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High-temperature optical constants, band-gap energies and in-situ growth monitoring of ZnO thin films

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Our messages

In-situ ellipsometry is a versatile technique for optical monitoring of PLD-grown ZnO thin films.

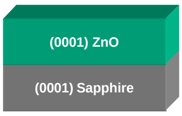
Sample temperature calibration versus heater power can be easily done.

We report the high-temperature band-gap energies and optical constants of ZnO.

The ZnO growth rate depends on deposition time, causing vertical gradients of optical constants and likely changes in the thin film microstructure. This gradient cannot be resolved anymore from a post-growth ex-situ ellipsometry experiment.

Goals: in-situ Ellipsometry control of novel flexible solar cells

In-situ monitoring and feed-back control of $CuInSe_2$ ($Cu(In,Ga)Se_2$) and ZnO (Zn(Cd,Mg)O) thin film growth

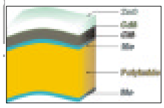


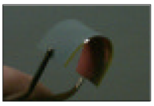
Here: ZnO thin films

- Attractive for developing short-wavelength optical devices:
  wide band gap (~3.37 eV) and high exciton binding energies
  band gap engineering: $Zn_{1-x}(Cd,Mg)_xO$ compound thin films
- Applications as transparent conducting oxide:
  front contacts for flexible solar cells

Future task: $CuInSe_2$/ZnO heterostructures

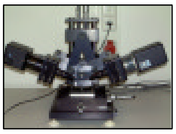
- CIGS absorber layers for high-efficient solar cells:
  New generation of thin film solar cell structures
  on flexible polymer sheets
  Band gap engineering: $Cu_{1-x}(In,Ga)_xSe_2$ compound thin films





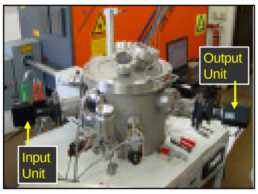
In-situ Ellipsometer setups

M-2000VI in-situ Ellipsometer (J.A.Woollam Co.)



- polarizer-sample-rotating-compensator-analyzer
- spectral range: 0.75-3.345 eV
- diode-array detector
- ex-situ mode possible
- typical measurement time: 0.5 … 2s

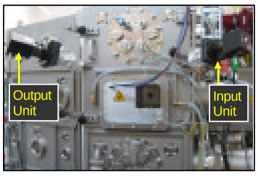
PLD chamber setup



Pulsed-Laser-Deposition

- Growth of wurtzite-type ZnO and $Zn_{1-x}(Cd,Mg)_xO$ compound films on a-, c-, and r- plane Al_2O_3
- KrF excimer laser ablation
- Optical ports at AOI of 70°

Roll-coater setup, Solarion GmbH, Leipzig



Ion-Beam-Deposition

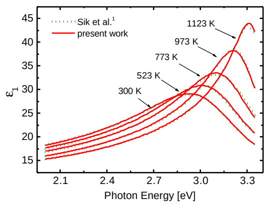
- Growth of $Cu_{1-x}(In,Ga)_xSe_2$-based solar-cells on flexible polymer sheets
- Optical access ports at AOI of 43° and 67°

PLD: temperature calibration

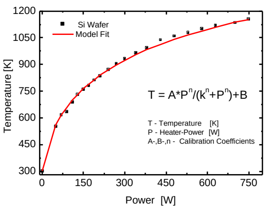
- SE-spectra of Si-wafer at different sample-heater power values
- Use of known temperature-dependent Si-optical constants[1]
- Calibration of the heater power to adjust the actual sample temperature

[1] J. Šik et al., J. Appl. Phys. **84**, 6291 (1998).

Si ε_1 at elevated temperatures



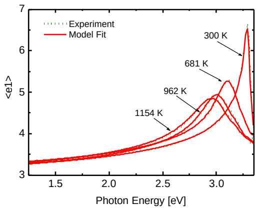
Sample temperature vs. heater power



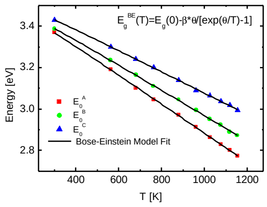
High-temperature ZnO band gap

- Temperature-dependent ex-situ SE spectra of a bulk (0001) ZnO from 300 K to 1154 K
- Strong red-shift and splitting of the $E_0^{A,B,C}$ band-gap energies with temperature:
  $dE_0^A/dT = -(7\pm1)\times10^{-4}$ eV/K
  $dE_0^B/dT = -(6\pm1)\times10^{-4}$ eV/K
  $dE_0^C/dT = -(5\pm1)\times10^{-4}$ eV/K
- Linear increase of the optical constants

ZnO $\langle\varepsilon_1\rangle$ at elevated temperatures



ZnO band-gap energies



PLD growth of (0001) ZnO thin film on (0001) Al_2O_3

Two-step-growth-process[2]

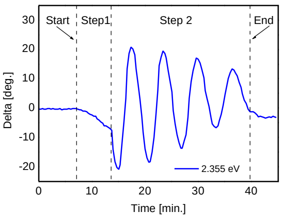
Growth Conditions

Step 1 → O_2-Pressure = 3*10^{-4} mbar
400 Laser pulses /1 Hz/600 mJ

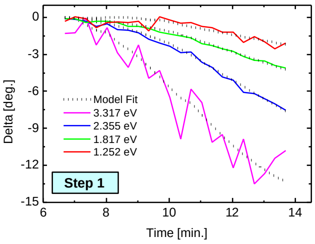
Step 2 → O_2- Pressure = 1*10^{-2} mbar
16000 Laser pulses /10 Hz/600 mJ

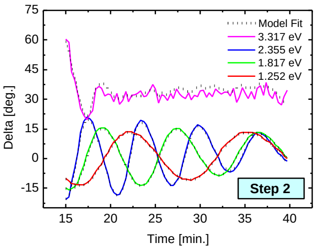
T=1053 K

[2] E. M. Kaidashev et al., Appl. Phys. Lett. **82**, 3901 (2003).

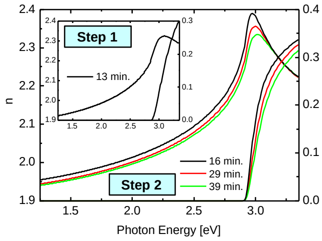


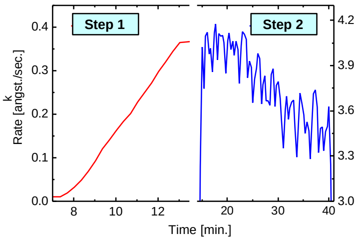
In-situ data analysis: Virtual-Interface-Approach[3]





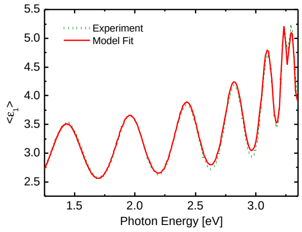
In-situ data analysis results





[3] D. E. Aspnes et al., Appl. Phys. Lett. **57**, 2707 (1990).

Ex-situ data analysis



In Summary

In-situ: Virtual-Interface-Approach
  Step 1. Nucleation-zone thickness: 15 nm
    Growth-rate increases
  Step 2. Growth-rate decreases
    Optical constants change
    Total film thickness: 630 nm
Linear-growth-rate analysis
  fails because the growth rates changes with time
Ex-situ-analysis
    Nucleation zone is not detectable
    Total film thickness: 634 nm
    Surface roughness: 4.7 nm
    Film-thickness-non-uniformity: 7.3%

Conclusions

Ex-situ effective thickness in good agreement with actual thickness, but gradient due to growth-rate-change and nucleation zone cannot be resolved

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