Phase Formation of Photoactive TiO$_2$ Thin Films by Metal Plasma Immersion Ion Implantation and Deposition

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CHAPTER 1 Introduction

Titanium dioxide (TiO\textsubscript{2}) belongs to the family of transition metal oxides. Among the semiconductors, TiO\textsubscript{2} (E\textsubscript{g} = 3.2eV) has proven to be the most suitable for widespread environmental applications, since it is biologically and chemically inert; it is stable with respect to photocorrosion and chemical corrosion; and it is inexpensive. Photoinduced processes are studied in a manifold ways and various applications have been developed since their first description. Beside an electrical use of this energy in solar cells, chemical effects (photochemical catalysis) or surface changes of the catalyst itself (superhydrophilicity) are observed. Titanium dioxide is one of the most important and most widely used compounds in all these application areas. By far, the most active field of TiO\textsubscript{2} photocatalysis is the photodegeneration of organic compounds. TiO\textsubscript{2} has become a photocatalyst in environmental decontamination for a large variety of organics, viruses, bacteria, fungi, algae, and cancer cells, which can be totally degraded and mineralized to CO\textsubscript{2}, H\textsubscript{2}O, and harmless inorganic anions. The ability to control photocatalytic activity is important in many other applications including utilization of TiO\textsubscript{2} in paint pigments and cosmetics.

However, to obtain the active phases anatase or rutile, conventional thin film deposition techniques need substrate temperatures of at least 400 – 700 °C, precluding the use of many temperature sensitive substrates, especially polymers. Using ion assisted deposition, it is known that the athermal energy provided by the impinging ions within the immediate surface region will results in a very short and spatially confined thermal spike, thus allowing the grows of high temperature phases while the substrate remains at room temperature.

TiO\textsubscript{2} can be prepared in the form of powder, crystals, or thin films. While powders are frequently utilized, thin films prepared by different methods, as magnetron sputter deposition, plasma immersion ion implantation and metal arc deposition, are also under investigation.

Metal Plasma Immersion Ion Implantation and Deposition (MEPIIID) is a relatively new method for surface modification of materials. Using this method, a pulsed regime is employed with accelerated, energetic ions arriving on the substrate during the high voltage pulses and low energy, respective hypersonic ions from the cathodic arc used to generate the Ti ions, between the pulses. Compared to continuous bombardment with 500-1500 eV ions, in this
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pulsed mode the total sputter rate of the growing film by the impinging ions is reduced. Oxygen gas backfill leads to a partial transfer of the kinetic energy from Ti ions to oxygen molecules during the transit from the cathode towards the substrate, thus partially ionizing the oxygen molecules. Furthermore, neutral oxygen atoms are preferentially adsorbed on the reactive TiO$_2$ surface and included in the film growth.

The aim of this work has been the formation of photoactive titanium dioxide thin films on temperature sensitive substrates using energetic ion bombardment to supply the necessary energy for anatase or rutile phase formation as well as heating the substrate up to 300 °C. According to published literature data on the phase formation of TiO$_2$, an average energy of 20 eV per deposited particle corresponds to substrate temperature around 700 °C. Using MEPIIID to accelerate the ions, a large variety of parameters is available to tailor the ion bombardment.

After reviewing the properties, structure and photoactive properties of TiO$_2$ in chapter 2, the basics of PIII and MePIIID are described in chapter 3. Experimetal setup used in this work and short overview of the used analytic techniques are presented in chapters 4 and 5. The main part of this thesis is presented in chapter 6 and 7.

In chapter 6 the results obtained from investigations of structure, morphology and photoactivity of the samples produced by MePIIID at room temperature, are presented and discussed. At a typical pulse length of 10 – 30 µs and duty cycles of 5 – 15%, average particle energies of up to 250 eV were achieved for 3 – 5 kV pulse voltage when taking the average charge state and ionized fraction into account. Phase formation, texture and morphology are investigated using SEM, TEM, X-ray diffraction and Raman spectroscopy. Silicon, Silicon oxide and fused silica wafers are used as substrates for these investigations. The photo-induced activity was evaluated into ways: (i) measuring the surface energy of the thin films using two different liquids (to allow the derivation of the surface energy and the polar/disperse fractions from the contact angle) as a function of UV illumination (time and intensity); (ii) determination of the decomposition rate of methylene blue, an organic model substance, used for evaluating the photo-activity of TiO$_2$. Thus, the deposited energy is supposed to be sufficient to induce the formation of the high temperature rutile phase. However, the nucleation processes were normally occurring on a much shorter timescale. Thus, it was established that rutile nucleates during the pulses and anatase or an amorphous phase between the pulses with a subsequent growth of both phases. Additionally, a variation
of the pulse voltage and the duty cycle was performed to keep the average energy constant while the pulse voltage was varied. Beside the athermal energy deposition by the energetic ions, damage formation proportional to the ion energy was occurring, which is especially critical for low temperatures and high ion energies as the subsurface damage cannot be annealed under these conditions, in contrast to the surface damage.

In chapter 7 the results obtained from investigations on TiO$_2$ thin film deposited with additional substrate heating using a different experimental setup from above chapter are presented. The energy/temperature phase diagram available in the literature which quantifies the replacement of thermal substrate heating with energetic ions was provided to exemplify the basic mechanisms during thin film deposition, especially the phase formation. However, as secondary effects as grain boundaries or crystallite size with their corresponding electronic defects are playing an important role in the photo-induced activity, a detailed investigation on temperature effects, especially annealing of defects and enhancement of crystallite growth with a reduced density of grain boundaries was performed.

These latter effects cannot be produced by ion bombardment alone, thus a process optimization with the substrate temperature or the temperature variation during the process (e.g. high energy bombardment during the nucleation phase at low substrate temperature with a reduced energy and increased substrate heating during the following growth phase) to find the highest photo-activity of the deposited thin films. Depending on the previous results, only selected methods, which are most representative and informative on the parameters determining the photo-activity, for thin film analysis are used during this stage.

Finally in chapter 8, a summary and conclusions are presented.
CHAPTER 2  Titanium Dioxide

In this chapter, after a short presentation of TiO$_2$ properties and applications, a description of TiO$_2$ structure with focus to photoactive properties is introduced.

2.1 TiO$_2$ Properties

TiO$_2$ has received a great deal of attention due to its chemical stability, non-toxicity, low cost, and other advantageous properties. Because of its high refractive index, it is used as anti-reflection coating in silicon solar cells and in many thin-film optical devices [1]. Due to its hemocompatibility with the human body, TiO$_2$ is used as a biomaterial (as bone substituent and reinforcing mechanical support) [2, 3, 4, 5, 6, 7, 8]. TiO$_2$ is also used in catalytic reactions [9] acting as a promoter, a carrier for metals and metal oxides, an additive, or as a catalyst. Rutile is investigated as a dielectric gate material for MOSFET devices as a result of its high dielectric constant ($\varepsilon > 100$) [10, 11], and doped anatase films (using Co) might be used as a ferromagnetic material in spintronics [12, 13]. In batteries, the anatase form is used as an anode material in which lithium ions can intercalate reversibly [14]. For solar cell applications, the anatase structure is preferred over the rutile structure, as anatase exhibits a higher electron mobility, lower dielectric constant, lower density, and lower deposition temperature.

The primary criterion for good semiconductor photocatalysts for organic compound degradation is that the redox potential of the H$_2$O/·OH (OH$^- = \cdot$OH + e$^-; E^0=-2.8$ V) couple lies within the bandgap domain of the material and that the material is stable over prolonged periods of time. Among various possible semiconductors such as metal oxides (TiO$_2$, ZnO, CeO$_2$, etc) and metal sulfide (CdS, ZnS, etc), titanium dioxide TiO$_2$ ($E_g = 3.2$ eV) has proven to be the most suitable for the photodegradation of toxic organic molecules due to its excellent photocatalytic performance with maximum quantum yields [15]. Semiconductor photocatalysis with a primary focus on TiO$_2$ as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification, for the destruction of microorganisms [16, 17], for the inactivation of cancer cells [18, 19], for the photosplitting of water to produce hydrogen gas [20, 21, 22, 23, 24] and for the cleanup of oil spills [25, 26, 27].
2.2 TiO$_2$ Phase Diagram

Titanium builds some stable oxides. In figure 2.1 is given the phase diagram of the titanium-oxygen [28].

The most important data from the above phase diagram are:
- Oxygen dissolves up to 30 atom % in the $\alpha$-titanium phase
- TiO crystallizes in NaCl missing state structure and can be found in a non-stoichiometric form of larger phase width TiO$_x$ ($0.70 \leq x \leq 1.30$).
- Ti$_2$O$_3$ has a corundum structure and above 200°C shows a transition from semiconductor to conductor.
- With increasing oxygen concentration oxide phases of Magnelli-type (Ti$_n$O$_{2n-1}$, with $4 \leq n \leq 9$) are formed. Here plates with a structure similar to Rutile under crystallographic shearing strain are connected to each other, thus stunt oxygen atoms by sharing of more edges between neighbor octahedra. These phases are semiconductors beside the Ti$_4$O$_7$ which is similar to metals.
- The most stable phase TiO$_2$ at normal pressure is rutile.

The last one requires an explanation because in the nature one finds three stable TiO$_2$ phases: rutile, anatase and brookite. The transition from brookite/anatase in rutile at higher temperatures.

![Figure 2.1: TiO$_2$ phase diagram](image-url)
temperatures is not reversible [28]. Therefore rutile is thermodynamically the most stable form of TiO$_2$ at normal pressure and 5 – 12 kJ/mol more stable than anatase [29].

### 2.3 The Structure of TiO$_2$

As stated, titanium dioxide crystallizes in three major different structures; rutile (tetragonal, $D_{4h}^{14} = P4_2/mnm$, $a = b = 0.459$ nm, $c = 0.296$ nm [30]), anatase (tetragonal, $D_{4h}^{19} = I4_1/amd$, $a = b = 0.379$ nm, $c = 0.954$ [31]) and brookite (rhombohedral, $D_{2h}^{15} = Pbca$, $a = 0.545$ nm, $b = 0.917$ nm, $c = 0.514$ nm) [32]. However, only rutile and anatase play any role in the applications of TiO$_2$ and are of any interest here. The unit cells of rutile and anatase are shown in figure 2.2, and the stacking octahedra of titanium dioxide major structures are depicted in figure 2.3.

![Figure 2.2: Bulk structures of rutile and anatase. The tetragonal bulk unit cell of rutile has the dimensions, $a = b = 0.459$ nm, $c = 0.296$ nm, and the one of anatase $a = b = 0.379$ nm, $c = 0.954$ nm. In both structures, slightly distorted octahedra are the basic building units. The bond lengths and angles of the octahedrally coordinated Ti atoms are indicated.](image-url)
The structures of rutile, anatase and brookite can be discussed in terms of \((\text{TiO}_2^-)^\) octahedrals. The three crystal structures differ by the distortion of each octahedral and by the assembly patterns of the octahedral chains. In rutile, neighboring octahedra share one corner along \(<110>\) – type directions, and are stacked with their long axis alternating by 90°. In anatase the corner-sharing octahedra form (001) planes. They are connected with their edges with the plane of octahedra below. In brookite, both vertices and edges are connected.

Particle size experiments affirm that the relative phase stability may reverse when particle sizes decrease to sufficiently low values due to surface-energy effects (surface free energy and surface stress, which depend on particle size) [33]. If the particle sizes of the three crystalline phases are equal, anatase is most thermodynamically stable at sizes less than 11 nm, brookite is most stable between 11 and 35 nm, and rutile is most stable at sizes greater than 35 nm [34].

The enthalpy of the anatase \(\rightarrow\) rutile phase transformation is low. A survey of the literature reveals widespread disagreement, with values ranging from -1.3 to -6:0 ± 0.8 kJ/mol [35, 36, 37]. Kinetically, anatase is stable, i.e., its transformation into rutile at room temperature is so
slow that the transformation practically does not occur. At macroscopic scale, the transformation reaches a measurable speed for bulk TiO$_2$ at $T > 600 \, ^\circ C$ [38, 39, 40]. The monotropic [41] anatase $\rightarrow$ rutile conversion has been studied for both mechanistic and application-driven reasons, because the TiO$_2$ phase (i.e., anatase or rutile) is one of the most critical parameters determining the use as a photocatalyst [42].

2.4 Photoactivity of TiO$_2$

The photoactivity of TiO$_2$ is one of its technological most attractive properties. The creation of electron-hole pairs through irradiation of light, either in TiO$_2$ itself, or in adsorbed molecules, and the following chemical or electron transfer reactions are at the heart of TiO$_2$ based photodevices applied in a range of areas. All photoinduced phenomena are activated by an input of super-band gap energy to the semiconductor TiO$_2$. Absorption of a photon with enough energy leads to a charge separation due to an electron promotion to the conduction band and a generation of a hole ($h^+$) in the valence band. The subsequent mode of action of the photogenerated electron–hole pair ($e^-h^+$), determines which of the phenomena is the dominant process, because even if they are intrinsically different processes, they can and in fact take place concomitantly on the same TiO$_2$ surface. Photocatalysis is a well-known process and is mostly employed to degrade or transform (into less harmful substances) organic and inorganic compounds and even microorganisms. The recently discovered wettability, termed as ‘superhydrophilicity’ [43], presents a large range of applications in cleaning and anti-fogging surfaces. The detailed material properties required for enhanced efficiency are different from each other. For enhanced photocatalysis, deep electron traps and high surface acidity are needed to lengthen the lifetime of photoexcited electrons and holes and to ensure better adsorption of organic substances on the surface. Meanwhile, low surface acidity and, most of all, a large quantity of Ti$^{3+}$ is essential for hydrophilic surface conversion. These differences are related to the fact that photocatalysis is more likely to be sensitive to bulk properties, while hydrophilicity can be definite as an interfacial phenomenon.

2.4.1 Photocatalysis of TiO$_2$

Semiconductor electronic structures are characterized by a filled valence band (VB) and an empty conduction band (CB), and can act as sensitizers for light-reduced redox processes. When a photon with an energy of $h\nu$ matches or exceeds the bandgap energy $E_g$ of the semiconductor, an electron $e^-_{cb}$, is promoted from the valence band, into the conduction band, leaving a hole, $h^+_{vb}$, behind. Excited state conduction-band electrons and valence-band holes
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Figure 2.4: Main processes occurring on a semiconductor particle: (a) electron–hole generation; (b) oxidation of donor (D); (c) reduction of acceptor (A); (d) and (e) electron–hole recombination at surface and in bulk, respectively [44].

can react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles or recombine and dissipate the input energy as heat, get trapped in metastable surface states. The above process in the photocatalysis is illustrated in figure 2.4.

For a semiconductor photocatalyst to be efficient, the different interfacial electron processes involving $e_{cb}^-$ and $h_{vb}^+$ must compete effectively with the major deactivation processes involving $e_{cb}^- - h_{vb}^+$ recombination, which may occur in the bulk or at the surface. Ideally, a semiconductor photocatalyst should be chemically and biologically inert, photocatalytically stable, easy to produce and to use, efficiently activated by sunlight, able to efficiently catalyze reactions, cheap, and without risks for the environment or humans. Titanium dioxide (with sizes ranging from clusters to colloids to powders and large single crystals) is close to being an ideal photocatalyst, displaying almost all the above properties. The single exception is that it does not absorb visible light.

TiO$_2$ photocatalysis mechanism can be described as below [15]:

Charge – carrier generation

$$TiO_2 + h \nu \rightarrow e_{CB}^- + h_{VB}^+ \quad (2.1)$$
Charge – carrier trapping
\[ h_{VB}^+ + [-Ti^{4+}OH] \rightarrow [-Ti^{4+}OH^{**}] \]
\[ e_{CB}^- + [-Ti^{4+}OH] \leftrightarrow [-Ti^{3+}OH] \]
or
\[ e_{CB}^- + Ti^{4+} \rightarrow Ti^{3+} \]

Charge – carrier recombination on the surface
\[ e_{CB}^- + [-Ti^{4+}OH^{**}] \rightarrow Ti^{4+}OH \]
\[ h_{VB}^+ + [-Ti^{3+}OH] \rightarrow Ti^{4+}OH \]

Interfacial charge transfer
\[ \begin{align*}
-[-Ti^{4+}OH^{**}] + R_{ed} & \rightarrow [-Ti^{4+}OH] + R_{ed}^{**} \\
[-Ti^{3+}OH] + O_s & \rightarrow [-Ti^{4+}OH] + O_s^- \\
Ti^{3+} + O_s & \rightarrow Ti^{4+} + O_s^-
\end{align*} \]

(2.4)

where \([-Ti^{4+}OH]\) represents a OH group of TiO2, \(e_{CB}^-\) is a conduction band electron, \(h_{VB}^+\) is a valence-band hole, Red is an electron donor (i.e., reductant), Ox is an electron acceptor (i.e., oxidant), \([-Ti^{4+}OH^{**}]\) is the surface-trapped VB hole (i.e., surface-bound hydroxyl radical), and \([-Ti^{3+}OH]\) is the surface-trapped CB electron.

Above reactions may be summarized as follows:
\[ (Ox_1)_{ads} + (Red_2)_{ads} \xrightarrow{h\nu>E_g} Red_1 + Ox_2 \]  

(2.5)

Depending on whether the sign of the change in Gibbs free energy (\(\Delta G^o\)) of the above reaction is negative or positive, the semiconductor-sensitized reaction may be an example of photocatalysis or photosynthesis, respectively [45].

Both crystal structures, anatase and rutile, are commonly used as photocatalyst, with anatase showing a greater photocatalytic activity [42, 46] for most reactions. It has been suggested that this increased photoreactivity is due to anatase’s slightly higher Fermi level, lower capacity to absorb oxygen and higher degree of hydroxylation (i.e., number of hydroxy groups on the surface) [46]. Reactions in which both crystalline phases have the same photoreactivity [47] or rutile a higher one [48] are also reported. Furthermore, there are also studies which claim that a mixture of anatase (70–75%) and rutile (30–25%) is more active than pure anatase [49, 50]. The disagreement of the results may lie in the intervening effect of various coexisting factors, such as specific surface area, pore size distribution, crystal size, and preparation methods, or in the way the activity is expressed.
2.4.2 Photoinduced Superhydrophilicity

UV illumination of TiO$_2$ may induce a patchwork of superhydrophilicity (i.e., photoinduced superhydrophilicity or PSH) across the surface that allows both water and oil to spread [51, 43]. This PSH is accompanied by photocatalytic activity, as both phenomena have a common ground; so the surface contaminants will be either photomineralized or washed away by water. One possible application is self-cleaning windows. PSH involves reduction of Ti(IV) cations to Ti(III) by electrons and simultaneous trapping of holes at lattice sites (usually bridging oxygen) or close to the surface of the semiconductor. Such trapped holes weaken the bond between the associated titanium and lattice oxygen, allowing oxygen atoms to be liberated, thus creating oxygen vacancies. The subsequent dissociative adsorption of water at the site renders it more hydroxylated. An increased amount of chemisorbed –OH leads to an increase of van der Waals forces and hydrogen bonding interactions between H$_2$O and –OH. Water can easily spread across the surface and hydrophilic properties will be enhanced [52, 53] (figure 2.5). Water adsorption does not occur uniformly but produces an amphiphilic surface with alternating hydrophilic and oleophilic regions at the scale of several nanometers (usually <10 nm in size) [51]. The hydrophilic domains align along the bridging oxygen sites. The reduced sites can be reoxidized by air and the weakly bound hydroxyl groups reactively desorbs (over some time, typically days in the dark) from the surface that returns to a more hydrophobic form. The longer the surface is illuminated with UV light, the smaller the contact angle for water becomes (a contact angles close to zero mean that water spreads perfectly across the surface). As far as the geometry of the surface is concerned, the hydrophilic properties are known to be enhanced by fine surface roughness [52, 53, 54, 55].

![Diagram of mechanism of photoinduced superhydrophilicity of TiO$_2$.](56)

**Figure 2.5:** *Mechanism of photoinduced superhydrophilicity of TiO$_2$. [56]*
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PSH was found to be of primary commercial importance due to the anti-fogging and self-cleaning properties of the deposits.
CHAPTER 3  Plasma Immersion Ion Implantation and Metal Plasma Immersion Ion Implantation and Deposition

Many methods are used for the preparation of TiO$_2$ in the form of powder, crystals or thin films, as extensively reviewed in the literature [56]. Methods correlated with the modification of surfaces are an attractive way to achieve the desired property at the surface of any bulk material. Surface modifications can be done by alloying/mixing elements at the surface of bulk materials or by an adherent overlayer on bulk materials. Plasma immersion ion implantation is one among the surface modification methods, which was developed about 20 years ago [57]. PIII is an emerging technology for the surface modification of semiconductors, metals and insulators. Materials to be treated are immersed in plasma and negative high voltage pulses are applied to the substrate holder. The positive ions are extracted from the plasma and accelerated towards the whole surface simultaneously. This technology offers a sufficiently uniform ion bombardment of components, there is no need for ion beam rastering as in conventional ion implanters, as well as providing a more simple way to treat large surface areas in a short time and cost-effective way. In the first section of this chapter the basic processes when energetic ions enter a solid, like energy loss per unit length and range, radiation damage and thermal spike, are presented. Furthermore, the principles of cathodic arc evaporation and MePIIID as a variation of PIII (where metal ions generated from cathodic arc evaporation are used), used in this work, are described.

3.1 Interaction of Ions and Electrons with Solid Surfaces

When an energetic atom or ion interacts with other particles, scattering processes occur. Elastic interactions with other atoms and inelastic scattering with electrons can be distinguished. For ion implantation within the laboratory reference system, kinetic energy is dissipated in both channels via nuclear collisions and electronic excitation, respectively. The energy loss or stopping power per length unit in the target can be given as the sum of nuclear (n) and electronic (e) stopping powers [58, 59]:

\[
\frac{dE}{dx} = \left( \frac{dE}{dx} \right)_n + \left( \frac{dE}{dx} \right)_e = -N[S_n(E) + S_e(E)]
\]  

(3.1)

where $N$ is the number density of atoms in the medium, $S_n(E)$ and $S_e(E)$ are the so-called nuclear and electronic cross sections. $S_n(E)$ determines the energy loss due to elastic collisions of the penetrating ion with target atoms and $S_e(E)$ determines the energy loss due to inelastic
processes (excitations of bound electrons of target atoms or bond breaking in a target consisting of molecules). This separation into elastic and inelastic processes can be made due to the large mass difference between ions and electrons.

An approximation for the nuclear stopping cross-section can be derived from an appropriate screened Coulomb potential [60, 61]:

\[ V(r) = \frac{Z_1 Z_2 e^2}{r} \Phi \left( \frac{r}{a} \right) \]  

(3.2)

Where \( \Phi \) is the so-called screening function, which screens the repulsive Coulomb forces of the nuclei, due to the partial shielding by the surrounding electron cloud. For shorter interaction distances, less screening is observed. For the commonly used krypton-carbon (Kr-C) potential [62], \( \Phi \) has the form:

\[ \Phi(x) = 0.190945 e^{-0.131825 x} + 0.473674 e^{-0.63717 x} + 0.335381 e^{-1.919249 x} \]  

(3.3)

\[ x = \frac{r}{a_L} \quad a_L = 0.8854 a_0 \left( Z_1^{2/3} + Z_2^{2/3} \right)^{1/2} \quad a_0 = 0.0529 nm \]  

(3.4)

Where \( a_L \) is the Lindhard screening radius for the Tomas-Fermi interaction between atoms and \( a_0 \) is the Bohr radius.

Following the notation of Lindhard et al [58, 59, 60], the nuclear stopping power then can be expressed:

\[ \left( \frac{dE}{dx} \right)_n = 509.6 \frac{\rho Z_1 Z_2 M_1 s_n(\epsilon)}{M_2 (M_1 + M_2) \left( Z_1^{2/3} + Z_2^{2/3} \right)^{1/2}} (eV \text{ nm}^{-1}) \]  

(3.5)

where \( M_1 \) is the projectile mass, \( M_2 \) is the target atom mass, \( \rho \) is the density (g cm\(^{-3}\)) and \( s_n(\epsilon) \) is the reduced stopping cross section. An analytical expression for \( s_n(\epsilon) \) based on Kr-C potential [62,63, 64, 65] was suggested by Wilson et al [64]. Another analytical expression of \( s_n(\epsilon) \) corresponds to the so-called Ziegler-Biersack-Littmark (ZBL) or universal potential [63].

Electronic stopping does only cause small scattering angles of the penetrating particle, because of the relative small electron mass, nevertheless a noticeable energy loss is recorded. At low projectile energies, following the so-called Lindhard-Scharff (LS) regime [59, 60, 63], the electronic stopping power becomes:

\[ \left( \frac{dE}{dx} \right)_e = 231.6 \rho Z_1^{1/6} \frac{Z_1 Z_2}{\left( Z_1^{2/3} + Z_2^{2/3} \right)^{1/2}} \frac{\sqrt{E(keV)}}{M_2 \sqrt{M_1}} (eV \text{ nm}^{-1}) \]  

(3.6)

Also the electronic stopping cross-section is often expressed in a dimensionless reduced form \( s_e(\epsilon) \).
The total path length or range of the ion can be calculated by integration over the energy losses:

\[ R(E) = \int dx = -\int_0^E \left( \frac{dE}{dx} \right) + \left( \frac{dE}{dx} \right)_0 \]  

(3.7)

Using the above equations in combination with the Kr-C potential, different energy losses and ranges can get estimates.

Recoil atoms (called primary knock-on atoms or PKAs) from collisions between the penetrating particle and atoms of the solid will, if sufficiently energetic, create secondary and higher-generation recoils and thus a collision cascade is produced (figure 3.1).

This leads to a distribution of vacancies, interstitial atoms and other type of lattice disorder in the region around the incident ion track. As the number of the incident ions increases, the individual disordered regions begin to overlap, and a heavily damaged layer or an amorphous region if formed. According to the radiation damage theories, a lattice atom struck by an energetic ion or recoiling target atom must receive a minimum amount of energy in the collision to be displaced from its lattice site. The minimum energy required to displace the lattice atom represents the displacement threshold and is called the displacement energy \( E_d \). If a lattice atom in a collision receives an energy greater than \( E_d \) a vacancy and an interstitial (Frenkel pair or Frenkel defect) are formed (figure 3.1). The average number of displaced atoms in a cascade produced by a primary knock-on of energy \( E \) is the displacement damage function \( N_d(E) \). A simple estimate was given by Kinchin and Pease [66], which gives for energies up to energies, where electronic stopping can be neglected (\( M/2 \) keV, i.e. 64 keV for Cu):

\[
N_d(E) = \begin{cases} 
0 & \text{for } E < E_d \\
1 & \text{for } E_d < E < 2E_d \\
E / 2E_d & \text{for } 2E_d < E 
\end{cases}
\]  

(3.8)

Equation (3.8) gives the number of displaced atoms produced by a PKA.

Another measure of irradiation damage is displacements per atom or dpa. A unit of 1 dpa means that, on average, every atom in the irradiated volume has been displaced once from its equilibrium lattice site.

Starting at energies of a few 10 eV the impinging ions have enough energy to create primary recoil atoms, which can be emitted from the target when they are located close to the surface and their momentum vectors points back to the surface. This leads to an erosion of the surface and is termed sputtering [67, 68]. Sputtering is the dominant process under ion impact, resulting in an effective surface erosion, in the energy range from 1 keV up to a few 10 keV.
During sputtering or surface erosion neutral, excited as well as ionized atoms, molecules and clusters are ejected, the bombarding particles are in part reflected, electrons as well as radiation can be emitted from the surface or from excited sputtered particles in front of the surface. The composition of the sputtered particle flux can change drastically depending whether oxygen or other electro-negative atoms are adsorbed or incorporated in the surface from almost exclusively neutral atoms and clusters to a large contribution of ions and excited atoms.

For high energy implantations where a large amount of energy is dissipated in a small volume, a thermodynamic approximation may be used to describe collective processes. A spike is defined as a high density cascade that possesses a limited volume in which the majority of atoms are temporarily in motion [70]. This highly damaged volume of material, composed of a core of vacancies surrounded by a shell of interstitial atoms (figure 3.2), is referred to as a displacement spike. In the spike regime the density of moving atoms is so high, that essentially all atoms in the “spike volume” are moving and thus collisions are dominantly between moving atoms.

At the point when the displacement spike comes to an end, the energy will be dissipated as lattice vibrations or heat. This period of lattice heating is known as the thermal spike phase of the collision cascade and may exists for several picoseconds before being quenched to ambient temperature. For a Maxwell-Boltzmann distribution of energy, the temperature is related to the mean deposited energy density in the spike by:
Figure 3.2: Schematic of a highly damaged volume of material, formed when the mean free path between collisions, $\lambda_d$, approaches the atomic spacing of the target atoms. The dense cascade is referred to as a displacement spike [71]

$$\Delta D = \frac{3}{2} k_B T$$, where $k_B$ is Boltzmann’s constant. \hfill (3.9)

The quench time, $t_q$, for a thermal spike of radius $r$ is extremely small and can be estimated by:

$$t_q = \frac{r^2}{4D_T}$$ \hfill (3.10)

where $D_T$ is the thermal diffusivity of the target.

3.2 **Plasma Immersion Ion Implantation**

In PIII, materials to be treated are immersed in a plasma containing ions of the species to be implanted. The PIII system does not use a separated ion source, extracting and accelerating coils or deflection plates as in conventional raster beam ion implanters. Usually the samples to be coated are subjected to negative potential pulses. When a negative potential is applied, electrons start moving away from the sample and the potential drops around the sample. Positive ions of the species present in the plasma accelerate normal toward the sample surface, and get implanted (shown schematically in figure 3.3).
Figure 3.3: Schematic showing the concept of PIII. a) Immersion of the sample holder in the plasma. B) Application of a high negative potential pulse to the sample holder results in an expanding plasma sheath. C) positive ions uncovered by the expanding sheath are accelerated by the high voltage and conformally implant into the substrate and substrate holder.

The PIII technique can be classified broadly based on the kind of source used for the production of the plasma. Plasma of species to be implanted can be produced from a gas or a solid material. The broad classification can thus be: (1) gaseous (conventional) PIII (PIII) and (2) metal PIII (MePIII). Metal plasma can be produced by the cathodic arc principle or by sputtering. Hence, MP III can be sub-classified as: (a) cathodic arc MP III and (b) sputter-assisted MP III.

3.2.1 Cathodic Arc Evaporation

The development of arc plasma physics is closely related to the development of electricity and thus can be traced back to the 18th century. Recent articles by Anders [72, 73] and Boxman [74] are tracking down the origin of arc plasma in pulsed, oscillating and continuous modes, and provide extensive references to early work.

Cathodic arc plasma deposition is among the oldest energetic thin-film deposition method. T.A. Edison and A.W. Wright were the first to use the arc discharge to process materials [75, 76, 77] with first commercial applications of the vacuum arc already developed in the early part of the 20th century. However, the use of arc to process materials has matured only in recent decades, due to the late availability of ultra high vacuum systems, atomic scale surface characterisation methods and modelling of deposition and transport processes.

An arc discharge can be defined as an electrical discharge of relatively high current at relatively low voltage. It is characterized by a collective mechanism of a self-sustaining discharge in front of an electrode where high current electron emission and supply of neutral atoms from the cathode are available. Vacuum arcs can be created either in a high-vacuum or
in a low-pressure gaseous environments, and films composed of metals, ceramics, diamond-like carbon (DLC), some semiconductors and superconductors, and other materials can be prepared. The method is a versatile and powerful tool for synthesizing novel and technologically interesting surfaces as a large combination of materials is available. The interest in the cathodic arc technique arises from the high deposition energy of the deposited particles which is important to promote the adhesion of the film and to disrupt columnar growth that is so detrimental for corrosion resistance for example.

3.2.1.1 Cathodic Arc Nature and Characteristics

An energetic deposition can be defined as a deposition process in which a large fraction of the depositing particles arrive on the substrate with a kinetic energy greater than the bulk displacement energy. This energy is not well defined as it depends on the crystallography of the substrate and the relative impinging direction of the bombarding particles. Displacement energies vary between 10 and 40 eV, depending on the material [78]. The bombardment induces the formation of defects such as Frenkel pairs. The flux of energetic particles can either be supplied from an independent source which assists the deposition process or the film-forming particles themselves can be energetic and the growth does not require assistance. Different techniques are available for energetic film deposition: ion-beam deposition, ion-beam-assisted deposition (IBAD), ionized and pulsed magnetron sputtering, pulsed laser plasma deposition, cathodic vacuum arc plasma deposition, and metal plasma immersion ion implantation and deposition (MePIIID). In the following, the vacuum arc and MePIIID will be developed.

Energy

Arc spots on the cathode are still a strange and fascinating phenomena. Tiny bright points of light run rapidly and irregularly across the surface. The consumable cathode is transferred to the plasma state at these microscopic (diameter of the order of 10 \( \mu \)m) non-stationary spots characterized by extremely high current density (~\(10^{11}\text{Am}^{-2}\)), power density (over \(10^{12}\text{Wm}^{-2}\)), and plasma density [79, 80]. These characteristics are due to a regime of electron emission that is totally different from the abnormal glow discharges used for example in sputtering. In arcing conditions, thermionic and field emission of electrons grow rapidly and lead to collective processes. To observe a strong thermo-field emission, the surface temperature of the spot root and the electric field strength at the surface must be high enough. Both conditions can be fulfilled by the discharge itself due to the ion flow from the plasma to the cathode surface:
1. The ions accelerated in the cathode sheath deliver their kinetic, thermal, and recombination energy during impact with the cathode surface [81]. The temperature of this surface increases strongly. In addition, resistive heating by the arc current contributes to the increase in surface temperature.

2. The space charge due to the ions flowing toward the cathode generates a high electric field. A high ion current density is only possible if the plasma density in front of the cathode is very high. Intense evaporation from the surface is necessary to provide this condition. These conditions for sufficient emission are only fulfilled if the arc spots contract. Avalanche ionisation of the emitted neutral atoms is observed across the gap between the surface and the actual plasma spot about 10 – 100 µm above the surface.

Arc spots move across the surface of the cathode very quickly, 0.1–100 ms\(^{-1}\), in most cases, and in random directions [82]. There are two possible explanations for this movement. The spot itself modifies local cathode properties by its own action until it can no longer survive. It then reignites nearby where local conditions are better. Another possibility is that the conditions remain satisfactory on the spot but better conditions develop suddenly in the neighbourhood. This could be due to the explosion of a pre-existing micro-protrusion, or formed by ejected liquid matter from the first spot. The arc spot leaves behind a crater that demonstrates the extremely intense interaction between the cathode spot and the solid surface [83]. In a few nanoseconds, intense heating and strong mechanical forces induce melting and excavation.

The ions leave the cathode spots towards the anode and the substrate with a very high kinetic energy. They are accelerated by three forces:

1. The pressure gradient within the cathodic plasma.
2. The electron–ion friction.
3. The electric field that has the opposite direction in the plasma expansion zone.

Multiply charged ions are formed by thermal and pressure ionization in the cathodic plasma [84]. The plasma jets reach speeds of \(10^3–10^4\) ms\(^{-1}\) with ion energies of 20–200 eV, depending on the nature of the evaporated material.

**Charge**

The ion charge distribution and energy as well as the cohesive energy and displacement energy for various materials and selected cathodic (vacuum) arc plasmas are reported in the literature [75]. Due to the thermal equilibrisation and the very high power density, multiply charged ions are observed at very high fractions. Higher average ion charge states are
observed for the materials with higher cohesive energies. The burning voltage, power density, average ion charge state, electron temperature, and ion kinetic energy are all related to the cohesive energy of the cathode material. Brown [85] measured these values for a large number of elements and Anders [81] presented them in the form of a periodic table. The flux of neutral atoms is usually negligible compared to the flux of ions. The ion charge states can be manipulated by magnetic fields and other methods [86].

**Time Scale**

As mentioned before, the cathode spots are moving very fast (residence time in the sub-microsecond range) and their characteristic size is smaller than 1 μm. The specifics depend on the cathode material and surface conditions [87]. Two main types of arc spots have been identified and are historically labeled types 1 and 2 (figure 3.4). Type-1 arc spots are comparatively fast, have a low brightness and arc current per spot. They are associated with surface contaminants and adsorbed gases on the cathode surface. Due to their characteristics, they do not contribute significantly to ablation of the cathode material. Type-2 arc spots are slower (around five times), have a high brightness and high current per spot. This type of spot is responsible for the ablation of the material. The transition between the two types of arc spot is especially important in the case of pulsed vacuum arc plasma sourced operating in reactive environments.

![Figure 3.4](image-url): **CCD images of an aluminum cathode showing transition from type-1 spot mode to type-2 mode. Image (a) is taken 8 pulses after the cathode was inserted into the vacuum system. After 49 pulses (b) the arc begins to operate initially in a type-2 mode before reverting to type-1 as contaminated regions are reached. After 62 pulses (c) the cathode surface has been cleaned of contaminants and the arc is operating purely in type-2 mode. Image size 6 cm x 6 cm (from Ref. [84]).**
It has been shown [88] that the composition of the plasma operated in an oxygen atmosphere depends on the arc pulse frequency. This is due to the formation of adsorbed gas monolayers on the cathode surface between pulses. The pulse frequency necessary to avoid the adsorption of significant amounts of contaminants and thus to operate in a stable regime will depend strongly on the background gas pressure.

**Macroparticles**

Unfortunately, the cathode spots not only generate a flux of ionized plasma, they are also the source of droplets and debris particles in the micrometer and sub-micrometer range commonly referred to as *macroparticles* (figure 3.5).

This is due to the explosive nature of plasma formation in a cathode spot. The formation and size distribution of macroparticles have been extensively studied (i.e. Refs. [89, 90, 91, 92]). The term “macroparticles” covers a wide range of sizes and should be understood for all particles that are much larger than atom clusters. For applications such as decorative or tool coatings, the presence of macroparticles could be tolerated. For higher end applications, such as precision optics and electronics, macroparticles must be removed or suppressed without significantly reducing the ion flux reaching the substrate. This is the main challenge for the development of industrial applications of cathodic arc plasma deposition.

![Figure 3.5: Cathodic arc erbium macroparticle deposited during growth of an erbia film (from Ref. [93]).](image)

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The most successful means to reduce film contamination by macroparticles are based on the great difference in charge-to-mass ratio between ions and macroparticles.

### 3.2.1.2 Continuous Arc (DC)

DC systems are able to provide very high deposition rates on large areas. They are especially convenient to deposit thick films for applications that do not require reduction or elimination of macroparticles. This mode of operation requires a suitable arc power supply and adequate cooling due to Ohmic heating. The cathode and the anode of the source are usually water cooled. DC sources typically operate from 30 up to 300 A. The requirements on cables and electrical feedthroughs are very demanding. The cathode is often relatively large. Without magnetic fields, cathode spots move randomly on a homogeneous surface. However, they have a tendency to reside longer on inhomogeneities such as contamination sites, grain boundaries, and inclusions. The resulting erosion rate is not smooth. A more detailed description of DC source design can be found in the literature [94].

Unfortunately, DC arcs can display density fluctuations on the millisecond time scale due to arc spot instabilities and on the second time scale due to variations in the degree of plasma coupling to the filtering system. The production of ultra-thin films with reproducible performance under these conditions is difficult [84].

### 3.2.1.3 Reactive Arc Deposition

In many cases, one of the elements is introduced as a gas in the deposition chamber. This gas interacts with the ion flux emitted by the cathode. In absence of gas, the ion energy distribution is described by a shifted Maxwellian curve. When a background gas is added, the distribution changes to one with higher Maxwellian temperature and smaller directed velocity. At still higher pressures, the distribution splits into two components: one of thermalized material and another of ions that had little interaction with the background gas [95].

The energy distribution of background gas ions shows a single contribution corresponding to a “cold” distribution. Simultaneously, the charge state distribution is modified: charge exchange collision processes and electron impact ionization both play an important role in determining the number of ions in each charge state. The total ion current is reduced. Boxman et al. modelled the interaction between a vacuum arc plasma jet and a neutral background gas [96]. The modifications of the ion energy and charge state distributions have an impact on the growth mechanisms of the films.
3.2.2 Interaction Between the Arc Plume and the Growing Film

As mentioned, the cathodic arc plasma is mostly ionized. A few neutral species may be present due to evaporation from macroparticles or from previously active sites on the cathode, but they do not represent a large fraction of the stream. Any modification of the substrate potential relatively to the plasma potential will induce the development of an electric sheath around the substrate that will act on all charged particles. By controlling the substrate bias it is thus possible to tailor the energy of plasma particles arriving at the substrate surface. By combining a cathodic arc plasma source with high voltage biasing, it is possible to implant species in the substrate.

3.2.2.1 Plasma Sheath

The basic physics of plasma sheath has been extensively reviewed in the literature (e.g. see Ref. [97]) but is mainly focused on steady-state conditions. When using pulsed high-voltage bias, it is necessary to consider transient sheaths.

When negative high-voltage pulses are applied to a sample, electrons are repelled from the sample surface leaving the ions to form an ion sheath. The ions are accelerated toward the sample surface. To sustain the ion flux, the ion sheath expands outwards until the end of the voltage pulse or until the vessel walls stop its progress. The development and stability of these transient sheaths have been modelled and characterized experimentally using Langmuir probes [98].

If we consider an electrically conductive substrate that is repetitively pulse biased, the ion density profile across the sheath depends on the repetition rate of the pulse. If the pulse frequency is high enough and the sheath sufficiently wide, the time between pulses is too short to allow the plasma to totally replenish the depleted region by diffusion. The current reaching the substrate during the second pulse is a lot smaller than the current observed during the first pulse (figure 3.6).

The lower plasma density in the depleted region allows a quicker expansion of the sheath during the first few pulses. Quickly, a multiple-pulse steady state will be established: the charge flowing continuously into the depleted region is completely used up during the pulse. The electrical conductivity of the substrate modifies the temporal sheath development. With an electrically insulating substrate, the sheath will expand and quickly collapse due to the accumulation of charges on the substrate. The collapse time depends on the plasma density and the magnitude of the high voltage applied to the substrate holder [99, 100].
3.2.2.2 Metal Plasma Immersion Ion Implantation and Deposition

If condensable plasma species such as ions of cathodic arc plasma are present, pulsing the substrate bias implies high-energy phases during which ion implantation takes place and low-energy phases during which deposition occurs. This surface modification technique combining PIII with cathodic arc deposition was introduced by Brown and co-workers at the beginning of the 1990s [101, 102] and was called plasma immersion ion implantation and deposition (PIIID). If metal ions are involved, the method is also called MePIIID, metal plasma ion immersion implantation and deposition. During the high-voltage pulse, ions implant in the substrate and also produce a recoil implantation of the deposited metal layer. Both deposition and implantation result in an adherent modified layer onto the substrate. The bias voltage can be adjusted during the surface treatment process. High voltages (a few kilovolts) can be applied during the early stages of the deposition process to sputter clean the substrate and to form a mixed interface by implantation. Low-voltage bias can be applied to provide ion assistance during the growth process. In this case, no foreign species are added, growth is self-assisted. The importance of the assistance low bias values or of sputtering and intermixing for high bias, is controlled by the biasing duty cycle. The duty cycle ($\delta_b$) is defined as the ratio between the bias on-time ($\tau_p$) and the total duration:

$$\delta_b = \tau_p / (\tau_p + \tau_{off})$$  \hspace{1cm} (3.11)

Apart from metallic films, a wide range of compound films and ceramics including oxides and nitrides can be deposited by flowing gases in the chamber during implantation and deposition.
processes. Various experimental set-ups have been designed to provide a wide choice of growth parameters. Figure 3.7 presents the set-up used at the IOM-Leipzig, Germany. It is based on a DC vacuum arc source.

A few aspects of PIIID using cathodic arc plasmas should be emphasized [95]. These points are related to the characteristic features of PIIID arc plasmas: multiply charged ions are present, the plasma is fully ionized, and the plasma flow velocity is supersonic:

(i) Multiple ion charge states give rise to multiple ion energies. If $E_0$ is the ion energy corresponding to the flow velocity ($E_0 = MV_0^2/2$) and $V_b$ is the negative bias voltage, in a collisionless situation, the ions acquire discrete energies depending on their charge state:

$$E_x = |ZV_b| + E_0$$

The energy input for the growing film depends on the composition of the plasma and on the charge distribution of each species. The sputter rate depends on the energy, and the observed sputter rate is an average determined by the abundance of the different ions. The sheath thickness is also influenced by the mean ion charge.

(ii) The ion flux, ion current densities, and deposition rates are relatively high in comparison with other implantation and techniques. The sheath is thus very thin and the potential drop is concentrated across a short distance. This can lead to the sheath breakdown by arcing to the substrate.

![Figure 3.7: Schematics of PIII equipment](image-url)
(iii) PIII is considered to be a three-dimensional process. This is only true if the plasma velocity is small compared with the thermal ion velocities. Vacuum arc plasmas do not fulfil this condition.

**Energy Release and Thermal Effects**

MePIIID is an energetic deposition technique. A large fraction of the incident particles have enough energy to penetrate under the surface. The impinging ions deliver a large quantity of energy (kinetic and potential) to the growing surface that will contribute to interface mixing, subplantation, texture and stress development or reduction, atomic scale heating, secondary electron emission and sputtering. The kinetic energy of condensing ions is taken into account in most of the published work, but potential energy is usually ignored despite its importance. Anders [81] has shown that potential energy of the impinging ions contributes significantly to atomic scale heating. An ion emitted by a cathodic arc acquires kinetic energy in three steps: first at the cathode spot, second in the sheath, and third extremely close to the growing surface (acceleration by the image charge). The last contribution is the smallest of the three. The ion kinetic energy determines the displacements and short collision cascades in the substrate. The different mechanisms involved in the loss of kinetic energy in the solid are well documented [103]. The displaced solid atoms vibrate around their new site with large amplitudes and are considered as “hot”. Thermal conduction quickly quenches them.

The ions potential energy includes the excitation energy \( E_{\text{exc}} \) of electrons but also rotational and vibrational energy for molecular ions, cohesive energy \( E_c \), and ionization energy \( E_Q \). So the total energy of an impinging ion can be expressed as follows:

\[
E(Q) = E_{\text{kin},0} + AQeV_{\text{sheath}} + E_w + E_c + E_{\text{exc}} + \sum_{Q'=0}^{Q-1} E_{Q'}
\]

where \( Q \) is the ion charge state, \( E_{\text{kin},0} \) is the kinetic energy corresponding to the initial velocity, and \( V_{\text{sheath}} \) is the potential drop across the sheath. The largest contribution to the potential energy is the ionization energy. For a multiply charged ion, each ionization energy must be taken into account.

Kinetic and potential energies delivered to the growing surface contribute to atomic scale heating, and usually exceeds the binding energy and activation energy for surface diffusion. They have significant effects on film formation and evolution.
Adsorption, Intermixing, and Adhesion

Generally, the deposition of dense films at practical growth rates requires sufficient energy as the atoms need to diffuse to form a coating microstructure more similar to the bulk material. A high degree of ionization is also often desirable in order to promote the formation of compound films. Cathodic arc PIIID processes can fulfill these conditions. In the present paragraph, we will only focus on few aspects that are characteristic of this technique. Arc technology often offers outstanding film properties and a wider process window for reactive deposition. The film properties can be tuned and tailored because cathodic arc plasmas are fully ionized. Non-equilibrium bonding states can be obtained in a coating by manipulating the ion kinetic energy.

Improved adhesion has been often observed for films deposited by the cathodic arc process. This is due to the higher energy of impinging ions which has multiple consequences. First the physisorbed impurities are desorbed either by direct impact or by local heating around the impact, leaving a cleaner surface for the condensing ions. In the case of reactive deposition, it is pointed out [104] that ion bombardment influences gas adsorption by increasing the sticking coefficient of gases such as nitrogen and changing the nature of adsorption sites from lower-energy physisorption sites to higher-energy chemisorption sites. This could explain why the cathodic arc process is so effective in forming nitrides and carbides.

The advantages of diffuse interfaces for enhancing coating adhesion do not need to be demonstrated here. The fully ionized flux emitted by cathode spots is ideal for forming this type of interface. The implantation profile can be tuned by varying the bias conditions. Implantation induces displacement of substrate atoms, breaking of bonds and formation of new bonds across the interface. A diffuse interface also spreads the stresses over a wider volume therefore decreasing the probability of delamination at the interface between the substrate and the coating. The bombardment by energetic ions can also, under certain conditions, roughen the interface and improve adhesion by mechanical interlocking.

However, care must be taken in choosing the initial deposition conditions to avoid significantly damaging the substrate, which would be detrimental for the performances of the coated piece.
CHAPTER 4  Experimental Methods

In this chapter, the experimental methods used for the investigation of the chemical composition, phase composition, morphology, structure and photocatalytic properties of the produced TiO$_2$ thin films deposited on different substrates are presented. With the aim to characterize the samples from different points of views, different analytic techniques are used: ion beam techniques for elemental composition, electron microscopy for structure and morphology investigation, atomic force microscopy for the surface topography, X-ray diffraction for the structure and contact angle measurements and absorption spectroscopy for the investigation of the photocatalytic properties.

4.1 Ion Beam Analysis

Ion beam analysis (IBA) plays an important role in modern materials analysis as a tool for the investigation of surfaces and thin films due to the possibility of element identification and quantitative element composition together with the feasibility of depth profiling at a high accuracy of a few nanometers. High-energy ions (typically > 1 MeV) impinge on a target and during collisions with the target atoms different events occur. In the case of elastic (Coulomb) scattering the backscattered incident particles are monitored via Rutherford Backscattering Spectroscopy (RBS), while the elastic generation of recoil atoms is utilized for Elastic Recoil Detection Analysis (ERDA) or Nuclear Reaction Analysis (NRA) is performed when nuclear reactions take place.

For elastic collisions the energy transfer is related with the incident energy by a kinematic factor $K$, defined as the ratio of the energies after and before the collisions, $E_p$ and $E_o$ respectively [105]:

$$K = \frac{E_p}{E_o} = \left(\frac{1 - \left(\frac{M_p}{M_T}\sin^2 \vartheta\right) + \frac{M_p}{M_T}\cos \vartheta}{1 + \frac{M_p}{M_T}}\right)^2,$$

depending on the mass of the ion $M_p$, the target atom $M_T$ and the scattering angle $\vartheta$ (in the centre of mass system). The probability for a collision event is given by the differential cross section:

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z_p Z_r e^2}{16\pi e_o E_o}\right)^2 \frac{4}{\sin^2 \vartheta / 2},$$

(4.2)
assuming a pure Coulomb interaction. \( Z_p \) and \( Z_T \) are the atomic numbers of the projectile and target, respectively, while \( e \) and \( \epsilon_0 \) are the elementary charge and the dielectric constant.

The high energy ions interact not only with the target surface, but also penetrate into the sample and the collisions may occur at a certain depth. There, the incident particles inelastically lose energy during the transit into the target and the reaction products lose energy during the transit out of the target, mainly by inelastic scattering with electrons in this energy range. As a first approximation, this energy loss can be assumed to be proportional to the depth (mean energy approximation [105]), and thus it is possible to calculate the depth of the reaction, hence allowing elemental depth profiling.

### 4.1.1 Elastic Recoil Detection Analysis (ERDA)

For the examination of the Stoichiometry of TiO\(_2\) thin films, Elastic Recoil Detection Analysis (ERDA) with a high-energetic heavy-ion-beam was employed [106, 107].

ERDA is an analytic technique which gives information about the depth profiling of the lighter elements in the surface. A focused high energy beam of heavy ions impinges at a shallow angle on a target. By elastic collisions with the sample-atoms, these are accelerated and (partially) are directed towards the surface. The lighter recoil atoms are detected in reflection geometry. Their energy again depends on the kinematic factor (see equation 1 above) and the depth of the reaction. A foil situated in front of the detector is usually used to prevent a detection of scattered incident ions while slightly decreasing the energy of the recoil atoms. The detector consists of two sections. The first section delivers a signal that is proportional to the linear energy loss; respective atomic number (mass) of the recoil atoms is recorded. In the second detector section, the recoil atom is stopped completely. Plotting of the atom energy given in both steps with the respect to each other gives elemental distribution according to the depth resolution. On the way to the surface, the atoms are slowed down through inelastic interaction with the electrons in the sample. The critical depth, from which an atom due to the energy loss can not be proved anymore, decreases with the square of the atomic number. For the titanium oxide layers on silicon substrate, this means that above a certain layer thickness the elements C and O reach the detector while titanium only partially, although it is still present at this depth. In this area (titanium proofing range), a part of the Ti-signals is missing at a constant oxygen and silicon signal. Ionization chambers are used as detectors in most experiments, allowing the measurement of the partial energy loss \( \Delta E \), while \( E_{tot} \) contains information about the depth where collision effect occurs.
The sensitivity of the ERDA for the lighter elements is 0.1 at%. Usually the detector energy resolution is near 1 %. The depth of analysis, as the sensitivity and the depth resolution, depends on the type of ion beam, the ion energy and the experimental setup with a value lower than 1 μm in most cases. The range of the investigated depth and detectable elements can be extended by using heavy ions with energies up to 240 MeV. Two advantages results from ERDA with heavy ions are almost the same sensitivity for all elements and the decreased ion beam current due to the higher cross section; thus the excessive sample heating is avoided.

The measurements on TiO$_2$ samples were performed at the accelerator laboratory of Munich in Garching with $^{197}$Au$^{+15}$ ions, that have an energy of 190 MeV and hit the surface at an incidence angle of 19°. The setup of the analysis-chamber of the ERDA at the Beamline in Garching is schematically represented in figure 4.1.

![Figure 4.1: Schematic presentation of the high vacuum facility for the Rutherford backscattering spectroscopy (RBS) and elastic recoil detection analysis (ERDA) and the ionisation chamber in Garching used for ERDA measurements. [106]](image)

4.1.2 Secondary Ion Mass Spectrometry (SIMS)

The mass spectrometry of ionized particles which are emitted when a surface, usually a solid, is bombarded by energetic primary particles, which may be electrons, ions, neutrals or photons, is called Secondary Ion Mass Spectrometry (SIMS). The majority of species emitted or “secondary” particles, which will be electrons, neutral species atoms or molecules or atomic and cluster ions, are neutral but it is the secondary ions which are detected and analyzed by a mass spectrometer. This process provides a mass spectrum of the surface and enables a detailed chemical analysis of the surface to be performed.
Two processes are important in SIMS, sputtering and ionization of the particles. Basically, a high energy (normally between 0.25 and 30 keV) beam of ions (usually Cs\(^+\), O\(^2+\), Ar\(^+\), Xe\(^+\) and Ga\(^+\)) or neutrals is used for bombarding the sample and the primary particle energy is transferred to the atoms of the sample to be analyzed by a short-lived collision “cascade” process occurring between the atoms in the sample (see figure 4.2). Some collisions return to the surface and result in the emission of atoms and atoms clusters (sputtering) some of which are ionized in the course of leaving the surface. These secondary emitted ions, which are only a small fraction (between 0.1 and 1 %) of all emitted particles (the final result is not only the emission of secondary ions but also the emission of low energy electrons, Auger electrons, photons, neutral particles and excited clusters [108]), are mass analyzed. As a matter of fact, secondary ions can be emitted from points well distant from the initial point of impact and in various directions from the sample surface with a range of energies that peaks around 10 eV and that is independent of the energy of the primary ions [109].

The basic equation of SIMS is:

\[
I_m = I_p Y_m \alpha \theta_m \eta
\]  

(4.3)

where \(I_m\) is the secondary ion current of species m, \(I_p\) is the primary ion flux, \(Y_m\) is the sputter yield, \(\alpha\) is the ionization probability, \(\theta_m\) is the fractional concentration of m in the surface layer and \(\eta\) is the transmission of the analysis system.

The two fundamental parameters are \(Y_m\) and \(\alpha\). \(Y_m\) is the total yield of sputtered particles of species m, neutral and ionic, per primary ion impact. It increases linearly with primary ion flux. It also increases with primary ion mass and energy although not linearly [110]. \(Y_m\) tends to maximize with energies at around 10 keV. Ionization occurs at, or close to, emission of sputtered particles with the consequence that the matrix participates in the electronic process.
This means that the secondary ion yield is strongly influenced by the electronic state of the material being analyzed and it is very sensitive to the electronic state of the atom or the molecule to be ionized and to the matrix from which they are emitted.

The resulting mass spectrum from SIMS provides information about the elemental identification and concentration of the sample as the measured intensity corresponds to particular elements and charge state. The atomic concentration can be quantified using reference standards. The depth distribution of several elements can be obtained simultaneously with a depth resolution, depending on the ion energy, of down to a few nm.

SIMS analysis of the TiO$_2$ samples was performed using ion mass spectroscopy in a time-of-flight setup with 15 keV $^{69}$Ga$^+$ primary ions for a scanned area of 100 x 100 $\mu$m$^2$. Sputtering for depth profiling was performed with 2 keV oxygen ions for the samples before PIII and the secondary ion beam was scanned across larger area to avoid crater edge effects. Additionally, spectroscopic ellipsometry was employed to measure the thickness of the oxide layer for the PIII samples. The sputter time in the SIMS measurement was converted into a depth-scale using the ellipsometry data and the total crater depth, as determined by mechanical profilometry. Thus, two independent sputter rates were obtained for the oxide layer on the surface and the bulk material. A single sputter rate was used to calibrate the depth scale for the samples after the marker and before the oxygen implantation.

4.2 Electron Microscopy

Electron microscopy is an analytic technique, which essentially uses various interactions between electron beam and a sample for an image formation as well as for structural and element characterization of materials. Requirements for high brightness and temporal and spatial coherence of the electron beam exist and they cannot be fulfilled by thermal emitted electrons from a tungsten wire. As an alternative lanthanium hexaborite (LaB$_6$) and field-emission cathodes are used for producing electron beams with less energy spread and higher gun brightness.

4.2.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a technique for the investigation of surface structures. An electron beam (up to 25 kV) is scanned across the sample surface and secondary electrons, back scattered electrons and X-rays are produced as the result of the interaction. Different detectors collect these particles and produce an image. The intensity of the secondary electrons and thus the brightness of the image depend on the local surface relief due to
asymmetrical location of the detector and therefore the topography is represented on the image.

The resolution is essentially determined by the beam spot size, which can be adjusted to an extremely small value between 5 and 20 nm. With SEM a magnification up to 40,000, a resolution down to 0.5 nm and a high focus depth can be achieved.

The backscattered electrons can also be collected by another detector as well as X-rays from the sample. The images from backscattered electrons give information about the distribution of elements with different atomic mass. The identification of the elements from the first micrometer of the surface is possible with X-ray analysis. Thus with energy dispersive X-ray analysis (EDXA) the elemental identification is also possible from SEM measurements.

SEM micrographs of TiO$_2$ samples were taken by a scanning electron microscope Carl Zeiss ultra 55 equipped with a Schottky field emission cathode with a resolution of down to 1.5 nm at 30kV.

### 4.2.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a well established technique for structure characterization of solids. Electron diffraction forms a physical basis of this method. The electron diffraction can be described analogously with the X-ray diffraction by the Bragg-equation. An electron beam, in the energy range of 100 – 300 keV, penetrates a sample and interacts with the electrons in the solid. TEM investigations are performed in different imaging modes typical among which are bright field imaging mode (BF), dark field imaging mode (DF) and high resolution TEM (HRTEM). In BF mode the image is formed using an objective aperture which produces the scattering and diffraction contrast. In the dark field mode the primary electron beam is intercepted in the focal plane of the objective lens by a shifted diaphragm, a tilted beam or a central beam stop. In high resolution TEM the image is only constituted by the phase contrast.

The selected area electron diffraction (SAED) mode is an electron diffraction mode which can be considered as a complementary mode to BF and DF image modes, revealing electron diffraction patterns of a sample area with size in order of 0.01 to 1 μm$^2$ and thus allowing a correlation with the TEM image. The diffraction patterns provide information about lattice constants, crystallographic orientation and lattice type. Two different approaches, plan view and cross-sectional TEM, are applied for investigations of thin films of TiO$_2$.

Point to point resolution of less than 1 nm is achieved using TEM. A disadvantage of this method is the requirement for the specimens to be transparent for the electron beam and
consequently sufficiently slim (depending on the material and in order of tens of nm), which leads to destruction of the sample along with a possibility of preparation artifacts.

TEM investigations of TiO$_2$ samples were performed on the equipments JEOL JEM at the Maks Planck Institute (MPI) for micro-structure-physics in Halle and HITACHI H-8100 at the IOM in Leipzig. Beside DF images also SAED and HRTEM images of the samples are produced. The high-resolution lattice layer image of the sample at 200°C is produced at the MPI equipment due to the higher acceleration voltage of 400 keV giving a better point resolution of 0.16 nm compared to the equipment at the IOM (200 keV acceleration-voltage, 0.23 point resolution; lattice constants of rutile: a = 0.458 nm, c = 0.295 nm, lattice constants of anatase: a = 0.373 nm, c = 0.937 nm).

### 4.3 X Ray Diffraction (XRD)

X-ray diffraction is a widely used, non-destructive technique for phase identification of materials and for texture characterization. The base of this method is diffraction of the incident X-ray beam from suitably oriented atomic planes in a crystal. The Bragg law gives the conditions at which such diffraction occurs and they are related by the equation:

$$2d \sin \vartheta = n\lambda$$

(4.4)

Where d is the planar distance, λ is the wavelength of the X rays, θ is the angle of diffraction and n the diffraction order.

The reflected radiation is then measured by a detector. For a polycrystalline sample diffraction is always occurring due to the random orientation of the crystallites. Typically, measurements are performed in $\vartheta/2\vartheta$ geometry, where 2θ is the angle of the detector with respect to the incident beam. Information about the crystal lattice (i.e. the phase composition)

![Figure 4.3: Schematic representation of XRD](image)
as well as the size of the crystals is obtained from the characteristic peak positions and the FWHM (full width at half maximum) in the XRD spectra.

In the standard $\theta/2\theta$ geometry a penetration depth of a few micrometers means a low sensitivity for investigation of thin layers. A glancing angle configuration is often applied to limit the penetration depth and thus to improve the sensitivity.

X-ray diffraction measurements of TiO$_2$ films were performed at the $\theta/2\theta$ geometry using a Seifert 3003 PTS diffractometer with monochromatic [Ge(220)-Crystal monochromator] Cu-K$_{\alpha}$-irradiation (wavelength $\lambda=0.15406$ nm) and 40 kV, 40 MA acceleration-voltage in the range from 20° to 80°, with steps of 0.1° and counting-time 90 s. Additionally, $\varphi/2\theta$ measurements at constant incidents angle $\varphi = 10^\circ$ with respect to the surface were performed at the Seifert XRD 7 diffractometer with monochromatic Cu-K$_{\alpha}$-irradiation (wavelength $\lambda=0.15406$ nm) and 40 kV, 40 MA acceleration-voltage in the range from 20° to 60°, with a step of 0.05° and a counting-time of 30 s. The slit width for the primary aperture and the detector aperture were 2 mm.

### 4.4 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a characterization method, with a very high resolution, that is applied for the investigation of the surface topography in the nanometer range [111, 112]. The main advantage of AFM is its sub-nanometer resolution and the possibility to give a direct real space image of the surface. With the AFM method, one scans the surface with very sharp tip mounted on a piezo-scanner that can be set in motion by applying a voltage on it.

Usually there are three modes used for be applied. One of measurements with AFM: i) contact mode, ii) non-contact mode and iii) TappingMode™ or dynamic mode. The last mode was developed as a method to achieve high resolution, without inducing destructive frictional forces between the sample and the tip. With this technique, the cantilever is oscillated near its

**Figure 4.4: Schematic representation of AFM system**
resonant frequency with constant amplitude as it is scanned over the sample surface. As the tip is brought close to the sample surface its amplitude will reduce. A feedback positioning unit takes care that the distance between the tip and the sample, i. e. the oscillation amplitude, remains constant during scanning, without getting in contact with each other. The measurements presented in this work, were all performed using Dimension 3000 with a Nanoscope IIIa controller, in TappingMode™ from Veeco Instruments [113], and MFP-3D, AFM, in dynamic mode from Asylum Research [114]. Compared to Nanoscope IIIa controller that can record up to 512 points per line, the MFP-3D offers the possibility to perform large area scans with high resolution up to 4096 points per line. The measurements were performed in air, using silicon tips with nominal radius smaller than 10 nm, and sidewall angles < 18 deg [115]. One important factor to be considered is the image size, the number of points one image has, and the spacing between points [116, 117]. If \( L \) is the image size, \( N \) the number of points, and \( d \) the data point spacing then \( L = N \cdot d \). Therefore, in order to have an accurate estimation and a better statistics, it is important that measurements with different size and high enough resolution are performed. For example, for a measurement with a scan size 4 \( \mu \)m \( \times \) 4 \( \mu \)m with 1024 \( \times \) 1024 data points gives a point spacing of \( \sim 4 \) nm. For structures with a mean size of 40 nm it means around 10 data points per structure.

The most important statistical quantity used to characterize the height fluctuations of the surface is the \( \text{rms} \)-root mean square roughness. It describes the fluctuations of the surface heights around an average height, and is given by:

\[
\text{rms} = w = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( h(x, y) - \overline{h} \right)^2}
\]

(4.5)

Here \( h(x, y) \) represents the surface height at a given point, and \( \overline{h} \) the mean height of the surface. For quantitative analysis of the surface roughness samples with scan size of 2 \( \mu \)m \( \times \) 2 \( \mu \)m and 4 \( \mu \)m \( \times \) 4 \( \mu \)m were used with 512 \( \times \) 512 and 1024 \( \times \) 1024 data points, respectively. This means a spacing \( d < 4 \) nm. However, a comparison with measurements having data point spacing \( d < 2 \) nm between points, showed no difference on the \( \text{rms} \) roughness value. This indicates that the largest contribution to the \( \text{rms} \) value comes from structures (ripples, dots) present on the surface.

### 4.5 Optical Methods

These methods may be summarized as involving the interactions of photons with surfaces which result in energy transfer to or from the surface adsorbed species via vibrational excitation. The discrete energies transferred of course correspond to vibrational quanta, and
analysis of these energies provides the means of determining the structure of the surface species.

4.5.1 Raman Spectroscopy

Raman spectroscopy is a non-destructive optical spectroscopic technique for studying lattice vibrations of materials. The Raman effect, which can be described as a scattering phenomenon, is the base of this analytic method (see figure 4.5).

The photons scatter inelastically at lattice phonons of a crystal resulting in an annihilation or creation of a phonon. The relation between the frequencies and the wave number of the incident photon ($\omega_i, k_i$), scattered photon ($\omega_s, k_s$) and emitted or adsorbed optical phonon ($\Omega$) ($k \sim 0$) is:

$$\omega_i = \omega_s \pm \Omega$$  \hspace{1cm} (4.6)

$$k_i = k_s \pm G$$  \hspace{1cm} (4.7)

where $G$ is a reciprocal lattice vector. A shift of the scattered photon frequency towards higher values, related with the adsorption of a phonon is called an anti Stokes shift, while a shift towards lower values is called Stokes shift. The intensity of the former is temperature independent while the intensity for the latter process increases with increasing temperature as (thermally created) phonons must be present in this case. Additionally, selection rules apply so that only lattice displacements $u(k,t)$ leading to a change in the polarisability of the crystal ($\frac{\partial \alpha}{\partial u} \neq 0$) are Raman active. The frequency of the incoming light is also important, as nearby optical modes can lead to a resonant enhancement of the cross section. For illumination below the optical gap, often only a very small cross section is observed.

![Figure 4.5: Schematic representation of the surface Raman experiment (FL-focusing lens, CL-collection lens, NF-notch filter)](image-url)
Monochromatic light (usually created by an intensive laser) is used to excite the Raman scattering. The spectrum of the scattered light is analysed by monochromators and recorded by photomultipliers. The identification of atomic bonding, symmetry of molecules or crystals is possible from the measured spectrum, as the Raman spectra for the most of materials are available and an immediate comparison is possible. Raman spectroscopy is also used for the determination of stress in thin films via the shift of Raman frequencies, which occurs as a result of deformation of the lattice. Usually, the size of the laser spot is about 100 μm, which is larger than the average size of the crystallites in the investigated sample, so a macroscopic average is obtained. Micro-Raman measurements are also possible with a focus between 2 and 15 μm.

The Raman spectra of TiO$_2$ samples were recorded in backscattering configuration with a Raman spectrometer equipped with a microscope. The 514.5 and 488.0 lines of an Ar$^+$ ion laser were used for the excitation. The laser intensity at the sample surface was between 3 and 5 mW for all measurements.

4.5.2 Spectroscopic Ellipsometry (SE)

Polarized light reflected from a surface provides a powerful non-invasive means for probing surface properties. When linearly polarized light interacts with a surface, the parallel and perpendicular electric-field components usually experience different absorption and phase modifications, resulting in elliptically polarized reflected light. The study of the reflection characteristics of polarized light is subsequently termed ellipsometry. If multiple photon energies are used the technique is termed Spectroscopic Ellipsometry (SE) (see figure 4.6). SE is an attractive method because it is noncontact, non destructive and does not require sample preparation.

Paul Drude [118] was the first to conduct fundamental experiments on ellipsometry in the 1880’s and is also responsible for deriving the equations that are still used to this day for analysis of ellipsometric data. It is the ability of ellipsometry to detect changes in reflection characteristics of a surface due to the presence of thin over-layers that makes it such a powerful and widely used technique. In theory, ellipsometry can resolve subatomic changes in film thickness and similarly small variations in optical constants. Whilst the precision of ellipsometric data is usually extremely high, it is often the inaccuracy of the model used to extract the desired information that limits the effectiveness of ellipsometry.
Ellipsometric data is generally represented by the ellipsometric parameters $\Delta$ and $\Psi$. These are defined by:

$$\tan(\Psi) \exp(i\Delta) = \frac{R_p}{R_s}$$  \hspace{1cm} (4.8)

where $R_p$ and $R_s$ are the complex Fresnel reflection coefficients for parallel (p) and perpendicular (s) polarised states. $R_p$ and $R_s$ can be acquired with relatively standard optical equipment. A simple experiment may consist of merely a light source and collimator, a rotating polariser, and a photodiode and amplifier that can detect the amplitude variations of the reflected light.

In order to correlate the optical measured data with the sample properties (film thickness, void fraction, refractive index, composition) a model of the sample structure is necessary. The calculated values of $\Psi$ and $\Delta$ are fitted to the measured one. Fitting variables are wavelength-independent parameters of the proposed model as a direct inversion of the data is in most cases not possible.

Spectroscopic ellipsometry measurements of TiO$_2$ thin films are performed over the spectral region from 250 to 820 nm at different angles of incidence between 50° and 80° using a SENTECH (SE800) instrument equipped with a Xe arc lamp, rotating analyzer and a spectrograph with a diode array. The analysed area was about 1 mm$^2$ and the measuring step size was 0.6 nm.
4.6 Photo Activity Analysis Methods

4.6.1 Contact Angle Measurements (CAM)

For the work described in this thesis goniometry was used to measure contact angles. With goniometry, the drop shape is analysed by observing the drop from the side. The contact angle can be determined by measuring the angle between the tangent of the drop surface at the contact line and the surface (see figure 4.7). The contact angle is measured by fitting a circle to the drop cross-section and determining the intersection with the projection of the surface. The surface energy of the samples was calculated from the experimental contact angle measurements under application of the mean value from the Young contact angle equation (Fowkes [119] and Owens – Wendt [120] methods). The leading force for the formation of new interfaces, liquid (L) - vapor (V), liquid-solid (S) and reduction of the solid-vapor interface, is the decrease of the free energy [121].

The Young contact angle equation:

\[
\cos \Theta = \left( \sigma_{VS} - \sigma_{LS} \right) / \sigma_{LV}
\]

(4.9)

with the interface energies \( \sigma_{LV} \), \( \sigma_{LS} \), \( \sigma_{VS} \) delivers a thermodynamic expression for the experimentally determined contact-angle \( \Theta \) between the interface of a liquid and a solid-surface. The method for the calculation of the surface-energy according to Fowkes comprises a division of the surface-energy into a dispersive and polar part:

\[
\sigma_{LV} \cdot \cos \Theta = \sqrt{\left( \sigma_{VS} \sigma_{VL} \right)_{\text{dis}}} + \sqrt{\left( \sigma_{VS} \sigma_{YL} \right)_{\text{pol}}} - \sigma_{LV}
\]

(4.10)

\[
\frac{1 + \cos \Theta}{2} \cdot \sigma_{LV} = \sqrt{\sigma_{VS}^{\text{dis}}} + \sqrt{\sigma_{VS}^{\text{pol}}} \cdot \sqrt{\sigma_{LY}^{\text{dis}}}
\]

The surface-energy of the solid is given from the sum of the dispersive and polar parts:

\[
\sigma_{VS} = \sigma_{VS}^{\text{dis}} + \sigma_{VS}^{\text{pol}}
\]

(4.11)

Figure 4.7: Schematic representation of the contact angle of a fluid drop on a surface.
In the above descript model the measure of contact angle of two different liquids is necessary to calculate the surface energy.

Contact angle measurements on TiO$_2$ samples were performed using a Krüss Contact Angle measuring system G2 and the results are obtained from the software DSA II (Drop shape analysis II). In dynamic CAM mode two different liquids are used, deionised water and ethylene glycol, employing manual drop position on the surface with 2-4 drops (because of high wettability of the samples surface after UV-irradiation). From each liquid a start-volume 3µl and end-volume 4µl, 10 successive snapshots for each drop were taken.

### 4.6.2 Absorption Spectroscopy

UV-Vis absorption spectroscopy is a method utilizing the absorption of photons ranging in energy from the near ultraviolet (33.000 cm$^{-1}$) over blue light (21.000 cm$^{-1}$) to near infrared (14.000 cm$^{-1}$). Radiation of this energy range is causing outer shell electron transitions in target molecules or atoms. The amount of light transmitted through a solution or suspension may be diminished by the absorption of light by colored compounds and/or the scattering of light rays by particulate matter. An instrument that measures the amount of light passing through a sample is called a spectrophotometer. The main requirement is that light be absorbed or scattered by some substance in the sample under investigation.

In order for absorption spectroscopy to be useful for quantitative studies, it is necessary to relate the absorbance of a compound to the amount of compound present. The Lambert-Beer law provides the mathematical basis of this relationship:

$$A = ε \cdot l \cdot c$$

where $A$ is the absorbance or optical density (no units), $l$ is the path length of the cuvette (in cm), $c$ is the concentration (in mol l$^{-1}$), and $ε$ is the extinction coefficient (in l mol$^{-1}$ cm$^{-1}$). The molar extinction coefficient is a constant that relates the absorbance of a particular substance to its concentration. According the Lambert-Beer law, an increase in the concentration of a compound leads to a linear increase in the absorbance of the solution. In practice, an increase in concentration produces a linear increase in absorbance only over a certain range because spectrophotometers are less sensitive to absorbance changes above a reading of 1.0 absorbance unit. If the extinction coefficient is known, the Lambert-Beer law (eq. 4.12) can be used to calculate the concentration of the solution.

The absorption spectroscopy measurements on TiO$_2$ samples were performed using a spectrometer SHIMADZU UV-2101PC. In the experiment, a methylene blue solution with an initial concentration of 0.007 mmol l$^{-1}$ was tested. Volumes of 20 ± 2 ml of this solution
together with the samples were irradiated for 1-3 hours time intervals (power density in air 1 mW cm\(^{-2}\)). As reference, a solution without TiO\(_2\) sample inside under the same parameters was irradiated. The respective maximum absorption was determined by the spectrophotometry with a split-width of the spectrometer of 1.0 nm, a resolution of 0.1 nm and a scanning interval of 0.2 nm.
CHAPTER 5 Experimental Setup

In this chapter the experimental parameters of the MePIIID of TiO$_2$ onto three different substrates are introduced. The experimental work is divided in three directions/procedures:

i. Variation of the oxygen flow in constant implantation energy/find “correct” O:Ti ratio;
ii. Variation of pulse voltage at room temperature and constant oxygen flow/Influence of HV;
iii. Variation of substrate temperature and pulse voltage at constant oxygen flow/Influence of heating/interplay with HV.

5.1 Variation of Pulse Voltage at Room Temperature and Constant Oxygen Flow/no Heating

A schematic of the experimental setup is depicted in figure 5.1.

**Figure 5.1:** Schematic representation of the experimental setup used at this stage for the MePIIID of TiO$_2$
Silicon (100), fused silica (f.s.) and 100 nm thermal oxide on Si (100) were used as substrate material. A cathodic arc with a pure titanium (99.99%) cathode, running at 100 A was employed to generate Ti ions. The vacuum chamber, with a base pressure better than $10^{-4}$ Pa, was backfilled with oxygen at a flow of 50 sccm (standard cubic centimeters per minute), resulting in a working pressure of 0.36 Pa, which decreased during the process to 0.2 Pa. The samples were mounted at a distance of 39 cm to the cathode for a treatment time of 5 minutes. The samples were normally at ground potential, additionally negative high voltage pulses between 1 and 10 kV with a length of 30 µs and a repetition rate of 3 kHz were applied. Between the pulses, electrons from the plasma will neutralize any remaining surface charges. The final sample temperature was less than 50 °C when no HV pulses were applied and less than 100 °C for 10 kV pulses after 5 minutes of deposition time.

The above experimental parameters are represented in table 5.1.

<table>
<thead>
<tr>
<th><strong>Experimental parameters</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Process gas</td>
<td>O₂, 50 sccm</td>
</tr>
<tr>
<td>Working pressure</td>
<td>0.2 Pa</td>
</tr>
<tr>
<td>Plasma source</td>
<td>Cathodic arc with a pure titanium (99.99%) cathode, 100 A, 19 V</td>
</tr>
<tr>
<td>Geometry</td>
<td>Sample holders with 7.5 cm diameter mounted at a distance of 39 cm from the cathode. No filter used</td>
</tr>
<tr>
<td>Substrate</td>
<td>Silicon (100), fused silica (f.s.) and 100 nm thermal oxide on Si (100)</td>
</tr>
<tr>
<td>Substrate High Voltage</td>
<td>1 kV - 10 kV</td>
</tr>
<tr>
<td>Pulse parameters</td>
<td>30 µs pulse length, 3 kHz repetition rate</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room Temperature (27°C)</td>
</tr>
<tr>
<td>Treatment time</td>
<td>5 min</td>
</tr>
</tbody>
</table>

**Table 5.1:** Experimental parameters used at this stage for the MePIIID of the TiO₂.
5.2 Variation of the Oxygen Flow/Additional Heating Possible

The schematic representation of the installation, in which the experiments for the production of titanium oxide by means of plasma immersion ion implantation and deposition were pursued, is depicted in figure 5.2.

The sample holder, from aluminium with a diameter of 7.5 cm of diameter, is positioned at a distance of 39 cm from the cathode (pure titanium (99.99 %) cathode) into a cylindrical vacuum chamber with 700 mm diameter and a height of 650 mm. Three different substrate materials, Silicon (100), fused silica (f.s.) and 100 nm thermal oxide on Si (100) were used, cut in coupons with 2.5 cm² x 2.5 cm² dimensions. A base pressure under $10^{-3}$ Pa was obtained. The plasma was generated by an arc discharge at the cathode. Over the treatment time of 5 min from the arc ignition, a constant oxygen flow in the range of 30 sccm up to 100 sccm was held in the chamber. The working pressure was in the range of 0.03 Pa up to 0.3 Pa. After the arc ignition, the pressure decreased because of the high reactivity of the titanium layer deposition.

Figure 5.2: Schematic of MePIIID experimental setup.
The sample holder is interconnected with a pulse voltage generator. In order to protect heating system from ion bombardment two shields are placed behind the substrate holder. So, the plasma sheath in this setup (figure 5.2) is completely different from the 1st experimental setup. Furthermore, in this experiment, negative high voltage pulses up to 10 kV with a duty cycle of 9%, are adopted. The experimental parameters are introduced in table 5.2.

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Process gas</th>
<th>O₂ → 30 sccm, 45 sccm, 55 sccm, 65 sccm, 75 sccm, 100 sccm.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Working pressure</td>
<td>0,03 - 0,3 Pa</td>
</tr>
<tr>
<td></td>
<td>Plasma source</td>
<td>cathodic arc with a pure titanium (99.99%) cathode, 100 A, 19 V</td>
</tr>
<tr>
<td></td>
<td>Geometry</td>
<td>Sample holders with 7,5 cm diameter mounted at a distance of 39 cm from the cathode. Shields used</td>
</tr>
<tr>
<td></td>
<td>Substrate</td>
<td>Silicon (100), fused silica (f.s.) and 100 nm thermal oxide on Si (100)</td>
</tr>
<tr>
<td></td>
<td>Substrate High Voltage</td>
<td>10 kV</td>
</tr>
<tr>
<td></td>
<td>Pulse parameters</td>
<td>30 µs pulse length, 3 kHz repetition rate</td>
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<tr>
<td></td>
<td>Temperature</td>
<td>Room Temperature (27°C)</td>
</tr>
<tr>
<td></td>
<td>Treatment time</td>
<td>5 min</td>
</tr>
</tbody>
</table>

**Table 5.2:** Experimental parameters for investigation of the variation of oxygen flow at constant ion energy in MePIIID of TiO₂.

### 5.3 Variation of Pulsed Voltage and Substrate Temperature/Additional Heating

The schematic representation of the installation is represented in figure 5.2. In this experimental work, the samples are produced on the same substrate holders (Silicon (100), 100 nm thermal oxide on Si (100) and fused silica) with variation of the high pulse voltage and substrate temperature up to 300 °C. In comparison to the melting point of Rutile at 1800 °C, the chosen temperatures lie under 20 percent of the melting point.
A cathodic arc with a pure titanium (99.99%) cathode, running at 100 A was employed to generate Ti ions. An oxygen backfill of 55 sccm was used to establish a working pressure of 0.36 Pa, which decreased during the process to about 0.1 – 0.2 Pa. An oxygen flow of 55 sccm at room temperature corresponds to approximately $3 \times 10^{19}$ oxygen-molecules per second. During the arc discharge, a titanium ion stream is built at the cathode of approximately 10 A, i.e. approximately $3 \times 10^{19}$ titanium atoms per second. Negative high voltage pulses between 1 and 5 kV with a length of 30 µs at repetition rate of 3 kHz (duty cycle 9%) were applied to increase the ion energy. Comparing the nominal Ti current from the cathode of about 10 A at an average charge state of 2.1 [84] with the oxygen flow, a O/Ti ratio of roughly 3:1 is established in the gas phase. The treatment time was 5 min.

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Process gas</td>
<td>O$_2$ → 55 sccm</td>
</tr>
<tr>
<td>Working pressure</td>
<td>0.1 - 0.2 Pa</td>
</tr>
<tr>
<td>Plasma sources</td>
<td>Cathodic arc with a pure titanium (99.99%) cathode, 100 A, 19 V</td>
</tr>
<tr>
<td>Geometry</td>
<td>Sample holders with 12 cm diameter mounted at a distance of 39 cm from the cathode. Shields used</td>
</tr>
<tr>
<td>Substratum</td>
<td>Silicon (100), 100 nm thermal oxide on Si (100) and fused silica.</td>
</tr>
<tr>
<td>Substrate High Voltage</td>
<td>0 kV, -1 kV, -3 kV, -5 kV</td>
</tr>
<tr>
<td>Pulse parameters</td>
<td>30 µs pulse length, 3 kHz repetition rate</td>
</tr>
<tr>
<td>Temperature at the substrate</td>
<td>27°C (RT), 200°C, 300°C</td>
</tr>
<tr>
<td>Heater</td>
<td>Halogen lamps (OSRAM, 400 W, 36 V), positioned at the sample holder's backside</td>
</tr>
<tr>
<td>Temperature calibration</td>
<td>Thermoelement RS 52</td>
</tr>
<tr>
<td>Treatment time</td>
<td>5 min</td>
</tr>
</tbody>
</table>

**Table 5.3:** Experimental parameters for the production of titanium oxide thin layers by MePIIID.
A heating system with IR lamps from the backside of the substrates was installed in the vacuum chamber (figure 5.2), the temperature itself was varied between room temperature (RT) with lamps in the vacuum system, but no heating, 200° and 300 °C. The experimental parameters are putted altogether in table 5.3. The temperature was calibrated by a thermocouple connected with the sample holder, in prior of the treatments. Comparing the present experimental setup with previous experiments [122, 123], the heating system massively disturbs the supersonic plasma flow around the substrate [124]. Instead of kinetic energies in the range from 50 eV without pulse voltage up to 1.5 keV with 10 kV pulse voltage, much lower values can be expected for the present geometry. The mean surface temperature of the implanted layer does not depend on the pulse voltage although, at 5 kV, an increase of less than 50 °C occurs during the deposition. An ending temperature of 330 °C, after 5 min of treatment started at 300 °C, was measured.
CHAPTER 6  Influence of Ion Energy on Phase Formation of Photoactive TiO$_2$ Films by MePIIID at Room Temperature

In the following experimental part, TiO$_2$ thin films are formed by metal plasma immersion ion implantation and deposition (MePIIID) [89] with a continuous flow of titanium ions, generated by a cathodic arc, and oxygen to the substrate. A general influence of the HV pulses on the film properties will be derived. Simultaneously, high voltage pulses are applied to the substrate, thus increasing the average particle energy from about 5 to 1000 eV. Using a pulsed mode, the average energy per incident particle can be increased without a massive reduction of the growth rate due to a sputter rate increasing with incident ion energy [122]. 1 ion at 10kV does lead to less sputtering than 10 ions at 1kV. For pure arc deposition, the kinetic energy is below the sputter threshold. At the same time, the substrate temperature will remain close to room temperature, allowing the deposition on temperature-sensitive substrates with the present method. Beside the phase formation, surface energy and photocatalytic activity are determined as a function of pulse bias and substrate.

6.1 Influence of Oxygen Flow at Constant Ion Energy

The examination of the Stoichiometry of variation of the oxygen flow using constant pulse voltage of 10 kV at room temperature is performed using ERDA measurements. They give information about the layer thickness, the elemental specific depth resolution and the elemental specific sputtering. The Stoichiometry primarily is determined by the oxygen flow, i.e. from the arrival ratio of titanium to oxygen atoms. On the basis of the final process pressure and the mean free path length of 10 cm – 100 cm, a restricted number of charge-exchange-collisions take place in the gas chamber, so that additionally titanium atoms and oxygen ions impact on the substrate surface. However, the main mounting of oxygen takes place as molecules from the gas-phase at the reactive surface.

In figure 6.1 are presented the depth profiles for 30 sccm, 55 sccm and 100 sccm oxygen flow rate. The atomic surface occupancy of the ERDA-measurements, that usually is expressed in atoms/cm$^2$, transferred into a metric depth scale under the approximation that the atoms are installed only on the Rutile lattice sites are plotted. The density used in the calculation of Rutile corresponds to 9,6·10$^{22}$ at cm$^{-3}$. The width of the profile edges is determined by the elemental specific depth resolution of the ERDA. In the depth profiles the dashed line gives
the limit for the measured titanium, after which the titanium spectra decreases, although titanium is also on the interface present. The depth profile from the surface up to the dashed line can be taken as credible.

![Graph](image.png)

**Figure 6.1:** *Comparison of ERDA depth profiles for the 30 sccm, 55 sccm and 100 sccm oxygen flow. Deposition conditions: RT, 10 kV. The verified limit for titanium is marked.*

The work pressure at low gas flow (30 sccm) lies at 0.03 Pa due to massive oxygen-adsorption on the titanium surface. The oxygen concentration between 50 nm and 150 nm lies at 50 at %, the oxygen is installed to 100% percent. The small titanium loss close to the surface is due to preferred sputtering of titanium for this Stoichiometry. The elemental profiles from 45 sccm are very homogeneous compared to those with 30 sccm on the basis of the oxygen saturation (figure 6.2) at the surface. The oxygen concentration reaches a value of 65 at %, above which the oxygen is no more completely adsorbed and therefore the working
pressure increases (0.3 Pa near 100 sccm). The oxygen/titanium ratio lies in the barely substoichiometric region of Titanium dioxide (1.9:1) and shows small variations with increasing the oxygen flow.

The decrease of the film thickness with increasing oxygen flow is represented in figure 6.3, and it is caused by the lower deposition rate due to the higher working pressure. An increase in pressure leads to more collisions that cause more scattering and slowing down of titanium, thus decreasing the guided titanium flow from the cathode to the substrate. The deposition rate on the surrounding walls of the chamber increases accordingly. The carbon impurity lies independently from the oxygen flow near 1 at %.

The X ray diffraction diagrams in dependence of the oxygen flow rate (figure 6.4) show a peak at 27.4°, which corresponds to Rutile, for an oxygen / titanium ratio of 1.9: 1. Due to this, the crystals show a strong preferred orientation of {110} - surfaces parallel to the sample surface. At 55 sccm, corresponding to an oxygen/titanium ratio slightly below 1.9:1, the peak due to the very small crystal size can only be guessed. The peak intensities increase with increasing oxygen flow (ratio of 2:1) on the basis of the increasing nucleation and coalescence of the nucleus. Altogether, the peak-intensities are very low. Hence rutile is present across a large variety of O/Ti ratios, starting around 1.75.

Can be summarized that the films obtained by this procedure are slightly substoichiometric titanium films with an O-Ti-ratio of 1.9 – 1, as determined by elastic recoil detection analysis.

![Figure 6.2: Particular oxygen titanium ratios for different oxygen flows.](image)

![Figure 6.3: Layer thickness as a function of the oxygen flow. Layer thicknesses are determined from SEM cross section images.](image)
The film thickness was always close to 300 nm, indicating a growth rate of about 1 nm/s and no strong influence of the varying ion bombardment, especially the concomitant sputtering, on the growth rate.

### 6.2 Stoichiometry

For a vacuum arc operating with a titanium cathode, an ionization of close to 100% with an average charge state of 2.1 is observed near the cathode [84]. At the same time, these positive ions are travelling from the cathode in a supersonic plasma stream with a kinetic energy of 10 – 50 eV [125]. Collisions with the oxygen gas will reduce this energy and the average charge state, nevertheless a variation of the energy per deposited particle between 2.5 and 450 eV is possible when changing the pulse bias from 0 to 10 kV at 9% duty cycle. The total titanium current of about 10 A corresponds to a deposition rate of 1 nm/s at the substrate.

The stoichiometry, film thickness and deposition rate were derived from Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS). The films obtained by this method showed a slightly substoichiometric O-Ti ratio of about 1.9 – 2.0, independent of the pulse voltage and without variation across the samples [126].
Influence of Ion Energy on Phase Formation of Photoactive TiO$_2$ Films by MePIIID at Room Temperature

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pulse Voltage (kV)</th>
<th>Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1</td>
<td>217</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>237.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>260.8</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>284</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>297.9</td>
</tr>
<tr>
<td>SiO$_2$/Si</td>
<td>5</td>
<td>338.9</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>347.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>358.7</td>
</tr>
<tr>
<td>f.s.</td>
<td>7.5</td>
<td>255.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>275.7</td>
</tr>
</tbody>
</table>

Table 6.1: Film thickness derived from Spectroscopic ellipsometry measurement for the samples deposited on different substrates and different pulse voltage for 5 min treatment time.

However, all samples were transparent in the visible region, as proved with spectroscopic ellipsometry. Contaminations as nitrogen or carbon were less than 0.5 at.%.

The film thickness (see table 6.1) was always close to 300 nm. So, the growth rate of about 1 nm/s depends only slightly on the pulse voltage, despite the massive ion bombardment during the film deposition. Two competing effects are responsible: sputtering of the surface by the impinging ions with the sputter rate increasing with the pulse voltage (higher current and higher sputter yield) and an increased deposition rate due to the expanding dynamic plasma sheath collecting more ions. The latter effect is dominating, however no monotonous increase of the growth rate was observed. No influence of the substrate material on the growth rate or stoichiometry was detected.

### 6.3 Phase Composition

X-ray diffraction measurements were performed on a laboratory machine equipped with a copper anode in 0/20-geometry. A step size of 0.05° and a step time of 80 s were employed. A strong dependency of the phase formation on the substrate and the pulse voltage was found, as depicted in Figure 1. For voltages lower than 3 kV, no discernible peaks from the deposited surface layers could be found in the XRD spectra. The forbidden Si (002) reflection is visible for the Si and SiO$_2$/Si substrates, whereas the f.s. substrates are visible as the increased background at smaller angles.
Rutile is dominating in the spectra of samples produced at 3 kV bias voltage and above, independent of the substrate, as the peak near 27.45° is growing with increasing pulse voltage. At the same time, admixtures of anatase and rutile are found with the respective intensities depending on the voltage and the substrate. For fused silica, anatase is only visible at 10 kV, merging with the background already at 7.5 kV. In contrast, finite peak heights for the anatase reflection near 38.58° above the noise level are observable for Si and SiO₂/Si substrates. The crystallite size, as determined from the line width by the Debye-Scherrer formula, increases from about 5 nm at 3 kV to 8 – 9 nm at 10 kV, again independent of the substrate. These obtained values are close to the detection limit for XRD.
Raman spectra were measured in backscattering geometry with a triple spectrometer and a spectral resolution of 1 cm$^{-1}$. The Ar$^+$ line at 488 nm was used for excitation of spot on the samples with a diameter of 1 – 2 µm.

The Raman spectra of the two samples with the highest anatase content (deposited on SiO$_2$/Si and Si at 10 kV bias) are shown in figure 6.6. Comparison with literature data for expected peak positions of rutile and anatase [127, 128] shows that only the rutile $E_g$ and $A_{1g}$ modes at 447 cm$^{-1}$ and 612 cm$^{-1}$ are clearly recognisable for the thin films deposited by MePIIID. Hints of the disorder bands near 250 cm$^{-1}$ and 320 cm$^{-1}$ can be identified in spectra.

Figure 6.6: Raman spectra of two samples deposited with 10 kV pulse voltage on SiO$_2$/Si and Si, together with reference spectra of a rutile thin film (from Ref. [122]) and anatase powder (APS 32 nm, Alfa-Aesar). The prominent peak at 520 cm$^{-1}$ arises from the Si substrate.
6.4 Surface Morphology

The film morphology was investigated with scanning electron microscopy (SEM), while the surface roughness was determined by atomic force microscopy (AFM). The spectra obtained here for films prepared with MePIIID are very similar to those of nanocrystalline rutile layer on Ti [129], shown as one reference. No similarity with the other reference spectrum of anatase powder, which is quite similar to that of bulk anatase [130], is observed. The low intensity of the signal should be a combination of small grain size and low crystalline quality. At the same time it should be kept in mind that the surface layer of TiO$_2$ is acting as an antireflection coating with a corresponding low amplitude of the electric field inside this layer and thus low Raman scattering. Despite the difference in the XRD and the Raman data, the surface morphology itself does not depend on the substrate; however significant variations with the pulse voltage are observed, with SEM viewgraphs of selected samples depicted in figure 6.7.
Very smooth sample surfaces without defects or droplets are obtained at 1 kV pulse voltage, whereas a microstructure is visible at 10 kV with the typical lateral dimensions about 30 – 60 nm. Atomically, the surfaces are not too smooth as shown by the comparison of the roughness of the one-crystalline silicon substrate (Rms 0.1 nm, figure 6.8).

**Figure 6.7:** SEM viewgraphs of four different samples, deposited at 1 and 10 kV pulse voltage on Si and f.s. substrates.
Influence of Ion Energy on Phase Formation of Photoactive TiO$_2$ Films by MePIIID at Room Temperature

Figure 6.8: AFM height profiles of (a) (100) Silicon (Rms 0.144 nm) surface, (b) SiO$_2$/Si (Rms 0.746 nm) surface and (c) Fused Silica (Rms 1.550 nm) surface.

Figure 6.9: AFM viewgraphs of six different samples, deposited at 1, 5 and 10 kV pulse voltage on Si and f.s. substrates. The corresponding roughness values Rrms are: a) 0.59 nm (1 kV/Si), b) 1.28 nm (5 kV/Si), c) 2.2 nm (10 kV/Si), d) 0.91 nm (1 kV/f.s.), e) 0.97 nm (5 kV/f.s.) and f) 2.7 nm (10 kV/f.s.)
At the same time, the surface roughness $R_{rms}$, obtained from AFM measurements, increases from 0.6 – 1.0 nm at 1 kV to 2.2 – 2.7 nm at 10 kV pulse bias (figure 6.9).

### 6.5 Surface Energy

The surface energy was derived from contact angle measurements employing water and ethylene glycol with the data analysis according to the Owens-Wendt method [131]. The samples were exposed to UV-A light, generated from an actinic tube with a spectral range of 300 nm – 460 nm and the maximum at 365 nm, with an irradiation power intensity of 1 mW/cm², for up to 3 hours. The ambient temperature and humidity was 21 °C and 25%, respectively. The results of contact angle measurements performed with water and ethylene glycol are presented in figure 6.10.

![Figure 6.10: Contact angle against water and ethylene glycol as a function of pulse voltage and illumination.](image)

Using two liquids with different surface energies, the surface energy of the thin film, as well as the dispersive and polar fractions, can be calculated. These results were obtained for an irradiation intensity of 1 mW/cm² after 3 hours. Even lower contact angles of 5° or less could be obtained for the 10 kV bias samples at intensities
of 2 – 3 mW/cm², however the error bars increase considerably for these measurements (not presented here).

The corresponding surface energies of the sample deposited on different substrates are shown in figure 6.11, comparing values of the pristine samples and those of samples after 3 hours continuous exposure to UV light. The time between end of the irradiation and the contact angle measurements was always less than 1 hour, while no influence of varying this delay time on the results was observed.

No effect of the UV irradiation on the contact angle was observed without bias or for pulse voltages up to 3 kV, the contact angle for water itself varies unsystematically between 75° and 85° for different substrates and pulse voltages. In contrast, at 5 kV and beyond, a strong reduction of the contact angle, correlated with an increased surface energy was observed with the effect increasing with rising pulse voltage and depending on the substrate. The highest value of close to 100 mN/m, corresponding to a water contact angle of 18° was observed after illumination for TiO₂ deposited on Si with no difference at 10 kV between SiO₂/Si and f.s. substrates. The obtained surface energies and their increase with UV irradiation are indicative of a photo-induced hydrophilicity [51]. Comparing the contact angle for water and ethylene glycol, the relative fraction of the disperse and the polar part of the surface energy could be

![Figure 6.11: Comparison of the surface energy before and after three hours of UV irradiation as a function of the pulse voltage.](image-url)
obtained. As shown in Figure 6.12, the dispersive part dominates over the polar part before illumination for all samples, whereas after irradiation with UV light the disperse part is tending towards zero and the surface energy is close to the polar part. The underlying process is the reduction of Ti(IV) cations to Ti(III) by electrons and the simultaneous trapping of holes, e.g. at bridging oxygen. Subsequent dissociative adsorption of water at oxygen vacancies created after the bond weakening by the trapped holes [56].

![Figure 6.12](image-url)

**Figure 6.12:** Deconvolution of the surface energy into disperse and polar fraction as a function of pulse voltage. Without illumination, all samples show a behaviour close to those deposited at 0 kV, hence only data for 0 kV are provided. Furthermore, the 0 kV samples did not show any change with illumination.

### 6.6 Photocatalytic Activity

The photocatalytic activity was investigated by spreading a diluted solution of methylene blue (MB), which is a well established model substance for photocatalytic activity, on the samples surfaces at a concentration of about $10^{-9}$ mol/cm$^2$. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was performed subsequently with a 15 keV Ga$^+$ ion beam, raster scanned over a surface area of $500 \times 500$ µm$^2$ for a total incident ion fluence of $2.5 \times 10^{12}$ ions/cm$^2$. This sample preparation and measurement mode ensures that only the MB film and the topmost layer of the thin films are investigated. In general, this increased hydrophilicity is accompanied by a photocatalytic activity. Using SIMS, it is possible to investigate directly the processes at the thin film surface [132]. Figure 6.13 depicts results from SIMS for different surface conditions. In the mass range from 230 to 300, pure Si exhibits some organic contaminations at low count rates around 265 and 280 amu. In contrast, after coverage with a
very thin film of MB, the typical fragmentation pattern is observed [132]. The most prominent peak at m/z = 284 corresponds to [MB]+, while m/z = 269 can be identified as MB after losing a methylene group ([MB-CH₃]+). Fragments where additional protons or more than one CH₃ group are missing, together with molecules containing ¹³C or ¹⁵N are completing the mass spectrum. The majority of this fragmentation behaviour of the secondary ions is due to the ion bombardment and the sputter process liberating the molecules from the surface.

**Figure 6.13:** SIMS spectra of the TiO₂ sample deposited onto Si at 10 kV bias voltage, covered with a methylene blue film and with and without UV irradiation. Additionally, data for a blank Si substrate, Si covered with MB, and TiO₂ deposited at 0 kV, covered with MB and illuminated are presented. Additionally, the chemical structure of MB is depicted in one panel. [MB-CH₃] indicates MB with one CH₃-group removed.

For MB on TiO₂ (deposited at 10 kV), a modified fragmentation pattern is observed with more protons missing from the MB molecules. After UV irradiation, no clear signal of the original MB is present and all heavy fragments above 230 amu are strongly suppressed. While some photocatalytic activity can be proposed for this sample with the highest surface energy
even without UV illumination, a complete destruction of the MB overlayer is observed after UV irradiation. No such effect is observed for samples deposited at 0 kV, where the SIMS spectrum after illumination is very similar to the spectrum without illumination.

These results can be also inferred from table 6.2, where the integrated peak intensities are shown as a function of the surface conditions. Again, it has to be distinguished between a complete destruction and a chemical modification of the adsorbed MB. For MB on pure Si and the film deposited at 0 kV after illumination, no differences in the MB/[MB-CH₃] ratio are observed, with the absolute difference most likely due to different adsorption rates of MB on the surface. This pattern should be purely due to the destruction by the primary ions during SIMS. For the film deposited at 10 kV and covered with MB before illumination, a shift of the MB/[MB-CH₃] ratio is observed, which can be explained by the abstraction of several hydrogen atoms, which is also featured in the corresponding spectrum. In contrast, the 10 kV film after UV illumination displays MB and its decomposition products barely above the background signal of the bare Si reference without MB coverage. It can be stated that the film with the highest surface energy has the strongest effect on MB decomposition, indicating a clear correlation between these two effects.

<table>
<thead>
<tr>
<th>Surface Condition</th>
<th>MB (283.5 – 286.5 amu)</th>
<th>MB-CH₃ (266.5 – 270.5 amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Reference</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>Si + MB</td>
<td>5599</td>
<td>4086</td>
</tr>
<tr>
<td>TiO₂/Si (10kV) + MB</td>
<td>598</td>
<td>1344</td>
</tr>
<tr>
<td>TiO₂/Si (10kV) + MB + UV</td>
<td>46</td>
<td>215</td>
</tr>
<tr>
<td>TiO₂/Si (0kV) + MB + UV</td>
<td>2354</td>
<td>2000</td>
</tr>
</tbody>
</table>

**Table 6.2:** Integrated SIMS signal intensities, the mass ranges were chosen to include either the main MB peak or the MB-CH₃ peak

### 6.7 Discussion

Summarizing the results, it can be stated that TiO₂ thin films were deposited onto three different substrates using MePIIIID with varying substrate pulse bias and without additional heating. While the surface energy without illumination is quite similar, strong differences are present after UV-A illumination. With increasing bias, i.e. ion bombardment, an increased
hydrophilicity was observed, accompanied by a photocatalytic activity. Corresponding changes in the phase composition were observed. The main factor influencing the phase formation during the film deposition is the ion bombardment as the temperature of 100 °C or less after the deposition runs of 5 minutes is much lower than the 300 °C reported in the literature necessary to form anatase without ion bombardment [133].

The correlation between the phase composition and the photoactivity of TiO$_2$ is well known, with anatase or rutile being more active than the amorphous phase [56]. At the same time, a correlation between the photocatalytic activity and the photo-induced hydrophilicity is established [134]. Instead, the discussion will concentrate on three points peculiar to the present experiments: (1) the apparent disagreement between the Raman and the XRD data, (2) the phase formation depending on the energy flux, and (3) the strong influence of the substrate on the surface.

XRD is sensitive to the long-range order of materials, thus providing average structural information across several unit cells. In contrast, Raman scattering is a local probe and very sensitive to local imperfections. As a very low substrate temperature compared to the melting temperature and a very high deposition rate existed during the thin film growth, the incorporation of a high defect density, including vacancies, interstitials and anti-site defect should occur. With XRD less sensitive towards these defects than Raman spectroscopy, the non-detection of anatase in the latter experiment is understandable.

The phase composition itself is depending on the substrate bias with crystalline rutile and anatase detected for pulse voltages between 3 and 10 kV, and an amorphous phase dominating at 0 and 1 kV. Comparing the growth rate of the thin films and the ion saturation current through the substrate [122], at least 50% of the arriving particles must be ionized. Making a conservative assumption on the average ion energy of 5 eV and an average charge state at the substrate of +1, the deposited energy per incoming atom is between 2.5 eV at 0 kV pulse voltage, 45 eV at 1 kV and about 450 eV at 10 kV.

According to the literature model for the energetic deposition of TiO$_2$ thin films [135], at room temperature, the transition from amorphous to a rutile/anatase mixture should occur around 5 eV (shifted to 1 eV around 100 °C). The establishment of pure rutile is supposed to happen beyond 30 eV at 0 °C and some 10 eV at 100 °C. These data were obtained at growth rates of 0.1 – 0.5 nm/s. In the present experiment, higher growth rates are present and the ion
Influence of Ion Energy on Phase Formation of Photoactive TiO$_2$ Films by MePHIID at Room Temperature

bombardment, favourable for the rutile nucleation, occurs in a pulsed mode with a duty cycle of 9% at a repetition rate of 3 kHz.

The first effect of a higher growth rate can shift the phase stability regions towards higher energies with especially the amorphous-crystalline transition affected. In contrast, the pulsed regime should allow an alternative nucleation of anatase and rutile with rutile being formed during the pulses and anatase between them. Varying the duty cycle or using DC bias could clarify this issue. Actually, the mixture of anatase and rutile could be more photoactive than pure anatase [56]. The increase in the substrate temperature from room temperature to 40 °C – 100 °C, small compared to 400 °C necessary to nucleate anatase with thermal particles, occurs roughly linear with time, thus the nucleation phase will always be completed at a similar temperature, while the thickness of the substrates is so small and the deposition time so short that different thermal conductivities of the substrates will not be important.

When trying to find the origin for the different activities of the thin films deposited onto Si, fused silica and thermal SiO$_2$/Si, the underlying influencing factors have to be examined. According to the literature, photoactivity and hydrophilicity is influenced by several parameters, including crystallite size, bandgap, oxygen vacancy density and electron-hole lifetime [56]. A direct influence of the substrate across a film thickness of 300 nm can be excluded, the range for such interface effects will be at most 5 – 10 monolayers, or even less. Thus, indirect effects must be responsible.

Figure 6.11 shows that the Si substrate leads to the most active thin films for 10 kV bias voltage with lower activity for the other two substrates. However, the intensity of the anatase phase is the lowest for the f.s. substrate with Si and SiO$_2$/Si yielding similar rutile/anatase intensity ratios. At the same time, the crystallite size and the surface roughness are identical for all films deposited at the same voltage (cf. figure 6.7 and 6.9).

During the deposition process, the surface region is subjected to intermixing by the ion bombardment. Especially during the initial stage of the growth process with the film thinner than the ion range, mixing of the TiO$_2$ and the substrate can occur with a 30 nm thick amorphous interface zone observed for deposition of TiO$_2$ on Si at 10 kV bias [136]. While the ion mixing efficiency is determined by a chemical driving force and not the ion range [137], an influence of the substrate on this mixing process is possible. However, at a layer
thickness of 300 nm and no thermal diffusion inside the film, the surface stoichiometry should not be influenced by this effect.

It can be summarized that a nanocrystalline structure with the crystallite size close to the XRD detection limit is present at higher voltages, in contrast to a presumably amorphous microstructure at lower voltages. At the moment, the microstructure itself, and the influence of the substrate on the crystallite nucleation and growth processes cannot be discerned, in addition to different effective surface areas. Further detailed investigation of the microstructure with TEM and measurements of the electronic properties of the films should help to elucidate the underlying mechanism as the macroscopic parameters do not allow an unequivocal identification.
CHAPTER 7  Ion Bombardment vs. Temperature

In the following experimental part, TiO$_2$ thin films are formed by metal plasma immersion ion implantation and deposition (MePIIID) [89] with additional substrate heating using a similar experimental setup from above experiments, now including additional heating. A correlation between phase composition, morphology and photoactivity is to be established.

7.1 Film Morphology

The film morphology was investigated with scanning electron microscopy (SEM) and the surface roughness was determined by atomic force microscopy (AFM). Furthermore, layer morphology was investigated using TEM.

7.1.1 SEM

The results obtained for the film morphology when investigating thin film cross-sections with SEM are presented in figure 7.1. As can be seen, no contrast is visible for a film deposited at room temperature with 5 kV pulse voltage. However, grain boundaries are visible for films formed at 200 °C and 300 °C. The column width decreases from 65 – 75 nm at 200 °C to about 50 nm at 300 °C. Nevertheless, dense and pore-free TiO$_2$ films were observed for all process conditions.
Figure 7.1: SEM cross-section viewgraphs of three different samples, deposited at 5 kV pulse voltage at room temperature, 200 °C and 300 °C

7.1.2 AFM

AFM results, depicted in figure 7.2 and 7.3, confirm the SEM results on the morphology. The surface roughness of the titanium oxide layers shows root mean square roughness (Rrms) between 1.5 nm to 2.8 nm. The AFM viewgraphs show, that with increasing pulse voltage
from 1 kV to 10 kV, a transition of dots structures with a size distribution below 50 nm to an overlapping micrometer size structures.

The structures are determined by the crystalline texture in the layer, since due to the ion bombardment the sputtering of the surface atoms is larger on grain boundaries due to their weaker bidding energy of these atoms. At 300 °C, the sputtering is negligible due to the increased surface movement of atoms (see the low roughness of 1.47 nm), but the grain size doesn’t increases as one would expect from the thermodynamical point of view.

**Figure 7.2:** AFM viewgraphs of three samples deposited at RT and 10 kV with oxygen flow (a) 30 sccm (Rms 1.48 nm), (b) 75 sccm (Rms 2.66 nm) and (c) 100 sccm (Rms 2.26 nm).

**Figure 7.3:** AFM viewgraphs of four samples, deposited at (a) 200 °C, 1 kV, (b) 200 °C, 3 kV, (c) 200 °C, 5 kV and (d) 300 °C, 5 kV. The corresponding roughness values Rrms are (a) 1.7 nm, (b) 2.0 nm, (c) 2.1 nm and (d) 1.5 nm.
Minor droplet contamination from arc deposition process is visible in some panels. A columnar structure is visible for all samples with slightly higher elevation between the grains and the grain boundaries for higher pulse voltages, indicating a preferential sputtering of grain boundaries. With increasing temperature, the surfaces become smoother as an increased surface mobility counteracts the localized sputter processes. At the same time, the surface roughness Rrms, decreases from 6.4 nm at RT to 1.5 nm at 300 °C.

7.1.3 TEM
The Selected Area Electron Diffraction (SAED) diagrams of the samples deposited on silicon substrate clearly show the evolution from a poor crystallinity at room temperature (RT) up to an ordered structure at 200°C (figure 7.4). At RT and 5 kV broader diffraction rings appear on the corresponding amorphous structure with crystallites showing a preferred orientation. The influence of the ion energy is not taken for the moment into account.

![Figure 7.4: SAED-Diagram of TiO₂ on (100) Silicon with beam direction parallel to [110] Si (200 keV acceleration voltage) a) 5 kV, RT b) 5 kV, 200°C (inverted) c) 5 kV, 300°C. The angle area of the azimutal grain tilt is marked.](image)

The dark-field view of the sample at RT shows a dense amorphous structure with rutile nanoclusters (figure 7.5). In contrast, a columnar structure with anatase/rutile mixture for 200 °C and 300 °C samples is visible in dark field (figure 7.5), column width decreases with temperature. Numerous Crystallites are visible in the dark field view, at higher temperature close to the layer surface, with correlating azimuthal orientation. The crystal formation is not very strong restricted by the azimuthal tilt of the diffracting lattice layers, because the hole aperture selects a limited area of the diffraction image. Beside the titanium oxide layer and silicon, there is also an amorphous inter-layer, with 25 nm thickness, visible due to the chemical mixing with the silicon substrate. The thickness of the amorphous inter-layer increases with increasing bias voltage and with a sufficiently high relationship from implantation to deposition. Additionally, the temperature has an influence on the diffusion. At
the additional oxygen implantation of titanium on silicon at temperatures above 350 °C, the oxygen diffusion from the titanium layer in silicon was proved. Also by simultaneous deposition of Ti and O, at room temperature, an amorphous layer created due to ion beam mixing is verified [106]. The comparison of the three texture structures shows that already at 200 °C nanosized crystallites grow on 50 nm broad columns orthogonal to the substrate, in which a correlated orientation pre-exists. The columns are aligned along ion beam direction. On high resolution images one can recognized that the amorphous areas between the crystallites, that are still present at 200°C, disappear completely at 300°C. At the same time a strong texture of the crystallites is visible. The texture development can be explained due to the ion bombardment. The investigation of the crystal growth with the MePIIID in dependence of the pulse voltage shows that with increasing pulse voltage from 5 kV to 10 kV the grain tilt goes over to a higher ordering of the crystals [123].

However, with temperature-increase, the opposite effect is to be observed. The dark field image of the sample at 300°C shows a weaker contrast. In the SAED Diagrams of the samples at 200°C and 300°C, the increase of the azimuthal tilting angle of particular lattice layers is visible. The angle-area marked in the figure 5 increases from 2.5° at 200 °C to 5° at 300 °C. In the high-resolution image of the sample at 300 °C a random coalescence of crystallites in the azimuthal layer is visible.

From the azimuthal orientation can be concluded that besides the interference lines also a dot structure appears caused by the crystallites on the beam direction tilted zone axis. From this

![Figure 7.5: Dark field images of layers deposited on silicon substrate at a pulse voltage of 5 kV at RT, 200°C and 300°C.](image-url)
Ion Bombardment vs. Temperature

orientation, a diffraction image using Fast Fourier Transformation (FFT) is built (figure 7.6d). The FFT was compared with calculated diffraction images for the individual structures of Anatase and Rutile (calculation by means of online-data base of the Centre Interdisciplinaire de Microscopie Electronique in Louseanne [138]) and was indexed. The lattice layer distances agree completely with Rutile. For the input of the lattice layer distances the FFT was used. If the FFT-Diagram was indexed right, then, the marked lattice layers are always perpendiculars to the corresponding g-Vectors (reciprocal lattice vectors). This gives us the plotted orientation relation. On the image of the sample at the 300 °C is clearly visible that the 010 -levels of Rutile are aligned parallel to the surface. The given lattice layer distances (d) have an error of 0.01 nm compare with standard lattice layer distances d(100) = 0.459 nm and d(110) = 0.325.

Figure 7.6: HRTEM-Images (cross section) of titanium oxide (Rutile) on (100) Silicon a), c): 5 kV, 200 °C. Image c is the marked area from a). The area between the crystallites is probably amorphous. b), d): 5 kV, 300°C. Image d) is the marked area of b). From the FFT image the beam direction parallel to [001] can be deduced.


7.2 Phase Composition

Ion bombardment and substrate temperature strongly influence the phase formation, as shown in the previous section. However, does allow only limited insights into local structures while XRD samples have larger areas and allow a more comprehensive viewpoint.

The structural characterization of the titanium oxide layers on silicon, silicon dioxide and fused silica substrates for different temperatures varying pulse high voltage, was done by X-ray diffraction measurements. Due to the strongly present preferred orientation of crystals the measurements at the Bragg-Brentano Diffractometer, that is actually a Powder Diffractometer, and the $\theta/2\theta$-measurements at incident glancing angles below 10° gave low peak intensities.

The layer thickness is sufficient for detection of layer crystallites. No phase formation could be detected at RT for the pulse voltage range from 0 to 5 kV, indicating either an amorphous structure or nanocrystallites with a size of less than 5 nm, whereas highly textured rutile and anatase could be observed from 1 kV voltage onwards. It has to be point out again that previous results showing rutile and anatase formation with similar pulse voltages were performed with a completely different substrate setup.

For 300 °C substrate temperature, two peaks at 27.7° and 38.2° (Figure 7.7 and 7.8) in samples deposited on silicon oxide and fused silica substrates appear. For 200 °C substrate temperature, qualitatively similar results were obtained, with only the 200 °C data from samples deposited on silicon substrate shown at figure 7.9. The substrate influence on the phase formation can be neglected. The peak at 27.7° correlates very well with the (110) reflection of standard Rutile. The peak at 38.2° can be assigned to the (004) orientation of Anatase. The intensity of the 110 peak of Rutile grows monotonically with increasing pulse voltage from 1 kV to 5 kV at constant peak width. At the same time the 004 peak of Anatase, with the highest intensity observed at 3 kV, loses on intensity at 5 kV.

With the PIIID and the related IBAD, beside the free standard energy of a crystal surface also the incidence geometry of energetic ions has an influence on the growth of lattice layers [139]. For IBAD was observed that through the recrystallization of the (100) layer, the (110) Rutile layers overgrow with increasing ion/atom relation [140]. This effect was explained that in the Rutile structure along [100] open channels exist through which the ions achieve effectively a larger range leading to a smaller contribution of their energy on the sputtering of the surface atoms.
Figure 7.7: XRD spectra of samples produced at 300 °C with different ion bombardment on SiO$_2$/Si substrates. The expected peak positions according to the powder diffraction files for anatase and rutile are indicated. The spectra are shifted vertically for clarity.

The intensity-decrease of the 004-peak of anatase could be due to stacking faults along [004] or grain tilting relative to the surface. Similar line of thoughts apply for MePIIID.

Through $\theta/2\theta$ measurement at constant incidence angle of 10° and the detector-position at variable $2\theta$ condition (27.7°) (figure 7.9) higher peak intensity was achieved. This allows grain tilting of 4° in the radiated sample volume to be accepted. The diffraction conditions at this asymmetric measurement are shown in figure 7.10.
Figure 7.8: XRD spectra of samples produced at 300 °C with different ion bombardment on fused silica substrates. The expected peak positions according to the powder diffraction files for anatase and rutile are indicated. The spectra are shifted vertically for clarity.

Figure 7.9: XRD spectra of samples produced at 200 °C and 300 °C with different ion bombardment on silicon substrates. The expected peak positions according to the powder diffraction files for anatase and rutile are indicated. The spectra are shifted vertically for clarity.
Figure 7.10: Diffraction geometry at a tilt $\alpha$ of the hkl layer compared to the Bragg angle

The XRD-Data of the samples deposited on silicon substrate (figure 7.11 and 7.12) were investigated regarding the temperature dependence of the diffraction intensity of the Rutile 110 peak and Anatase 004 peak.

At 200°C, the (110) and (004) layers are oriented parallel to the surface. It can be recognized that the intensity of the 004- peak decreases at 5 kV similar to the layers on the glass and silicon oxide substrates. At higher temperature, (300 °C), the coherent scattering areas in form of (004) layers parallel to the surface increase at the cost of (110) layer. This shows that from a threshold of 300°C the temperature dominates over the energetic effect. The increased temperature probably influences grain tilt. In this case the 110 - layers don’t lie parallel to the surface anymore.
**Figure 7.11:** XRD spectra of samples produced at 200 °C with different ion bombardment on silicon substrates. The expected peak positions according to the powder diffraction files for anatase, rutile and silicon are indicated. The spectra are shifted vertically for clarity.

**Figure 7.12:** XRD spectra of samples produced at 300 °C with different ion bombardment on silicon substrates. The expected peak positions according to the powder diffraction files for anatase, rutile and silicon are indicated. The spectra are shifted vertically for clarity.
The crystallite size, inferred by the Debye-Scherrer formula:

\[
D = \frac{0.89 \cdot \lambda}{\Delta 2\theta (\text{rad}) \cdot \cos \theta}
\]  

(7.1)

increases from about 5 nm at 3 kV to 10 nm at 5 kV and listed in Table 7.1.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pulsed Voltage</th>
<th>hkl: 110 D (nm)</th>
<th>hkl: 004 D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) Silicon</td>
<td>3 kV</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 kV</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>Silicon oxide</td>
<td>3 kV</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 kV</td>
<td>5.8</td>
<td>9.2</td>
</tr>
<tr>
<td>Quartz glass</td>
<td>3 kV</td>
<td>10.4</td>
<td></td>
</tr>
</tbody>
</table>

**Table 7.1:** Calculated crystal size using Bragg Brentano diagrams for rutile and anatase at 300 °C

The Raman spectroscopy and Ω/20-Measurements (Rocking curves) were not used for the present experiments, although additional information is to be expected from both methods [127,129]. The Raman spectroscopy is a more sensitive method in comparison to the X ray diffraction for the phase-analysis of polycrystalline thin layers with a strong preferred orientation. The intensity of Raman modes of the respective phase similar to X ray diffraction for very small crystals and high defect density, that disturbs the lattice coherence, is very small. Grain boundaries and other lattice misfits create, due to the inelastic scattering processes in the misfit ordering conditions, additional Raman modes. Ω/20-Measurements (Rocking curves) can be applied for the determination of the grain tilting for the epitaxical layer-adhesion. For the present samples, due to the strong grain tilting relative to the substrate, this method is not suitable.

### 7.3 Surface Energy

The power intensity of the irradiation on the sample surface was set constant at 1 mW cm\(^{-2}\) by calibrating measurements with a light sensitive UV-A measuring instrument.

The surface energy was derived from contact angle measurements employing water and ethylene glycol with the data analysis according to the Owens-Wendt method [131]. As the contact angle of two liquids against the thin films was measured, it was possible to calculate the surface energy before and after illumination with UV light. No systematic differences were found before illumination, however a strong effect was found after illumination.
7.3.1 Variation of Oxygen Flow
Figure 7.13 shows the development of the water contact angles and the calculated surface energies in dependence of the oxygen flow before and after irradiation with light in the wavelength range from 315 nm up to 400 nm (UV light) with wavelength-maximum at 365 nm (iradiator F15W/T8/BL -350).

In section 6.1 it was shown that by the variation of oxygen flow one can tune the Stoichiometry of the layer. This can lead to a saturation of the oxygen concentration at higher oxygen flows. In the figure 7.13, one can recognize that this only slightly substoichiometric titanium oxide layer at higher oxygen flows achieve a higher wettability after photo-activation.

7.3.2 Variation of HV Pulses and Temperature
Figure 7.14 shows the time dependence of the water contact angles of TiO$_2$ layers on (100) silicon after UV irradiation for different temperatures, deposited at constant oxygen flow of 55 sccm and unified pulsed voltage of 5 kV. The sample at room temperature shows the highest activity. The contact angle decreases within 2 hours at $10^\circ$ (strong wettability). The sample at 200 °C after 3 hours reaches the same condition. However, the sample at 300°C doesn't show any photo-activity.

The surface energies as a function of pulse voltage and deposition temperature are presented in figure 7.15. No substrate influence on the surface energy was observed.

The time between end of the irradiation and the contact angle measurements was always less than 1 hour, no influence of small changes in this delay time on the results was observed.
Figure 7.14: Irradiation time dependence of the water contact angles of TiO$_2$ on (100) silicon after UV irradiation for different temperatures, deposited at constant oxygen flow of 55 sccm and unified pulse voltage of 5 kV.

For all temperatures, some samples with a surface energy of 100 mN/m or more, indicating photocatalytic activity were obtained. For 200 °C deposition temperature, all samples showed this value, whereas low pulse voltage at 300 °C and high pulse voltages at room temperature were necessary to obtain these values.

Figure 7.15: Surface energy of titanium oxide layers deposited on silicon and silicon oxide substrates after 3 hours of UV illumination as a function of substrate temperature and substrate bias.
Comparing the contact angle for water and ethylene glycol, the relative fraction of the disperse and the polar part of the surface energy could be obtained. As shown in figure 7.16, the dispersive part dominates over the polar part before illumination for samples deposited on silicon substrate at 200 °C, whereas after irradiation with UV light the disperse part is tending towards zero with increasing irradiation time and the surface energy is close to the polar part. The underlying process is the reduction of Ti(IV) cations to Ti(III) by electrons and the simultaneous trapping of holes, e.g. at bridging oxygen. Subsequent dissociative adsorption of water at oxygen vacancies created after the bond weakening by the trapped holes [56].

The area of higher surface-energy corresponds to the mean parameter-region with higher ion energy (3.\,kV - 10\,kV) and lower temperature (RT - 200°C) or lower ion energy (1 - 3\,kV) and higher temperature (300°C). The area of high energy and high temperature as well as low energy and room temperature lie outside the area the photo-activity. The question on the large difference on the correlation of the surface energy between the samples at 300 °C with the structural properties of the surface cannot be answered with the results presented here. The surface morphologies of the samples at 300°C don't differ essentially between them.

Figure 7.16: Deconvolution of the surface energy into a disperse and a polar fraction as a function of pulse voltage for the samples deposited on silicon substrate at 200 °C.
7.4 Photocatalytic Activity

The photocatalytic activity was examined by exposing the samples to UV light, generated from an actinic tube with a spectral range of 300 nm – 460 nm with the maximum at 365 nm, at an intensity of 1 mW/cm², for up to 3 hours.

The photocatalytic activity of the samples was investigated by the decolorization of Methylene blue (figure 7.17), that is used as standard substance also in the literature. In this case, can be assumed that the superhydrophilic activity is strongly correlated with the photocatalytic activity [141,134]. The superhydrophilic property as like as the photocatalytic activity of titanium dioxide is based on the generation of electron-hole pairs by activation with photon-energies in the range of the band-gap energy.

\[
\begin{align*}
\text{Figure 7.17: Schematic representation of the Methylene blue [142]} \\
\end{align*}
\]

Initially, the adsorption and dissociation of water takes place at the surface of titanium dioxide. The water binds at oxygen-atoms at the surface, that are coordinated by fivefold titanium atoms. The role of the titanium coordination of the oxygen is essential. The reduced oxygen then becomes transferred in the Thiazinring (NC4S) of the Methylene blue under formation of a Sulfoxids and reduction of the nitrogen through hydrogen on the Thiazinring. The Sulfoxid is colorless since the aromatic system of the Methylene blue was changed. The kinetics of the catalytic demineralization from Methylene blue to Carbon dioxide and nitrate-ammonium and sulphate ions through titanium oxide in form of Nanoparticle dispersion is already described [143].

The linear area of the absorption of Methylene blue near 664 nm is depicted in Figure 7.18. With increasing irradiation time, the spectrum of a product that forms as an intermediate, overlapped with the absorption spectrum of Methylene blue. After 27 hours of UV Irradiation, only the spectrum of the product remained. Under the assumption, that the concentration of the product at this time corresponds to the exit-concentration of Methylene blue, the sum absorption spectrum can be separated into two shares. Afterwards, the concentration \( c \) of Methylene blue at a time \( t \) could be expressed using the following formula:

\[
\begin{align*}
\Delta c &= I - c_{\text{exit}} \\
\Delta \varepsilon &= \varepsilon - \varepsilon' \\
\end{align*}
\]

(7.2)
with the absorption $I$, the extinction coefficient of Methylene blue $\varepsilon$ (79.51 lmmol$^{-1}$) and the extinction coefficient of the product $\varepsilon'$ is calculated.

![Graph showing absorption vs. Methylene Blue concentration]

**Figure 7.18: Absorption of different concentrations of Methylene Blue solution**

By comparing the concentration decrease for solutions without titanium oxide layer and with titanium oxide layer three photoactivity regions can be distinguished: (i) neglecting, (ii) middle and (iii) high. Altogether, a relatively low photocatalytic activity is to be observed. This can be connected with the phase composition. The layers consist mainly of Rutile and the photocatalytic activity of anatase is usually higher compared to Rutile [143]. The results obtained for three different samples are presented in figure 7.19. The absorption of the solution without titanium oxide doesn't show any photo-chemical reduction reaction of Methylene blue within the error by the absorption measurement. Therefore, the observed decrease of the absorption results from the photocatalytic activity of the titanium dioxide layers. The sample, which was produced with a pulse voltage of 5 kV and a substrate temperature of 300 °C, doesn't show any photocatalytic activity. The sample at 3 kV and 300°C shows the highest activity. The results from the contact angle measurements and the decolorization of the Methylene blue show the correlation of both effects. The disappearance of the photoactivity cannot be explained with the results of this work due to characteristic structural layer properties. Regarding the structure of the layers, that shows an extreme distinction in photoactive properties, no differences were observed (see the TEM dark field views and X ray diffraction diagrams). Furthermore, no difference in the phase composition was observed.
Figure 7.19: Photocatalytic degradation of Methylene blue from titanium dioxide layers deposited on (100) silicon substrate.

7.5 Correlation of the Photoinduced Effects with Film Properties

A summary of these results on the photoactivity is schematically presented in Figure 7.20, using the published phase formation behavior [135] as a reference. A good agreement between the photoactive thin films and a phase composition of anatase or an anatase/rutile mixture is observed. When interpreting these data, two caveats have to be considered. First, the absolute quantification of the particle energies in the present MePIIID experiments is still unfinished. Plasma density measurements and energy flux measurements reported earlier for an experimental setup without additional substrate heating [122] are not valid for the present experiment due to the completely different plasma flow in the new setup. A reduction of the energy of the Ti ions arriving at the surface from 50 eV towards 1 – 3 eV is very likely, which would also explain the variation in the microstructure found for nominally identical pulse voltages without heating in Reference [124] and here.

Second, the published model [135] is purely empirical and summarizes the experimental observations. The replacement of substrate temperature with energy roughly implies an increase in the energy by a factor of 10 for a decrease of 300 °C. The implied logarithmic scale is counter-intuitive as a linear reduction of temperature should be compensated by a linear increase in energy.
Figure 7.20: Identification of process window to obtain photoactive thin films using the correlation between phase composition and temperature/energy.

As a corollary, the phase composition is more important than the microstructure for the photoactivity. The nanocrystalline or amorphous film obtained at 5 kV and RT is photoactive, similar to the columnar structured film at 5 kV and 200 °C. In contrast, the film deposited with 5 kV pulse voltage at 300 °C, which is structurally nearly identical except for slightly smaller grains, is not photoactive at all.

At the same time, temperature is counteracting ion bombardment as additional defects are produced by the impinging ions, which can only anneal at higher temperatures. Thus, a complete compensation of substrate heating by athermal ion energy will not be beneficial for the electronic properties. The exact influence of the radiation defects produced during the film growth on the electronic density of states and, hence, corresponding changes in the efficiency of electron-hole separation after photo-excitation and the subsequent lifetimes of trapped holes [56] have to be investigated in future experiments.
CHAPTER 8  Summary and Conclusions

In this work the possibility of metal plasma immersion ion implantation and deposition (MePIIID) as a method for the formation of photoactive TiO$_2$ thin films is presented. MePIIID using a titanium plasma in an oxygen atmosphere at low pressures leads to the production of titanium dioxide layers with 300 nm thickness in a time of 5 minutes. In this process the substrate was immersed in an arc plasma and a regime of ion implantation and deposition in a gas atmosphere was used. In this work the average ion energies between 10 eV (without HV pulses) and 1500 eV (10 kV HV pulses) were employed. This ionic energy allows the reduction of the substrate temperature. So the deposition on temperature sensitive substrates is possible.

Examining the stoichiometry in the dependence of the oxygen flow, we see a strong influence on the stoichiometry due to surface adsorption of oxygen molecules from the gas phase, and saturation effects at high oxygen partial pressures. The incorporation of oxygen should not be affected by the ion bombardment. Slightly substoichiometric TiO$_{1.95}$ thin films were used in further experiments.

In a second step, hydrophilic, photoactive TiO$_2$ films were prepared near room temperature using MePIIID with a pulse bias voltage of at least 5 kV necessary to induce this effect. For these energies, a mixture of rutile and anatase was found by XRD, while the amorphous films obtained at 1 kV and below did not show changes in the contact angle and surface energy after UV-A illumination. Thus, deposition of photoactive films is possible with energetic bombardment at temperatures below 100 °C without subsequent annealing steps, allowing the transfer of this process towards flexible and temperature sensitive polymer substrates. A strong influence of the substrate was found for a film thickness of about 300 nm with Si showing the largest effect, compared to fused silica and thermal SiO$_2$/Si substrates.

Furthermore, for the investigation the influence of ion energy and temperature, TiO$_2$ layers at a constant oxygen flow are produced. The investigation enables a clear separation of both influences. The characterization of the layers showed that the phase formation was determined from the high ion energy of MePIIID process. Increasing the process temperature from 200 °C to 300 °C has no further influence on the phase formation. Formed rutile and anatase phases with energetic ion bombardment are related to the crystal size, which lay in the range
of 10 nm. The nano-sized rutile and anatase crystals grow in columnar areas parallel to the incident ion direction. Simultaneously, a strong texture of the crystals can be seen, that does not change with temperature. There is no coalescence of the epitaxial rutile crystals with the (100)-oriented silicon substrate. At the silicon surface an amorphous layer of 25 nm thickness was produces by mixing of atoms and ions with the substrate atoms. Summarizing and comparing these results from TEM and XRD with previous results of MePIIID can be said that a relationship exists between the correlated orientation of the crystals and the ion energies used in this work.

XRD diagrams of samples with high ion energy and increasing deposition temperature from 200 °C to 300 °C give an indication that the tendency to the polycrystalline layer formation with arbitrary orientation of the grains alone was caused by increasing the temperature. The examination of surface texture using AFM indicates a fine-grained texture, which is produced by sputtering of the surface atoms at the grain boundaries. The fine structure that arises from the individual grains is overlaid with increasing ion energy from larger structures. The larger structures are similar with regard to the diameter of the columnar crystal areas that are visible in the TEM dark field images. From a threshold of the deposition temperature of 300 °C the sputtering effect is significantly lower in existing columnar growth. This is explained by the increased mobility of surface atoms at 300 °C. In the High Resolution images, the temperature effect on surface mobility can be also recognized. The amorphous regions between the crystals, which are still present at 200 °C, disappear at 300 °C.

By photo-activation of the titanium dioxide layers in the wavelength range 315 nm to 400 nm improved wettability and photocatalytic activity could be detected. The contact angle measurements on the layers, which all have a smooth non-porous surface, and the experiment for the photocatalytic decolorization of methylene blue confirm the correlation of both photoactive effects of titanium dioxide. The photoactivity is commonly seen with the overlapping area of the anatase and rutile phase in context. This phase area corresponds to a middle ion energy and temperature of the used MePIIID process. The parameter sets high energy and low temperature and low energy and high temperature to produce titanium dioxide, show only a low or no photoactivity. So, the replacement of substrate heating with ion energy was possible in a restricted process window, thus enabling the formation of photoactive TiO$_2$ thin films on temperature sensitive substrates. However, no exact correlation between microstructure or phase composition with the photoactivity was found.
The origin of the photo-induced phenomena in TiO$_2$ is broadly understood with the underlying process being the charge separation due to an electron promotion to the conduction band and a generation of a hole in the valence band. However, detailed dependencies on material properties are still open questions with various coexisting factors, i.e. grain size, phase composition, co-existence of a second phase, being discussed in the literature.

Further work is necessary to quantify the energy flux impinging on the substrate, which is much more complicated for MePIIID processes than for conventional ion beam assisted deposition. At the same time, detailed investigations of the electronic properties and their changes under different process conditions are necessary to explain and optimize the present findings.
CHAPTER 9  Bibliography


