \).}
Ion Energy ($E$): In the present study Ar$^+$ ions were used to sputter Ag, Ge and Si targets. According to Sigmund [150], the yield $Y$ increases with $\sqrt{E}$ and reaches a maximum value for ion energies $E \leq 20$ keV. Thus, energies of the incident ions $E \leq 20$ keV are required to gain high yields and high deposition rates of the sputtered particles. The sputtering yields can be estimated using an empirical formula deduced by Matsunami et al. [152] and Yamamura et al. [153, 154]. An approximate estimation of sputtering yields of Ag, Ge and Si are determined using this empirical relation. Figure 3.1(a) depicts a plot of sputtering yields of Ag, Ge and Si with Ar$^+$ ions having energies between 100-2000 eV. Evidently, with increasing ion energy the sputtering yield increases in this energy range.

Incidence Angle ($\alpha_{ST}$): The incidence angle is an important factor that controls the sputtering yield. The yield reaches a maximum value for $\alpha_{ST}$ ranging between 60° to 80°, independent of the ion and target material combination. The ratio of sputtering yield at a given angle of incidence and the yield at normal incidence is found to be a function of the cosine of $\alpha_{ST}$:

$$Y(\alpha_{ST}) / Y(0^\circ) \approx \cos^f (\alpha_{ST})$$

(3.2)

where $f$ depends on the mass ratio of the target and bombarded ions ($M_T / M_i$). Figure 3.1(b) depicts yield dependency on the incidence angle for Ge, Ag and Si by Ar ions with energies used in the present work. For very large incidence angles, ions are reflected and the yield $Y$ decreases.
3.1 Experimental setup, deposition method and analysis

While a maximum yield is obtained at $60^\circ \leq a_{ST} \leq 80^\circ$. The highlighted area in Fig. 3.1(b) illustrates ion incidence angle $a_{ST} \approx 70\pm 5^\circ$ used in the present work.

**Angular distribution of the particle flux:** The particle flux polar angular distribution is typically described to be of ‘cosine type’ [151]. With an angle of particle emission $\zeta$ (with respect to the target normal), the sputter particle emission intensity $I(\zeta)$ with respect to the emission intensity along the normal $I_0$ is given by $I(\zeta)/I_0 = \cos (\zeta)$. But many studies suggest certain deviations from the ‘cosine’ distribution [155-157], where the angular distribution is observed to be ‘over-cosine’ distribution.

**Energy distribution of the particle flux:** The energy distribution of sputtered particle flux is a strongly dependent function of the ion energy $E$, the incidence ion angle $a_{ST}$ and the emission angle $\zeta$. The average energy of the sputtered particles is observed to be lowest for sputtered atoms in normal direction, while it decreases rapidly with an increase of $\zeta$. With increasing ion energy $E$, the energy of emitted atoms $E_0$ increases until the maximum value at $E_0 = U_0 / 2$ is reached and thereafter it decreases with $1/E^2$ [158]. If the surface-binding energy $U_0$ is to be approximated [159] as the sublimation energy of Ag, Si and Ge (which are: 2.95 eV, 4.63 eV and 3.85, respectively [160]), it represents that the majority of sputtered atoms of each Ag, Si and Ge emitted in normal direction should have energies as $E_{Ag} \approx 1.48$ eV, $E_{Si} \approx 2.31$ eV and $E_{Ge} \approx 1.93$ eV, respectively. However, more often deviations from this rough approximations are found [151] and thus the estimation is considered to be a rule of thumb. Additionally, the energy of the sputtered particles increases with an increase in $\zeta$. For instance in Ref. [161], Kr$^+$ ion ($E = 1$ keV, $a_{ST} \approx 60^\circ$) sputtered Si atoms at $\zeta \approx 5^\circ$ have a low average energy $<E_{Si}(5^\circ)> \approx 13$ eV, whereas it increases with $\zeta$ value at $<E_{Si}(45^\circ)> \approx 34$ eV. Hence, the sputtered species retains the emission energy that ranges from 0.1 to 100 eV, while the energy distribution extends over the range of 5-20 eV [161]. A small number of sputtered atoms, however, can also possess much higher ion energies.

3.1.2 Deposition chamber setup and experimental parameters

All experiments were performed in a high vacuum load-locked deposition chamber depicted in Fig. 3.2(a). The stainless steel chamber with a cylindrical geometry is constituted of 400 mm internal diameter and a 610 mm height. All ion beam sputter deposition experiments were carried out in the chamber with a base pressure better than $1.0 \times 10^{-8}$ mbar. For a quick sample change
and transfer in and out of the deposition chamber, the deposition system is equipped with a load-lock chamber. The HF ion beam source\(^3\) [162] was used to sputter the desired material (Ag, Si, or Ge) from the target. The sintered target discs (diameter 15 cm) of choice are freely rotatable around the x-axis. Subsequently, this compound target holder enables rapid swipe from one-target to other during multilayer thin film deposition. With this experimental arrangement, the distance between the target and the substrate measures approximately 12 cm, and the ion beam source to target distance is approximately 16 cm. During deposition, the Ar gas flow \(f_{Ar}\) through the ion beam source was adjusted to \(3.3 \text{ sccm} < f_{Ar} < 6.3 \text{ sccm}\). Subsequently, the working pressures measured \(6.0 \times 10^{-5} \text{ mbar} < p_{dep} < 1.0 \times 10^{-4} \text{ mbar}\). The angular beam divergence was controlled utilizing a slit aperture placed in between target and substrate.

**Ion beam source:**

A high-frequency (HF) ion beam source was used to generate the \(\text{Ar}^{+}\)-ions [162], that are required for the sputtering process. The gas inlet provides the process gas Ar, while an Ar plasma is generated within a ceramic discharge housing. The schematic sketch of the ion beam source is depicted in Fig. 3.2(b). An inductively coupled HF field in the discharge housing, that is used to ionize the inert gas, is generated by a HF supply energized (13.56 MHz) with a 5-turn coil, which surrounds the housing. The beam voltage (positive) \(U_B\) determines the energy of the Ar ions and

\(^3\)Ion beam source is in-house assembled high frequency \(\text{Ar}^{+}\) ion source.
is expressed as $E = e \cdot U_B$, where $e$ is the elementary charge. For the extraction of the ion beam out of the discharge chamber, three multiple aperture grids of diameter 40 mm are assembled within the ion source. The grids are made of graphite and have several small apertures to collimate and direct the ion beam.

The positively biased screen grid is connected to the anode and therefore, the beam voltage $U_B$ is adjusted by regulating the positive bias 850 eV < $U_B$ < 1200 eV. The accelerator potential $U_A$ is regulated by the negatively biased accelerator grid. Positive ions and electrons in the generated electric field are separated between the grids, where positively charged Ar ions are extracted out of the discharge chamber and accelerated, while the electrons are repelled by the negative potential. The deceleration grid is connected at ground potential, and therefore extracted ions bear a net ion energy of $E = e \cdot U_B$. The extracted ion beam is well directed towards the target, which is used for the sputtering process. The sputtered particle flux is then directed towards the substrate to deposit thin films on it. Under the working pressures $p_{dep}$, the mean free path of the particle ($\bar{l}$) can be calculated as following:

$$\bar{l} = \frac{k_B \cdot T}{\sqrt{\pi} \cdot d_{RG}^2 \cdot p_{dep}} \quad (3.3)$$

where $k_B$ is the Boltzmann constant, $d_{RG}$ the atomic diameter of the residual gas (or working gas) and $T$ the temperature [163]. At $p_{dep} = 1.0 \times 10^{-4}$ mbar, $T = 300$ K and $d_{RG} \approx 0.32$ nm, the mean free path becomes $\bar{l} \approx 0.7$ m. Thus, $\bar{l}$ is about 6 times larger than the target-substrate distance and the scattering probability of sputtered particles becomes negligible.
3.1 Ion beam sputter glancing angle deposition

**Target:**
The target assembly is freely rotatable around its axis and is constituted of a dual target attachment setup as depicted in Fig 3.3(a). Two sintered disc targets (Si and Ge) each with a diameter of 15 cm can be attached to the target holder assembly. A shield is attached to the back of each target holder to avoid cross-contamination between the targets. The maximum sputtering yield is obtained for $60^\circ < \alpha_{ST} < 80^\circ$ [150, 151, 153], and thus the angle between target and ion beam source was adjusted to $\alpha_{ST} \approx (70\pm5)^\circ$ to attain a maximum deposition rate for constant deposition conditions. For multilayered thin film growth, the required target can be sputtered sequentially by rotating from Si to Ge target as illustrated in Fig. 3.3(a).

**Aperture: particle flux collimator**
As described in the previous section, for the sputtered particle flux the angular distribution is described to be of over-cosine type and the target is not to be considered as a point source. Consequently, the sputtered area spans an elliptical shape and spreads over a few cm$^2$. Therefore, the emitted (i.e sputtered) particles do not necessarily travel in normal direction from the target surface, while a significant fraction of sputtered particles are likely to arrive at the substrate surface with undesired deposition angle (non-glancing angle $\beta^*$) that diverges from $\beta$ value. Thus, for a highly directional particle flux, an aperture is used to collimate the incoming particle flux. As displayed in Fig. 3.3(b), the aperture averts the particles arriving at non-glancing angle $\beta^*$ and restricts the minimum deposition angle to $\beta_{\text{min}} \approx 90^\circ - \arctan(\varepsilon/60)$, where $\varepsilon$ defines the opening (in mm). For the usual deposition angle $\beta = 86^\circ$, the approximate value of $\varepsilon = (15\pm3)$ mm results in an angular divergence of $\Delta\beta \approx (9\pm2)^\circ$, or in other words $\beta_{\text{min}} \approx (77\pm3)^\circ$. Under constant deposition conditions and under a deposition angle $\beta \approx 86^\circ$, in the presence of slit aperture the deposition rate amounts $r_a = 3.6\pm0.3$ nm/min, while in the absence of the slit aperture it increases to $r_b = 7.2 \pm 0.4$ nm/min.

**Substrate manipulator and heater**
The substrate manipulator is used to align the substrates in desired x-,y- and z-direction. This substrate manipulator is also equipped with a substrate rotator and substrate heater. It is feasible to rotate the holder around the z-axis (to set the deposition angle $\beta$). Moreover, the substrates can be rotated azimuthally around the substrate normal with a rotation velocity $0.01 < \omega < 0.2$
The azimuthal substrate rotation is aided by computer controlled step motor, which can be utilized to adjust stepwise or continuous substrate rotation around the substrate normal. The substrate temperature $T_S$ can be increased and measured by a tantalum wire resistance heater and a thermocouple, respectively, attached below the substrate holder. The dependence of the substrate temperature $T_S$ on the measured thermocouple temperature $T_{TC}$ is observed to be linear [164] and is given by: $T_S = 0.8 \cdot (T_{TC} - 6.5)$ K. Here, with the temperature controller the substrate temperature can be regulated between $RT \leq T_S \leq 400$ °C.
3.2 Substrate pre-patterning methods

**Nanosphere Lithography (NSL)**

Nanosphere lithography is a versatile method that enables the realization of periodic nanostructure arrays over a large area [165]. In general, widespread arrays of polystyrene (PS) or SiO$_2$ nanospheres of diameter $D$ are achieved by means of methods like spin coating [166]. Self-assembly of nanospheres, with the help of surfactants, leads to single monolayers$^4$ (SL) or double layers (DL) in planar-closed-packed arrangement, depending upon nanosphere suspension density [165]. Further, self-assembled monolayers are used as an evaporation mask, where the evaporant is deposited on the substrate surface through the quasi-triangular spaces between the nanospheres. Subsequent removal of nanospheres in a wet-chemical or mechanical process (with the use of scotch tape) leads to a periodic array of evaporant dots in a honeycomb-like arrangement on the substrate surface. In particular, usage of different nanosphere sizes $D$ allows varying the distances between the seeds. Previously, self-assembled nanospheres [14, 45, 59, 76, 113] or metal seeds in honeycomb-like arrays [76, 77, 79-81, 167] have been utilized for the GLAD growth of periodic nanostructures. But, reactive ion beam etching or reactive ion etching methods in combination with NSL can provide an alternative to form Si seeds of the Si substrate itself for a large area periodic growth. The Si seeds arranged in honeycomb-like and planar hexagonal-closed-packed (planar-hcp) arrays are achieved in the following way:

**Combination of NSL and reactive ion beam etching**

In this process, Si(111) substrates (size: 20 mm x 20 mm) are patterned with planar-closed-packed monolayers of polystyrene nanospheres (Fig. 3.4(a)) of diameter $D = 508$ nm, 780 nm and 1390 nm in a self assembly process [59, 165, 168]. Subsequently, a thin layer of Au (nominal thickness of $h_S = 100$ nm) is deposited onto the substrates by evaporation. In the following steps, the nanospheres are removed, thus leaving honeycomb-like arranged Au dots as illustrated in Fig. 3.4(b). Au seeds formed by this patterning technique are quasi-triangular shaped. To achieve Si seed arrays, this Au honeycomb array is subjected to a reactive ion beam etching process with a mixture of CHF$_3$ and O$_2$ (50% / 50%) as the etching gas. After this pattern

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$^4$ In this study only monolayers are used for substrate patterning and the evaporant used is either Al or Au.
transfer step, a honeycomb pattern is formed\(^5\) that consists of Si seeds at the locations of Au dots as shown in Fig. 3.4(b).

![Figure 3.4: Substrate pre-patterning processes: (a) self assembly of nanospheres; (b) evaporation of Au dot array followed by RIBE process to obtain Si dots; (c) O\(_2\) plasma etching of nanosphere array followed by RIE process to obtain Si seed array; Subsequent top-view micrographs depicting a honeycomb-like array (d) and a planar-hcp array (e).](image)

The etching times are varied between 7 to 9 min to obtain Si hillocks\(^6\) with different seed heights\(^7\). In a honeycomb arrangement, each seed (Fig. 3.4(d)) has three first-nearest neighbors at a distance \(d_1 = D/\sqrt{3}\), six second-nearest neighbors at a distance \(d_2 = D\) and three third-nearest

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\(^5\)Due to a higher etching rate of Au as compared to Si, the honeycomb pattern is transferred within the substrate exhibiting self-elevated Si dots within the Si substrates.

\(^6\)Energy dispersive X-ray (EDX) fluorescence measurements of a honeycomb substrate before and after the etching confirmed the pattern transfer process exhibiting Si hillocks formed after the RIBE process.

\(^7\) Measurement of seed heights before and after the etching process was done using atomic force microscopy (AFM) and scanning electron microscopy (SEM).
neighbors with a distance $d_2 = 2d_1 = 2D/\sqrt{3}$ (where $D$ is nanosphere diameter). For instance, the first nearest neighbors are located at a distance $d_1 \approx 293$ nm ($D = 508$ nm), $d_1 \approx 450$ nm ($D = 780$ nm) and $d_1 \approx 802$ nm ($D = 1390$ nm).

**Combination of nanosphere self-assembly and reactive ion etching**

In this process, Si(100) substrates (size: 20 mm x 20 mm) are patterned with planar-closed-packed monolayers of polystyrene nanospheres (PS) (Fig. 3.4(a)) of diameters $D = 535$ nm and 722 nm, in a self-assembly process [168]. Subsequently, the patterned substrates are etched isotropically with an oxygen plasma [169], in a reaction chamber (Diener electronic GmbH LF-plasmadevice NANO, 40 kHz and 300 W), under a low working pressure. The mass flow of $f_{O_2} = 160$ sccm is kept constant for $t_{O_2} = 10$ and 14 min (for $D = 535$ nm) and $t_{O_2} = 14$ and 35 min (for $D = 722$ nm) to achieve isolated PS nanospheres of diameters $D_{\text{plasma}} = 200$ and 100 nm respectively, as schematically sketched in Fig. 3.4(c). Subsequently, in order to produce cylindrical Si seeds on these substrates, inductively coupled plasma reactive ion etching is performed [170, 171] (ICP-RIE: Plasmalab 100 Oxford Instruments Plasma Technology) with an ICP source (2 MHz, 1200 W) and a RIE source (13.56 MHz, 45 W). A mixture of $C_4F_8$ and $SF_6$ (77% / 23%) is used as etching gas. The seed heights of $h_s \approx 100$ nm and seed widths $w_s = 100$ and 200 nm are achieved respectively for both periods. The polystyrene nanospheres are removed in an ultrasonic bath with dichloromethane ($CH_2Cl_2$), and subsequent rinsing with acetone and deionized water. Following the removal of PS spheres, Si seeds of width $w_s$, height $h_s$ with a seed separation distance $R_s$ are produced for GLAD growth (see Fig. 3.4(e)). The Si seed pattern formed after the etching process on a template $D = 535$ nm with a seed width $w_s = 200$ nm is shown in Fig. 3.4(e).
3.3 High temperature thermal annealing

In order to obtain crystalline nanostructures, the samples can be thermally annealed at high temperature condition in a controlled environment. In the present work, high temperature annealing was conducted in an infrared lamp heating furnace (MILA-5000, ULVAC-RIKO Inc. Yokohama, Japan). The heating system consists of an infrared lamp fixed at the focus of a parabolic reflector. Typically, the assembly is made in such a way that the emitted IR rays converge within the iso-thermal zone of the furnace where the sample can be placed on the sample holder. For different heating methods, two types of lamps can be used: a near infrared lamp with high energy density (100 V, 1 kW/piece) suitable for the heating to a high temperature range within a short interval or a far-infrared lamp (100 V, 250 W/piece) suitable for a steady and uniform heating process. The heating lamps are embedded in an isolated condition within a quartz glass tube to allow clean heating. The furnace is equipped with a water cooling system and the sample holder assembly is provided with air-tightening-rings to allow controlled heating. The sample can be heated in a controlled environmental condition, for instance at ambient atmospheric condition, under vacuum condition aided with a vacuum pump system at the evacuation port or in an inert gas flow (e.g. N₂ or Ar) controlled through gas flow unit. The sample assembly, consisting of a transparent quartz glass tube and a thermocouple with a Pt ribbon end, is then fixed to the water-cooled aluminum alloy flange and subsequently the sample can be heated with the infrared lamp with a suitable temperature ramp adjusted with a computer software.

In the present work, annealing of Ge-GLAD samples was performed in the annealing oven within an inert Ar-atmosphere with a continuous gas flow. The temperature ramp-up was adjusted to a heating rate ~ 55-60 °C/sec. The GLAD-grown samples were annealed at temperatures ranging from \( T_A = 300 \) °C to 800 °C. The samples were kept at different annealing temperatures for durations between 10 to 30 min, followed by a ramp-down at a cooling rate ~ 2-4 °C/sec during the cooling step.
3.4 Sample analysis

3.4.1 Scanning electron microscopy (SEM)

The surface structures were investigated and analyzed by Scanning Electron Microscopy (SEM). With the aid of a primary electron beam the sample surface can be visualized on a micro- and nano-meter scale. The electrons emitted out of the cathode are accelerated towards the sample surface. With the electron beam voltage different secondary signals are generated and typically the acceleration voltage of primary electrons lies in the range of approximately 0.1- 30 kV. Secondary electrons generated in the near-surface region and backscattered electrons generated deep inside the excitation volume were used as signals for the visualization. The inelastic scattering process of the primary electrons at the electron shell of the atoms of the sample generates secondary electrons that are of low energy (<50 eV) at the near surface region of the excitation volume. On the other hand backscattered electrons have more energy than 50 eV and are generated by elastic scattering of primary electrons. These secondary and backscattered electrons are generated at a depth of approximately 50 and 100 nm inside the surface. Apart from that, Auger electrons, x-rays, and cathode luminescence can be excited by the primary electrons. However, the secondary electrons are mainly useful for imaging the surface topography and structure, while the backscattered electron signal intensity is dependent upon the atomic mass of the elements. Hence, backscattered electrons contain information about the elemental distribution within the sample. Semiconductor or Everhart-Thornley (scintillator-photomultiplier system) detectors are used to detect secondary and backscattered electrons.

In the present work, a Carl Zeiss SMT AG, Ultra 55 with Gemini column SEM, equipped with a tungsten Schottky field emission cathode, was used to analyze the samples. The system is capable of working at a beam voltage in the range of 0.5-50 kV. The lateral resolution limit of the microscope is approximately 3 nm. The primary electrons, through the field emission tip, are emitted and accelerated via an electron tube and thereby pass through multiple electromagnetic lenses to reach the sample surface, where secondary signals are excited. The SEM is equipped with two secondary detectors: a ring-shaped in-lens detector\(^8\) positioned within the electron tube and one other located outside the electron column pointing towards the sample stage. On the

\(^8\)In the present work, an in-lens detector is mostly used for top-view and cross-sectional analysis.
other hand, the detector for backscattered electrons is generally used for elemental distinction. In this work, the cross-sections and top-views of the sample were analyzed. For cross-sectional measurements, samples were cut before mounting them on the sample holder. Most of the samples were analyzed with a relatively low beam voltage in the range of 1.5-2.5 kV in order to avoid surface charging. The working distance between the sample surface and the in-lens detector was maintained at approximately 5 mm in all the case.

The obtained SEM micrographs were analyzed using computer software programs, for instance SPIP (version 3.2.6.0) [172] and ImageJ (version 1.35) [173]. Specifically, for precise characterization SEM micrographs were obtained at different locations of the sample, and for the average structure diameter \( w \) and average structure height \( h \) calculation several iteration measurements were performed. The SPIP software identifies the term diameter as:

\[
    w = 2\left(\sqrt{A/\pi}\right),
\]

where \( A \) is the area detected by SPIP.

### 3.4.2 Transmission electron microscopy (TEM)

Transmission electron microscopy is a technique used for the visualization and investigation of thin specimen on an atomic scale. Typically, an electron emission source consists of a filament connected to a high voltage source (in the range of ~ 200-400 kV) to enable electron emission under vacuum condition. The electron beam extracted out of the emission source interacts with the specimen under observation. Hence, secondary electrons and backscattered electrons are generated during elastic or inelastic scattering process along with Auger electrons, x-rays, and cathode luminescence, which can be excited by the primary electrons. The condenser lenses focus the electron beam on the sample, and then an objective lens is used to form the diffraction in the back focal plane and the sample image in the image plane. Additionally, some multiple lenses are used to magnify the obtained image or the diffraction pattern. The amplitude contrast, while analyzing the crystalline and amorphous phases within the sample, can be obtained by inserting objective diaphragm in the back focal plane to gather the transmitted beam. In this condition, the crystalline parts (i.e. Bragg orientated) appear dark and the amorphous (not Bragg oriented parts) appear bright. This imaging mode is termed as ‘bright field’ mode. On the other hand, if the diffraction consists of many diffracting phases, each one can be differentiated by selecting it with the objective diaphragm. Therefore, the incident beam can be tilted and
diffracted beam is adjusted on the objective lens axis to avoid aberrations. This imaging mode is termed as ‘dark field’ mode. Additionally, a particular area diaphragm can be selected out of the imaged sample area and diffraction patterns can be obtained. These selected area electron diffraction (SAED) patterns are useful for the investigation of the lattice symmetry and to calculate inter-planar distances.

In the present work, the sample analysis was done in an electron microscope HITACHI H-8100 with an acceleration voltage of 200 kV and in an JEM 4010 (HRTEM) with an acceleration voltage of 400 kV. The sample preparation for TEM measurements was done with either by mechanical and ion beam thinning or by Focused Ion Beam (FIB) cutting. The FIB-lamella was prepared with FIB machining (Carl Zeiss Auriga equipped with a Cobra column and a gas injection system). For that purpose a Ga\(^+\) beam (30 kV) was used to cut out a lamella from a selected area. A micromanipulator was used to lift the lamella and to attach it to a TEM lift-out (Cu) grid with the aid of a cracked Pt precursor gas.

### 3.4.3 X-ray diffraction

X-ray diffraction is a versatile technique used for the thorough investigation of the crystallographic structure of a sample. Typically, for such measurements radiation with a short wavelength in the range of a few angstroms to 0.1 angstroms (Å) is used. When the incident x-rays penetrates into the material and gets diffracted due to a specific atomic arrangement, reflective constructive interference occurs.

Figure 3.5 shows a schematic sketch of x-ray diffraction at parallel lattice planes. A crystal lattice consists of a regular three-dimensional distribution of atoms in space with specific inter-planar spacing \(d\). When a x-ray beam (electromagnetic radiation, energy in the range of 100 eV - 100 keV) with a wavelength \(\lambda\) is directed onto a crystalline material with an angle \(\theta\), diffraction pattern can be obtained. In such a case, the diffracted x-rays retain the original wavelength after the elastic scattering process, while the non-elastic scattering leads to the alterations in the wavelength. Diffraction can be measured only when the following Bragg’s
condition is fulfilled: \(2d \sin \theta = n\lambda\), where \(n\) is the order of diffraction.

In the present work, a Seifert XRD 3003 PTS diffractometer was used to perform x-ray diffraction measurements. The instrument is equipped with a graded multilayer mirror to collimate the incident x-ray and with a single crystal Ge(220) monochromator. The crystallographic analysis of the samples was done with Cu-K\(\alpha_1\) radiation (wavelength \(\lambda = 0.15406\) nm). The diffracted x-rays pass through a slit system and were gathered with a scintillation detector equipped with an electron multiplier system.

For 0/20 measurements the x-ray tube remains stationary while the sample tilts with the angle \(\theta\) and subsequently the detector moves with the 2\(\theta\) angle as depicted in 3.6. When the Bragg’s condition for \(d_{hkl}\) is fulfilled, corresponding diffraction peaks at \(\theta\) can be measured. With this method lattice plane distances can also be calculated.

With Rocking curve measurements the crystalline quality, as represented by the tilt distribution of crystallites in the film, can be investigated. Typically, in this method the x-ray source and the detector are kept fixed so that the Bragg’s condition of a specific reflection is fulfilled and \(\omega\) scans are performed. Here, the full width half maximum (FWHM) of an \(\omega\) scan peak is inversely proportional to the dislocations in the crystalline film.

Phi-scans (\(\phi\)) are used to determine the in-plane orientation of the film. In this measurement, the sample is rotated about its normal from 0 to 360°, while keeping \(\theta\), 2\(\theta\) and polar angle \(\chi\) fixed.

In a polycrystalline film, typically texture goniometry measurements are used to evaluate the orientation distribution of the crystallites the film is comprised of. A Pole figure is plotted in polar coordinates with the specific tilt and rotation angle with respect to a given crystallographic

Figure 3.6: Schematic diagram of a goniometer.
orientation and it is measured with a series of \( \varphi \) scans (in-plane rotation around the sample normal) at different polar angles \( \chi \).

### 3.4.4 Time of flight secondary ion mass spectrometry (TOF-SIMS)

This analysis technique is used for the investigation of thin film elemental depth distribution profile. The primary ion source (several keV) beam is focused on the sample surface and secondary ions sputtered from the surface are detected and analyzed. Although most of the particles emitted out from the surface are neutral, a small fraction of the particles is charged and can be detected. These sputtered ions can be mass analyzed as they represent the elemental/molecular composition of the sample on the basis of the intensity of the elements, compounds and their charge states. Different analyzers, for instance quadrupole or time of flight (as in the present work) are used for this mass analysis. In TOF-SIMS measurements, an electric field accelerates the secondary ions that are ejected from the sample towards the detector. As the mass-to-charge ratio determines the velocity of the ions, different ions require different times to arrive the detector and hence it is feasible to mass analyze the detected ions. For example, heavier ions ejected at the same time than lighter ions will reach the detector at a later time interval. Therefore, it is possible to gather a mass spectrum. In order to record a depth profile of a sample, typically a dual ion beam mode is employed, in which one high current ion beam (for instance, \( \text{O}_2^+ \) or \( \text{Cs}^+ \)) is utilized to sputter a crater within the sample, while for analysis at the bottom of this crater a second ion beam (for example: \( \text{Ga}^+ \)) is used.

In the present work, in order to sputter a crater 2 keV \( \text{Cs}^+ \) ions were used on the area of 300 \( \mu \text{m} \times 300 \mu \text{m} \), while the analysis was done using 15 keV \( \text{Ga}^+ \) ions on the area of 75 \( \mu \text{m} \times 75 \mu \text{m} \) in the middle of the sputtered crater. In the case of sample charging, an electron flood gun was used to suppress the effect by charge compensation. All depth profiles presented here were obtained from negative ion mass spectra.
Chapter 4

Ion beam sputter deposition of silver films at elevated substrate temperature

In this chapter, the growth of Ag nanostructures and Ag compact thin films with ion beam sputter deposition on Si substrates will be examined. For GLAD-grown multilayered Si/Ge nanostructures, a Ag layer can potentially be used as a promising conductive capping layer. The growth of the capping layers on GLAD films has been studied previously by a few groups [26-30]. However, such capping layers on the top of GLAD nanostructures must necessarily be defect free to ensure high characteristic performance of the thermoelectric device. Moreover, particularly the properties of GLAD films ($\beta = 86^\circ$) differ from the dense films deposited with normal particle incidence ($\beta = 0^\circ$) due to the differences in growth mechanism, porosity, surface-to-volume ratio etc. Hence, in principle it is required to examine the growth characteristics of Ag films on Si substrates with the ion beam sputter deposition method, before investigating the capping layer properties of Ag films.

Here, the growth of compact thin Ag films deposited on native oxide covered Si(100) substrate and Ag films deposited under GLAD conditions are investigated. Among several variables that influence the growth of the film, the substrate temperature $T_S$ plays a key role which can attribute enhanced surface diffusion effects. Hence, in particular substrate temperature influence on the growth of Ag films will be presented in this section.

4.1 Growth of Ag thin films on native oxide covered Si(100) substrates

Some recent studies concerning the growth of hetero-epitaxial layers on native oxide covered Si surfaces highlight a vital role of the native oxide [35-39]. Besides, Ag films deposited by radio-frequency magnetron sputtering on Si substrates covered with native oxide demonstrated an epitaxial relationship with the underlying Si(100) substrate at elevated deposition temperature (550 °C) [37, 38]. However, most of the previous investigations carried out regarding the epitaxial growth of Ag films are devoted towards molecular beam epitaxial (MBE) growth of Ag on oxide layer free Si substrates under ultra-high vacuum (UHV) conditions [31-33]. Further, in some studies it was shown that with MBE growth Ag films do not exhibit an epitaxial relationship with Si(100) substrates having a thin SiO$_2$ layer on top [34].
4.1 Growth of Ag thin films on native oxide covered Si(100) substrates

In the present work, however, the influence of the substrate temperature on the growth of ion beam sputter deposited Ag epitaxial films is studied. The deposition of Ag films on native oxide covered Si(100) substrates was done at various substrate temperatures ranging from $T_s = $ RT to 300 °C. The deposition angle was adjusted to normal particle incidence ($\beta = 0^\circ$) to form compact thin films. Most of the films studied in this section were of thickness of ~200-500 nm ($t_{\text{dep}} = 6$-16 min) deposited with a constant deposition rate $r_{\text{Ag},0} \approx 31.2$ nm/min. At first, the influence of the substrate temperature is examined, while in the later subsections the epitaxial growth of Ag on Si(100) substrate is discussed in detail with a specific focus on the role of a native oxide layer.

4.1.1 Influence of substrate temperature

Figure 4.1(a) depicts XRD $\theta/2\theta$ diffraction diagrams of Ag films deposited at different substrate temperatures ranging from $T_s = $ RT to 300 °C. The film deposited at RT was observed to be polycrystalline, but with a preferred (111) orientation. Particularly, for a Ag powder standard sample, the ratio of intensity of (200) and (111) reflections is 0.4. Here it is observed to be ~ 0.002. With increasing deposition temperatures from $T_s = $ RT to 100 °C, 150 °C, 250 °C and 300 °C, the intensity of the (200) reflection increased, while the intensity of the (111) reflection decreased. Even at a substrate temperature as low as $T_s = $ 100 °C, the (200) reflection was observed to be stronger compared to the very low intense (111) reflection. The intensity ratio $I_{(200)}/I_{(111)}$ as a function of the substrate temperature from $T_s = $ RT to 300 °C has been plotted in Fig. 4.1(b). Due to the dominant (111) reflection at RT the intensity ratio was observed to be

![Figure 4.1: (a) XRD $\theta/2\theta$ diffraction diagrams of the Ag films deposited at various temperatures ranging from $T_s = $ RT to 300 °C, (b) Corresponding intensity ratio of $I_{(200)}/I_{(111)}$ at different substrate temperatures.](image)
minimum. But for increasing substrate temperature from \( T_S = RT \) to 300 °C, the intensity ratio increased due to a highly intense (200) reflection. Thus, it can be concluded that the volumetric fraction of Ag crystallites with (100) orientation increases with increasing substrate temperature.

### 4.1.2 Epitaxial growth of Ag on Si(100) substrate

As the intensity of (200) reflections were observed to increase with increasing substrate temperature, azimuthal scans of reflections corresponding to the films and to the Si(100) substrates were accumulated. Figure 4.2 illustrates such x-ray (111) \( \phi \)-scans of Si(100) substrate (Fig 4.2(a)) and Ag films deposited at \( T_S = 100 \) and 300 °C (Fig. 4.2(b) and (c), respectively). The \( \phi \)-scan of the Si(100) substrate demonstrates an extremely narrow FWHM (full width half maximum) for the observed equidistant four peaks. The \( \phi \)-scan of the corresponding Ag film deposited at \( T_S = 100 \) °C illustrates a single favourable in-plane orientation of (100) with four fold matching symmetry on Si(100) substrate. It is evident that the Ag film exhibits an epitaxial relationship with the underlying Si(100) substrate. For the Ag film deposited at \( T_S = 300 \) °C it is worth noting that the orientation still matches with the substrate orientation but the FWHM becomes narrower in comparison to the film deposited at \( T_S = 100 \) °C. This indicates that the twist distribution of Ag crystallites gets narrower with increasing \( T_S \).

![Figure 4.2: X-ray (111) \( \phi \) scans for the Si(100) substrate (a) and Ag film deposited at different temperatures: (b) \( T_S = 100 \) °C, (c) \( T_S = 300 \) °C.](image-url)
distinct equidistant pole density maxima\(^9\) at \(\chi \approx 55^\circ\), originated by the (200) oriented epitaxial Ag film, as well as four weak pole density maxima at \(\chi \approx 16^\circ\) and eight at \(\chi \approx 79^\circ\) that can be correlated to 1\(^{st}\) order twinning. This twin formation is a consequence of the relatively low growth temperature of the films.

For the films deposited at 75 °C, the (200) reflection was found to be intense in comparison to (111), however Ag\{111\} pole figures showed extremely low intense pole density maxima at \(\chi \approx 55^\circ\). In addition, as the temperature increased from \(T_S = 100\) to 300 °C, the pole density maxima became more intense and narrower, and at \(T_S = 300\) °C a strong evident (200) texture is observed. Figure 4.3(f) shows a plot of intensity ratios of the average intensity of pole density maxima at \(\chi \approx 55^\circ\) to the average intensity of the 1\(^{st}\) order twin related pole density maxima at \(\chi \approx 16^\circ\) as well as at \(\chi \approx 79^\circ\) with respect to deposition temperatures. Both intensity ratios increase with increasing deposition temperature. It is obvious that with increasing deposition temperature an increase in the crystalline quality was observed with a narrowing mosaic distribution of

\[^9\]The angle between (111) and (200) planes in the cubic crystal structure is 54.74°.
crystallites and a decrease in the fraction of 1\textsuperscript{st} order twins. Ag(200) rocking curve measurements performed on the epitaxial films confirmed the improving crystalline quality of the films with increasing substrate temperature. Figure 4.3(g) displays a plot of FWHM values of the rocking curves as a function of substrate temperature. As for RT, the Ag film was not epitaxial but had a (111) preferred orientation, the rocking curve of that Ag(111) reflection was used for the RT value plotted in Fig. 4.3(g). As the temperature increased from $T_S = \text{RT}$ to 300 °C, the FWHM values decreased indicating a narrowing mosaic spread of crystallites. Here, it is worth noting a decrease in FWHM of almost two orders of magnitude.

In this case, ion beam sputter deposition of Ag on native oxide covered Si substrate can result in high-quality epitaxial Ag films. Obviously, the presence of a native oxide layer did not prevent the epitaxial growth of the Ag film on Si(100) substrates. This has been shown by other groups [37, 38]. The native oxide layer thickness at RT is usually observed to be approximately 2-3 nm, while it contains a lower percentage of oxygen, when compared to thermally grown SiO$_2$[174]. Generally, desorption of native oxide from the Si surface needs a high temperature treatment (~800-1000 °C) in ultra-high vacuum condition. However, under ion beam sputter deposition conditions, the stability of a native oxide layer is still unclear.

High energetic sputtered particles that impinge on the substrate surface at high temperature might reduce the stability of the oxide layer. Additionally, the native oxide is likely to have a certain degree of voids with a loose open structure due to lower stoichiometry [174] and due to the formation of voids in the oxide layer as an effect of thermal decomposition [175, 176]. According to the investigations of Hur et al. [37, 38], a higher growth temperature and the sputtering method can activate the oxide desorption process and therefore, impinging sputtered Ag atoms can reach the Si(100) substrate surface. Considering the ratio of the lattice constants of Si (0.543 nm) and Ag (0.409 nm) it matches to approximately 3-to-4 ratio [19]. Thus, it can be expected that a 4×4 mesh of unit cells of Ag(100) grows with cube-on-cube domain epitaxy on a 3×3 mesh of unit cells of Si(100) with a lattice mismatch of 0.4% [42]. In the present experiments it was observed that the (200) reflection was intense in comparison to the very low intense (111) reflection even at 100 °C and the Ag film also demonstrated an evident epitaxial relationship with the substrate, as proven by the Ag{111} pole figure measurements. These
results partially differ from the results of Hur et al. [37, 38]. At this point the question arises, if the native oxide layer is a necessity to obtain epitaxial growth.

4.1.3 The function of native oxide layer on Si(100) substrate

In order to check the necessity of the presence of a native oxide layer prior to the growth of an epitaxial film on a Si(100) substrate, films were deposited on Si substrates that were treated with HF (etch duration: 10 min) prior to the Ag deposition. This removes the native oxide (and all the organic impurities) completely. Such HF treated substrates were then immediately loaded into the vacuum chamber and ion beam sputter deposition was carried out at different substrate temperatures.

Figure 4.4(a) shows a comparison of XRD \( \theta/2\theta \) diffraction diagrams of Ag films deposited on Si(100) substrates with and without native oxide at \( T_S = 300 \, ^\circ\text{C} \). Here, the Ag film on the substrate covered with a native oxide layer showed a highly intense (200) reflection, signifying the already described epitaxial relationship with the Si(100) substrate. On the contrary, the film deposited on the HF rinsed Si(100) substrate exhibited a dominant (111) reflection, and no epitaxial relationship with the underlying Si(100) substrate was observed. The corresponding pole figure measurement of the Ag film deposited on the HF treated substrate, displayed in the inset of Fig. 4.4(a) confirms non-epitaxial growth on the oxide free Si(100) substrate. It must be concluded that the native oxide layer may play the key role in the growth of epitaxial Ag film on the Si(100) substrate.

The topographical comparison of the films deposited on Si(100) substrate with and without native oxide layer (Fig. 4.4 (c)-(f)) further illustrates the growth differences. The film deposited on native oxide covered Si(100) substrate contains diminutive pores, but the overall morphology of the film depicts an uniform film thickness with a relatively smooth surface (Fig. 4.4(b) and (d)). In contrast, the cross-sectional and top-view SEM micrographs of the film on the HF treated substrate, which exhibited non-epitaxial Ag film growth, shows a non-uniform, very rough, and porous film morphology (Fig. 4.4(c) and (e)).

The fact of the non-epitaxial growth on an oxide-free Si substrate must have to do with the energetic impinging of Ag particles. This could be understood on the basis of the fundamental difference of native oxide coverage on the substrate surface. For a similar case, Si(100) native
oxide free substrate (HF treated) Lamontagne et al. [177, 178] demonstrated that during a Au sputter deposition process an amorphization of the crystalline-Si surface can occur by the energetic Au sputtered particles, as Si atoms from the silicon matrix are displaced, causing a disturbance in the Si atomic arrangement of the substrate surface. Similarly, this effect could also be the case of the non-epitaxial growth of Ag film on native oxide-free substrates.

The present experimental observations displayed growth of non-epitaxial Ag films only on HF treated Si substrates. Although, the inherent substrate matrix governs the epitaxial growth process, the stability during ion beam sputter deposition of Ag at elevated substrate temperature still remains unclear. Moreover, the XRD θ/2θ diffraction diagrams, ϕ-scans, pole figure measurements and SEM analysis demonstrated significant dissimilarities between the films deposited on HF treated substrates in comparison to the epitaxial films grown on native oxide covered Si(100) substrates. Consequently, the presence of native oxide layer prior to the film deposition is observed to be an elementary requirement to grow epitaxial Ag films on Si(100) by ion beam sputter deposition method.

Up to this point, only the Ag films themselves were investigated, but not the oxide layers. Therefore, to examine the actual state of the native oxide layer on Si substrate, TOF-SIMS measurements were performed on the films deposited at various substrate temperatures, and the film deposited on the HF treated Si substrate.
4.1 Growth of Ag thin films on native oxide covered Si(100) substrates

Figures 4.5(a)-(c) show TOF-SIMS depth profile analyses of the elements Si, O and Ag within the films deposited at temperatures $T_S = RT$, $100 \, ^\circ C$ and $300 \, ^\circ C$ on native oxide covered Si substrates. At RT, a distinguishable peak of O content is visible at the Ag/Si interface, while a reduced intensity within the Ag film can be observed, which remained almost constant throughout the film. In fact, O and Ag intensities decreased rapidly at the Si substrate surface, and the depth profile measurement did not show any significant intermixing of Ag and Si layers at $T_S = RT$. The lowest epitaxial growth temperature was observed to be $T_S = 100 \, ^\circ C$. The depth profile measurements on this film showed an O signal peak at the Si/Ag interface too (see Fig. 4.5).

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4.5(b)). In this case, a considerable interfacial oxygen content was detected, but the overall oxygen content at the Ag/Si interface decreased in comparison to the film deposited at RT. Further, a notable difference in the O depth profile was observed at \( T_s = 300 \, ^\circ \text{C} \), where the O content decreased significantly and the O peak at the Ag/Si interface broadened. This might be due to a local oxygen desorption process at the beginning of the Ag deposition. Additionally, the O content within the Ag film decreased in comparison to the films deposited at RT and 100 \( ^\circ \text{C} \). It is worth noting that for a \( \sim 500 \, \text{nm} \) thick epitaxial film a small amount of oxygen was observed at the Ag/Si interface as well as within the Ag film. In order to comparatively understand the underlying presence of oxygen at the Ag/Si interface, the interfacial area of oxygen peaks in the TOF-SIMS measurement were integrated for the films deposited at different temperatures. Figure 4.5(d) shows the peak area integration of oxygen peaks at the Ag/Si interface as a function of the substrate temperature. Clearly, at RT a large oxygen content was observed at the interface, while with an increasing substrate temperature the oxygen content reduced significantly. Nonetheless, it was observed that even though the oxygen content at the interface reduced, a considerable fraction was still detected at the Ag/Si interface and within the epitaxial Ag films. For a substrate temperature of 300 \( ^\circ \text{C} \), the O peak area is still half of the O peak area for the RT sample. This proves, that there is still a more or less intact oxide layer present. This is also in contradiction to the conclusions of Hur et al. [37, 38]

From literature, it is known that the desorption process of native oxide layer is initiated through the formation and growth of voids [175]. Subsequently, Si atomic self-diffusion over the clean Si surface within the voids attributes a surface reaction \( \text{Si} + \text{SiO}_2 \rightarrow 2\text{SiO(volatile)} \), while the coalescing of such voids results in the desorption of the oxide layer from the Si substrate [175, 176]. But, the stability of such a native oxide on a Si substrate under a flux of high energetic Ag sputtered particles at elevated substrate temperature is yet unknown. According to Hur et al. [37, 38], the native oxide desorption process is typically initiated under high vacuum conditions at elevated substrate temperatures and leads to the complete desorption at 550 \( ^\circ \text{C} \). In the sputter deposition process the impinging atoms have a considerably large kinetic energy. Most of the sputtered Ag atoms have energies between 2-30 eV. As against the atoms deposited with MBE, where the energy of impinging atoms is relatively low in the region of thermal energies (0.1-0.3 eV) [179]. Hence, in the present case impinging Ag atoms might enhance the oxide desorption...
4.1 Growth of Ag thin films on native oxide covered Si(100) substrates

process, which could ultimately lead to the deposition of Ag atoms on the exposed Si surface. From the TOF-SIMS measurements, a reduction of the oxygen intensity at the interface confirmed the partial desorption of the native oxide layer. However, a non-negligible oxygen fraction at the interface indeed suggests only local desorption of the native oxide at the beginning of Ag deposition that leads to the epitaxial growth. In fact, Barski et al. [36] and Shklyaev et al. [35] reported the growth of epitaxial Ge nanodots on thin-oxide covered surfaces, where the local oxide desorption was detected. Besides, annealing treatment of post-deposited Co layers at 500-700 °C on oxide covered Si surface illustrated epitaxial growth of CoSi$_2$ [180], where silicide formation is mediated by the thin oxide layer. These studies explicitly suggest diffusion of the deposited-over-layer atoms through the oxide layer to reach the exposed substrate surface, where local desorption can lead to the growth of epitaxial nanoislands on the exposed Si surfaces.

In summary, the process of hetero-epitaxial growth that occurs in this study strongly relies upon the substrate temperature, energy of impinging particles and oxide desorption mechanism. From the XRD and SEM measurements it is evident that Ag films are comprised of an arrangement of crystallites with a corresponding number of grain boundaries. Though the overall topography of each epitaxial film was observed to be smooth a close inspection of for example Fig. 4.4(d) indicates the existence of minute pores, which could be correlated with certain grain boundaries, voids and defects within the film. Moreover, SIMS measurements not only presented a decreasing oxygen content at the Ag/Si interface with increasing substrate temperature, but it also depicted a non-negligible content at the interface for epitaxially grown Ag films. This primarily, suggests local-oxide-desorption at the beginning of the growth of epitaxial films. Further investigations, in particular in-situ investigations, about the interfacial kinetic processes could certainly improve the understanding of the essential function of the oxide layer, the substrate temperature and the particle energy influence on the oxide desorption process.
4.2 Temperature altered morphology of silver nanostructures

In this section, the growth characteristics of Ag GLAD nanostructures deposited at various substrate temperatures will be presented. First, the fundamental differences between the growth modes of Ag nanostructures at room temperature on planar and pre-patterned substrates are studied. Afterwards, the influence of diffusion-driven processes on GLAD nanostructures is examined.

For the experiments in this section, the substrate temperature $T_S$ was varied between $RT \leq T_S \leq 350 \, ^\circ C$. In particular, the effect of particle flux collimation in the case of ion beam sputter deposited films is investigated. Subsequently, the growth differences on planar and pre-patterned substrates are also studied. The deposition of Ag GLAD films discussed in this section was carried out with or without a slit aperture placed between target and substrate. In the presence of a slit aperture, an opening of $15 \pm 3 \, mm$ collimates the particle flux arriving at the substrate surface and restricts the minimum angle of incidence for the incoming particle flux with respect to the substrate normal to $77 \pm 3 \, ^\circ$. At $T_S = RT$, the deposition rate at $\beta \approx 86 \, ^\circ$ amounted $r_a = 3.6 \pm 0.3 \, nm/min$. The absence of the slit aperture fosters a broad angular distribution of the particle flux resulting in a higher deposition rate $r_b = 7.2 \pm 0.4 \, nm/min$ ($\beta \approx 86 \, ^\circ$) at $T_S = RT$.

4.2.1 Growth on planar and pre-patterned substrates (at $T_S = RT$)

- **Growth on planar substrates**

As described in section 2.1.3, the morphology of the growing structure depends on the ratio $\rho = \frac{r}{\omega}$ of deposition rate $r$ and rotational velocity $\omega$. Independent of $\rho$ values, growth of the structures will commence on the seeds that are formed at an early stage of the growth with approximate seed-dimensions within the range of $\approx 20$-30 nm [61, 115]. For a constant deposition rate $r_a = 3.6 \pm 0.3 \, nm/min$, the $\rho$ value can be adjusted for a continuous substrate rotation to form a vertical column-like morphology. Figures 4.6(a) and (b) show respective cross-sectional and top-view SEM micrographs of Ag vertical columns deposited with continuous substrate rotation ($\rho \leq 18 \, nm/rev$). Through the early stages of growth, due to the self-shadowing mechanism the rate of column extinction is high, until a stable ratio of average column separation and average column width is reached [118]. In particular for column-like structures, the average column diameter and inter-column separation increases with growing...
4.2 Temperature altered morphology of silver nanostructures

The structure height as a result of column extinction and column merging [4, 6, 58]. The self-shadowing favours the predominant larger structures, while the growth of smaller seeds stops prematurely, as observable in Fig. 4.6(a). As a result the surviving columns become broader with increasing height, as visible from Fig. 4.6(b).

As described in section 2.1.2, the column inclination angle $\gamma$ can be deduced using different models as a function of deposition angle $\beta$ for obliquely deposited films. Figure 4.6(c) and (d) show cross-sectional and top-view SEM micrographs obliquely grown Ag films (without substrate rotation). Here, the column inclination angle $\gamma$ measured $69\pm2^\circ$. Other researchers reported values of $\gamma(85^\circ) = 67^\circ$ [136] and $\gamma(86^\circ) = 71.3^\circ$[181] for e-beam evaporation of Ag nanorod arrays. Thus, the experimentally obtained data for $\gamma$ values for the oblique angle deposition case at $T_S = RT$ is in agreement with both the published results and the model put forward by Tait et al. [90].

To evaluate the growth exponent $p$ of the scaling law $w \propto h^p$ (Eq. 2.5), the $w(h)$ data is plotted in Fig. 4.7 (the $w(h)$ data is the calculated over the average value of 6-10 columns) and fitted to the scaling law. According to the predictions, [101] the $p$ value should vary between 0.3 and 0.5, and decrease with increasing surface diffusion. Here, the scaling exponent value is observed to be $p = 0.36\pm0.02$ at $T_S = RT$. In an earlier study, Zhao et al. reported $p = 0.14\pm0.1$ for e-beam evaporated Ag nanorod arrays [182]. Even though the obtained values for the experimental measurements differ slightly from the published data, the present experimental value is consistent with the theoretically predicted $p$ values by Karabacak et al. for a negligible surface diffusion scenario [101].

Generally, a discrepancy between the theoretical predictions and experimentally measured values can occur due to the differences in deposition conditions. For instance, the $\rho$ values used to
obtain ($\rho \approx 18$ nm/rev) in the current experimental part are large as compared with published data [51, 101]. Secondly, even though an aperture is used to collimate the particle flux, there will be a certain variance ($\Delta \beta \approx 9^\circ$) in the angular distribution of the particle flux arriving at the substrate surface. Thus, non-glancing angle $\beta^*$ values, in principle, can certainly attribute to the fluctuation in $p$ above $p = 0.5$ [51].

- **Growth on patterned substrates**

As described earlier, growth on planar substrates results in randomly arranged structures due to the statistical behaviour of the growth process [99, 119, 120, 183], where the structure dimension and periodicity can not be controlled precisely [4]. Instead, by utilizing pre-patterned substrates, a defined surface structure periodicity can be attained [5]. On such pre-patterned substrates, artificial seeds serve as growth-seeds for the periodic nanostructure arrays. Out of several templates used till date, the growth of Ag nanostructures on honeycomb-like arranged Al seeds is briefly discussed here.

For planar substrates it was found that the column diameters increase with increasing structure height (Fig. 4.7) and follow a power scaling law. However, it is known that for pre-patterned substrates column diameter $R$ quickly saturates [116] to a value $R_{Sat}$ for tetragonal templates as a
4.2 Temperature altered morphology of silver nanostructures

dependent function of inter-seed distance $d_s$ as explained in equation (2.7). But, the geometry of
the underlying template controls the overall morphology of the columnar structures grown
thereon. Specifically, for the honeycomb-like pattern, due to the rotationally non-symmetric
template the columnar evolution is significantly influenced by the nearest neighbouring seeds.

To gain a thorough idea about geometric effects on the growth of the structures, the temporal
evolution of Ag nanorods on honeycomb-like arranged template ($D = 517$ nm, $h_S = 35$ nm) is
depicted in Fig. 4.8. The underlying honeycomb pattern is formed with the NSL method as
described in section 3.2. The deposition angle $\beta = 86^\circ$ results in a shadowing length $l \approx 500$ nm.
With increasing deposition time $t_{dep}$, shape and width of the nanorods change as observable in
Fig. 4.8(a)-(c). At an early stage of growth the shape of a nanorod can be compared to a circular
cross-section ($t_{dep} = 28$ min), while later it transforms into a comparable triangular cross-sectional
shape ($t_{dep} = 84$ min).

This can be understood by considering following effects. For a honeycomb-like patterned
substrate\footnote{Growth under GLAD conditions on honeycomb-like arranged templates is discussed in detail in section 5.3 and a
more descriptive analysis will be presented.}, each seed has three first-nearest neighbours, six second-nearest neighbours and three-
third-nearest neighbours which influence the shape and dimension of the subsequently grown
nanorods \cite{79, 81}. As a result, the honeycomb-like patterns, unlike a tetragonal template, provide
a less rotational symmetric shadowing effect. The first nearest neighbours ensure early saturation
in $d_1$ direction, leading to the formation of a flat side in that direction. Due to the fact that $d_2 > d_1$
and $d_3 > d_1$ nanorods have more space to “fill” in the direction of $d_2$ and $d_3$ neighbouring seeds.
Hence, the “saturating radius” in that case will be greater, affirming in the growth of pikes,
which in turn resemble the triangular shape of the nanorod. Moreover, with increasing deposition
time ($t_{dep} = 140$ min, $h \approx 500$ nm) eventually a column merging effect is observed (Fig. 4.8(d))
which could be attributed to the enhanced column competition on such honeycomb-like
patterned substrates \cite{77}. As a consequence on the honeycomb patterned substrate the
morphological evolution of columns is strongly influenced by inter-seed distances, seed heights,
and consequently shadowing lengths.
4.2.2 Growth at elevated temperatures: Effect of flux collimation on the film morphology

To examine the effects of particle flux collimation on the film morphology, films were deposited with and without a slit aperture at $RT \leq T_S \leq 350 \degree C$. The slit aperture collimates the particle flux arriving at the substrate surface and restricts the minimum angle of incidence for the incoming particle flux with respect to the substrate normal. Without aperture, the deposition rate of the film was observed to be twice ($r_b = 7.21 \text{ nm/min at } T_S = RT$) compared to that of the films deposited in the presence of the aperture ($r_a = 3.6 \text{ nm/min at } T_S = RT$). The films in the absence of the aperture were prepared with a deposition time $t_{dep} = 70 \text{ min}$, while the deposition time was increased to $t_{dep} = 140 \text{ min}$ in the presence of the aperture.

At RT, clusters of non-uniform sizes distribute randomly in the early stages of growth and serve as seeds for the growing nanostructure on the planar substrates. Furthermore, these nanostructures tend to broaden with increasing height [101] and compete in growth, which leads to the extinction of some of the structures [4, 6]. On the contrary, when the substrate temperature is increased, an immense morphological difference appears. This can be attributed to the enhancement in the diffusion lengths of the adatoms. Figures 4.9 (a)-(f) show a comparison between Ag-STFs deposited on bare Si(100) substrates at $\beta = 86\degree$, in the absence and in the presence of the slit aperture at $T_S = RT$ and at $T_S = 300 \degree C$. At $T_S = RT$, with the exception of a larger column density for the aperture-free case, no significant differences were observed for the films deposited.

![Figure 4.9: SEM micrographs of samples prepared in presence (t = 140 min) and absence (t = 70 min) of a slit aperture: (a) without aperture at $T_s = RT$, (b) with aperture at $T_s = RT$, (c) without aperture at $T_s = 300 \degree C$, (d) with aperture at $T_s = 300 \degree C$, (e) top-view of (c), (f) top-view of sample (d).]
with and without collimation slit. At $T_S = 300$ °C, ‘mountain-like’ (without aperture) and ‘nanorod-like’ (with aperture) structures evolve as observable in Fig. 4.9(c) and (d), respectively. The growth of such shaped structures is atypical for glancing angle deposited films. Here, the maximum height of the mountain-like structures measured ~ 800 nm, but no uniformity of the thickness is observed, as these structures are found to form separate islands. From the top-view (Fig. 4.9(e)), large island- and mountain-like structures, typically greater than 2 μm in length, can be observed, while no presence of nano-rod/-whiskers can be detected.

In contrast, in the presence of the slit aperture nanorods of length 3.6 μm grow amidst multifaceted grains as observable in Figs. 4.9(d) and (f). As whiskers of different thicknesses could be observed, in the further description for convenience “nanorods” are classified to have diameters greater than approximately 120 nm, and “nanowires” to have diameters below that value. Vapor phase growth of identical Al whiskers was reported by Suzuki et al. for oblique angle deposition conditions [46, 47, 125]. The critical temperature of the formation of such GLAD-grown Al-whiskers was noticed to be between $180 \degree C \leq T_S \leq 290 \degree C$ [46]. However, these OAD-grown Al-whiskers were grown with electron beam evaporation method, which certainly attributes comparatively lesser angular beam divergence and thus a collimated particle flux. With the present experimental conditions, mountain-like (without aperture) and nanorod-like (with aperture) structures evolve at elevated temperatures depending upon particle collimation. Therefore, it is evident that for ion beam sputter deposition, the particle flux divergence certainly plays a key role in the resultant film morphology.

**Growth model: Particle flux collimation effect**

The absence of the slit aperture results in a rather broad angular distribution of the particle flux due to the usage of the sputtering process. This results in a distinct amount of Ag particle flux reaching the substrates under ‘non-glancing angle deposition conditions’, as schematically shown in Fig. 4.10(a). At $T_s = RT$, irrespective of the presence of a slit aperture, GLAD-grown films show the typical columnar morphology (see Fig. 4.9 (a) and (b)). An obvious morphological difference is detected only for the films deposited at higher substrate temperatures.
Thus, the enhanced surface diffusion lengths \([82, 83, 124]\) at elevated temperatures \(T_S / T_M \approx 0.46\) for \(T_S = 300\,^\circ\text{C}\) trigger the growth of large island- and mountain-like structures. At elevated \(T_S\), large nuclei evolve on the substrate surface at the beginning of growth, having even larger capture radii for the impinging Ag particles. In the absence of a slit aperture, the particles approaching the substrate (Fig. 4.10(a)), at glancing angle \(\beta\) as well as at non-glancing angle \(\beta^*\), get caught by those large nuclei, before they reach the stable crystalline sites that would ideally be required for the growth of columnar structures. In such a condition, the arriving particles are even able to diffuse to otherwise shadowing overruled locations due to a higher deposition rate, broad angular distribution, and enhanced surface diffusion. In addition, with continuous deposition process these adatoms get buried by the following particles, leading to the formation of mountain-like structures.

In presence of a slit aperture, the flux collimation lowers the deposition rate \((r_a = 3.6\,\text{nm/min})\), while the adatoms reach the substrate surface under a defined angle of divergence \((\Delta\beta \approx 9\,^\circ\)).
other words, in the GLAD case the slit aperture prohibits incoming particles from reaching the substrate at an incidence angle less than approximately 77°, if $\beta \approx 86°$. Clearly, this results in a higher probability of an adatom, with enhanced diffusion capability at high temperatures, to diffuse along a growing rod or wire and, reach the top thereof before getting trapped and buried by the following adatoms, as sketched in Fig 4.10(b). According to Sears [184], low supersaturation, large mobility of the adatoms on the growing side of the nanorods, and a sufficient particle flux are important requirements for the continuous growth, which is in agreement with the experimentally observed results.

Previously, it has been demonstrated that metal adatoms get incorporated on the top of growing nanorods in the high temperature GLAD case [46, 47, 125], from where they can diffuse along the whisker sides, thus contributing to the whisker growth [184, 185]. Additionally, an increase in the substrate temperature enhances the adatom diffusion length not only for adatoms that get incorporated in whiskers from the top, but also of those that reach the substrate surface. Subsequently, this increases the capture radius of Ag nuclei already present there, and hence the size of the nuclei enhances. Some predominant grains with large particle capture lengths receive a large amount of adatoms, which, depending on the growth conditions, under certain circumstances might also contribute to the elongation of nanorods that evolve out of the seeds by diffusing along the whisker sides from bottom to top. Thus, grains with intermediate heights as well as long nanorods or nanowires can be found. If, however, those multifaceted grains with an appropriate crystal orientation receive particles which get incorporated continuously, they can attain local height maxima to become nanorods.

### 4.2.3 Substrate temperature influence on different substrates

At elevated substrate temperature, crystalline Ag whisker-like structures evolve only in the presence of the slit aperture. On pre-patterned substrates and under negligible surface diffusion, the presence of artificial seeds leads to the growth of periodic nanostructure arrays in comparison to the random growth on planar substrates. From previous reports [44, 45] it is known that on pre-patterned substrates an increased adatom mobility at high substrate temperature enhances the competitive growth mechanism between adjacent columns. In this subsection, growth of Ag films deposited on planar Si(100) substrates and on honeycomb-like patterned substrates ($D =$
200 and 780 nm) is discussed. Additionally, films deposited at high temperature with and without substrate rotation are compared.

Figures 4.11(a)-(f) show cross-sectional SEM micrographs of the films deposited at \( T_S = 350 \, ^\circ C \) in the presence of a collimation slit with continuous substrate rotation (left) and without substrate rotation (right). At RT, for \( t_{dep} = 140 \) min deposition time, the film accumulates a thickness of approximately 500 nm. However, at \( T_S = 350 \, ^\circ C \), no thickness value could be stated as the usual columnar appearance of the glancing angle deposited films cannot be observed. For the films deposited at elevated temperatures (\( T_S = 350 \, ^\circ C, 300 \, ^\circ C \)) both without substrate rotation and with substrate rotation, nanorods are found to grow independent of the direction of particle flux.

Figure 4.11: SEM cross-section of Ag GLAD films deposited on different types of substrate at \( T_S = 350 \, ^\circ C \) for \( t_{dep} = 140 \) min in the presence of a slit aperture with substrate rotation: (a), (c), (e) and without substrate rotation: (b), (d), and (f). Types of substrates used: Si(100), and Si(100) patterned with honeycomb-like arranged Al dots with pattern period \( D = 780 \) nm \( D = 200 \) nm.

In particular, for the films deposited with continuous substrate rotation (left), even though nanorods mostly grew in upright direction, some of the nanorods also grew making an acute angle with the substrate. On the other hand, GLAD films deposited without substrate rotation and under negligible surface diffusion conditions (\( T_S = RT \)) exhibit columnar nanostructures that evolve with a column tilt towards the direction of particle source [26]. However, it is worth noting that due to enhanced surface diffusion nanorods evolve independent of the direction of particle source as observable in Fig. 4.11(b, d, f) (white arrows show the direction of particle
flux). Moreover, few nanorods also grew in vertical direction or making an arbitrary angle not necessarily pointing towards the direction of particle flux.

The length of the nanorods and nanowires on both planar and patterned substrates is observed to vary between 1.8 µm and 4.0 µm for most of the whiskers, however, some of the nanorods are found to be rather long (>5 µm) in comparison to the STF thickness reached at $T_s = RT$ (accumulated film thickness ~ 500 nm). In general it was observed that a similarity in the thickness of the nanorods is detected and this thickness of the nanorods is maintained throughout the length. Most of the nanorods have a diameter between 300 nm and 500 nm, while the nanowires of equivalent lengths exhibit thicknesses of approximately 60 -120 nm.

The absence of any kind of pattern on the bare Si(100) for the adatoms impinging on the substrate leads to nucleation at random places. The governance of the self-shadowing mechanism is prominent at room temperature [26]. In contrast, on honeycomb-like patterned substrates nanorod growth adapts the periodicity of the underlying seed pattern at RT [77, 79, 80]. But at $T_s = 350 °C$, 300 °C no such periodicity is observed due to surface diffusion effects. The nanorod density at elevated substrate temperatures on bare Si(100) is observed to be higher, as against that on the pre-patterned honeycomb type substrates, and could be understood as an effect of high adatom surface diffusion associated with high substrate temperatures and absence of any kind of pre-patterning in the case of bare Si(100) substrates. For $D = 780$ nm, the first-nearest-neighbour\(^{12}\) seed is located at a distance of $d_1 \approx 450$ nm, while for $D = 200$ nm, the first-nearest-neighbour is situated at approximately $d_1 \approx 115$ nm. Therefore, more agglomerates and clusters of varied sizes and shapes are found around the Al-dots\(^{13}\) in both cases. However, nanorods and nanowires were found to grow on these patterned seeds as well as in void spaces available in between the patterned seeds (discussed in detail in 4.2.3). Clearly, the intermediate void space is larger for $D = 780$ nm, compared to $D = 200$ nm, raising the possibility to grow nanorods on the non-patterned area.

\(^{12}\) For honeycomb substrates three nearest neighbours are located at distances: $d_1 = D/\sqrt{3}$, $d_2 = D$ and $d_3 = 2d_1 = 2D/\sqrt{3}$ (where $D$ is nanosphere diameter).

\(^{13}\) Here, as pre-patterned substrates are patterned with Al dots ($h_s \approx 35$ nm), probable alloying of Ag and Al at concerned substrate temperatures might commence as Ag reacts with Al at rather low temperatures. However, as similar type of growth of nanorods was observed on both the substrates namely bare Si(100) substrate and pre-patterned substrate with Al dots, a possible influence of Ag-Al alloy formation has not been addressed in the current work.
4.2.4 Growth on honeycomb-like arrays: Influence of substrate temperature

A distinct growth behaviour can be observed on pre-patterned substrates at elevated substrate temperature conditions. Figures 4.12(a)-(d) show Ag films prepared with deposition time $t_{\text{dep}} = 140$ min on honeycomb-like patterned substrates ($D = 780$ nm) at $T_S = \text{RT}$ and $T_S = 350$ °C. At room temperature, the GLAD-inherent shadowing mechanism dominates the film growth and nanorods adapt the periodic seed arrangement, as visible in Figs. 4.12(a) and (c). For the given seed height and incidence angle, a shadowing length results being approximately $l \approx 500$ nm on the range of the nearest neighbour distance for the case of $D = 780$ nm. At RT, the surface diffusion of the adatoms is negligible, and most of the particles that impinge on the substrate get trapped by the seeds. Thus, the nanorods perfectly evolve on the Al seed patterns. Enhanced surface diffusion at $T_S = 350$ °C, on the other hand allows particles to diffuse through regions otherwise shadowed at RT, thus enhancing the possibility of increased inter-seed condensation. For instance, Fig. 4.12(b) shows a nanorod of length $\sim 2.4$ μm and thickness $\sim 360$ nm, grown on the void space in-between the artificial seeds. The existence of nanowires can be noticed on the right part of the same micrograph, with a wire diameter $\sim 20$ nm and a wire length of approximately 600 nm. Agglomerated clusters of various sizes are found around the nanorod, as visible from Fig 4.12(d). As the deposition time is increased, more and more particles are deposited on the substrate surface, which either get agglomerated around the pre-patterned seeds, or diffuse over the surface and contribute to the growth of inter-seed islands. Thus, grains of discrete sizes are found with no significant trace of pre-patternning as an effect of agglomeration around the artificial seeds and on the void space between the Al seeds.
The morphology of the film completely changes when the pre-patterning period is decreased \((D = 200 \text{ nm})\) at otherwise constant deposition parameters\(^{14}\). In this case, the shadowing length is much larger than the nearest neighbour distance \((l \approx 500 \text{ nm} >> d_1 \approx 115 \text{ nm})\), which leads to a loss of nanostructure periodicity as visible in Fig. 4.13(a) and (c). This can be understood from the fact that the nearest neighbouring seeds are located in a close proximity, and thus the competitive growth mode dominates \([72, 77]\) the nanorod evolution attributing the loss of periodicity. Further, the column number density and column diameter both are limited due to the column competition on pre-patterned substrate having considerably narrow periods \([72]\). Thus, columns do not grow separately, but merge together as the deposition goes on and are difficult to identify as separate entities. In contrast, at elevated substrate temperature enhanced adatom mobility leads to the growth of sub-micron length nanorods and loss of nanostructure periodicity. For instance, Fig. 4.13(b) shows a nanorod of approximate length 1.9 \(\mu\text{m}\) and approximate diameter of 470 nm possessing smooth facets, while the top-view (Fig. 4.13(d)) depicts multifaceted grains around the pre-patterned seeds.

In order to investigate the early evolution of the rods on pre-patterned substrates at elevated temperatures, the deposition time was decreased\(^{15}\) to \(t_{\text{dep}} = 28 \text{ min}\). Figures 4.14(a) and (b) show the growth of Ag nanostructures on honeycomb-like pre-patterned substrates \((D = 780 \text{ nm})\) at \(T_s = 350 \degree\text{C}\). Clearly, the effects of enhanced surface diffusion can be observed here: agglomerates of various sizes can be seen all over the sample.

\(^{14}\)\(T_s = RT\) and \(350 \degree\text{C}\), deposition time \(t_{\text{dep}} = 140 \text{ min}\).

\(^{15}\)Deposition time is reduced to one fifth of that of samples described in Figs. 4.12 and 4.13.
Moreover, large agglomerated clusters gather around the pre-patterned Al dots. It is found that nanorods also evolve in between the void spaces of the pre-patterned seeds, as marked in Fig. 4.14(a). On the contrary, in Fig. 4.14(b) it is shown that nanorods also evolve on pre-patterned seeds. This is a clear indication that, the patterning of the substrate does not necessarily govern the evolution of nanorods and wires. Moreover, nanorods not necessarily grow in each of the void spaces or on every pre-patterned seed point. As the deposition time increases, a larger amount of material is deposited in between and around the pre-patterned seeds, effectively increasing the overall structural density of the film.

### 4.2.5 Atypical growth and structural characteristics of nanorods

In the present study, collimation is found to be a critical prerequisite in order to grow Ag nanorods or nanowires having (sub)micron lengths, when the ion beam sputtering technique is used. The directional reliance governs the growth of nanostructures at \( T_S = RT \), where the self-shadowing mechanism is persistent and hence the growing columns tilt towards the direction of the source for non-rotated substrates [26]. On the contrary, at an increased substrate temperature of up to 300 °C and 350 °C the adatom diffusion overrides the GLAD inherent self-shadowing. As a consequence, the directional dependence of the incoming particle flux is suppressed, and nanorods grow in random directions on those crystal planes having complementing axial development. Figures 4.15(a)-(d) demonstrate such atypical-GLAD features observed on different substrates.

The directional diffusion of adatoms over the whisker-sides and incorporation on the top of the whisker is proposed to be the driving force for the elongation of whiskers [184, 185]. Moreover, especially at increased substrate temperatures, the surface diffusion lengths of these adatoms can be greater than the radius of the nanorods [47], which obviously can assist the growth dimension of nano-rods and -wires. Figure 4.15(a) depicts such an extremely long nanorod of length ~ 5.1
μm and diameter ~ 400 nm, grown at $T_S = 300 \, ^\circ C$ on a honeycomb-like pre-patterned substrate ($D = 780 \, nm$). At $T_S = RT$ and with the same deposition parameters, the film thickness accumulated to a thickness of approximately ~ 508 nm. Clearly, a significant amount of material is provided to the nanorod to grow up to 10 times in length in comparison to the film thickness at RT. Likewise, a nanowire of length of approximately 1.6 μm and diameter of approximately 50 nm is displayed in Fig. 4.15(b). This nanowire was observed to grow on a honeycomb-like pre-patterned substrate ($D = 780 \, nm$) without substrate rotation at $T_S = 350 \, ^\circ C$. Besides, it grows on a multifaceted grain of indefinite shape. Figures 4.15(c) and (d) show nanorods of length ~ 1.8 μm and ~ 2.1 μm grown at $T_S = 300 \, ^\circ C$ and 350 °C, respectively, on a bare Si(100) substrate. Even though these multifaceted nanorods are observed on the same substrate type with the same deposition conditions, the thicknesses of these nanorods vary quite significantly. In addition, Fig 4.15(d) depicts a sharp bend near the top of the nanorod, which might be attributed to crystal defects that led to a change in the growth direction.

The films deposited at higher temperatures under glancing angle conditions ($\beta = 86^\circ$), irrespective of the presence of a slit aperture, were observed to be polycrystalline and non-epitaxial, while the Ag films deposited at elevated temperatures demonstrated a higher degree of crystallinity, as analysed from XRD $\theta/2\theta$ measurements (Fig. 4.16 (a)). On the other hand, the films deposited at $T_S = RT$ exhibited (111) and (200) reflections. Concerning the mountain-like
structures that evolved in the absence of the slit aperture, the intensity of the (111) reflection is observed to be higher than that of the (200) reflection. On the contrary, a highly intense (200) reflection in comparison to the (111) reflection is detected for the nanorod samples grown under collimation geometry. However, no epitaxial growth is detected for GLAD-grown samples (\( \beta = 86^\circ \)), even though the film with Ag nanorods exhibited a higher intensity of the (200) reflection in comparison to the (111) reflection. Closer investigation of one of the nanorods of length ~1.25 \( \mu \text{m} \) and diameter ~200 nm deposited at \( T_S = 300 \, ^\circ \text{C} \) \( (t_{\text{dep}} = 60 \, \text{min}) \) (Fig. 4.16(b)) by TEM reveals that a twin plane exists along the nanorod axis. The selected area diffraction pattern (inset) illustrates \([2 \bar{1} 1]\) as the nanorod growth direction. Besides, a strongly excited diffraction pattern with relatively weak diffraction spots attributes the twin orientation domains within the nanorod.
4.3 Summary

_Growth of Ag thin films on native oxide covered Si(100) substrates_

- With ion beam sputter deposition Ag(200) epitaxial films can be realized on native oxide covered Si(100) substrates at elevated deposition temperatures. High energetic Ag sputtered particles impinging the substrate surface and high substrate temperature are observed to be essential parameters for the epitaxial Ag film growth.

- With increasing deposition temperatures from $T_S = RT$ to 300 °C, the intensity of the (200) x-ray reflection increased, while the intensity of the (111) reflection decreased. The lowest epitaxial growth temperature is observed to be 100 °C.

- The XRD (111) φ-scan of the Si(100) substrate demonstrated equidistant four peaks with extremely narrow FWHM, while the corresponding Ag(111) φ-scans of the film deposited at $T_S = 100 \, ^\circ C$ and 300 °C illustrated a single favourable in-plane orientation of (100) oriented Ag crystallites with four fold matching symmetry on Si(100) substrate.

- Ag{111} pole figures exhibited four distinct equidistant pole density maxima at $\chi \approx 55^\circ$, originated by the (200) oriented epitaxial Ag film, as well as four weak pole density maxima at $\chi \approx 16^\circ$ and eight at $\chi \approx 79^\circ$ correlated to 1st order twinning.

- With increasing deposition temperature the improving crystalline quality of the films was confirmed with Ag(200) rocking curve measurements indicating a narrowing mosaic distribution of crystallites combined with a decrease in the fraction of 1st order twins.

- In comparison, the Ag films deposited on HF rinsed Si(100), oxide layer free substrates exhibited a dominant (111) reflection and no epitaxial relationship with the underlying Si(100) substrate was observed, while the SEM analysis illustrated a non-uniform, very rough, and porous film topography.

- A considerable amount of oxygen content at the Ag/Si interface for epitaxially grown films suggested local-desorption of the native oxide layer.

_Temperature altered morphology of silver nanostructures_

- Under glancing angle deposition condition geometrical self-shadowing effects led to the evolution of columnar films at RT. With the exception of a larger column density for the aperture-free case, no significant differences were observed for the films deposited with and
without collimation slit. At elevated substrate temperatures an increase in the crystallinity of the Ag-GLAD films is seen, and the morphology of the films changed significantly. At \( T_S = 300 \) and \( 350 \) °C (\( T_S / T_M \approx 0.46 \) and 0.50, respectively) increased surface diffusion length of adatoms caused atypical growth depending upon particle flux collimation.

- In the absence of the collimation slit aperture, the impinging particles get trapped by early stage mounds formed on the substrate surface and are concealed by the subsequent incoming adatoms before they reach stable crystal sites that are required for the growth of columnar structures. Thus, islands of size of more than ~ 2 µm in length are observed in the aperture-free case.

- The particle flux collimation was observed to be an important requirement in order to grow single crystalline Ag nanorods and nanowires with ion beam sputter GLAD at elevated \( T_S \). As an effect of the collimation (\( \Delta \beta \approx 9^\circ \)), impinging particles that arrive under non-glancing angle conditions (\( \beta^* \)) are averted by the aperture, and adatoms under glancing angle (\( \beta \)) reach the substrate surface and are capable of contributing to the growth of nanorods before they are captured by the existing grains and are buried by the following impinging particles.

- The growth direction of the nanorods and nanowires was found to be independent of the direction of the particle flux. Nanorods and nanowires of varying lengths (1-4 µm) are found to grow on pre-patterned and un-patterned substrates. In few cases, nanorods of more than 5 µm in length evolved on the substrate. A higher density of nanorods was exhibited on the un-patterned substrates, which can be attributed to the absence of pre-patterned hillocks. The rod- and wire like growth on a pre-patterned substrate is not necessarily governed by the existence of the seeds, as nanorods were also found to grow on void spaces between the patterned seeds.
Chapter 5

Glancing angle deposition of Germanium

In this chapter, the growth of Ge nanostructures with ion beam sputter GLAD will be examined. Initially, the particular structure growth reliance on deposition conditions, deposition time, and substrate rotation at room temperature condition is discussed. Subsequently, the influence of substrate temperature $T_S$ on the growth of glancing angle deposited structures is evaluated. The high temperature-induced surface diffusion is believed to be counterproductive as against self-shadowing mechanism\(^\text{16}\) [104]. However, in recent years researchers have devoted considerable attention towards GLAD nanostructures deposited at elevated substrate temperatures in order to understand the diffusion-driven effects on the morphology. In the current study, however, the temperature altered morphology of Ge nanocolumns is studied with a specific attention towards column merging behavior, column density and structure diameters on planar and pre-patterned substrates.

In the later sub-sections, two substrate patterning methods are discussed and subsequent Ge GLAD growth on these templates is presented in detail considering the influence of inter-seed distances, seed heights and shadowing lengths. As described in Chapter 2.2, in the past several methods including nanosphere lithography (NSL) [13, 15, 44, 45, 59] or e-beam lithography [72-75] have been adapted for substrate pre-patterning and controlling the columnar morphology of GLAD nanostructures grown thereon. But the approaches discussed here demonstrate alternative methods to attain Si seeds on the substrate surface. Moreover, the growth on such Si patterned substrates can be optimized by adjusting the template dimensions. This method could be advantageous for obtaining crystalline nanostructures through controlled annealing and to retain distinct GLAD columnar morphologies.

More often numerous applications require crystalline nanostructures instead of amorphous ones that can, in principle, be obtained by depositing films at high substrate temperature. Post-deposition annealing could serve as an alternative method to realize crystalline Ge nanostructures with columnar morphologies [63-67]. Therefore, post-deposition thermal annealing of Ge

\(^{16}\)According to the Structure Zone Model surface diffusion becomes prominent once $T_S / T_M \geq 0.3$, where $T_M$ is the melting temperature of the material to be deposited.
nanostructures grown on planar and pre-patterned substrates in a continuous Ar-flow is studied in the final sub-section of this chapter. In particular, morphological changes induced by the annealing process on Ge nanostructures grown on planar and pre-patterned substrates are discussed for the temperature range $T_A = 300$-$800$ °C.

### 5.1 Ge-GLAD on planar substrates at RT

The deposition of Ge GLAD films discussed in this section was carried out with a slit aperture placed between target and substrate. In the presence of a slit aperture an opening of $15\pm3$ mm collimates the particle flux arriving at the substrate surface and restricts the minimum angle of incidence for the incoming particle flux with respect to the substrate normal to $77\pm3^\circ$, i.e. an angular divergence $\Delta \beta \approx 9^\circ$. Under these constant conditions ($T_S = RT$) the deposition rate at $\beta \approx 86^\circ$ amounted to $r_a = 3.4\pm 0.3$ nm/min.

The morphology of the growing structure depends on the ratio $\rho = r / \omega$ of deposition rate $r$ and rotational velocity $\omega$ as described in section 2.1.3. Independent of $\rho$ values, the growth of the structures commences on the seeds that are formed at the beginning of the growth process with an approximate seed-dimension within the range of $\approx 20$-$30$ nm [61, 115]. For a constant deposition rate $r_a = 3.4\pm 0.3$ nm/min, the $\rho$ value can adjusted for a continuous substrate rotation to form a vertical column-like morphology. Specifically, for such column-like structures formed under competitive growth conditions, the average column width $w$ and inter-column separation increases due to column extinction and column merging in the early stages of growth [6, 58, 104]. The self-shadowing effect favors predominant larger seeds to grow, while the growth of smaller seeds stops prematurely. Thus, the column number density is continuously reduced as deposition goes on as illustrated in Fig. 5.1.
To evaluate the scaling exponent $p$ of the scaling law $w \propto h^p$ (Eq. 2.5), the $w(h)$ data is plotted\textsuperscript{17} in Fig. 5.2(a). The obtained experimental values marginally diverge from the theoretically predicted range. According to the predictions [101] $p$ value should vary between 0.3 and 0.5, and decrease with increasing surface diffusion length. Here, it is observed that at $T_S = RT$, $p = 0.59 \pm 0.02$. The inconsistency between theoretically predicted $p$ and experimentally measured values can be explained with the following considerations. The $p$ values ($p \approx 18$ nm/rev) in the current experimental part are large when compared with published data [51, 101]. Secondly, even though an aperture is used to collimate the particle flux as an effect of the sputter deposition method, there will be a certain variance ($\Delta \beta \approx 9^\circ$) in the angular distribution of the particle flux arriving at the substrate surface. Therefore, non-glancing angle $\beta^*$ values can certainly attributes to the fluctuation in the exponent value above $p = 0.5$ [51].

Figure 5.2(b) shows inter-column separation $\lambda$ shifts from $\lambda \approx 45$ nm to $\lambda \approx 158$ nm in the power spectral density plots as deposition time increased from $t_{dep} = 20$ min to $t_{dep} = 200$ min, respectively. Evidently, with increasing structure height, the lateral size of the growing structures increased (from the range of ~20-30 nm) while inter-column separation gets amplified.

\textsuperscript{17} The $w(h)$ data is calculated over the average value of 6-10 columns and fitted to the scaling law.
In general, different substrate rotation schemes [6] allow growth of various types of isolated, free-standing nanostructures under glancing angle deposition conditions. For a constant deposition rate $r_a$, the substrate rotational velocity $\omega$ can be adjusted to obtain different $\rho$ values for the growth of spiral-, screw- and column-like morphological structures, as depicted in Fig. 5.3. In this case, for a slow substrate rotation with $\rho \geq 100$ nm/min spiral-like morphology is observed, while for a fast substrate rotation and with $\rho \leq 20$ nm/min column-like morphology is attained. For an intermediate $\rho$ value, screw-like structures can be obtained that typically evolve from the isolated spiral-likes structures. However, it is observed that this shape distinction holds only until the critical structure merging height is reached [61]. It was found that for Si nanostructures deposited with ion beam sputter deposition this broad classification is valid only for structure heights $h \leq 800$ nm [58]. In the case of Ge nanostructures the critical structure merging height is detected to be $h \leq 700$ nm.

In comparison to the continuous substrate rotation, $n$-fold structures can be grown by stepwise substrate rotation. A two-fold 5 arm chevron structure was deposited on a planar Si(100) substrate by keeping the substrate stationary while depositing each arm, and then rapidly rotating the substrate azimuthally through 180° to grow each subsequent arm. Figure 5.4 displays such a chevron structure grown by stepwise substrate rotation.
5.2 Influence of the substrate temperature

In this section, the influence of substrate temperature $T_S$ on the growth of Ge nanostructures deposited with glancing angle deposition is discussed. For evaluation, the deposition of Ge GLAD films was carried out on planar Si(100) and substrates patterned with one monolayer of SiO$_2$ nanospheres (diameter $D = 351$ nm) at different substrate temperatures ranging from $RT \leq T_S \leq 350 \degree C$. In the presence of a slit aperture, the deposition rate (at $\beta = 86\degree$) amounted to $r_a = 3.1 \pm 0.2$ nm/min. For planar substrates, the deposition time was kept constant at $t_{dep} = 140$ min. On patterned substrate the deposition was carried out for two different durations $t_{dep} = 157$ min and $t_{dep} = 218$ min.

5.2.1 Effect of $T_S$ on planar substrates

Under shadowing deposition conditions at RT clusters of non-uniform sizes distribute randomly in the early stages of mound formation and serve as seeds for the growing nanostructure on planar substrates. These nanostructures tend to broaden with increasing height [101] and compete in growth, which leads to the extinction of some structures [4, 6]. The inherent columnar morphology of Ge-GLAD films is strongly influenced by the substrate temperature due to enhanced surface diffusion. At $T_S = RT$, the film accumulates an overall thickness of $h(RT) = 443$ nm (Fig. 5(a)-(b)). The typical columnar appearance of the film remained persistent until $T_S = 100 \degree C$. However, for the films deposited at $T_S = 150 \degree C$, temperature induced film densification is observed to modify the film morphology, where numerous fiber-like structures evolved.
From Fig. 5.5(c) and (d), it is distinctly noticeable that the single columns are constituted of many thin fibers of width $w \approx 20-30$ nm. Hence, the individual existence of a single column is complicated to trace. However, these fibers are so densely packed that they bunch together to transpire as a single column. Moreover, it is evident that some of the thin fibers do not necessarily start evolving from the base of the substrate, but the growth also commenced at an intermediate stage of the thin film.

The densification of the Ge-GLAD films gets even more pronounced at $T_s = 200$ °C, where the films start turning into crystalline state. Although, the substrate was rotated continuously with $\omega = 0.2$ rev/min receiving an even particle flux from all directions, columns essentially did not grow in exact vertical direction, but grew in the void space in the peripheral region available between two successive growing seeds, where an increased column number density can be noticed (Fig. 5.6(a) and (b)).

At an elevated substrate temperature adatoms diffuse over the surface for larger distance before they eventually contribute to the growing structures. Due to this increased adatom mobility otherwise shadowed void spaces are filled with diffusing adatoms [45] that induces intra-columnar growth. The fibrous growth of the nanocolumns observed at $T_s = 150$ °C vanished at $T_s = 200$ °C; however, with a close inspection and comparison of Fig. 5.5(d) and 5.6(b), it appears as if the fibers (at 150 °C) merge and coalesce to emerge as an individual (at 200 °C). As a consequence, the column number density increased by a large quantity.

Figure 5.6: Cross-sectional (left) and top view (right) micrographs of Ge nanocolumns ($t_{dep} = 140$ min) prepared on Si(100) substrates at different substrate temperatures $T_s$. (a) and (b): $T_s = 200$ °C, (c) and (d): $T_s = 300$ °C.
The film growth at $T_S = 300$ °C is strongly affected by the diffusion-driven mass transport, where crystal facets emerged (Fig. 5.6(c) and (d)). Further increase in substrate temperature to $T_S = 340$ °C ($T_S / T_M \approx 0.51$) resulted in the merging and coalescing of neighbouring columns suggesting the possible influence of bulk diffusion.

The trends observed in column number density $n$ and average column width $w$ as a function of increasing $T_S$ are plotted in Fig. 5.8(a). At RT, even separation of columns results in an average column width $w = 220 \pm 8$ nm. Although at $T_S = 75$ °C and 100 °C ($T_S / T_M \approx 0.28$ and 0.30, respectively), a low adatom mobility condition is applicable, the column width increased to $w = 243 \pm 5$ nm and $283 \pm 2$ nm, respectively. At $T_S = 150$ °C ($T_S / T_M > 0.3$), surface diffusion starts influencing the film morphology [82, 83, 124]. In other words, on the contrary to negligible surface diffusion at RT, where impinging particles stick to the growing columns where they land, diffusion-driven mass transport for $T_S / T_M \geq 0.3$ allows impinging particles to travel some distance along column sides after attachment. Hence, for closely packed fibers observed at $T_S =$

\[\text{Figure 5.7: Cross-sectional (a) and top view (b) micrographs of Ge nanocolumns deposited on Si(100) substrates at substrate temperature of } T_S = 340 \text{ °C}\]

\[\text{Figure 5.8: Trends followed in column width } w \text{ and column number density } n \text{ (a) as well as overall film height (b) as a function of the substrate temperature } T_S.\]

\[\text{The homologous temperature } T_S / T_M \text{ is expressed in Kelvin scale. The melting temperature } T_M \text{ of Ge is 1210 K.}\]
150 °C the film density increases. Subsequently, the column number density reduces to 34% of its initial value from RT to 150 °C. The intra-columnar growth observed at \( T_S = 200 \) °C is responsible for the sudden increase in the column number density as much as four times than is observed at \( T_S = 150 \) °C. As a consequence, the average column width decreases and reaches a minimum. At further elevated temperature \( T_S = 250 \) °C, lesser dominance of the intra-columnar growth enhances the average column width. This trend continues and the column width broadens from \( w(200 \) °C\) = 186 ± 26 nm\) to \( w(340 \) °C\) = 396 ± 24 nm\).

With an increase in \( T_S \) from RT to 200 °C the overall film thickness was reduced. The changes in the overall film thickness \( h \) for \( T_S \) ranging from RT to 340 °C are plotted in Fig. 5.8(b). Temperature induced densification caused a decrease in the overall film thickness from \( h(\text{RT}) = 443 \) nm to \( h(200 \) °C\) = 313 nm. In contrast, once the film turned crystalline \( (T_S > 200 \) °C\), the overall film height \( h \) increased to \( h(340 \) °C\) = 382 nm. This effect is a consequence of the improvement in the crystalline quality of the film above 200 °C. In other words, the film overall film thickness increased as a result of increased shadowing correlated with crystal faceting and decreased layer density, which emerges because of enhanced column competition.

In order to investigate the sudden increment in column number density, Ge films were deposited at \( T_S = 200 \) °C with decreased deposition time \( (t_{dep} = 20 \text{ min}) \) to examine the influence of the early stage seed layer on the overall film growth. Figure 5.9 (a) shows structures of height 48 ± 3 nm grown at \( T_S = 200 \) °C. At an elevated substrate temperature adatoms diffuse over the substrate surface for larger distance before they contribute to the growing structures. Hence, intra-columnar void spaces are filled with diffusing adatoms [45]. As a consequence, the average
size of some of the structures enhances and the surface mound density decreases. The early growth mounds can be evaluated to be of two different sizes as marked with solid circles and dashed circles in Fig. 5.9 (a) having average widths of 92 ± 7 nm and 41 ± 11 nm, respectively. Therefore, due to the bimodal size distribution of early stage seeds and increased mound density, emerging columns exhibit a broad width distribution and an increase in column number density. In contrast, the film deposited at $T_s = 340$ °C (Fig. 5.9(b)) to compare the nucleation behaviour (thickness $h \approx 68 \pm 8$ nm) demonstrated merging and coalescing of emergent mounds as a result of strong surface diffusion. As the growth continues, due to competitive growth mechanism, the mounds receive a slightly higher particle flux and benefit from surplus adatoms that diffuse after attachment [44, 45, 61]. Hence, further growth with impinging adatoms causes broadening and a decrease in column number density [45, 61].

The amorphous nature of the fiber-like structures at $T_s = 150$ °C is revealed by the bright field TEM micrograph (Fig. 5.10(a)). As described earlier, some fibers grow at the intermediate stage of column growth and identification of a single column becomes complicated to trace. In the dark field TEM image (Fig. 5.10 (b)) the growth at $T_s = 340$ °C of a large crystallite within the broad column is apparent. Here, the thickness of the initial seed layer measured ~ 80-90 nm, which is in good agreement with the measurements discussed earlier (Fig. 5.9(b)). Moreover, the bases of those successive nanocolumns are not separate, but are inter-connected indicating layer-plus-island growth [186-189].
5.2.2 SiO\textsubscript{2} nanosphere patterned substrates

In order to assess the influence of substrate patterning on the overall growth morphology of Ge nanocolumns at different substrate temperatures, Ge nanocolumns were deposited on the SiO\textsubscript{2} nanosphere patterned substrates\textsuperscript{19} (\(D = 351\) nm) for \(t_{\text{dep}} = 157\) and \(218\) min. Figures 5.11 (a)-(f) show top-view and cross-sectional micrographs of Ge nanocolumns deposited on SiO\textsubscript{2} patterned substrates for \(T_s = \text{RT}, 200^\circ\text{C}\) and \(340^\circ\text{C}\), respectively. The morphology of GLAD-grown Ge nanocolumns on SiO\textsubscript{2} patterned substrates is strongly influenced by the substrate temperature. The temperature induced alterations in the nanocolumn dimensions are illustrated in Table 5.1. At RT, with deposition time \(t_{\text{dep}} = 218\) min nanocolumns accumulated to a height of \(h_{\text{tot}} \approx 972\) nm. At RT negligible surface diffusion resulted in the growth of uniform nanorods with moderate broadening. On the patterned substrates with spheres of size \(D = 351\) nm, the Ge nanocolumns attained an average column width \(w = 487 \pm 23\) nm (Fig. 5.11 (a) and (b)). But the increased adatom mobility \([82, 124]\) at \(T_s = 200^\circ\text{C}\) provoked strong column competition \([44, 45, 113]\). For planar substrates, as substrate temperature was increased to \(T_s = 200^\circ\text{C}\), the morphology of the film was prominently affected by intra-columnar growth as intra-columnar void spaces are filled by diffusing adatoms \([45]\). Identical growth is detected for the patterned substrates, where column growth on each SiO\textsubscript{2} sphere is comprised of multiple sub-branches.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>(T_s) (°C)</th>
<th>(h_{\text{tot}}) (nm)</th>
<th>(h) (nm)</th>
<th>(w) (nm)</th>
<th>(h_0) (nm)</th>
<th>(w_0) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>157</td>
<td>RT</td>
<td>812</td>
<td>551</td>
<td>480±18</td>
<td>495</td>
<td>216±19</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>632</td>
<td>402</td>
<td>431±33</td>
<td>348</td>
<td>179±27</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>677</td>
<td>424</td>
<td>450±29</td>
<td>389</td>
<td>392±21</td>
</tr>
<tr>
<td>218</td>
<td>RT</td>
<td>972</td>
<td>704</td>
<td>487±23</td>
<td>670</td>
<td>231±24</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>941</td>
<td>512</td>
<td>410±47</td>
<td>527</td>
<td>187±37</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>897</td>
<td>638</td>
<td>507±39</td>
<td>602</td>
<td>411±34</td>
</tr>
</tbody>
</table>

Table 5.1: Influence of substrate temperature \(T_s\) on total structure height \(h_{\text{tot}}\), column height \(h\), average column width \(w\) of the nanocolumns grown on SiO\textsubscript{2} patterned substrates for different deposition durations \(t_{\text{dep}} = 157\) and \(218\) min. For comparison, effects of substrate temperature on the height of Ge columns on planar substrates \(h_0\), average column diameter on planar substrates \(w_0\) for similar deposition time and deposition conditions.

\textsuperscript{19} For comparison, planar Si(100) substrates were also mounted along with pre-patterned substrates on the substrate holder deposition and subsequently column characteristics on both types were studied.
5.2 Influence of the substrate temperature

The effect is attributed to diffusion-driven mass transport due to the elevated substrate temperature \( T_S / T_M \approx 0.34 \). The average column width and column height decreased to \( w = 410 \pm 47 \) nm and \( h_{\text{tot}} = 742 \) nm, respectively. As films grown above 200 °C were found to be crystalline (XRD measurements discussed in the next paragraph), a further increased substrate temperature \( T_S = 340 \) °C induced strong coalescing and merging of neighbouring nanorods (see Fig. 5.11(e) and (f)). Additionally, the average column width enlarged to \( w = 507 \pm 39 \) nm and the total height of these nanorods increased from \( h_{\text{tot}}(200 \) °C\( ) = 742 \) nm to \( h_{\text{tot}}(340 \) °C\( ) = 897 \) nm. The transitions of

Figure 5.11 Top-view (left) and cross-sectional (right) SEM micrographs of Ge nanocolumns deposited on Si(111) substrates patterned with SiO\(_2\) nanospheres (\( D = 351 \) nm) at different substrate temperatures \( T_S \). (a) and (b): \( T_S = RT\); (c) and (d): \( T_S = 200 \) °C; and (e) and (f): \( T_S = 340 \) °C.
Glancing angle deposition of Germanium

column width and height with respect to the substrate temperature (above 200 °C) on patterned substrates are in agreement with the growth behaviour noticed for the planar Si(100) substrates. Additionally, on patterned substrates an increased adatom mobility at elevated growth temperatures caused an identical morphology modification, that was noticed on the planar Si(100) substrates. The enhanced adatom mobility induced effects are not averted by the nanosphere substrate patterning. Therefore, it can be concluded that the temperature induced growth modifications of Ge nanocolumns are independent of substrate type.

Crystal orientation studies

X-ray diffraction diagrams of Ge GLAD films deposited on planar Si(100) are depicted in Fig. 5.12. The samples deposited at $T_S \geq 200 \, ^\circ C$ were found to be polycrystalline\textsuperscript{20} exhibiting (111), (220) and (311) reflections. It can be clearly seen that the (111) reflection dominates at $T_S = 200 \, ^\circ C$, while the presence of the less intense (220) and (311) reflections can be noticed indicating preferential growth in (111) orientation. XRD measurements show an increased intensity of the (220) reflection as the substrate temperature increased from $T_S = 200 \, ^\circ C$ to 340 °C. For $T_S = 200 \, ^\circ C$ an intensity ratio $I_{(220)} / I_{(111)}$ of 0.16 was observed, while for $T_S = 340 \, ^\circ C$ this intensity ratio increased to 1.54. On the other hand, for $T_S = 200 \, ^\circ C$ the intensity ratio $I_{(220)} / I_{(311)}$ of 1.08 was observed, while for $T_S = 340 \, ^\circ C$ this intensity ratio increased to 3.30 signifying preferential shift to (220) orientation.

Likewise, films were deposited ($t_{dep} = 20$ min, thickness at RT: $h \approx 500 \, \text{nm}$) under normal deposition angle ($\beta = 0^\circ$) at elevated substrate temperatures to compare the crystallinity of the as-grown films with GLAD-grown films. Identically the samples deposited at $T_S \geq 200 \, ^\circ C$ were found to be

\textsuperscript{20} XRD measurements on SiO$_2$ patterned substrates are also in agreement with the results obtained on planar Si(100) substrates.
5.2 Influence of the substrate temperature

polycrystalline exhibiting (111), (220) and (311) reflections, and a change of orientation from (111) at \( T_S = 200 \, ^\circ C \) to (220) at \( T_S = 340 \, ^\circ C \) was noticed. For \( T_S = 200 \, ^\circ C \) the intensity ratio \( I_{(220)}/I_{(111)} \) of 0.68 was observed, while for \( T_S = 340 \, ^\circ C \) the intensity ratio increased to 1.07.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>GLAD films</th>
<th>Compact films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( I_{(220)}/I_{(111)} )</td>
<td>( I_{(220)}/I_{(311)} )</td>
</tr>
<tr>
<td>200</td>
<td>0.16</td>
<td>1.08</td>
</tr>
<tr>
<td>250</td>
<td>1.02</td>
<td>1.12</td>
</tr>
<tr>
<td>300</td>
<td>1.28</td>
<td>2.73</td>
</tr>
<tr>
<td>340</td>
<td>1.54</td>
<td>3.30</td>
</tr>
</tbody>
</table>

Table 5.2: Intensity ratio of \( I_{(220)}/I_{(111)} \) and \( I_{(220)}/I_{(311)} \) for GLAD and compact films deposited at elevated substrate temperature on planar Si(100) substrate.

Hence, an increased substrate temperature causes growth with preferential (220) orientation. Even though the (111) planes are lowest surface energy planes [190, 191], the final texture of the film also relies upon growth of lower strain energy planes [167]. In the case of Ge films, (220) planes are lower strain energy planes as compared to (111) planes [167]. Additionally, the orientation of the film is strongly influenced by the deposition conditions; while relative low temperature growth leads to (111) orientation and high temperature growth results in preferential (220) orientation [192]. Thus, with diffusion constrained surface kinetics relatively low temperature crystal growth and consequent strains induced in the Ge films could also attribute the growth in (220) as a preferential orientation.
5.3 Growth on Si patterned honeycomb template

Till date several patterning methods have been adapted for substrate patterning and the use of tetragonal template is well described in the GLAD-literature [5, 72-74, 106, 107, 109, 110, 193-195]. In comparison, growth on NSL patterned honeycomb-like arrays [77-81] is relatively less examined in terms of effects of asymmetric shadowing on the film morphology. Hence, in this section growth on such honeycomb-like template is studied with a particular focus on the influence of seed heights and inter-seed distances on the growth process. For this purpose, reactive ion beam etching (RIBE) was performed to obtain seeds of various heights by transferring a Au dot pattern to a Si seed pattern on Si(111) substrates. In addition, the patterning process was performed on three different template periods \( D = 508, 780, \) and 1390 nm, where \( D \) is nanosphere diameter) to inspect the effects on the nanorod evolution. In the following section, morphological shape variations, which are introduced through the influences of pattern arrangement and seed dimension on Ge nanorods grown on both types of honeycomb substrates containing Au dots and RIBE templates, are discussed.

All the experiments were done using a slit aperture placed between target and substrate and the deposition angle was adjusted to \( \beta = 86^\circ \). In the presence of the slit aperture the deposition rate measured \( r_a \approx 3.4\pm0.3 \) nm/min. During the deposition of Ge nanorods the substrates were rotated continuously at \( \omega = 0.2 \) rev/min to form vertical nanorods. The deposition on all template periods was carried out for \( t_{dep} = 133 \) min and 210 min.

5.3.1 Honeycomb pattern transfer by RIBE

Before performing GLAD, a three step patterning process was used to achieve Si honeycomb arrays on Si substrates as described in section 3.2. Figure 5.13(a) depicts a top-view SEM micrograph of a Au dot template obtained before the reactive ion beam etching process. Two different etching durations of 7 and 9 min resulted in different Si seed heights.
Even though Au dots with the same nominal thickness of $h_S = 100 \text{ nm}$ for each template period were used in the RIBE process, dissimilar volumes of the Au dots on the original template are responsible for the different seed heights for a same etching time. Due to a higher etching rate of Au as compared to Si, the honeycomb pattern is transferred onto the substrate exhibiting self-elevated Si dots on the Si substrates. The subsequently formed honeycomb pattern with Si dots is shown in Fig. 5.13(b). Table 5.3 summarizes the average seed heights formed after 7 and 9 min etching duration determined by AFM and SEM measurements.

<table>
<thead>
<tr>
<th>RIBE duration</th>
<th>Average seed height $h_S$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D = 508 \text{ nm}$</td>
</tr>
<tr>
<td>7 min</td>
<td>30</td>
</tr>
<tr>
<td>9 min</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 5.3: Average seed heights $h_S$ of Si dots formed after RIBE process of durations 7 and 9 min. $D$ is the nanosphere diameter.

### 5.3.2 Ge nanorod growth on Au patterned NSL template

As already explained, in a honeycomb-like arrangement each seed has three first-nearest neighbors at a distance $d_1 = D/\sqrt{3}$, six second-nearest neighbors at a distance $d_2 = D$ and three third-nearest neighbors with a distance $d_3 = 2d_1 = 2D/\sqrt{3}$ (where $D$ is nanosphere diameter) which influence the shape and dimension of the subsequently thereon grown nanorods [79, 81]. Sputtered Ge particles that arrive at the substrate surface with glancing angle ($\beta = 86^\circ$) are captured by the Au hillocks (Fig. 5.14 (a)), resulting in growth at each seed location while depleting the growth over the inter-seed shadowed flat surface. Figures 5.14(b)-(d) show top-view micrographs of Ge nanorods deposited on Au honeycomb substrates, with pattern period $D = 508 \text{ nm}$, 780 nm and 1390 nm, respectively. As is clearly noticeable, the Au dots ($h_S = 100 \text{ nm}$) serve as growth seeds for Ge nanorods that adapt the honeycomb-like periodic arrangement. For a Au seed height of $h_S = 100 \text{ nm}$, the shadowing length for the deposition angle of $\beta = 86^\circ$ becomes $l \approx 1430 \text{ nm}$. For $D = 508 \text{ nm}$, a triangular shape of the nanorods is a result of nearest neighbors that are located at $d_1$, $d_2$ and $d_3$ distances. Likewise for honeycomb $D = 780 \text{ nm}$, $l > d_2$ and $l > d_3$ prohibited a supplementary particle flux from the directions of $d_2$ and $d_3$ seeds resulting in triangular shaped nanorods with nearly curved edges.
A significant difference could be noticed in the case of the honeycomb pattern with $D = 1390$ nm (Fig. 5.14(d)), where the shape of the nanorods become almost hexagonal. This effect could be attributed to the additional particle flux arriving from the direction of $d_3$ neighboring seeds and increased inter-seed growth, which resulted in flattening of pikes. Here, as $d_3 > l$, three third-nearest neighbors located at distance $d_3 \approx 1604$ nm ($l \approx 1430$ nm, $h_S = 100$ nm) are insufficient to shadow the entire inter-seed space.

For GLAD-grown nanostructures with continuously rotating quadratic pre-patterned substrates with distinct seed period $d$, the nanorod radius $R_{sat}$ obeys a power law $R_{sat} \sim d^q$, where $q$ is a growth exponent [116]. However, for the rotationally asymmetric, complex honeycomb-like pattern, nearest neighbors $d_1$, $d_2$ and $d_3$ determine the shape and diameter of the growing structures. In the case of $D = 508$ nm and 780 nm, as $d_2 > d_1$ and $d_3 > d_1$ the nanorod growth
5.3 Growth on Si patterned honeycomb template

rapidly saturates in direction of each \( d_1 \) neighboring seeds demonstrating flat sides and forming pikes in \( d_2 \) of triangular shaped nanorods [79].

<table>
<thead>
<tr>
<th>Honeycomb substrate type</th>
<th>Nanorod width ( w ) [nm]</th>
<th>Nanorod height ( h ) [nm]</th>
<th>Nanorod aspect ratio ( h/w )</th>
<th>Inter-seed growth ( f ) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au dot</td>
<td>508</td>
<td>297±14</td>
<td>522</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>358±53</td>
<td>517</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>1390</td>
<td>650±18</td>
<td>521</td>
<td>0.80</td>
</tr>
<tr>
<td>RIBE 9 min</td>
<td>508</td>
<td>299±19</td>
<td>462</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>370±25</td>
<td>480</td>
<td>1.29</td>
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<td></td>
<td>1390</td>
<td>627±28</td>
<td>485</td>
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<td>RIBE 7 min</td>
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<td>780</td>
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</tr>
<tr>
<td></td>
<td>1390</td>
<td>590±39</td>
<td>480</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Table 5.4: Characteristics of Ge nanorod honeycomb arrays grown on different templates \( t_{dep} = 133 \) min.

But for \( D = 1390 \) nm, \( d_2 > d_1 \) and \( d_3 > d_1 \) nanostructures formed three flat sides in \( d_1 \) directions, while \( d_3 > l \) and subsequently increased inter-seed growth leads to the flattening of three more sides in \( d_3 \) direction. In other words, \( d_3 > l \) asserted additional particle flux from \( d_3 \) direction and thus corresponding seed benefited with a surplus amount of particle flux, causing growth in otherwise shadowing overruled direction. On the other hand, enhanced inter-seed condensation from \( f \approx 47 \pm 5 \) nm \( (D = 508 \) nm) to \( f \approx 140 \pm 20 \) nm \( (D = 1390 \) nm) induces growth saturation and flattening of the growing nanorods in \( d_3 \) direction due to self-undesired shadowing effect of inter-seed condensation. As a result nanorods attain almost a hexagonal shape.

In addition, when the template period was increased from \( D = 508 \) nm to \( D = 1390 \) nm, the average nanorod width increased from \( w \approx 297\pm 14 \) nm to \( w \approx 650\pm 18 \) nm, respectively. Thus, it was observed that the nanorod diameter increases with an increase in template period [77]. Additionally, the aspect ratio of the nanorods decreased from 1.75 to 0.81 for \( D = 508 \) to \( D = 1390 \) nm, respectively (see Table 5.4).

5.3.3 Growth on Si patterned RIBE templates

The pattern transfer process to gain Si dots on Si substrates was realized by the RIBE method and subsequent Ge deposition on all templates was carried out for \( t_{dep} = 133 \) min and 210 min. Table 5.3 summarizes the average seed heights formed after 7 and 9 min etching duration.
Figures 5.15(a)-(f) show top-view and cross-sectional micrographs of Ge nanorods grown on 9 min etched RIBE templates \((t_{\text{dep}} = 133 \text{ min})\). Here, the Si hillocks act as growth seeds to form a honeycomb-like nanorod array. Those changes in the shape and dimension of the nanorods observed on different Au dot honeycomb arrays discussed earlier (section 5.3.2) are also observed on RIBE templates.

As summarized in Table 5.3, for \(D = 508 \text{ nm}\) a seed height \(h_S \approx 40 \text{ nm}\) achieved after 9 min etching can sufficiently shadow\(^{21}\) the inter-seed space as \(d_3 > l\). Additionally, \(d_2 > d_1\) and \(d_3 > d_1\) assure early saturation in \(d_1\) direction resulting in triangular shape of nanorods as illustrated in Fig. 5.15(a) and (b). Identical growth characteristics are observed for Ge nanorods grown on 7 min etched template, where \(h_S \approx 30 \text{ nm}\) adequately depletes inter-seed condensation. Likewise, for RIBE honeycomb \(D = 780 \text{ nm}\) (Fig.5.15 (c) and (d)), growth of Ge nanorods follow the periodic Si seed arrangement. Moreover, with a close inspection of Fig. 5.15(d), a Si seed of height \(\approx 50 \text{ nm}\) can be noticed beneath the Ge nanorod. Here, seeds located in \(d_2\) directions \((l \approx 715 \text{ nm})\) just adequately shadowed inter-seed spaces in \(d_2\) direction \((d_2 \approx 780 \text{ nm})\). But \(d_3 \approx 900 \text{ nm}\) caused greater inter-seed growth and further “cured” pikes of the nanorods. A consistent growth pattern of triangular shaped nanorods with curved edges and amplified inter-seed growth, attributed to surplus particle flux from \(d_2\) and \(d_3\) directions, were observed for 7 min etched RIBE template \((h_S \approx 40 \text{ nm})\).

For the RIBE honeycomb pattern with \(D = 1390 \text{ nm}\), a significant difference in the shape of nanorods was noticed (Fig. 5.15(e) and (f)). From the top-view micrograph a hexagonal shape of the nanorods could be noticed. Here, 9 min etching provided a seed height \(h_s \approx 65 \text{ nm}\) and subsequently shadowing length of \(l \approx 929 \text{ nm}\). As a consequence, additional particle flux can reach each growing nanorod from \(d_2\) and \(d_3\) direction as \(d_2 > l\) and \(d_3 > l\). Hence, the shape of nanorods changed from a triangular shape (observed for \(D = 508 \text{ nm}\) and \(D = 780 \text{ nm}\)) and attained nearly a hexagonal shape for \(D = 1390 \text{ nm}\). For some nanorods the shape roughly resembled circular rather than hexagonal. This could be due to slight variations in shape and size of adjacent seeds and corresponding nanorods.

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\(^{21}\) The shadowing length for the seeds of height \(h\) and deposition angle \(\beta = 86^\circ\) is given by \(l \approx h_S \cdot \tan (86^\circ)\)
5.3 Growth on Si patterned honeycomb template

Fig. 5.15 depicts a Si seed (~ 65 nm) formed after the RIBE process which can be noticed beneath the nanorod. Thus, obvious differences in subsequent nanorod growth and dimensions could be observed. It is evident that the seed height $h_s$, seed size and pattern period $D$ strongly influence the growth and shape of the nanorods. As the pattern period increased from $D = 508$ nm to 1390 nm, the average nanorod width also increased from $w \approx 299 \pm 19$ nm to $627 \pm 18$ nm, respectively. Hence, scaling up of nanorods is nearly proportional to the nanosphere diameter $D$, which is in good agreement with the previously reported studies [77, 79]. Nonetheless, the distinctions in growth conditions (including deposition method, deposition angle, growth rate,
substrate rotation) and intrinsic material properties would influence the scaling of nanorods. Furthermore, due to inadequate shadowing of Si hillocks, inter-seed condensation increased from $f \approx 80 \pm 18$ nm ($D = 508$ nm) to $f \approx 225 \pm 35$ nm ($D = 1390$ nm) and the subsequently shape of the nanorod changed and broadened from triangular to almost hexagonal with increasing pattern period $D$. Comparable results were seen in the case of 7 min etched templates. The trends concerning average column width $w$, inter-seed growth height $f$ and total height of the nanorods observed for Au patterned substrates and RIBE templates are summarized in Table 5.4.

**5.3.4 Inter-seed growth dependent morphological variation on enlarged pattern period**

To understand the close-to-hexagonal shape evolution of nanorods on the honeycomb-like template on an enlarged pattern period, influences of seed height, inter-seed distance and the effects on the shadowing mechanism needs to be inspected in detail. For instance, if Ge nanostructures deposited on the honeycomb pattern with $D = 1390$ nm with Au dots and RIBE templates etched for 9 min and 7 min are compared (Fig. 5.16 (a)-(c)) the growth differences on enlarged pattern templates can be examined. Thus, the morphological variation should be evaluated on the basis of seed heights and resulting shadowing lengths.

The complex geometry due to neighboring seeds located at three different distances affirms an asymmetric shadowing effect. As described earlier, each Au dot ($h_s \approx 100$ nm) effectively shadowed the inter-seed space resulting in comparatively lower inter-seed condensation for $D =$
5.3 Growth on Si patterned honeycomb template

508 nm and $D = 780$ nm. But, for the Au honeycomb pattern with $D = 1390$ nm, the conditions $l > d_2$ and $l < d_3$ result in each growing nanorod benefiting from the surplus particle flux from $d_3$ direction. For RIBE templates, 7 min and 9 min etching durations produced seed heights of $h_s \approx 50$ nm and 65 nm, respectively. Consequently, respective shadowing lengths $l$ are also insufficient to deplete the inter-seed growth. Even though $d_2 > d_1$ and $d_3 > d_1$ assured early saturation in $d_1$ direction [79], the surplus particle flux reached the growing nanorods from $d_2$ and $d_3$ directions ($d_2 > l$ and $d_3 > l$). For 7 min etched RIBE template (Fig.5.16(c)), particle flux reaching each nanorod from $d_2$ and $d_3$ directions is larger than for the 9 min etched RIBE template (Fig. 5.16(b)). Evidently, the shape of the nanorods grown on the 7 min etched template tends to a comparable circular cross-section. As summarized in Table 5.4, with decreasing seed height from $h_s \approx 100$ nm to 50 nm, the average nanorod width decreased from $w \approx 650 \pm 18$ nm to $590 \pm 39$ nm and the inter-seed condensation increased from $f = 140 \pm 28$ nm to $255 \pm 52$ nm, respectively. Effectively, increased inter-seed condensation provoked unwarranted shadowing and as a consequence nanorod growth in $d_3$ direction saturated and flattening of pikes resulted in nearly hexagonal shape of the nanorods.

To further evaluate the geometrical influence of surplus particle flux arriving from $d_2$ and $d_3$ directions and inter-seed growth $f$ on the temporal shape evolution of nanorods (on both Au patterned and RIBE templates with $D = 1390$ nm), the deposition time was increased to $t_{dep} = 210$ min. The trends observed in average column width $w$ as a function of seed height $h_s$ are plotted for two different deposition times ($t_{dep} = 133$ and 210 min) in Fig. 5.17 (a) for honeycomb templates with $D = 1390$ nm. As discussed earlier, altered shadowing lengths $l$ are responsible for the variation in the average column widths. For $D = 508$ nm and 780 nm, the supplementary particle flux from $d_2$ and $d_3$ directions is adequately depleted due to the Au dots ($h_s \approx 100$ nm). However for $D = 1390$ nm, the large pattern period suppressed the column competition [72, 77], resulting in a surplus particle flux from $d_2$ and $d_3$ directions and enhanced inter-seed condensation. Furthermore, for a constant pattern period $D$, the amount of surplus particle flux enhances and consequently the inter-seed condensation amplifies as seed heights reduce from $h_s \approx 100$ nm (for Au honeycomb template) to $h_s \approx 50$ nm (7 min etched RIBE template).

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22 The inter-seed condensation bears a maximum height at the center and a declining height towards the honeycomb seeds, as illustrated in Fig. 5.15 cross-sectional micrographs.
Accordingly, the average column width decreases from $w \approx 682 \pm 24$ nm ($h_s \approx 100$ nm) to $w \approx 638 \pm 28$ nm ($h_s \approx 50$ nm) for $t_{dep} = 210$ min, which is also in agreement with lower deposition time measurements ($t_{dep} = 133$ nm). Additionally, hexagonal shape evolution for period $D = 1390$ nm is also consistent as respectively indicated in the top-view micrographs (for $h_s \approx 50$, 65 and 100 nm and $t_{dep} = 210$ min) in Fig. 5.17(b).

Inter-seed growth has a congruent influence on the shape and width of the nanorods, and it has a strong dependence on the seed heights and the template period. Fig. 5.17(c) shows this inter-seed growth dependence as a function of seed height. Besides, with decreasing seed height insufficient shadowing occurs and thus, the nanorod width decreases and the inter-seed growth increases. For instance, with $t_{dep} = 210$ min, as the seed height decreases from $h_s \approx 100$ nm to $h_s \approx 50$ nm, the inter-seed growth increases from $f \approx 216 \pm 40$ nm to $f \approx 445 \pm 60$ nm, respectively. Therefore, for $D = 1390$ nm, even if on one hand an enlarged pattern period suppresses the competitive growth [72, 77], surplus particle flux from second and third nearest neighbors results in enhanced inter-seed growth. Thus it can be concluded that nanorod width and inter-seed growth are inter-dependent parameters as a function of seed height.

The following schematic sketch (Fig. 5.18) illustrates the morphological shape variations on the basis of geometrical influences observed in the experiments. The cross-sectional SEM micrographs (left) display nanorod evolution on different seed heights ($h_s \approx 100$ nm to $h_s \approx 50$ nm for $t_{dep} = 133$ min). The shape of the nanorod strongly depends on the seed height $h_s$ and on
inter-seed growth. From the schematic sketch, the particle flux $\beta$ contributes to the inter-seed growth due to large pattern period, while $\beta^0$ contributes to the growth of nanorods for $h_s \approx 100$ nm. Thus, the surplus particle flux from $d_2$ and $d_3$ directions has to arrive “over” the inter-seed condensation conditionally in order to contribute to the growth of subsequent nanorods. Otherwise, this particle flux will be embedded in the inter-seed condensation.

As deposition continues, inter-seed growth increases, averting the growth of triangular shaped nanorods and the flattening of otherwise observed pikes (for $D = 508$ and $780$ nm) in direction $d_3$. This additional flattening of three sides of the nanorod results in the growth with a hexagonal shape. Moreover, in accordance with the seed height the shape of the nanorod varies from hexagonal to nearly circular shape as described earlier (see Fig. 5.16(a)-(c)). Corresponding cross-sectional evolution could be understood from Fig. 5.18. For decreasing seed height, inter-seed growth increases (Fig.5.17(c)) resulting in a lower amount of particle flux contributing to the growth of nanorods and subsequently decreasing nanorod width. The particle flux $\beta$ and $\beta^0$ from $d_2$ and $d_3$ directions in the case of $h_s \approx 50$ nm contributes to the inter-seed growth rather than to the nanorod as a consequence of increased inter-seed condensation (Fig. 5.18). Thus, nanorods attain nearly circular shaped cross-sections. Therefore, apparent effects of inter-seed distances, seed heights and consequently shadowing lengths influence the shape and dimension of nanorods grown on a honeycomb patterned substrate.

Figure 5.18: Cross-sectional SEM micrographs (left) of films deposited on templates consisting of different seed heights ($h_s \approx 100$ nm to $h_s \approx 50$ nm) ($t = 133$ min) and corresponding schematic sketches (right) describing influences of seed height and inter-seed growth on the
5.4 Growth on Si patterned planar-hcp template

Rectangular templates and their usage for the growth of GLAD nanostructures is well established in the GLAD-literature [5, 72-74, 106, 107, 109, 110, 193-195]. On the other hand, nanosphere self-assembled templates usually consist of a SiO$_2$ or polystyrene (PS) nanosphere pattern [44, 45, 59] or when used as an evaporation mask, metal hillocks arranged in honeycomb [77-81, 196] or planar hexagonal-closed-packed (planar-hcp) [79, 81] array for the GLAD growth. Instead, a combination of nanosphere self-assembled monolayer and reactive ion etching (RIE) process could offer an alternative method to the e-beam lithography process to form Si seed patterns onto the substrate itself. Moreover, for many applications such ‘Si’ hillocks on a Si substrate for a large area periodic growth of GLAD nanostructures will be essential. One previously reported method to obtain Si patterns in an etching process, applied for the growth of two-level porosity [76, 78], utilized Cr network films formed after a NSL procedure. However, this approach produced the growth of inter-connected columns that grew on the Cr ridges of pattern holes. Thus, in order to realize post-deposition arrays with isolated columns in a periodic arrangement, the reactive ion etching procedure represents a method to utilize “metal-free” patterns for the growth of GLAD nanostructures.

In this section, the growth of Ge nanorod arrays on Si patterned substrates is demonstrated. All experiments were done using a slit aperture placed between target and substrate and the deposition angle was adjusted to $\beta = 86^\circ$. In the presence of the slit aperture the deposition rate measured $r_a \approx 3.2\pm0.3$ nm/min. During the GLAD experiments, substrates were rotated constantly with $\omega = 0.2$ rpm and deposition was carried out for $t_{dep} = 66$ min to 330 min to form vertical Ge nanorods of height $h \approx 200, 400, 500, 700, \text{ and } 1000$ nm.

5.4.1 Planar-hcp pattern transfer by RIE

Before performing GLAD, a three step patterning process as described in section 3.2 was used to achieve Si planar-hcp arrays on Si substrates. The required Si seed dimensions were achieved by a combination of self-assembly of polystyrene nanospheres (PS) and reactive ion etching (RIE). Figures 5.19(a)-(b) depict top-view SEM micrographs of a Si template obtained after the patterning process.
At the beginning, a PS self-assembled monolayer was subjected to isotropic etching in an oxygen plasma. The resulting pattern was used as an etch mask in a reactive ion etching process to form Si seeds. This planar-hcp Si seed arrays with different seed widths $w_s$ and the inter-seed separation distances $R_s$ were utilized for the growth of Ge nanorods. The deposition was carried out on the templates with inter-seed distances: $R_s = 335$ nm ($D = 535$ nm), $R_s = 435$ nm ($D = 535$ nm), $R_s = 522$ nm ($D = 722$ nm), and $R_s = 622$ nm ($D = 722$ nm). Figure 5.19(a) and (b) depict examples of Si seed patterns formed after the etching process with template periods $R_s = 435$ nm ($w_s = 100$ nm) and $R_s = 522$ nm ($w_s = 200$ nm). In the following subsections, the growth optimization of Ge nanorod arrays achieved through the systematic alterations of the pattern period and the seed dimension is described in detail.

### 5.4.2 Morphological evolution during extreme column competition

The differences in the seed arrangement of tetragonal, honeycomb-like and planar-hcp templates in terms of geometrical shadowing effects have a significant influence on the nanostructure evolution and resulting morphology under GLAD conditions with fast substrate rotation. In an earlier section (5.3) an asymmetric shadowing effect on a honeycomb-like array was demonstrated. On the contrary, in a planar-hcp arrangement each Si seed is surrounded by six equidistant neighbors located at a distance $R_s$ as depicted in Fig 5.19(b) and hence, each growing nanorod experiences a symmetric shadowing effect from its neighboring seeds. Thus, in this highly symmetric case generally columnar nanostructures emerge with close-to-circular cross-sections [58, 79]. But as discussed in section 2.2, seed dimensions also have a strong influence on the nanostructure evolution under shadowing conditions. Figure 5.20(a) shows top-view SEM micrographs of Ge nanorods of height ~ 200 nm, ~ 400 nm, and ~ 1000 nm deposited on the template with a pattern period $R_s = 335$ nm and seed width $w_s = 200$ nm. The seeds of height $h_s$ ~
Glancing angle deposition of Germanium

100 nm (shadowing length \( l \approx 1430 \) nm, thus \( l > h_s \)) sufficiently circumvent the inter-seed growth (Fig. 5.20 (b)), where a clear Si seed step is visible. The prominent column competition [5, 105] results in the growth of closely bunched multiple-structures that evolve on each broad Si seed (\( w_s = 200 \) nm).

Furthermore, growth on the side walls of the Si seed pattern can also be noticed. This growth could be attributed to the exposure height described by the ratio [105] \( a_s \approx R_s / l \) and a broad angular distribution of the particle flux due to the sputtering method.

The growth on these broad Si seeds (\( w_s = 200 \) nm) can be compared to the individual seeds, which are formed on a flat surface at the early stage of mound formation and receive particle flux for subsequent growth. The evolution of GLAD structures on planar substrates usually starts with the formation of seeds having small dimensions in the range [115] of 20-30 nm. Therefore, if template seeds are introduced prior to GLAD, whose dimensions exceed this size, the condensation and emergence of multiple sub-structures can be expected, as schematically depicted in Fig. 5.20(c). Additionally, under shadowing conditions, competitive growth increases for narrow inter-seed distances [5, 77]. Moreover, these structures tend to broaden with increasing height [6, 72], which leads to an extinction of some of the structures. Besides, with increasing structure height the predominant seeds receive more particle flux, which results in the growth of these structures, while the growth of smaller seeds stops prematurely. This is an effect that is distinctly visible from Fig. 5.20(a), where the number of structures decreases with increasing height from \( h \approx 200 \) to 1000 nm. Evidently, under

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Figure 5.20: (a) Top-view SEM micrographs of Ge nanorod arrays (\( h \approx 200 , 400 \) and 1000 nm) grown on Si patterned substrates with the inter-seed distances: \( R_s = 335 \) nm, \( w_s = 200 \) nm; (b) corresponding cross-sectional view of Ge nanostructures of height \( h \approx 200 \) nm; (c) Schematic diagram illustrating competitive growth on such templates.
competitive growth conditions, when \( w_s \) is over-sized, in relation to the equilibrium structure dimension on planar substrates, growth of multiple-structures (i.e., the survival of more than one structure per seed) on each artificial seed is more likely to occur [72, 115].

### 5.4.3 Growth optimization on enlarged pattern period

In order to investigate the effects of the template period and the seed width on the growth of Ge nanostructures, the deposition was also carried out on Si patterns with enlarged inter-seed distances \( R_s = 435 \text{ nm} \) (\( w_s = 100 \text{ nm} \)), \( R_s = 522 \text{ nm} \) (\( w_s = 200 \text{ nm} \)) and \( R_s = 622 \text{ nm} \) (\( w_s = 100 \text{ nm} \)). The column competition can be suppressed by means of increased inter-seed separation [72, 77]. Besides, when \( w_s \) is optimized within the equilibrium structure dimension, growth of multiple-structures on a single seed can be averted, and singular structures can emerge on each seed [103, 104].

Figures 5.21(a) and (d) show top-view and cross-sectional micrographs of the planar-closed-packed Ge nanorod array grown on Si seeds with an inter-seed distance \( R_s = 435 \text{ nm} \). The decreased seed width (\( w_s = 100 \text{ nm} \)) and consequently decreased ratio \( w_s / R_s \approx 0.22 \) facilitated the growth of isolated nanorods (Fig. 5.21(d)). Here, at an early stage of growth, formation of multiple seeds on each individual Si seed within the 20–30 nm range [115] would be expected. The top-view Fig. 5.21(a) shows small branching or bifurcation within each nanorod. But after the mound formation, under extreme shadowing conditions and for sufficiently narrow seeds, fiber-like structures emerge on the early stage seeds. Subsequently, inter-column competition and merging of neighbouring structures sets in, which eventually results in the growth of an isolated, large structure that then incorporates multiple sub-branches and bifurcated structures. This can also be attributed to the broadening effect during a competitive growth mode, an effect clearly noticed from the cross-sectional SEM image Fig. 5.21 (d), where the growth of isolated Ge nanorod and a clear Si seed step beneath the nanorod are visible.

For rectangular templates Ye *et al.* reported [197] the growth of multiple nanorods on each individual seed of relatively large seed width (\( w_s = 360 \text{ nm} \)). The growth of single isolated nanorods was achieved [197] on each seed by merely reducing the seed width to \( w_s = 150 \text{ nm} \) and subsequently altering the inter-seed distance. For these rectangular templates, each seed is surrounded by eight adjacent seeds (four first-nearest neighbors located at \( R_s \), and four second-
nearest neighbors located at $\sqrt{2}R_s$ [74, 81]. However, in the current experiment, Si seeds, arranged in a planar-hcp array, experience highly symmetric shadowing from the six nearest neighbours that are located at a distance $R_s$. Therefore, with the present rotationally symmetric planar-hcp templates, columnar structures emerge with a close-to-circular cross-section. From Fig. 5.21(a) and (d), isolated nanorods of height $h \approx 200$ nm and average width $w \approx 418\pm43$ nm that evolved on each Si seed can be noticed. The growth on the entire side walls of the Si seeds and inter-seed condensation $f = 63\pm8$ nm can be attributed to the broad angular distribution of the particle flux due to the sputtering method. Additionally, for $R_s = 435$ nm a significant difference in the growth process can be observed in comparison to the nanorods grown on $R_s = 335$ nm. Moreover, as an attempt to “fill” the additional inter-seed space, these nanorods broadened [116] with increasing height.

Likewise, Ge nanorods grew on a planar-closed-packed array of Si seeds separated by inter-seed distance, $R_s = 522$ nm ($D = 722$ nm) as illustrated from Fig. 5.21(b). In spite of relatively broad seeds ($w_s = 200$ nm), growth of isolated Ge nanorods can be observed. The top-view shows small

![Figure 5.21: Top-view and corresponding cross-sectional SEM micrographs of Ge nanorod arrays ($h \approx 200$ nm) grown on patterned substrates with the inter-seed distances: $R_s = 435$ nm, $w_s = 100$ nm [(a) and (d)], $R_s = 522$ nm, $w_s = 200$ nm [(b) and (e)] and $R_s = 622$ nm, $w_s = 100$ nm [(c) and (f)], respectively.](image-url)
5.4 Growth on Si patterned planar-hcp template

branching and fissures within each nanorod. However, the merging of adjacent structures during the growth eventually leads to the growth of a singular structure that incorporates multiple sub-branches and bifurcated structures. An example of such individual nanorods is depicted in Fig. 5.21(e), where a distinct Si seed step underneath the nanorod and sub-branches are visible. As an effect of increased inter-seed separation to $R_s = 522$ nm ($D = 722$ nm) (Fig 5.21(b) and (e)) as opposed to $R_s = 335$ nm ($D = 535$ nm) (Fig. 5.20(a) and (b)), the column competition is suppressed [72, 77] considerably. Thus, successive merging of early stage seeds during continuous deposition caused each nanorod to grow as an uniform entity, with branched or bifurcated features, on each Si seed despite identical seed width $w_s$. In other words, the increased inter-seed distance $R_s$, strongly influenced the growth on these Si seeds, enabling the formation of singular nanorod structures.

Here, the average nanorod width amounted to $w \approx 549\pm29$ nm, while the inter-seed condensation increased up to $f = 77\pm6$ nm, due to the increased inter-seed separation. For decreased seed width $w_s = 100$ nm, and consequently increased inter-seed distance $R_s = 622$ nm, analogous nanorod arrays with an average width $w \approx 498\pm39$ nm, were observed. The reduced broadening effect could be attributed to the decreased seed width $w_s$ (Fig. 5.21(c) and (f)). Here, an increased inter-seed condensation up to $f = 82\pm7$ nm and growth covering the complete side walls of Si seeds can be seen from the cross-sectional SEM micrograph. From the top-view (Fig. 5.21(c)), lesser branching or column-bifurcation can be noticed in comparison to Fig. 5.21(a) and (b). Evidently, consecutive merging during continuous deposition conditions leads to the growth of individual nanorods, with branched and bifurcated features, on each Si seed. It is worth noting that, for an optimized pattern period, the smaller the seed width, the lesser the branching observed.

5.4.4 Influence of deposition time

In order to assess the temporal evolution on each pattern period, deposition was carried out for $t_{dep} = 66$ min to 330 min to form vertical nanorods of height $h \approx 200, 400, 500, 700, \text{ and } 1000$ nm. As known from previous studies [116, 197], the inter-seed separation distance and the seed width dominate the growth process as well as the morphological evolution of the nanorods. The influence of $R_s$ on the nanorod width $w$ on these patterned substrates consisting of different seed widths $w_s$ is demonstrated in Fig. 5.22. The inter-seed distance $R_s = 335$ nm and the broad seed width $w_s = 200$ nm resulted in an increased column competition on an individual seed. Thus, the
growth of closely bunched multiple-structures on each Si seed was observed. For $h \approx 200\,\text{nm}$, the average nanorod width measured $w \approx 62\pm 22\,\text{nm}$, while on the other hand, due to the nanorod broadening at $h \approx 1000\,\text{nm}$, the average width measured $w \approx 210\pm 52\,\text{nm}$. Consequently, the column competition for closely bunched multiple-structures becomes even more severe with increasing height of the structure.

The growth process optimization on the Si seed patterns with the increased inter-seed distances and narrow widths could be attributed to the merging of growing structures during continuous deposition on each seed, and the suppression of growth competition on enlarged pattern periods [72, 198]. Figures 5.23(a)-(c) show top-view micrographs of different heights ($h \approx 400, 700$ and $1000\,\text{nm}$ nanorods) and cross-sectional micrographs of the nanorods of height $h \approx 1000\,\text{nm}$ grown on templates with $R_s = 435\,\text{nm}, 522\,\text{nm},$ and $622\,\text{nm}$, respectively. The cross-sectional micrographs evidently demonstrate that under continued deposition conditions, singular nanorod structures attain an uniform columnar shape with increasing structure height.

The nanorods of height $h \approx 1000\,\text{nm}$ grown on the template with inter-seed distance $R_s = 435\,\text{nm}$ and seed width $w_s = 100\,\text{nm}$ attained the average rod width $w \approx 464\pm 43\,\text{nm}$ (Fig 5.23(a)). While for an increased inter-seed distance $R_s = 522\,\text{nm}$, nanorods exhibited an average width of $w \approx 636 \pm 20\,\text{nm}$ (see Fig. 5.23(b)). In contrast to the multiple-structures that were observed on broad Si seeds, and narrow inter-seed separations, isolated nanorods could be grown on enlarged inter-seed patterns in spite of analogous seed widths.
For the ratio \( w_s / R_s \approx 0.59 \), strong column competition resulted in the growth of multiple nanorods on each Si seed. While for the decreased ratio of \( w_s / R_s \approx 0.38 \), they evolve as a single entity [199]. Evidently, on a pre-patterned substrate comprising of considerably narrow periods, \( R_s \), column number density and column diameter are both limited due to the column competition [198]. For a relatively narrow seed width \( w_s = 100 \) nm and increased inter-seed distance \( R_s = 622 \) nm the nanorod width decreased to \( w \approx 610 \pm 29 \) nm as shown in Fig. 5.23(c). Further, from Fig. 5.22, for \( R_s = 435 \) nm, 522 nm, and 622 nm, it is noticeable that once the nanorod height \( h \approx 500 \) nm is attained, the nanorod widths do not show much broadening with further increasing height. This represents near saturation diameters of the nanorods. Clearly, the nanorod growth processes and the resultant nanorod dimensions on the planar-closed-packed arrays of Si seeds are strongly controlled by the seed widths \( w_s \) and inter-seed distances \( R_s \).
5.5 Effects of annealing on Ge GLAD nanostructures

In this section, effects of annealing on the morphology of Ge GLAD nanostructures deposited on planar and pre-patterned substrates will be presented.

Several materials have been investigated for the feasibility to scale up three-dimensional nanostructures to avail size limited confinement effects. Although the required crystalline Ge-Glad nanostructures can, in principle, be obtained by depositing films at elevated substrate temperatures, the GLAD-inherent columnar morphology is significantly altered by diffusion-driven processes [200]. Instead, post-deposition annealing could be a possible alternative to realize crystalline Ge nanostructures with columnar morphologies. So far, only few reports concerning the effects of annealing on glancing angle deposited nanostructures exist, for example assessing surface melting and a coalescing effect of obliquely grown Cu nanorod arrays annealed under vacuum conditions at ~300-800 °C [67], describing the morphology alteration in Ge nanowire arrays at ~400-600 °C [65], or evaluating the recrystallization behavior of Si nanostructures above ~800 °C [64, 126]. In the present study, however, the morphological effects on glancing angle deposited Ge nanocolumn arrays annealed within an Ar-atmosphere at different temperatures ranging from $T_A = 300 - 800$ °C are discussed. Most of the deposition experiments were carried out with a slit aperture placed between target and substrate. The deposition angle was adjusted to $\beta = 86^\circ$ to form columnar nanostructures, whereas to deposit compact thin films the deposition angle was set to $\beta = 0^\circ$. To evaluate the time-dependent crystallization process, nanocolumn arrays possessing different structure heights were annealed for varied time intervals. Additionally, compact thin Ge films deposited with normal angle incidence of Ge particle flux ($\beta = 0^\circ$) were subjected to an equal annealing process. To assess the influence of substrate patterning, nanostructures grown on pre-patterned substrates were also annealed at different temperatures and for different time durations.

5.5.1 Thickness dependent morphological changes

To investigate the film thickness dependent morphological alterations on Ge nanocolumn arrays, as-deposited samples of various thicknesses ($h \approx 200, 300, 400,$ and $500$ nm) were annealed in a continuous Ar-flow at different temperatures ranging from $T_A = 300 - 700$ °C for $10$ min. Figures
5.5 Effects of annealing on Ge GLAD nanostructures

5.24(a)-(b) show top-view micrographs of as-deposited (at RT) Ge nanocolumns of height \( h \approx 200 \) and 500 nm grown on planar Si(100) substrates, respectively.

The average nanocolumn width increased from \( w \approx 102 \pm 33 \) nm to \( w \approx 174 \pm 51 \) nm, and the average column number density decreased from \( n \approx 72 \pm 17 \) µm\(^{-2}\) to \( n \approx 38 \pm 8 \) µm\(^{-2}\), with an increase in structure height from \( h \approx 200 \) nm to 500 nm, respectively. Figures 5.24(c)-(d) and (e)-(f) show respective top-view and cross-sectional SEM micrographs of Ge nanocolumn arrays of height \( h \approx 200 \) and 500 nm annealed in Ar-flow at \( T_A = 700 \) °C. With a close inspection column coarsening and faceted structures can be noticed. For \( T_A = 600 \) °C \((h \approx 200 \) nm\), moderate nanocolumn merging and comparatively less prominent faceted structures were detected, while for annealing temperatures below \( T_A = 600 \) °C no considerable morphological alterations were observed. This coarsening of adjacent nanocolumns can be attributed to the temperature induced densification during the annealing process. Likewise, a moderate coalescing of adjacent nanocolumns is apparent for \( h \approx 500 \) nm at \( T_A = 700 \) °C (see Fig. 5.24(d) and (f)), in comparison to \( h \approx 200 \) nm. Apart from average column width variation, nanocolumns did not show any considerable modifications for annealing temperatures \( T_A < 600 \) °C \((h \approx 500 \) nm\)).
Evidently, the temperature at which Ge nanocolumns exhibit coarsening is significantly lower than the bulk melting temperature of 938 °C. This coarsening leads to the minimization of surface-to-volume ratio. Specifically, GLAD nanostructures inherit very high surface-to-volume ratio [52] in contrast to the bulk material. On the planar surfaces, due to GLAD-inherent competitive growth mechanism [1, 2, 89], nanocolumns have smaller circumferences and narrow inter-column separation [6, 115] near the substrate surface, while the nanocolumn widths increase with structure height [101]. Hence, during the annealing treatment, at an adequately high temperature, physically adsorbed atoms at the surface may detach and diffuse as adatoms over the surface curvature causing column coarsening. This diffusion process, driven by the surface energy minimization occurs to smooth the surface morphology and is proportional to the divergence of the surface curvature [201].

The nanocolumn arrays annealed at $T_A = 300$ and 400 °C were found to be amorphous and did not show any reflection, while the nanocolumns annealed at $T_A \geq 500$ °C were found to be polycrystalline exhibiting (111), (220) and (311) reflections. Figure 5.25(a) depicts x-ray diffraction diagrams of the nanocolumn arrays ($h \approx 500$ nm) annealed at different temperatures ranging from $T_A = 300$ °C – 700 °C. For Ge-GLAD nanocolumns deposited at elevated substrate temperatures [200] a shift of preferential crystallite orientation from (111) to (220) was observed.
as the growth temperature increased from $T_S = 200 \, ^\circ\text{C}$ to $340 \, ^\circ\text{C}$. This effect was attributed to the lower strain energy of (220) oriented Ge during growth. However, here no such shift of preferential crystal orientation is observed for an increasing annealing temperature. For $T_A = 700 \, ^\circ\text{C}$, the ratios $I_{(111)}/I_{(220)}$ and $I_{(111)}/I_{(311)}$ were observed to be $\sim 1.20$ and $\sim 1.15$, which increased with annealing temperature$^{23}$.

For the nanocolumns ($h \approx 200$ to $500 \, \text{nm}$) annealed at $T_A = 700 \, ^\circ\text{C}$, average nanocolumn widths decreased by approximately $9-11\%$ in comparison to as-deposited nanocolumn widths. Figure 5.25(b) depicts a plot of the average column width as a function of film thickness for as-deposited and annealed nanocolumns at different temperatures ranging from $T_A = 300 \, ^\circ\text{C} - 700 \, ^\circ\text{C}$. The width variation can be attributed to the densification induced by the annealing process. The inset of Fig. 5.25(b) displays the scaling exponent $[51, 101]$ $p$ values ($w \propto h^p$, where $p$ is calculated on log-log plot) for the as-deposited and annealed nanocolumns. For as-deposited nanocolumns, the growth exponent is observed to be $p(\text{RT}) \approx 0.59$. With an increase in the annealing temperature up to $700 \, ^\circ\text{C}$ a slight tendency of an increase of $p$ can be observed. The discrepancy of measured $p$ value and predicted values ($p$ should vary between 0.3 to 0.5 and should decrease with increase in diffusion length as predicted [101]) at $\beta = 86^\circ$ could be attributed to the deposition chamber geometry and differences in the deposition conditions (including deposition rate, pressure, substrate rotational speed, etc.). Moreover, due to the principle of sputter deposition method, a certain deviation in the angular distribution of the particle flux should be taken into account. This causes the particle flux to arrive at ‘non-glancing angle condition’ ($\Delta \beta \approx 9^\circ$), which certainly increases [51] the $p$ values above 0.5 (for as-deposited films at RT).

In general two separate temperature regions have to be identified. First, for $T_A < 500 \, ^\circ\text{C}$ even though nanocolumn arrays exhibited a width variation, structures were found to be in the amorphous state. On the other hand, for $T_A > 500 \, ^\circ\text{C}$ temperature induced densification leads to morphological alterations, typically column coarsening, and structures turn into crystalline state, exhibiting random orientation.

$^{23}$ In comparison, the ratio of intensities $I_{(111)}/I_{(220)}$ and $I_{(111)}/I_{(311)}$ in Ge standard powder diffraction diagrams are 1.75 and 2.56, respectively.
5.5.2 Influence of annealing duration on the film morphology

In order to examine the effects of annealing duration, nanocolumn arrays of height $h \approx 500$ and 1000 nm were annealed at different temperatures ranging from $T_A = 400 - 800$ °C for 30 min in continuous Ar-flow. Figures 5.26(a)-(d) and (e)-(h) show top-view and corresponding cross-sectional SEM micrographs of as-deposited (RT) and annealed Ge nanocolumns ($h \approx 1000$ nm). Significant changes in the morphology can be seen with an increasing annealing temperature from $T_A = 500$ to 700 °C in comparison to as-deposited films. For $T_A = 500$ °C, nanocolumns did not exhibit a considerable modification within the columnar structures. At $T_A = 600$ °C, a prominent coarsening of adjacent nanocolumns can be noticed, where multi-faceted structures are apparent. However, the GLAD-inherent columnar morphology persists (at $T_A = 600$ °C), as displayed in Fig. 5.26(c) and (g).

For further increased annealing temperature $T_A = 700$ °C, immense morphological alterations are observed (see Fig. 5.26(d) and (h)), as clusters of Ge agglomerates were formed. Here, even though the morphology is apparently porous, the typical GLAD columnar appearance of the film completely degenerated. Annealing at a temperature $T_A = 800$ °C resulted in identical Ge agglomerates. Likewise, for the nanocolumn arrays of height $h \approx 500$ nm annealed for 30 min, entirely comparable observations were noted.

![Figure 5.26: Top-view and corresponding cross-sectional SEM micrographs of Ge nanorod arrays ($h \approx 1000$ nm) on Si(100) substrates: as-deposited [(a) and (e)] and annealed in continuous Ar-flow for 30 min at $T_A = 500$ °C [(b) and (f)], $T_A = 600$ °C [(c) and (g)] and $T_A = 700$ °C [(d) and (h)], respectively.](image)
X-ray diffraction diagrams of the nanocolumns \((h \approx 500 \text{ nm})\) annealed at different temperatures ranging from \(T_A = 400 - 800 \text{ °C}\) revealed recrystallization of nanostructures after the annealing process. Identical to those nanocolumns annealed for 10 min duration, diffraction diagrams demonstrated polycrystalline evolution at \(T_A \geq 500 \text{ °C}\). Besides, an extended annealing duration (30 min) exhibited small intensities of (331) and (422) reflections in addition to (111), (220), and (311) reflections. Hence it can be concluded that with an increased annealing duration the crystalline quality improved. From the comparison of Fig. 5.24 and 5.26 it is evident that the morphological alterations are strongly influenced by the annealing duration. Complete disintegration of columnar structures and formation of Ge agglomerates at \(T_A = 700 \text{ °C}\) (30 min) clearly indicates that the thermally stimulated crystallization process is time-dependent [202].

The enhanced surface diffusion during the annealing treatment induces premelting [203] at the surface of nanostructures. The surface energy constraints the stability during annealing of such nanoscale structures, due to its inverse proportionality with the nanowire radius and width [204]. In such cases, nanostructures generally change their shape to reduce the surface free energy. Hence, coalescing or disintegration processes of the nanostructures strongly depend on nanocolumn/nanowire width. Further, method of preparation, thermal treatment, and experimental conditions can also influence the crystallization process. A previous report [65] concerning e-beam evaporation GLAD-grown Ge ‘nanowires’ (width ~ 50 nm) annealed at 600 °C showed a complete disintegration of nanowires and formation of Ge agglomerates for a short annealing interval of 5 min. Choi et al. [65] attributed this disintegration to the perturbations generated within the nanowires of small widths (width ~ 50 nm), which either induce ‘bundling’ (at 410 °C) or ‘disintegration’ (at 600 °C). However, as discussed in section 5.2, drastic growth differences were observed [200] for ion beam sputter Ge-GLAD

Figure 5.27: X-ray diffraction diagrams of Ge nanorod arrays \((h = 500 \text{ nm})\) annealed in continuous Ar-flow for 30 min at temperatures \(T_A = 400 \text{ °C} - 700 \text{ °C}\).
‘nanocolumns’ grown at different substrate temperatures in comparison to the reported [65] e-beam evaporation-grown Ge ‘nanowires’. Besides, it is theoretically predicted that the disintegration of ‘nanowires’ strongly depends upon nanowire circumference [205]. Consequently, the current experimental observations evidently demonstrate that the stability of Ge-GLAD ‘nanocolumns’ is determined by the nanostructure characteristics including deposition methods, growth process, and differences in the deposition conditions (including deposition rate, pressure, substrate rotational speed etc.)

To examine the effects of annealing on dense Ge films, compact thin films of thickness \( h \sim 500 \) nm deposited by normal particle incidence (\( \beta = 0^\circ \)) were annealed at \( T_A = 400\text{-}800 \degree C \) for 30 min in continuous Ar-flow. Figures 5.28(a)-(c) show top-views of thin compact films annealed at \( T_A = 600 \degree C, 700 \degree C \) and \( 800 \degree C \), respectively. With a close inspection it is apparent that diminutive pores and faceted surfaces were observed after the annealing process at \( T_A = 600 \degree C \).

![Figure 5.28](image.png)

Figure 5.28: Top-view SEM micrographs of compact Ge films deposited with normal incidence (\( \beta = 0^\circ \)) of thickness \( h \approx 500 \) nm on Si(100) substrates annealed in continuous Ar-flow for 30 min at (a) \( T_A = 600 \degree C \), (b) \( T_A = 700 \degree C \) and (c) \( T_A = 800 \degree C \), (d) Corresponding X-ray diffraction diagrams of compact Ge films annealed at temperatures \( T_A = 400 \degree C - 700 \degree C \), (e) A plot of grain sizes of (111), (220) and (311) grains calculated by measuring FWHM of respective reflections at different temperatures. Dotted line is a guide to the eyes.
5.5 Effects of annealing on Ge GLAD nanostructures

However, the film thickness remained consistent and did not show any cluster agglomeration. For $T_A = 700 \, ^\circ\text{C}$ (see Fig. 5.28(b)), although a similar type of faceted surface evolved, pore enlargement occurred. But the thickness and overall uniformity remained undisturbed, as investigated by cross-sectional SEM. An immense morphological difference was detected for the films annealed at $T_A = 800 \, ^\circ\text{C}$, where the film consistency was significantly affected and the film completely disintegrated. Typically, pre-melting [203] and interior-melting [206] processes can lead to the alterations in shape and likely detachment of the surface atoms and subsequent adatom rearrangement. From the top-view micrograph (Fig. 5.28(c)), agglomerated granules with faceted structures are visible amidst a relatively porous film. The shapes and sizes of these clusters vary considerably. Evidently, a compact thin film also exhibits nanostructure coarsening at elevated annealing temperatures. At such a high annealing temperature ($T_A = 800 \, ^\circ\text{C}$) and relatively long annealing interval of 30 min results in the thickness inconsistency and a drastic morphological alteration.

Fig. 5.28(d) shows x-ray diffraction diagrams of the temperature series ($T_A = 400 - 800 \, ^\circ\text{C}$) of the compact annealed films (thickness ~ 500 nm). The films annealed at $T_A \geq 500 \, ^\circ\text{C}$ exhibited (111), (220), (311), (331) and (422) reflections. Fig. 5.28(e) shows a plot of average grain size estimation of (111), (220) and (311) oriented grains as a function of annealing temperature of a ~500 nm compact dense film. The approximate grain sizes were estimated by measuring the peak widths (FWHM) of each reflection (Fig. 5.28(d)) for the temperature series ($T_A = 500-800 \, ^\circ\text{C}$) and using the Scherrer formula. With an increase in the annealing temperature the average grain size increases from about ~ 8-10 nm at $T_A = 500 \, ^\circ\text{C}$ to ~ 20-22 nm at $T_A = 800 \, ^\circ\text{C}$ for (111), (220) and (311) oriented grains. The estimated average grain size of three different orientations does not vary considerably for a given annealing temperature.
5.5.3 Influence of substrate patterning on annealed Ge nanorods

To assess the influence of the annealing process on the morphology of Ge nanocolumns grown on SiO\(_2\) templated substrates, samples annealed at different temperatures were examined. Figures 5.29(a)-(b) and (c)-(d) show cross-sectional and top-view SEM micrographs of Ge nanocolumn arrays (\(h \approx 700\) nm and total nanorod height \(h_{tot} \approx 1000\) nm) deposited on SiO\(_2\) nanosphere patterned substrates (\(D = 351\) nm) annealed for 10 min at temperatures \(T_A = 600\) °C and 700 °C, respectively. As distinctly noticeable, the shape of the nanocolumns and overall morphology after the annealing process remained intact. For an annealing interval of 10 min on planar substrates, a strong column coarsening appeared at \(T_A = 600\) and 700 °C (discussed in section 5.5.1). However, for SiO\(_2\) patterned substrates coalescing or disintegration of the nanocolumns was not observed after the annealing treatment. This effect could be attributed to the relatively broad and uniform nanocolumn widths, presence of SiO\(_2\) nanospheres at the substrate surface and thus a relatively stable nanostructure.

The altered periodic arrangement of nanocolumns (see Fig. 5.29(b) and (d)) can be attributed to densification induced by the annealing treatment. A reduction of the sphere size by about 5% was reported for post-annealing of SiO\(_2\) nanospheres [207, 208] due to densification. Thus, during such an annealing procedure likely disarrangement of Ge nanocolumns could occur, which might induce a tilt or shift towards the adjacent columns in the periodic arrays as notices from the top-view SEM micrographs. A previous investigation [209] indicated diffusion of Ge within silicon oxide layers on silicon substrates during rapid thermal annealing, but in the current experiments such inter-diffusion characteristics have not been
5.5 Effects of annealing on Ge GLAD nanostructures

investigated. The formation of diminutive pores within the nanocolumns are apparent at $T_A = 600 \degree C$. But the faceted structures emerge only at $T_A = 700 \degree C$ (see Fig. 5.29(c)).

An intensive column broadening was noticed on such SiO$_2$ patterned substrates during the growth of Ge nanocolumns at increased deposition temperatures [200]. On the contrary, the annealing treatment caused a column width reduction from $w \approx 467 \pm 38$ nm to $w \approx 420 \pm 47$ nm with increasing annealing temperatures from $T_A = 300 \degree C$ to 700 °C (see Fig. 5.30(a)). This effect is in agreement with the column width reductions described in section 5.5.1. Fig. 5.30(b) shows x-ray diffraction diagrams of the annealing temperature series ($T_A = 400 - 800 \degree C$) of Ge nanocolumns. The nanocolumns annealed at $T_A \geq 500 \degree C$ were found to be polycrystalline exhibiting (111), (220), (311), (331) and (422) reflections. It is worth noting that on one hand, the crystallization temperature ($T_A \geq 500 \degree C$) for the columns deposited on SiO$_2$ patterned substrates ($D = 351$ nm) is identical to the observations on planar substrates. On the other hand, morphological modifications differ, as the nanocolumn coarsening effect is not detected on pre-patterned substrates. This is a consequence of the relatively large inter-structure distance on SiO$_2$ nanosphere patterned substrates.

Figure 5.30: (a) A plot of average column width as a function of annealing temperature. Red dots correspond to the adapted data for comparison of average column width at high substrate temperature from chapter 5.2. Dotted line is a guide to the eyes. (b) Corresponding X-ray diffraction diagrams of annealed Ge nanorod arrays grown on SiO$_2$ patterned substrates at temperatures $T_A = 400 \degree C - 700 \degree C$. 

5.5.4 Shape consistency on Si patterned substrates

The effect of annealing on the shape consistency of GLAD-grown nanostructures was examined by annealing zig-zag shaped two-arm-chevrons deposited on Si patterned substrates (with a pattern period \( R_S = 435 \) nm) in the temperature range \( T_A = 500 - 700 \) °C. Figures 5.31(a) and (b) show cross-sectional and top-view SEM micrographs of as-deposited (at RT) two-arm-chevrons formed on Si patterned substrates. The first and second arm of the two-arm-chevron structures measured \( h_1 \approx 757 \pm 11 \) nm and \( h_2 \approx 687 \pm 21 \) nm on a Si patterned substrate, respectively. The angle between the two arms of the chevron structures measured approximately \( \sim 79 \pm 2^\circ \). From Fig. 5.31(a) the Si seed of \( h_s \approx 100 \) nm beneath the chevron can be noticed along with the inter-seed condensation \( f \approx 84 \pm 7 \) nm. The cross-sectional and top-view SEM micrographs depict the ‘rough’ surface of chevron structures. Moreover, there exist finer features that branch out from the individual chevron (see Fig 5.31(b)).

Figures 5.31(c) and (d) show cross-sectional and top-view micrographs of Ge chevron structures annealed at \( T_A = 600 \) °C for 30 min in continuous Ar-flow. The shape, dimension and overall morphology of the chevron structures remained completely intact after the annealing treatment. Cross-sectional and top-view micrographs show the absence of merging or coalescing of adjacent chevrons. The ‘rough’ surface of chevrons apparent from Fig. 5.31(b) was retained after the annealing process as seen from Fig. 5.31(d). The angle between the two arms of the chevron did not exhibit any deviation and measured \( \sim 80 \pm 3^\circ \). For the chevrons annealed at \( T_A = 500 \) °C and 700 °C, identical observations were seen. The
5.5 Effects of annealing on Ge GLAD nanostructures

XRD measurements of the films annealed at $T_A \geq 500$ °C exhibited (111), (220), (311), (331) and (422) reflections. The intensities of all the reflections increased slightly with increase of the annealing temperature. No preferential crystallite orientation emerged due to annealing. The stability of the two-arm-chevron structure on Si patterned substrates under the annealing treatment could be attributed to the relatively broad nanostructure dimension and well separated structures. For instance, the growth of vertical nanorod arrays on such Si patterned substrates (discussed in detail in section 5.4) exhibit well separated structures. For the nanorod height $h \approx 1000$ nm grown Si seeds (with $R_S = 435$ nm, $w_s = 100$ nm) nanorods attained an average width $w \approx 464 \pm 43$ nm and demonstrated a wide inter-rod separation $\lambda \approx 140 \pm 26$ nm. Hence, on Si patterned substrates a relatively broad nanostructure width in comparison to the nanocolumns formed on planar substrates (discussed in section 5.5.1 and 5.5.2) and larger inter-column distance provide a stable structure that withstands extensive annealing treatment. Besides, a considerable inter-structure spacing on the pre-patterned substrates also prohibits adjacent structure merging.

In order to assess the local crystallographic structure of annealed chevron nanostructures, TEM investigations were performed. Figure 5.32(a) depicts a cross-sectional bright field TEM image of the two-arm-chevron structures annealed ($T_A = 700$ °C) in continuous Ar-flow for 30 min.

![Figure 5.32: TEM images of two-arm-chevron structures annealed in continuous Ar-flow for 30 min at $T_A = 600$ °C](image)
A close inspection reveals that multiple grains are formed within each individual chevron structure. The annealing treatment induces crystallization of the individual chevrons as well as of the inter-seed condensation. Considering the extensive annealing treatment at $T_A = 700$ °C for 30 min, it is worth noting that the small inter-seed features ($f \approx 84\pm7$ nm) do not disintegrate or evaporate. In addition it is found that small crystallites evolve within the finer branched features of the chevron structures. The exterior surface of Ge chevron structures contains a very thin amorphous state, which could be attributed to the oxide layer that has formed after the annealing treatment. The inset of Fig. 5.32(a) shows selective area electron diffraction (SAED) pattern obtained from the corresponding chevron structures (marked with the white circle). It confirms the crystallization process upon the annealing treatment as there are polycrystalline diffraction rings visible. Figure 5.32(b) illustrates nanocrystalline domains that are present within the chevron structure. The grain sizes vary considerably from 5-30 nm (in diameter) and are comparable to the grain sizes calculated by measuring the peak width (FWHM) of each x-ray reflection for the compact Ge film annealed in Ar-flow for 30 min (Fig. 5.28(e)). High-resolution TEM reveals illustrated multiple-grains that are oriented randomly, while no preferential crystal orientation is observed. These results are consistent with the XRD measurements discussed in the earlier sections, which demonstrate evolution of polycrystalline nanostructure exhibiting (111), (220), (311), (331) and (422) reflections.
5.6 Summary of results: Glancing angle deposition of Germanium

\textit{Ge-GLAD on planar substrates at RT}

- On the planar substrates growth of Ge nanostructures commences on the early stage seeds and with appropriate substrate rotation scheme spiral, screws vertical columns and n-fold structures can be achieved. In the case of continuous substrate rotation for $\rho \geq 100$ nm/min spiral-like and for $\rho \leq 20$ nm/min column-like morphology is obtained, while intermediate $\rho$ values leads to screw-like structures.

- Strong influence of inter-column competition led to the effects of structure merging and structure extinction. The widths of the surviving structures increased with an increase in structure height according to a power scaling relationship ($p = 0.59 \pm 0.02$). Besides, inter-column separation distance $\lambda$ increased with an increase in deposition time.

\textit{Influence of the substrate temperature}

Concerning Ge nanostructures deposited at elevated substrate temperatures the following main results can be drawn:

- Surface diffusion-driven mass transport altered column width, column number density and overall film thickness with an increase in $T_S$. The usual GLAD-inherent columnar appearance was observed until $T_S = 100$ °C.

- Growth of unusual fiber-like structures is observed at $T_S = 150$ °C. Moreover, these closely packed fibers ($w \approx 20$-30 nm) decrease the column number density to 34% of its initial value from RT to 150 °C.

- Intra-columnar growth at $T_S = 200$ °C induced significant modifications in the column width and the column number density and as a consequence, the average column width $w$ decreased and reached a minimum. A bimodal size distribution of early stage seeds and enhanced adatom mobility induced increased column competition, where intra-columnar growth is noticed.

- With further increasing temperature, merging and coalescing of adjacent columns resulted in the growth of broad columns of average width $w(340$ °C) = 396 ± 24 nm.
- Identical growth behaviour was noticed on SiO$_2$ nanosphere patterned substrates, where nanorod width, total height and overall column density changed with increasing substrate temperature.
- XRD measurements showed growth of polycrystalline films for $T_S \geq 200 \, ^\circ C$. Increment of $T_S$ above 200 $^\circ C$ resulted in shift of preferential crystal orientation from (111) to (220).

**Growth on Si patterned honeycomb template**

For the growth of periodic nanostructure arrays, NSL patterned substrates comprising of Au dots were used as an etch mask in a RIBE process. Following main results can be drawn from the growth Ge nanostructures on Au and Si seed honeycomb template:

- The artificial seeds act as growth seeds for the growth of periodic nanostructures and Ge columns replicate the underlying honeycomb-like template.
- The evolution of nanostructures on a honeycomb-like template is strongly influenced by the pattern periods and the seed heights. Identical growth behavior is observed on both Au dots prepared by NSL method as well as on Si dots formed by the RIBE process.
- For honeycomb-like pattern nearest neighbours located at distances $d_1$, $d_2$ and $d_3$ induced asymmetric shadowing effect. As a consequence, with increasing pattern period from $D = 508 \, \text{nm}$ to $1390 \, \text{nm}$ the shape of the nanorod changed from triangular to nearly hexagonal due to insufficient shadowing from the third-nearest neighbours.
- For narrow pattern period ($D = 508$ and 780 nm) nanorod width saturates early in $d_1$ direction, while in $d_3$ direction width saturated later resulting in triangular shape. In contrast, for enlarged pattern period ($D = 1390$ nm) insufficient shadowing from the direction $d_3$ neighbours ($l < d_3$) resulted in additional particle flux contributing to the growth of nanorods and inter-seed condensation. As a consequence, the nanorod growth saturated in $d_3$ directions leading to the hexagonal shape of the nanorods grown thereon. Additionally, reduction in seed height caused amplified inter-seed condensation and reduction in average nanorod widths. Moreover, on enlarged pattern period ($D = 1390$ nm) with decreasing seed height (from $h_s \approx 100$ to 50 nm) nanorod shape changes from hexagonal to nearly circular cross-section.
5.6 Summary of results: Glancing angle deposition of Germanium

**Growth on Si patterned planar-hcp template**

In the case of planar-hcp template: each Si seed is surrounded by six neighbouring seeds located at distance $R_S$ that induce symmetric shadowing effect. Following are the main results concerning the growth of Ge nanostructure arrays on Si patterned planar-hcp template:

- Strong column competition on the templates with narrow inter-seed distance and broad seed ($w_S / R_S \approx 0.59$) resulted in the growth of multiple structures on each Si seed. However, through the systematic variation of Si seed dimensions the growth of singular nanorod structures on each Si seeds can be achieved.

- The growth on these Si patterns starts with individual seeds that are formed at the early stage of structure formation. Under competitive growth mode, the predominant seeds receive more particle flux, which results in the growth of these structures, while the growth of smaller seeds stops prematurely. As a consequence, when $w_S$ is oversized in relation to the equilibrium structure dimension on planar substrates, growth of multiple structures ($w_S = 200$ nm, $R_S = 335$ nm) is observed.

- In contrast, on optimized seed patterns singular structures evolved on each Si seed. In this case, at an early stage of growth formation of multiple seeds on each Si seed within the 20-30 nm range is expected. However, after the seed formation, under extreme shadowing conditions and for sufficiently narrow seeds, inter-column competition and merging of adjacent structures sets in, which eventually results in the growth of isolated, large structures that then incorporates bifurcated structures. Moreover, through the variation of seed width resulting column widths and branching effect can be optimized. It is observed that the smaller the seed width lesser the branching observed.

- The temporal evolution on pattern periods $R_S = 435, 522$ and $622$ nm suggested that once the nanorod height $h \approx 500$ nm is attained; the nanorod widths do not show considerable broadening with further increasing height. This represents near saturation radius of the nanorods.

*Effects of annealing on Ge GLAD nanostructures*

Concerning the effects of annealing on Ge nanostructures grown on planar and pre-patterned substrates in continuous Ar-flow following main results can be listed. Typically, GLAD grown
Ge nanostructures exhibited drastic morphological difference depending upon substrate type, annealing duration and nanostructure characteristics:

- **On planar substrates:**
  - Short annealing duration (10 min) caused reduction of nanocolumn widths by 9-11% for annealing temperature $T_A = 700$ °C. Additionally, nanocolumns neither showed strong merging effect $T_A < 500$ °C nor exhibited disintegrate effect $T_A = 700$ °C. For nanocolumn arrays ($h \approx 100$-500 nm) the coarsening effects are observed to independent of nanocolumn height.
  - For extended annealing duration (30 min) nanocolumn arrays demonstrated strong column coalescing at $T_A = 600$ °C and degeneration at $T_A = 700$ °C. Hence, thermally activated annealing process is time-dependent.
  - Two separate temperature regimes have to be distinguished: For $T_A < 500$ °C although nanocolumns showed width reduction, structures demonstrated amorphous phases. While for $T_A > 500$ °C temperature induced densification led to the column merging effect and structures turned crystalline, exhibiting (111), (220) and (311) reflections.

- **On pre-patterned substrates:**
  - For Ge nanocolumns deposited on SiO$_2$ nanosphere patterned substrates densification induced column width reduction and alteration in the periodic nanocolumn arrangement. However, column merging effect is not observed due to larger inter-column distance and relatively stable nanostructure.
  - On Si patterned substrates after extended annealing interval nanostructures retain the shape and uniformity. For instance, the angle between the two arms of the chevron structures did not exhibit any significant deviation and column merging effect was absent.
  - Large inter-column distance ($\lambda \approx 147\pm26$ nm) prevents the merging or coalescing of adjacent columns and relatively broad nanostructure prevents nanostructure degeneration at elevated annealing temperatures.
  - HRTEM investigations illustrated multiple-grains of the order of 5-30 nm (in diameter) present within nanostructures after the annealing treatment.
6.1 Growth of multilayered Si/Ge heterostructures

Chapter 6

Glancing angle deposition of multilayered Si/Ge nanostructures

In this chapter, ion beam sputter glancing angle deposition of multilayered Si/Ge hetero-
nanostructures will be presented. Initially, it will be shown that with the use of a dual target
system, multilayered nanostructures can be deposited with alternating material supply.
Subsequently, the influence of the substrate temperature $T_S$ on the growth of glancing angle
deposited structures is evaluated, with a specific attention towards column merging behavior,
column number density and structure diameters on planar substrates. Later, growth of
multilayered nanostructures on Si patterned substrates is discussed. Additionally, the
experimental realization of a Ag capping layer on such multilayered Si/Ge nanostructures is
briefly presented.

6.1 Growth of multilayered Si/Ge heterostructures

Most of the reported investigations on three-dimensional nanostructures deposited with GLAD
focused on structures consisting of only one particular material system, while only few studies
[13-18] concentrated on the fabrication of heterostructures by combining different materials. In
fact, multi-component GLAD nanostructures with high porosity (thus increased surface-to-
volume ratio) and manifold shapes could find a wide range of applications. Specifically, the
promising efficiency of SiGe thermoelectric systems [56, 146-149, 210, 211] encourages the
investigation of multilayered Si/Ge GLAD nanostructures for the realization of thermoelectric
power generation modules.

With the aid of a dual target system and alternating material supply, multilayered thin films can
be achieved. For this purpose, Si and Ge targets were attached on opposite sides of the target
holder assembly, which is rotatable around its axis through 360°, as shown in section 3.1. Thus,
each material was sputtered sequentially and the deposition was carried out with a slit aperture
placed between target and substrate. In the presence of the slit aperture, an opening of 15±3 mm
collimates the particle flux arriving at the substrate surface with a resulting deposition rate $r_a =
3.5± 0.3 \text{ nm/min (at } \beta \approx 86^\circ)$. 

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Substrate temperature influence on planar substrates

Figure 6.1(a) illustrates a compact multilayered film deposited with normal angle incidence ($\beta \approx 0^\circ$) by sequential alternate sputtering of Si and Ge targets. The SEM micrograph depicts two layers of each Si and Ge, where the thickness of each layer amounts to $h \approx 200$ nm. At normal angle incidence the deposition rates were $r_{\text{Si}_0} = 28.5 \pm 0.3$ nm/min and $r_{\text{Ge}_0} = 27.8 \pm 0.3$ nm/min. The micrographs depict sharp interfaces and low surface roughness. Thus, interfacial characteristics could be investigated by the depth profile analysis. The TOF-SIMS depth profile measurement (Fig 6.1(b)) demonstrates a sharp increase and decrease of the intensities of $^{30}\text{Si}$ and $^{74}\text{Ge}$ signals at the respective layer interfaces. Additionally, a certain amount of inter-mixing is detected from the intensity of the $^{28}\text{Si}^{-}$-$^{74}\text{Ge}^{-}$ signal at each Si/Ge interface. The depth profile of the $^{30}\text{Si}^{-}$ signal demonstrates Si negligible diffusion into the Ge layer. Likewise, the depth profile of the $^{74}\text{Ge}^{-}$ signal reveals a small fraction of Ge within each Si layer. Typically, quantification by Rutherford backscattering (RBS) spectrometry\textsuperscript{24} on such multilayered samples delivered a Ge concentration of $\sim 0.7$ at. % within the Si layer.

In a similar approach, multilayered GLAD nanostructures were deposited by adjusting the deposition angle ($\beta \approx 86^\circ$) and sequential alternate sputtering of Si and Ge targets. Figure 6.2 depicts multilayered Si/Ge GLAD nanocolumns deposited on planar Si(100) substrates at $T_S =$

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\textsuperscript{24} For the RBS measurements, the scattering cross-section is directly proportional to the square of the target material atomic number ($\sigma \propto Z_T^2$) and therefore in this case the sensitivity for Ge ($Z_T=32$) is significantly higher than for Si ($Z_T=14$).
6.1 Growth of multilayered Si/Ge heterostructures

RT. From the cross-sectional views each layer with distinct material contrast is clearly visible. It is apparent that the layer height remains intact for a constant deposition time ($t_{dep} = 50$ min) for each layer. The GLAD inherent columnar appearance of the film can be noticed for both the films, where the overall film thickness accumulated to $h(\text{RT}) \approx 476$ nm. Although, the top-most layer in each film differed, both the top-view micrographs depicted large similarities in terms of inter-column separation and column widths. Hence, independent of the starting layer nanocolumns exhibit identical morphologies at $T_S = \text{RT}$.

To understand the growth differences at elevated substrate temperatures, nanocolumns comprising of two layers of each material were deposited at temperatures ranging from $\text{RT} \leq T_S \leq 300$ °C. Additionally, as the growth characteristics of Si and Ge nanostructures at elevated substrate temperatures diverge considerably [61, 200], multilayered nanocolumns were also deposited with a starting layer of Si and Ge in each case. Subsequently, the effects of substrate temperature on column merging behavior, column density and structure diameter on planar substrates were examined.

For Si nanocolumns, with increasing substrate temperature $T_S$ diffusion-driven mass transport ($T_S / T_M \geq 0.3$) induces column broadening, while the average column number density decreases with increasing temperature [58, 61]. At an elevated substrate temperature, adatoms diffuse over the substrate surface for larger distances before they contribute to the growing seed. Hence, intra-columnar spaces are filled with diffusing adatoms [45]. As a consequence, the average size of some of the mounds enhances and the surface mound density decreases.

As described in section 5.2 for Ge nanocolumns, intra-columnar growth at $T_S = 200$ °C provokes a sudden increase in the average column number density. But column broadening dominates the overall film morphology for $T_S \geq 200$ °C, which leads to a decrease in average column number.
density. Hence, during multilayered nanocolumn growth, the starting layer influences the overall morphology as demonstrated in Fig 6.3.

Figures 6.3(a) and (b) show the temperature series of multilayered Si/Ge nanostructures deposited on planar Si(100) substrates, with starting material Si and Ge, respectively. In both cases, the typical columnar appearance was observed to be persistent at $T_S = 100^\circ$C, and on a larger extent a morphology resemblance is noticed.

However, depending on the starting layer (either Si or Ge) the columnar evolution of multilayered nanocolumns differs for $T_S = 200$ and $300^\circ$C due to enhanced surface diffusion effects. The SEM cross-sections demonstrate significant differences in the growth processes. With increased surface diffusion, inter-mixing of Si and Ge layers and column merging occur, and individual layers become complicated to trace. But in general with increasing substrate temperature independent of the starting layer, the column width increases and the average column number density decreases as depicted in Fig 6.4(a) and (b).
The XRD measurements\textsuperscript{25} demonstrated growth of polycrystalline Ge films above 200 °C, corresponding to the reflections only associated to polycrystalline Ge. This in agreement with the observations discussed in section 5.2, where Ge film turned crystalline for $T_S \geq 200$ °C. Moreover, for Ge nanocolumns deposited at elevated substrate temperatures the overall film thickness increased\textsuperscript{26}, due to increased shadowing correlated with crystal faceting and improvement of the crystalline quality of the film (above 200 °C) [200]. However, for Si nanocolumns with increasing substrate temperature the densification caused a reduction of the film thickness [61]. In the case of multilayered nanocolumns a mixed trend is identified, where the film thickness decreased from RT to 200 °C and further increased with increasing temperature at 300 °C, as shown in Fig. 6.4(c).

\textsuperscript{25} XRD measurements revealed Ge(111), Ge(220) and Ge(311) reflections, while no Si reflection was detected suggesting amorphous phase.

\textsuperscript{26} Discussed in detail in section 5.3: For equal deposition time ($t_{dep}=140$ min), the overall film thickness decreased from $h$(RT) = 443 nm to $h$(200 °C) = 313 nm. Whereas, once the film turned crystalline ($T_S > 200$ °C), the overall film height $h$ increased to $h$(340 °C) = 382 nm.
6.2 Multilayered Si/Ge nanostructures on patterned substrates

As described in the earlier chapters, due to the statistical nature of the growth process on planar substrates columnar structures randomly evolve on the substrate surface [99, 120, 183], and the structure dimensions cannot be controlled precisely [4]. Hence, various substrate pre-patterning methods are used in order to control the lateral periodicity of growing nanostructures [3, 5, 74, 77, 79, 105, 195, 197, 212, 213]. Among several pre-patterning methods, Zhou et al. [14, 15] used a self-assembled monolayer of nanospheres to obtain periodic arrays of multi-component nanorods. Instead, it may be possible to grow multilayer Si/Ge nanostructures on Si patterned substrates at room temperature. Moreover as described in section 5.5.4, on such Si patterned substrates it is possible to retain the distinct GLAD columnar morphology, upon post-deposition annealing. It is therefore of high interest interesting to investigate growth of multilayered Si/Ge nanostructures on Si patterned substrates.

For the growth of multilayered Si/Ge nanorod arrays, Si patterned substrates\(^{27}\) with different seed widths \(w_S\) and inter-seed distances \(R_S\) were used. Subsequently, multilayered nanorod arrays comprising of 2, 6, 9 and 18 layers of each, Si and Ge, were deposited with sequential alternate deposition. Figure 6.4 illustrates multilayered Si/Ge

Fig 6.5: Cross-sectional and top-view SEM micrographs of multilayered Si/Ge nanorod arrays deposited on Si patterned substrates with pattern period : [(a)-(b)] \(R_S = 435\) nm, \(w_S = 100\) nm; [(c)-(d)] \(R_S = 522\) nm, \(w_S = 200\) nm; [(e)-(f)] \(R_S = 622\) nm, \(w_S = 100\) nm. The arrow indicates Si pattern seed.

\(^{27}\) Substrates were patterned by a combination of self-assembly monolayers of PS nanospheres and RIE (as described in section 3.2)
nanorod arrays on such Si patterned substrates with patterned periods $R_s = 435$, 522 and 622 nm. Two layers of each, Si and Ge, are deposited alternately with the starting layer being Si. The growth of GLAD structures on planar substrates usually starts with the formation of seeds having small dimensions in the range of 20-30 nm [115]. Likewise, the growth on Si pattern features can be compared to the individual seeds which are formed on a flat surface at an early stage of mound formation and receive particle flux for the subsequent growth. As discussed in section 5.4, under extreme shadowing conditions and for sufficiently narrow seeds, fiber-like structures emerge on the early stage mounds. Subsequently, inter-column competition and merging of neighbouring structures sets in, which eventually results in the growth of an isolated, large structure that then incorporates multiple sub-branches and bifurcated structures. Figures 6.5(a), (c) and (e) show multilayered Si/Ge nanorods deposited on Si patterned substrates with pattern period $R_s = 435$, 522 and 622 nm, respectively. On the Si patterned substrate with inter-seed distance $R_s = 435$ nm, each nanorod is constituted of 1-3 branches (Figures 6.5(a) and (b)), while the average nanorod width measured $w \approx 453 \pm 37$ nm. Here, alternate Si and Ge layers can be distinguished due to the different material contrast.

As discussed in section 5.4, for Ge nanorods deposited on Si patterned substrates with period $R_s = 522$ nm and relatively broad Si seed width $w_s = 200$ nm growth of isolated nanorods was observed. However, during multilayer growth, for each Si or Ge layer the initial growth front is formed by a prior deposited layer that exacerbates the branching effect, as clearly noticed from Fig. 6.5(c) and (d) where increased branching is detected within each nanorod. But merging of adjacent structures during the growth eventually leads to the growth of isolated structures that incorporate 2-4 sub-branches and bifurcated structures (Fig. 6.5(d)). An example of such a nanorod is depicted in the cross-sectional view (Fig. 6.5(c)), where a distinct Si seed step underneath the nanorod and sub-branches are visible, with alternate Si and Ge layers marked by dotted lines. The growth on the side walls of the Si seed pattern can be attributed to the exposure height [105]. Here, due to the increased column competition on a broad Si seed ($w_s = 200$ nm)[199], more branching is observed in comparison to the nanorods grown on a pattern with

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28 The substrate patterning method (described in section 3.2) presents the following pattern dimensions: (a)-(b) $R_s = 435$ nm, $w_s = 100$ nm, (c)-(d) $R_s = 522$nm, $w_s = 200$ nm, and (e)-(f) $R_s = 622$ nm, $w_s = 100$ nm.
period $R_s = 435$ nm. Moreover, the average column width increased to $w \approx 626\pm28$ nm caused by to the increased seed width and inter-seed space.

With increasing pattern period, the column competition is suppressed [72, 77] for $R_s = 622$ nm ($w_s = 100$ nm) and consequently, lesser branching or column-bifurcation can be noticed from the top-view (Fig. 6.5(f)) in comparison to the pattern period $R_s = 435$ and 522 nm (Fig. 6.5(b) and (d)). But analogous a multilayered Si/Ge nanorod array with an average width $w \approx 593\pm31$ nm is observed. The reduced broadening effect could be attributed to the decreased seed width $w_s$. Evidently, consecutive merging during continuous deposition conditions leads to the growth of isolated structure with branched and bifurcated features, on each Si seed. It is worth noting that for an optimized pattern period, the smaller the seed width, the lesser the branching observed.

By adjusting the deposition angle, dense Ag layers can be deposited on the top of multilayered Si/Ge nanostructures, which can potentially serve as a promising conductive capping layer. The growth of the capping layers on GLAD films has been studied previously by a few groups [26-30]. With the deposition angle set to $\beta = 45^\circ$, a dense Ag capping layer can be deposited on GLAD grown of Si/Ge nanorod arrays ($h \approx 900$ nm) on planar (Fig 6.5 (a)) and pre-patterned (Fig 6.6(b)) substrates\(^29\). With a constant deposition rate $r_45 \approx 26.6$ nm/min and deposition time $t_{dep} = 15$ min, a capping

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\(^29\) Multilayered Si/Ge nanostructures were deposited with 6 alternate layers of Si and Ge on planar Si(100) and Si patterned substrates $R_s = 622$ nm. Before depositing Ag capping layers post-growth samples were rinsed with buffered HF solution to prevent any contamination and then immediately loaded in the vacuum chamber.
layer of thickness ~ 400 nm was attained on Si/Ge nanorod arrays, as illustrated in Fig 6.6(c)-(f). On planar Si(100) substrates (Fig 6.6(c) and (e)), due to narrow inter-column distribution ($\lambda \approx 132$ nm) a compact Ag capping layer is formed. On the other hand, on Si patterned substrates, inter-column separation is significantly large ($\lambda \approx 227$ nm) as displayed Fig. 6.6(b). Therefore, the capping layer deposited on the nanorod arrays consists of cracks and voids, as noticeable from Fig. 6.6(d). Moreover, the cross-section SEM micrograph (Fig. 6.6(f)) reveals that obliquely deposited Ag enhances the overall width of the nanorod as Ag adatoms diffuse and coats the exterior nanorod surface. In contrast, narrow inter-column separation on planar Si(100) prevents such diffusion over the nanorod surface and subsequently a uniform, dense capping layer is obtained (Fig. 6.6(e)). It can be concluded that the uniformity and consistency of the capping layer depends upon the inter-column separation and the capping layer thickness. Further, the uniformity of such a capping layer can be improved by optimizing the inter-column separation.
6.3 Summary of results

Following are the main results concerning basic understanding of the growth of multilayered Si/Ge heterostructures on planar and pre-patterned substrates:

*Growth of multilayered Si/Ge heterostructures*

- With the aid of alternate sputtering of Si and Ge targets multilayered Si/Ge nanostructures can be deposited. For multilayered Si/Ge dense film SEM micrographs depicted sharp interfaces and low surface roughness.
- TOF-SIMS measurements of the multilayered Si/Ge dense film revealed sharp decrease in the intensities of Si and Ge at the respective interfaces.
- Influence of substrate temperature on GLAD grown multilayered Si/Ge nanostructures:
  - At RT with alternate material supply multilayered Si/Ge nanostructures can be deposited, where distinct columnar morphology is observed. But, at elevated substrate temperature surface diffusion influences the resulting morphology of the film depending on the starting layer material.
  - For Si/Ge nanostructures with Si as the starting layer: an increase in the substrate temperature leads to the column broadening effect.
  - For Si/Ge nanostructures with Ge as the starting layer: intra-columnar growth (~200 °C) and extensive column broadening (~300 °C) is observed for Ge nanocolumns. This influences the resulting morphology of multilayered film. Additionally, film deposited above 200 °C exhibited polycrystalline growth with the reflections associated with crystalline Ge structures.
  - Correspondingly, temperature induced surface diffusion caused distinct effects that are attributed to both Si [61] and Ge [200] structures. As a consequence, during the multilayer growth column merging, coalescing and broadening effects are dependent upon the starting layer material and distinct morphologies associated with temperature effects on both Si and Ge nanostructures.
6.3 Summary of results: Glancing angle deposition of multilayered Si/Ge nanostructures

**Multilayered Si/Ge nanostructures on pre-patterned substrates**

- On Si patterned planar-hcp templates multilayered Si/Ge nanocolumn arrays can be grown with alternate material deposition, where each layer can be identified using different material contrast in SEM micrograph.
- With substrate patterning nanostructure periodicity can be precisely controlled and desired number of layers can be deposited systematically.
- Ag capping layer can be deposited by adjusting deposition angle to $\beta \approx 45^\circ$ and a dense layer on the top of multilayered Si/Ge nanostructures can be formed. On planar substrates due to narrow inter-column distribution ($\lambda \approx 132$ nm) a compact Ag capping layer is formed. In contrast, on Si patterned substrates, inter-column separation is significantly large ($\lambda \approx 227$ nm) and thus capping layer deposited on the nanorod arrays is comprised of cracks and voids.
Chapter 7

Summary and conclusions

In this work, the effects of deposition conditions on the morphological evolution of ion beam sputter deposited Ge, Ag and multilayered Si/Ge nanostructures were investigated. Several experimental parameters were systematically varied and their influence the nanostructure growth was examined.

At the beginning, influence deposition geometry on the growth of Ag films at elevated substrate temperature $T_S$ was examined in detail. On native oxide covered Si(100) substrates ion beam sputter deposition under normal angle incidence resulted in the growth of epitaxial Ag film at elevated substrate temperature. Moreover, on oxide-free (HF treated) Si(100) substrates similar deposition led to non-epitaxial film growth. According to the investigations by Hur et al.[37], a combination of higher growth temperature and the magnetron sputtering method can activate the oxide desorption process and therefore, impinging sputtered Ag atoms can reach the exposed Si(100) substrate surface. However, TOF-SIMS study detected a considerable fraction of O content at the Ag/Si interface for the epitaxial Ag films, even though the intensity of the O content decreased with increasing substrate temperature. For Ag-GLAD nanostructures an immense morphological difference was noticed in the absence and in the presence of particle flux collimation at elevated substrate temperature. The particle flux collimation was observed to be an essential control to grow atypical ‘whisker-like’ Ag nanorods of sub-micron length. In contrast, the absence of aperture leads to a broad angular distribution of particle flux which resulted in the emergence of ‘mountain-like’ nanostructures. The slit aperture restricts the incoming particles ($\Delta\beta \approx 9^\circ$) and thereby increasing the probability of an adatom, with enhanced diffusion capability at high temperatures, to diffuse along a growing nano-rod or -wire and to reach the top thereof before getting trapped and buried by the following adatoms.

In the later part, the influence of various deposition conditions on the glancing angle deposited Ge nanostructures on planar and pre-patterned substrates was presented. Additionally, the influence of vertical deposition rate and substrate rotational velocity was examined in order to achieve free-standing manifold nanostructures like spiral-, screw-like structures on planar substrates. Besides, influence of substrate temperature on the nanostructure growth on planar and
pre-patterned substrates was presented. For vertical column-like structures it was found that there exists a transition temperature at 200 °C at which intra-columnar growth changes the morphology of the film drastically and nanostructures turn crystalline. In order to obtain Ge nanostructures on Si seed patterns honeycomb-like and planar-hcp templates were utilized for GLAD growth. For rotational asymmetric honeycomb-like template it was observed that the inter-seed distances and the seed heights strongly influence the shape of the nanorods grown thereon. Moreover, on the enlarged pattern periods surplus particle flux due to inadequate shadowing from the direction of second and third nearest neighboring seeds caused increased inter-seed condensation and a change nanorod shape evolution from usual triangular to hexagonal shape. On the contrary, on rotationally symmetric planar-hcp pattern narrow inter-seed distance and broad seed width led to multiple column growth on each Si seed. However, on optimized pattern period singular nanorod structures evolved with nearly circular cross-section. Post-deposition annealing of Ge nanostructures grown planar Si substrate demonstrated recrystallization at ~ 500 °C), while morphological coarsening and column disintegration effect were seen for extended annealing durations. In contrast, on Si patterned templates nanostructures retained the shape and column merging effect was absent. HRTEM investigation revealed nanocrystalline domains of the order of 5-30 nm (in diameter) present within the nanostructures.

Finally, the growth of multilayered Si/Ge nanostructures realized by alternate sputtering of Si and Ge targets on planar substrates was presented. Besides, the effects of substrate temperature on the growth of multilayered Si/Ge nanostructures were examined. It was found that due to the different growth modes of Si and Ge with respect to substrate temperature the initial growth layer influences the resulting morphology to a considerable extent. Additionally, growth of multilayered Si/Ge nanostructures on planar-hcp templates was examined. Moreover, the feasibility of Ag capping layer on the top of such multilayered structures on planar and pre-patterned substrates was demonstrated. Such hetero-structures could offer promising future prospects in for e.g: multilayered Si/Ge thermoelectric devices.
Bibliography


[182] Zhao YP, Chaney SB, Zhang ZY: Absorbance spectra of aligned Ag nanorod arrays prepared by oblique angle deposition. *Journal of Applied Physics* 2006, 100(6).


List of variables

\( \beta \) Deposition angle with respect to substrate normal \([^\circ]\)  
\( h_S \) Seed height \([\text{nm}]\)  
\( l \) Shadowing length \([\text{nm}]\)  
\( \delta \) Column tilt angle with respect to substrate normal \([^\circ]\)  
\( \Phi \) Azimuthal angle \([^\circ]\)  
\( \omega \) Rotation speed \([\text{rev/min}]\)  
\( r \) Deposition rate \([\text{nm/min}]\)  
\( t_{\text{dep}} \) Deposition time \([\text{min}]\)  
\( \rho \) Ratio of vertical deposition rate to rotational speed \([\text{nm/rev}]\)  
\( D \) Nanosphere diameter \([\text{nm}]\)  
\( d_S \) Inter-seed distance in honeycomb-pattern \([\text{nm}]\)  
\( R_S \) Inter-seed distance in hexagonal planar closed packed pattern \([\text{nm}]\)  
\( w_S \) Seed width in hexagonal planar closed packed pattern \([\text{nm}]\)  
\( w \) Column width \([\text{nm}]\)  
\( h \) Column height \([\text{nm}]\)  
\( n \) Column number density \([\mu\text{m}^{-2}]\)  
\( p, q \) Growth exponents  
\( R_{\text{Sat}} \) Column saturation radius \([\text{nm}]\)  
\( F \) Inter-seed condensation \([\text{nm}]\)  
\( T_S \) Substrate temperature \([\text{°C}]\)  
\( T_M \) Melting temperature \([\text{°C}]\)  
\( T_S/T_M \) Homologous temperature \([\text{°K}]\)  
\( T_A \) Annealing temperature \([\text{°C}]\)  
\( E \) Ion energy \([\text{eV}]\)  
\( Y \) Sputtering yield  
\( U_0 \) Surface binding energy \([\text{eV}]\)  
\( N \) Atomic density of target material \([\text{nm}^{-3}]\)  
\( \alpha_{ST} \) Ion incidence angle on with respect to target normal \([^\circ]\)  
\( \zeta \) Atomic emission angle from target \([^\circ]\)  
\( <E> \) Average energy of sputtered particles \([\text{eV}]\)  
\( p_o \) Base pressure \([\text{mbar}]\)  
\( p_{\text{dep}} \) Deposition pressure \([\text{mbar}]\)  
\( f_{\text{Ar}}, f_{\text{O2}} \) Gas flow \([\text{sccm}]\)  
\( t_{\text{O2}} \) Oxygen flow duration \([\text{min}]\)  
\( U_B \) Beam voltage \([\text{V}]\)  
\( U_A \) Acceleration voltage \([\text{V}]\)  
\( I_B \) Beam current \([\text{mA}]\)  
\( I_A \) Acceleration current \([\text{mA}]\)  
\( P_{\text{HF}} \) RF power \([\text{W}]\)  
\( E \) Slit aperture opening \([\text{mm}]\)  
\( \phi \) In plane rotation angle around the sample axis \([^\circ]\)  
\( \theta \) Angle of incident x-ray beam \([^\circ]\)  
\( \chi \) Azimuthal angle in XRD analysis \([^\circ]\)
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>GLAD</td>
<td>Glancing angle deposition</td>
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<tr>
<td>OAD</td>
<td>Oblique angle deposition</td>
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<td>PVD</td>
<td>Physical vapor deposition</td>
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<td>CVD</td>
<td>Chemical vapor deposition</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>FIB</td>
<td>Focused ion beam</td>
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<td>XRD</td>
<td>X-ray diffractometry</td>
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<td>TOF-SIMS</td>
<td>Time-of-flight secondary ion mass spectrometry</td>
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<td>PS</td>
<td>Polystyrene</td>
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<td>NSL</td>
<td>Nanosphere lithography</td>
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<tr>
<td>EBL</td>
<td>Electron beam lithography</td>
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<tr>
<td>Planar-hcp</td>
<td>Planar-hexagonal closed packed</td>
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<tr>
<td>RT</td>
<td>Room temperature</td>
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<tr>
<td>FFT</td>
<td>Fast fourier transformation</td>
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<tr>
<td>PSD</td>
<td>Power spectral density function</td>
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<tr>
<td>SPIP</td>
<td>Scanning probe image processor</td>
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Supervisor: Prof. Dr. Dr. h.c. Bernd Rauschenbach
List of publication

The contents of this thesis have been published in the following articles, are submitted, or in-preparation for future publication.


10. A. Shalabney, C. Khare, B. Rauschenbach and I. Abdulhalim, Surface Enhanced Raman Scattering from metallic nano sculptured thin films - a comparative study, (*submitted*).

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Chinmay Khare