Semiconducting Zn-(IV)-Nitride films, Deposited by Reactive Magnetron Sputtering

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3. Challenges for the preparations of Zn-IV-N_2 semiconductors
4. Reactive sputter deposition of Zn_3N_2 films
5. Reactive co-sputter deposition of $ZnSnN_2$-films
6. Summary

IGF-project Nr. 20963 BG

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Bundesministerium für Wirtschaft und Klimaschutz
aufgrund eines Beschlusses des Deutschen Bundestages

Short introduction of OUT

Non-profit industrial research institute since 1991

Location:	Berlin / Innovationspark Wuhlheide (IPW)
Staff (2024):	19 employees
Research funding (2022):	1,8 Mio. €

Manfred-von-Ardenne-Gewerbezentrum im IPW

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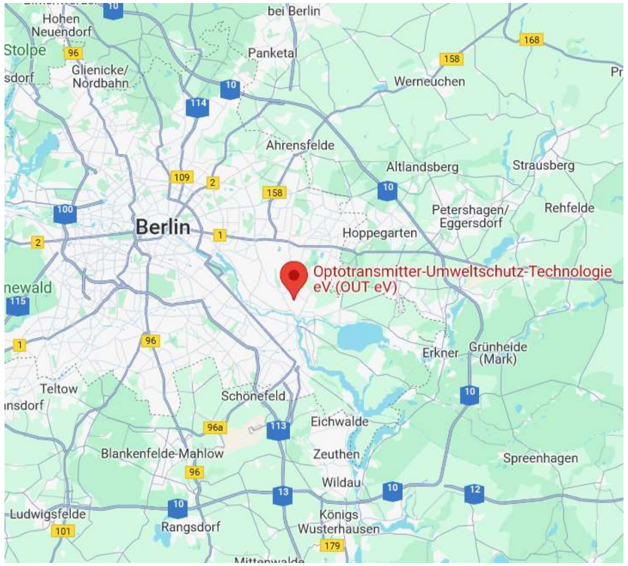
OUT Geschäftsräume im Haus 201



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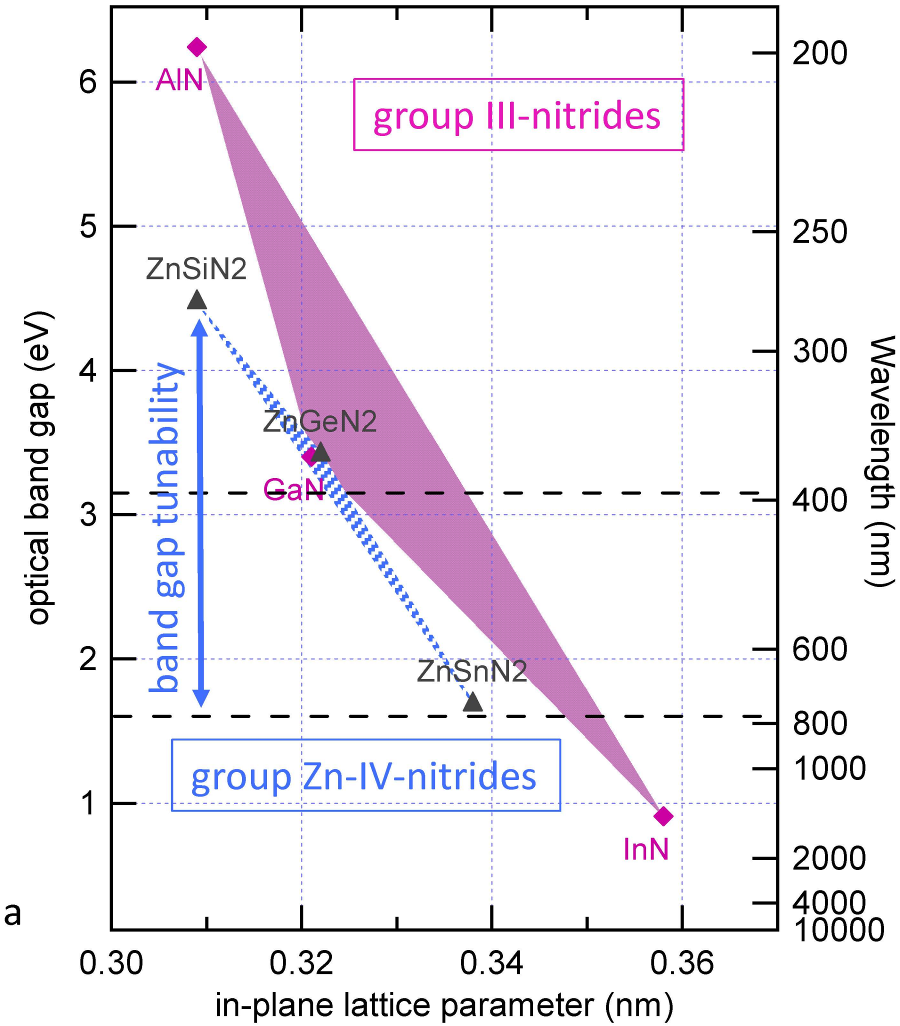
Benefits of Zn-IV-N_2 semiconductors

- earth-abundant base materials (Si, Zn, Sn, N_2) for the preparation of $ZnSnN_2$, $ZnSiN_2$
- direct band gap semiconductors
- band gap tunability in Zn-IV-N_2 due to heterovalent substitutions
- $ZnGeN_2$ is analogous and has a lattice-matched to GaN



Prospects and Applications:

- $ZnSnN_2$ as photovoltaic absorber (E_g = 1.5 eV)
- Optoelectronics: GaN-$ZnGeN_2$ hetero-epitaxy as a low-cost alternative to InGaN

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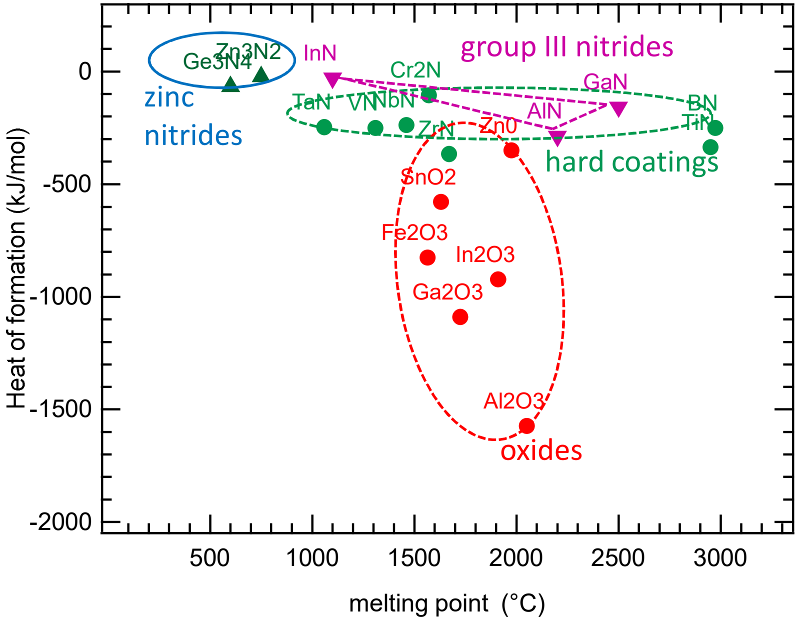
Challenges for the reactive sputter deposition of Zn-IV-N_2 semiconductors

Nitride Thermodynamics

- N_2-molecules have a high bond energy of -9.75eV, which makes them chemically inert.
- The phase equilibrium is driven towards nitrogen-poor compositions, which have a metal-like electronic structure, due to the small heat of formation.
- Nitrides are cohesive solids due to mixed ionic-covalent bonding, which makes them strong and hard.



Why magnetron sputtering deposition for synthesizing Zn-IV-N_2 semiconductors?

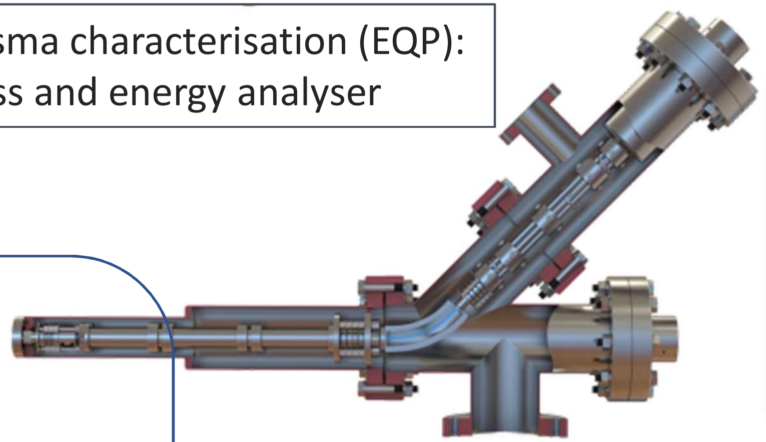
- Nitrides can be synthesized by sputtering pure metal targets in an argon-nitrogen gas mixture.
- Highly reactive nitrogen species can be formed in the plasma through radio frequency excitation.
- The desired nitride phases can then be epitaxially grown at moderate substrate temperatures.

Goals: **1. To prepare semiconducting nitride films with low carrier densities ($n_e < 1 \times 10^{18}$ cm^{-3}).**
2. To enhance the crystalline quality of nitride films through sputtering processes.

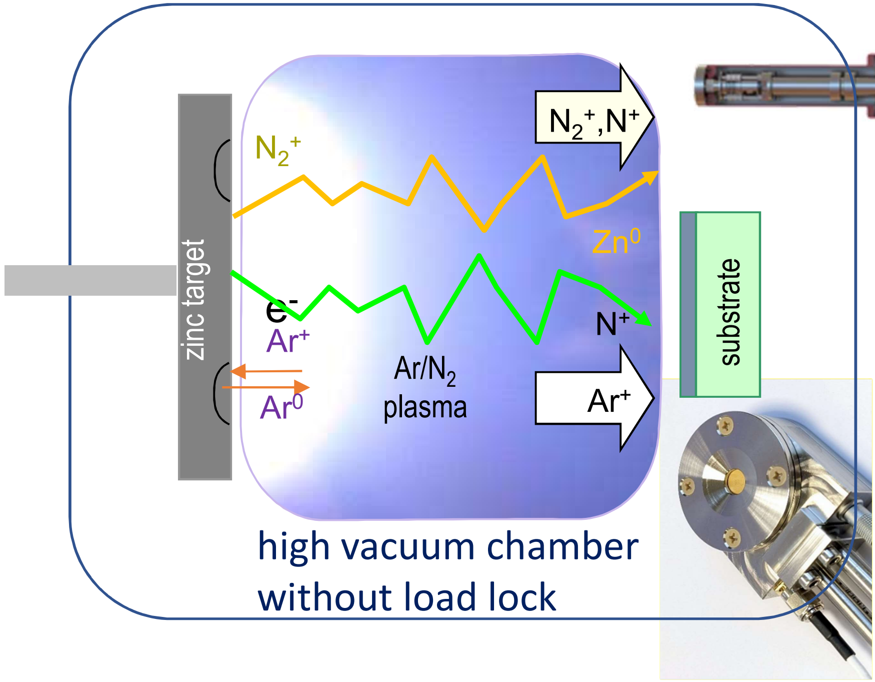
Reactive sputter deposition of Zn_3N_2: Plasma Process Characterization

- sputtering power: 50 - 150 W (2” target and 3”target) and 300 W - 750 W (6” target)
- vacuum base pressure: $5x10^{-7}$ mbar
- argon/nitrogen gas ratio: 5% to 100%
- total gas pressure: 0.5 Pa to 1.5 Pa
- substrates: borosilicate glass and Si/SiO_2
- heater temperature: up to 600 ºC

plasma characterisation (EQP):
mass and energy analyser



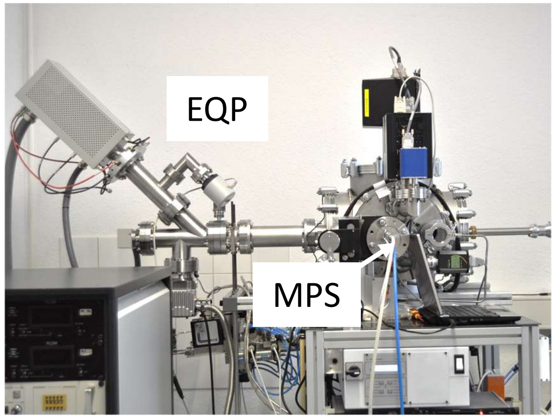
plasma excitation:
dc
rf 13.56 MHz
rf 27.12 MHz
(pulsed 10 kHZ)

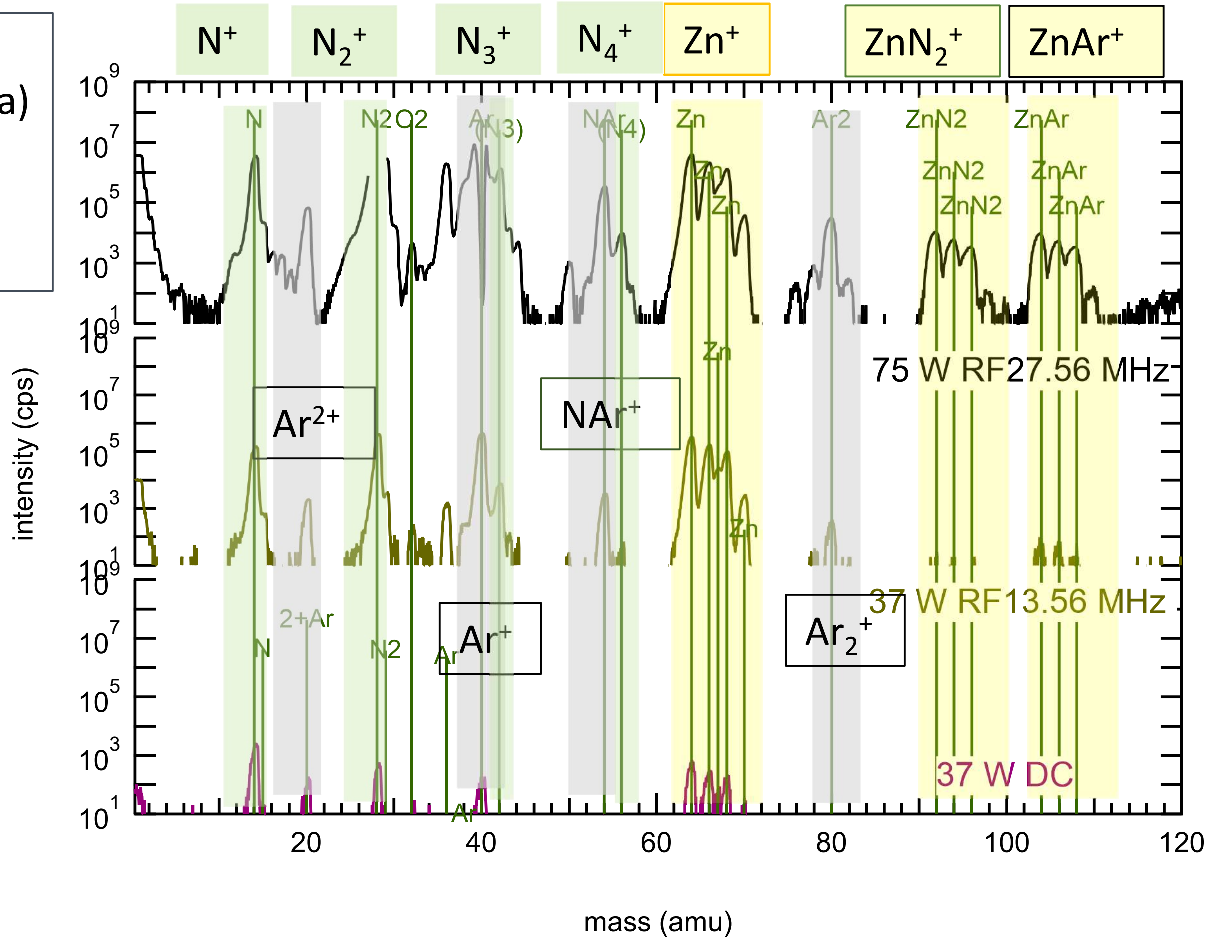


plasma sensor (MPS):
measuring of the
energy flux and the
deposition rate

Reactive sputter deposition of Zn_3N_2: Plasma Process Characterization

plasma excitation:
p=0.35 Pa, 0.5 N_2/Ar gas ratio (*1.5Pa)
dc (ENI) P = 37 W
rf 13.56 MHz (Dressler) P = 37 W
rf 27.12 MHz (COMET) P = 75 W





The plasma species were identified using the mass analyzer (EQP) during sputtering in a 0.5 N2/Ar gas ratio. The intensity of atomic nitrogen (N+) and molecular nitrogen species (N_2^+, N_3^+, N_4^+,) increased with rf plasma excitation.

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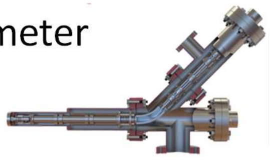
Reactive sputter deposition of Zn_3N_2: Plasma Process Characterization

EQP-measurement: process parameter
p=0.35 Pa, 50% N_2/Ar gas ratio
target-to-sensor distance 220 mm



Increasing the plasma excitation frequency:

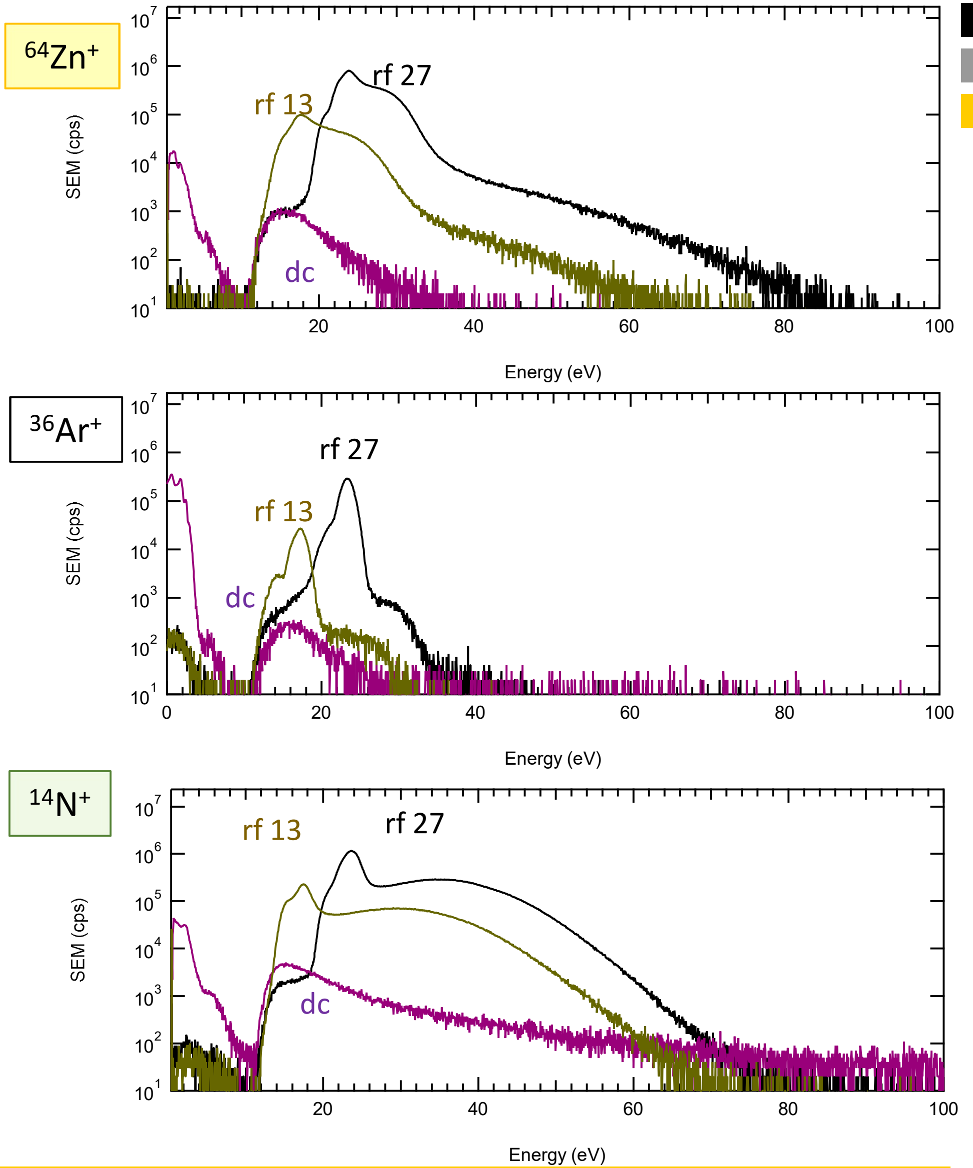
- high ion energies in the rf plasma
- the reactivity of plasma increases with the energy of nitrogen ions ($^{14}N^+$)

MPS-measurement: process parameter
p=1. 5 Pa, 50% N_2/Ar gas ratio
target-to-sensor distance 50 mm

Increasing the Plasma Excitation Frequency:

- deposition rate decreases (MPS)
- total energy flux increases (MPS)

Plasma Excitation	P (W)	V_{dis} (V)	E (MPS) (mW/cm²)	Rate (MPS) (nm/Min)
DC	37	-341	15.0	57.0
RF13.56 MHz	37	-190	14.5	30.0
RF27.27 MHz	75	-103	28.3	32.5



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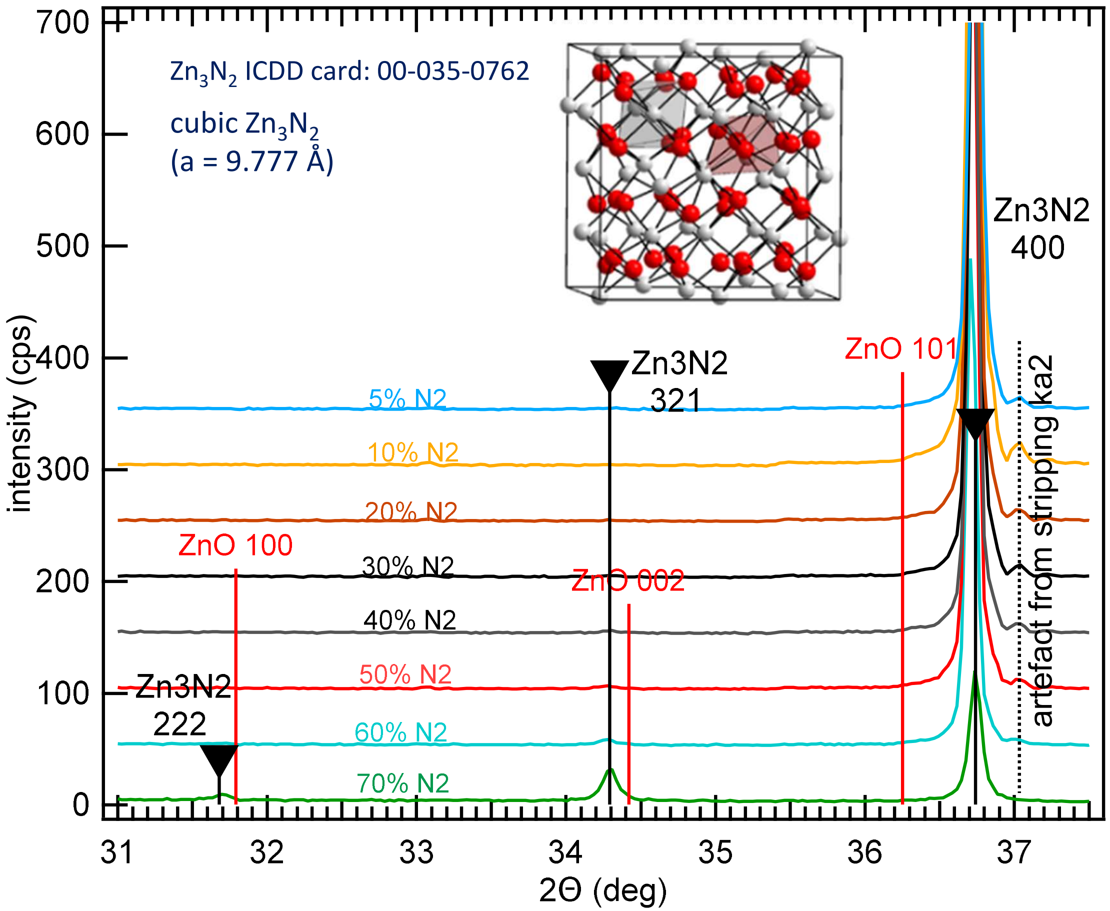
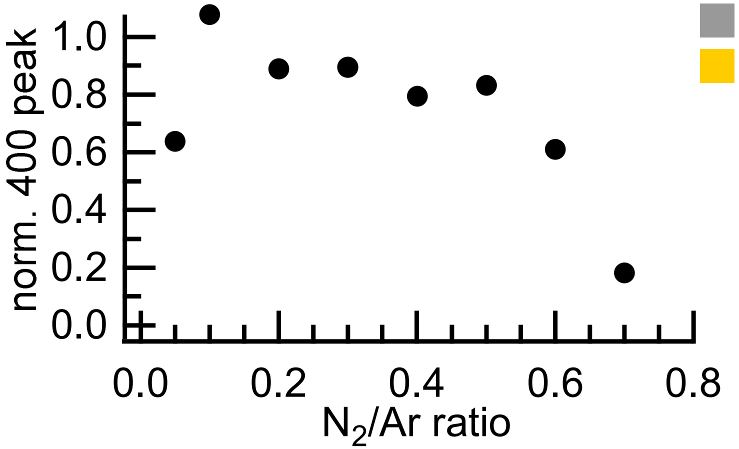
Reactive sputter deposition of Zn_3N_2 films: Variation of the N_2/Ar gas ratio





Process parameters:

300 W Rf-27.12 MHz (pulsed 10kHz)
zinc target (200 mm)
p= 1.5 Pa, N_2/Ar gas ratio (0.05 to 0.7)
unheated glass and Si/SiO_2

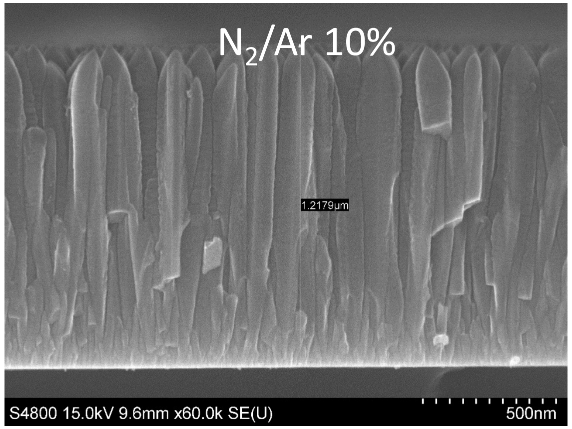
X-ray diffraction analysis:

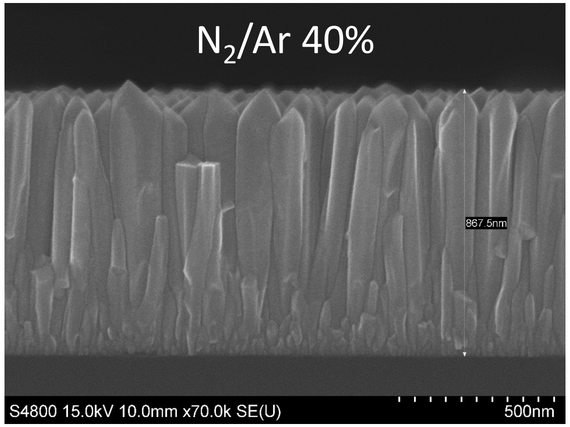
- At N_2/Ar gas ratios less than 0.6, the Zn_3N_2 films grow with the 400 orientation of the crystallites
- At higher N_2-to-Ar gas ratios, the Zn_3N_2 films grow polycrystalline with small crystallites.

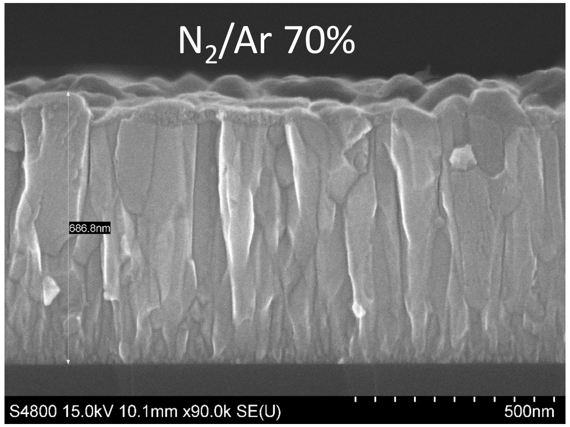
Reactive sputter deposition of Zn_3N_2 films: Variation of the N_2/Ar ratio

SEM analysis:

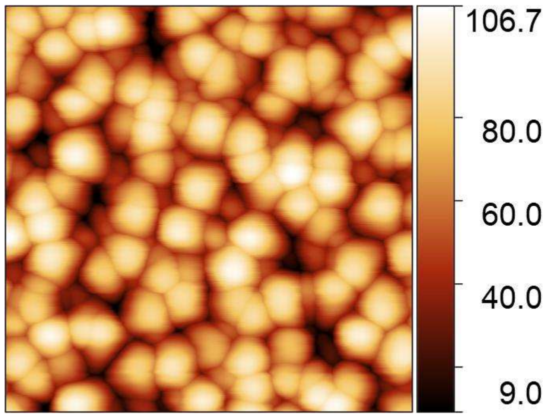
- columnar crystallites at N_2/Ar gas ratio < 0.6
- compact film growth at N_2/Ar gas ratio = 0.7, **but** surface oxidation after a few days (ZnO formation)



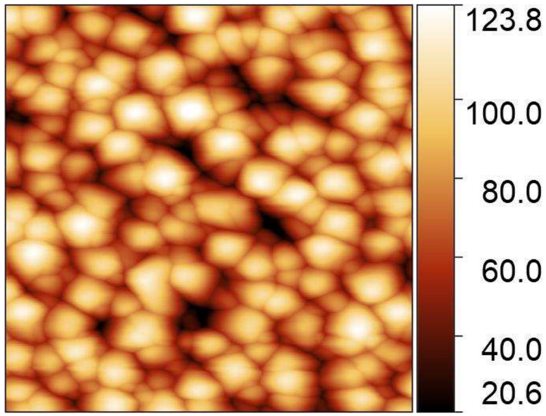




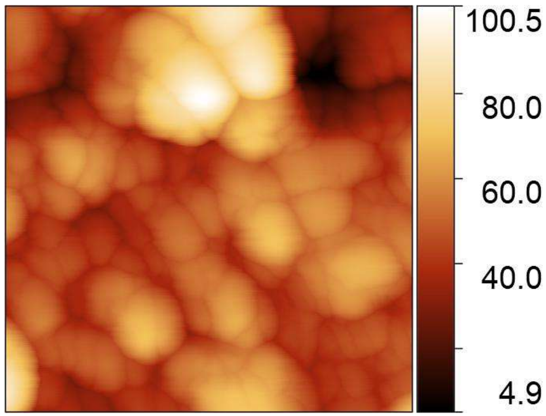
AFM analysis: 1x1 µm²



rms= 20.02 nm

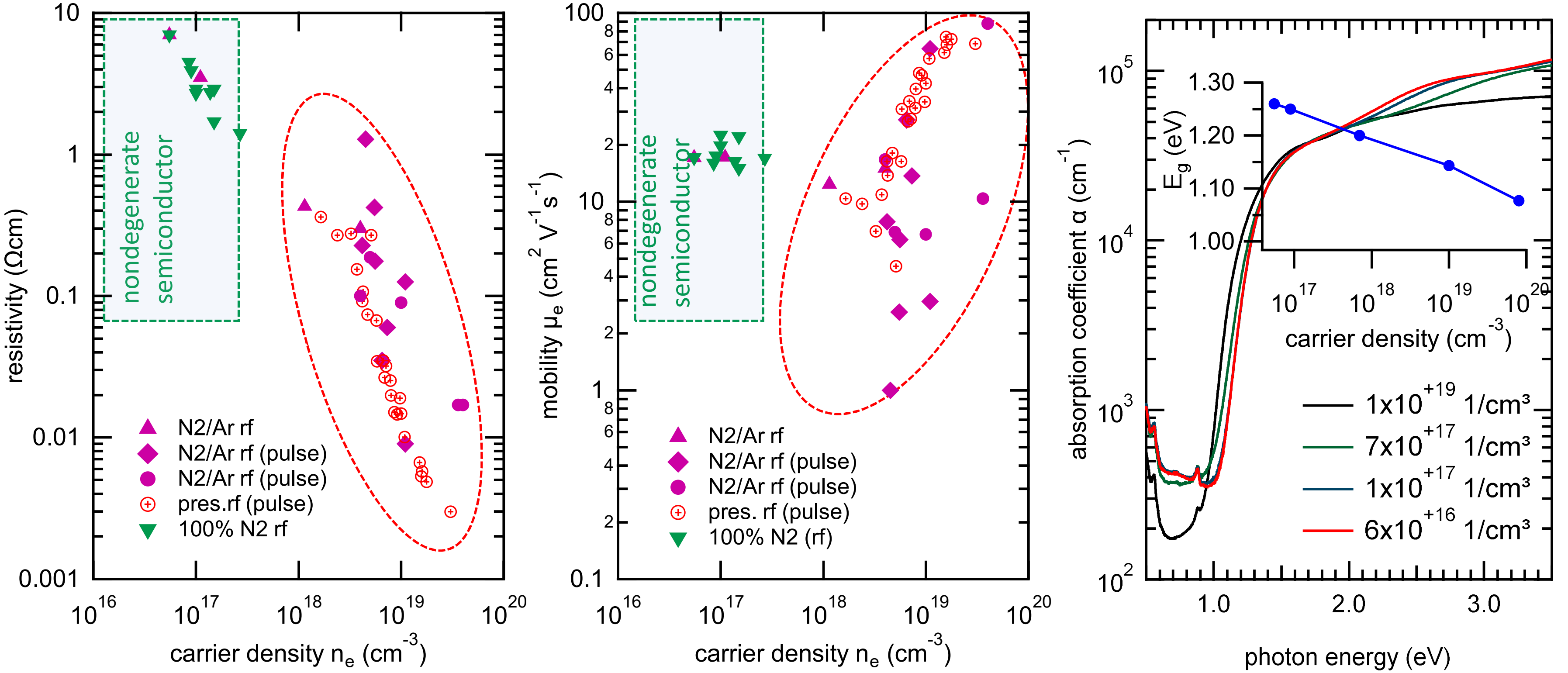


rms= 19.51 nm



rms= 14.72 nm

Zn_3N_2-Film Sputter Deposition: electrical and optical properties



- rf-sputter deposition in N_2/Argon gas mixtures results in high carrier densities $n_e > 10^{18}$ cm^{-3}
- rf-sputtering in N2 gas reduces carrier density in nanocrystalline Zn_3N_2-films to below 10^{17} cm^{-3}
- Semiconducting Zn_3N_2-films have a band gap of $E_g \approx 1.25$ eV

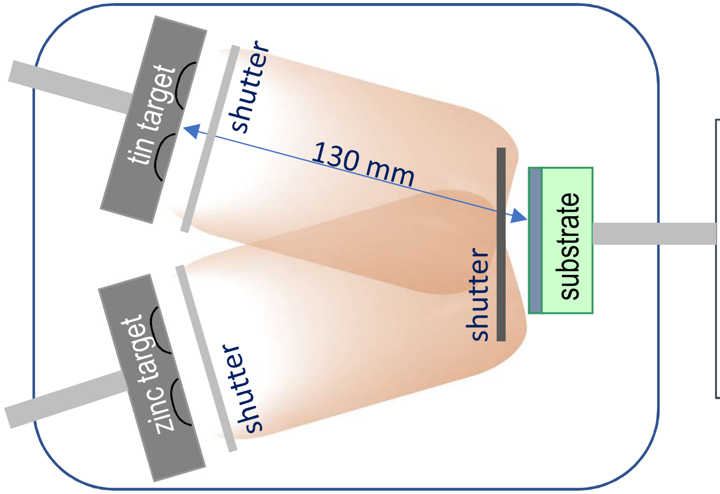
nondegenerate Zn_3N_3 $n_e < 2 \times 10^{17}$ cm^{-3}	Yong Wang, Takeo Ohsawa, Yu Kumagai, Kou Harada, Fumiyasu Oba, and Naoki Ohashi , "Achieving nondegenerate Zn_3N_2 thin films by near room temperature sputtering deposition", Appl. Phys. Lett. 115, 092104 (2019)

Reactive Co-sputter deposition of $ZnSnN_2$ films from Zn-target and Sn-target

- vacuum base pressure: 2 x 10^{-7} mbar
- argon/nitrogen gas mixture: 0.05% to 100%
- total gas pressure: 1.5 Pa
- substrates: borosilicate glass and Si/SiO_2
- heater temperature: up to 600 ^{o}C
- target-to-subtrate distance: 130 mm
- tin target 2“ (99.99%)
- zinc target 2“(99.99%)

tin target
dc power: 40 W to 60 W

zinc target
rf power (27.12 MHz)
100 W



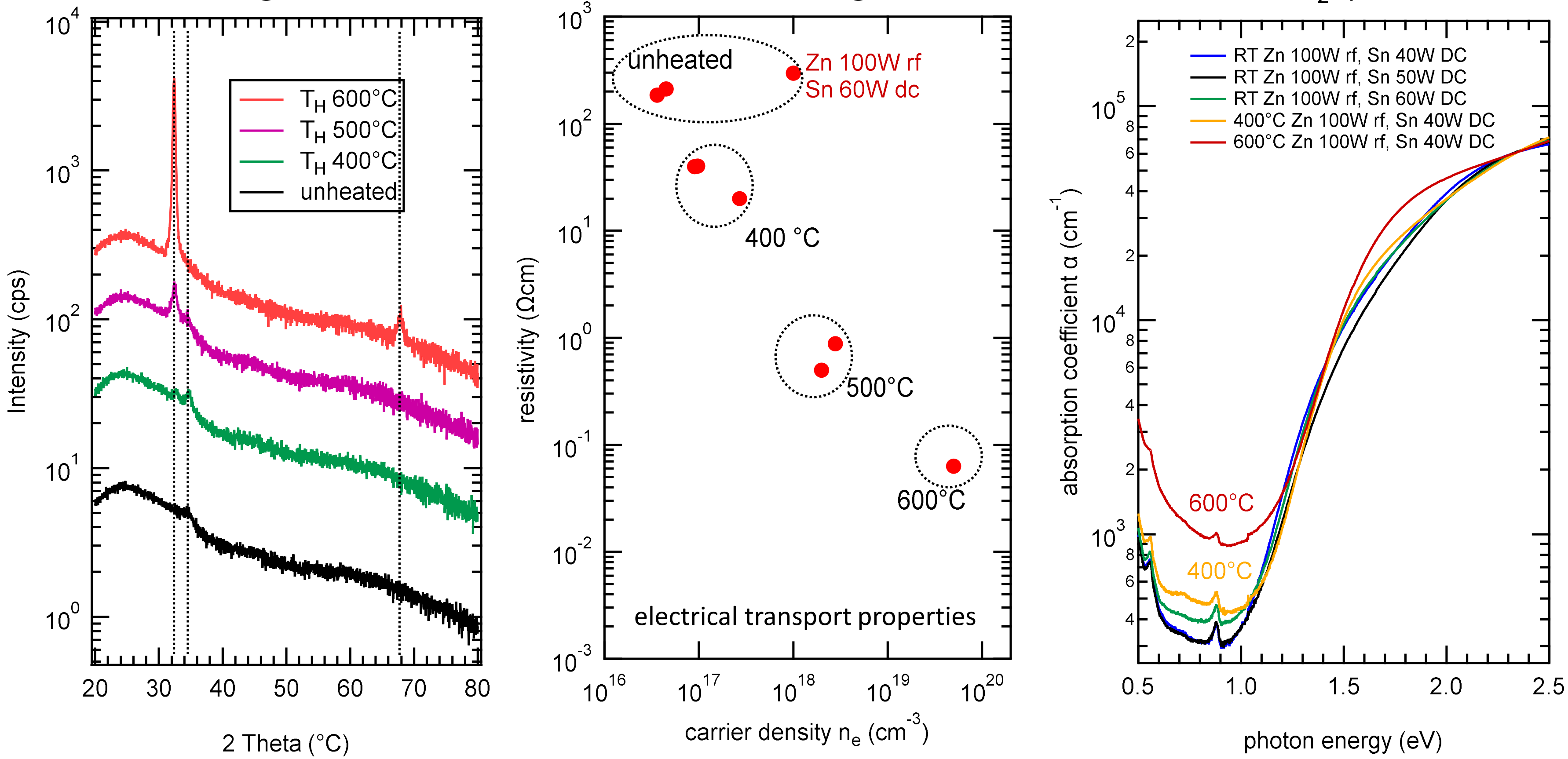
2” substrate holder:

- heating up to 600°C
- 14 rpm rotation speed
- floating substrate potential

high vacuum chamber without load lock p=2 x 10^{-7} mbar

Reactive Co-sputter deposition of $ZnSnN_2$ films from Zn-target and Sn-target

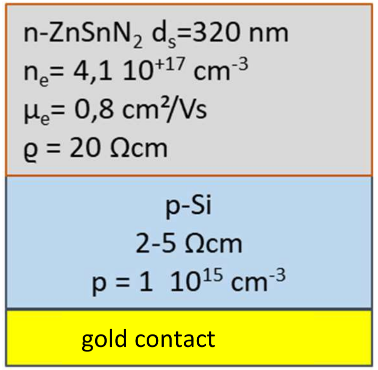
2” zinc target: 100 W Rf-27.12 MHz and 2” tin target: 40/50/60 W dc in 100% N_2, p=1.5 Pa

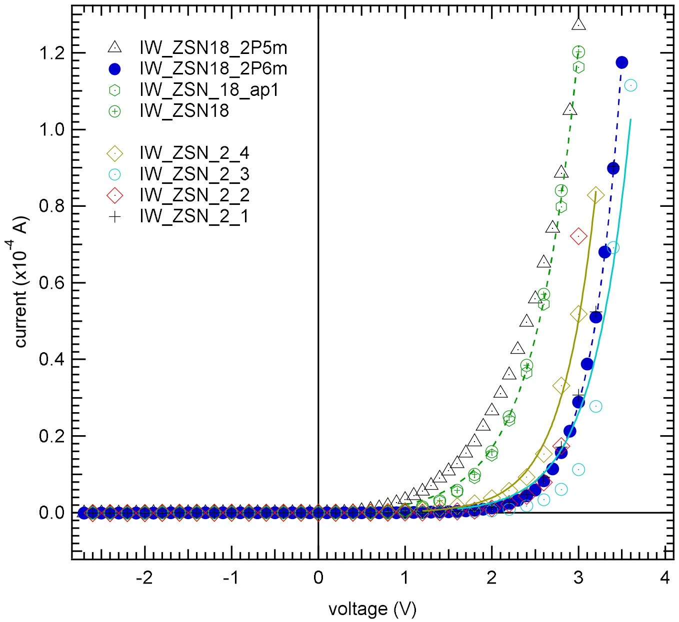


- without substrate heating, the $ZnSnN_2$ films grow nanocrystalline with low carrier densities $n_e \approx 5 \times 10^{16}$ cm^{-3} ($\mu_e \approx 1$ $cm^2 V^{-1}s^{-1}$)
- optical band gap energies $E_g \approx 1.5$ eV (suitable for photovoltaic applications)

Application possibilities for novel Nitride Semiconductors

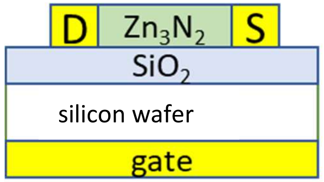
$ZnSnN_2$ heterojunction on p-silicon

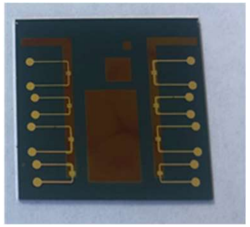


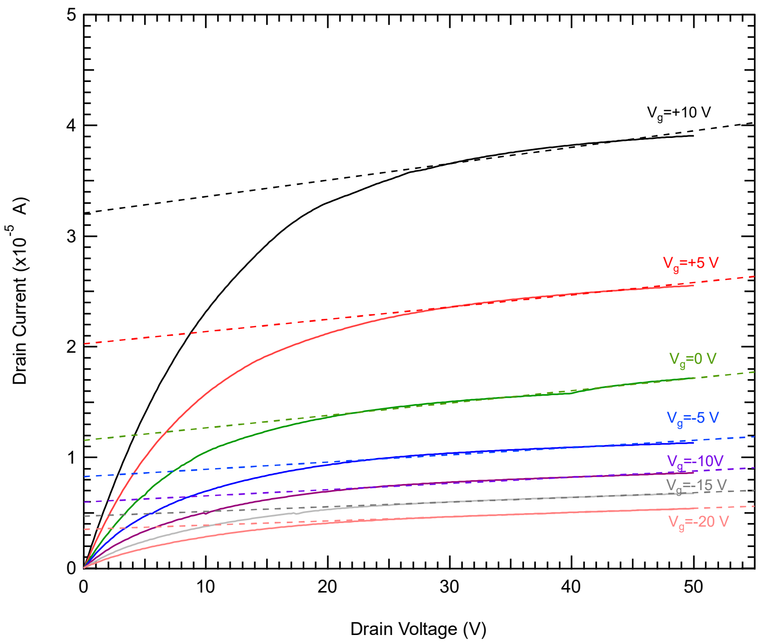


n-channel Field-Effect Transistor (FET)

- Zn_3N_2 (thickness 56 nm):
- n_e=6.8 x 10^{+17} cm^{-3}, μ_e= 20 cm²/Vs)







Summary

Reactive rf-Magnetron Sputter deposition processes can create a highly reactive nitrogen plasma (N^+) which is ideal for growing semiconducting Zn_3N_2 and $ZnSnN_2$ films. However, raising substrate temperatures results in unintentional oxygen doping.

Semiconducting Zn_3N_2 films:

- nanocrystalline Zn_3N_2 films ($n_e \approx 2 \times 10^{17}$ cm^{-3}) grow in nitrogen plasma without substrate heating
- Zn_3N_2 films with 400 crystallite orientation are more stable against oxidation

Semiconducting $ZnSnN_2$ films (Co-sputtering from a zinc-target and tin-target):

- nanocrystalline $ZnSnN_2$ films have low carrier densities $n_e \approx 5 \times 10^{16}$ cm^{-3}
- optical band gap energies $E_g \approx 1.5$ eV (suitable for photovoltaic applications)

Thank you for your attention!

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ReSpuN
Reaktive **Spu**tterabscheidung von **N**itridischen Halbleiterschichten
IGF-project Nr. 20963 BG

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Bundesministerium für Wirtschaft und Klimaschutz
aufgrund eines Beschlusses des Deutschen Bundestages

ZIM Zentrales Innovationsprogramm Mittelstand

EURONORM

AiF Forschungsnetzwerk Mittelstand

EFDS