Defect studies of thin ZnO films prepared by pulsed laser deposition

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Introduction

Preparation of high-quality ZnO films is of great interest for efficient excitonic UV lasers exploiting externally pumped lasing observed in epitaxial ZnO films at room temperature [1]. Furthermore, ZnO films have favorable properties for application in flat panel displays and optical coatings for solar cells [2]. Several techniques for production of ZnO films were developed, e.g. dip coating, sol-gel, magnetron sputtering and pulsed laser deposition (PLD) [3]. In this work we will present studies of defects in thin ZnO films prepared by PLD.

Experimental details

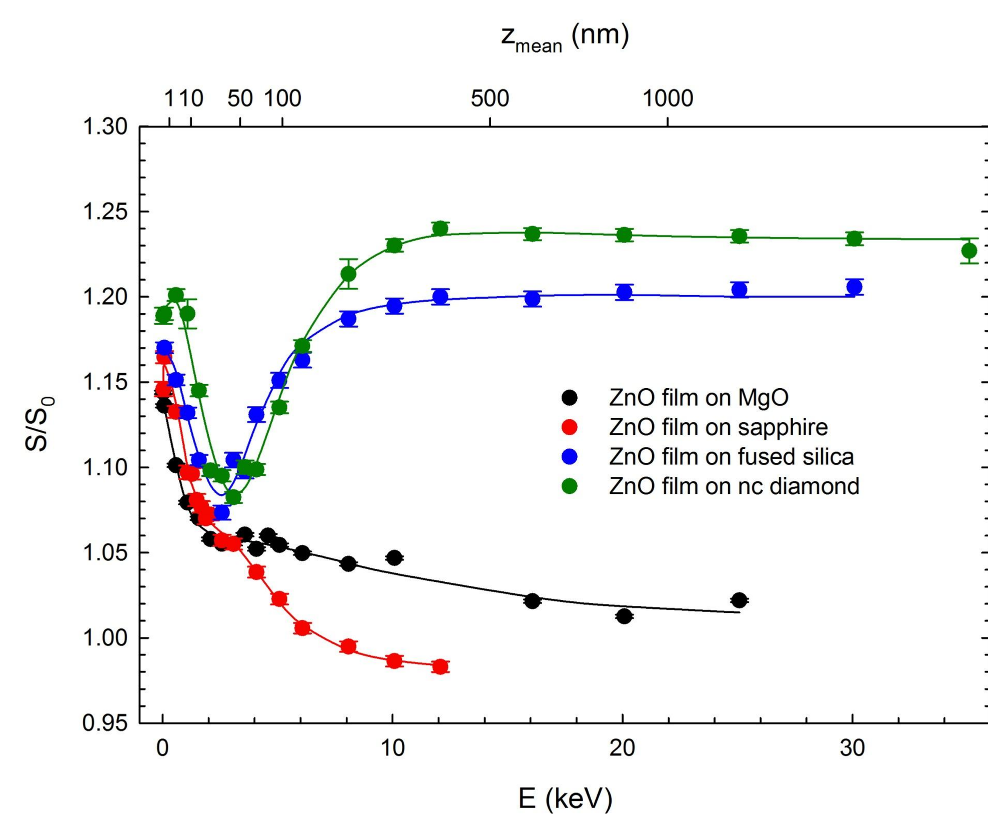
SPIS studies were carried out using slow positron beam SPONSOR:

- Magnetically guided beam
- Positron energy range from 30 eV to 36 keV
- High-purity germanium detector with resolution of 1.09(1) keV at 511 keV

Doppler broadening measurements were evaluated using the line shape *S* parameter calculated from energy interval 510.07 to 511.93 keV. *S* parameter for the reference ZnO bulk single crystal is S_0 = 0.5068(5). Measured data were analyzed by VEPFIT software package [5].

Results (1)

XRD investigations revealed that ZnO films deposited on all substrates exhibit wurtzite structure. ZnO films deposited on single crystal substrates (Mg0, sapphire) exhibit local epitaxy while films deposited on amorphous fused silica or nanocrystalline diamond show (0 0 0 1) fiber texture with random lateral orientation of crystallites in the plane of substrate. At the lowest energy E = 0.03 keV almost all positrons annihilate on the surface of the ZnO film. With increasing energy positrons penetrate into the ZnO film and subsequently into the substrate. Largest fraction of positron annihilates in ZnO film at $E \approx 3$ keV.



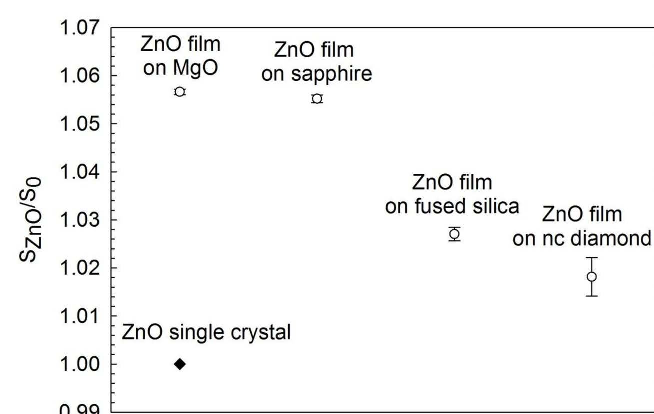
S(E) curves of ZnO films deposited on various substrates

At energies E > 20 keV virtually all positrons annihilate in the bulk of the substrate and measured *S* parameters approach bulk values for corresponding substrates. Fused silica and nanocrystalline diamond substrates exhibit significantly higher *S* parameters than MgO or sapphire due to lower electron density in inter-atomic regions.

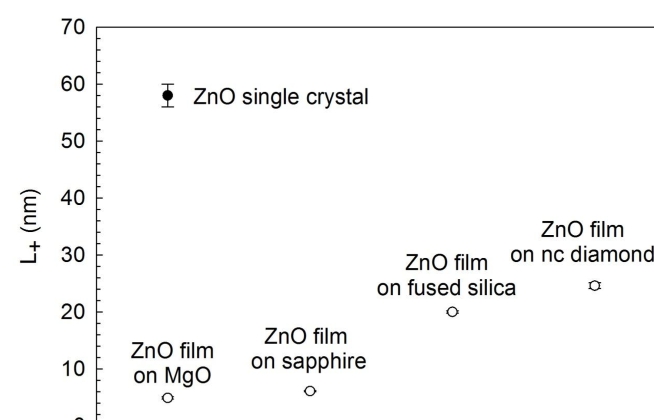
Measured data were analyzed by VEPFIT software package [5] using two-layer model system. Values for the S parameter and mean positron diffusion length L_+ of the ZnO model layer were obtained by fitting of experimental data. Trapping rate *K* was calculated from measured diffusion length L_+ of ZnO films using the expression:

$$K = \frac{1}{\tau_B}\left(\frac{L_{+,B}^2}{L_+^2} - 1\right) \qquad (1)$$

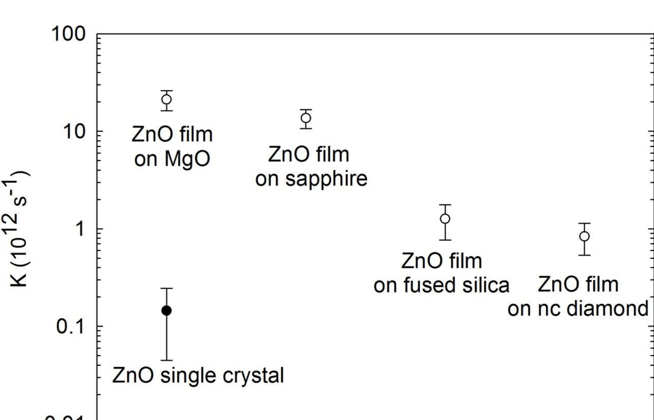
The diffusion length $L_{+,B}$ = 280 nm and the bulk positron lifetime τ_B = 154 ps for a defect-free ZnO crystal were obtained by theoretical calculations. All ZnO films exhibit higher *S* parameters and shorter diffusion lengths than those for the bulk ZnO single crystal. Therefore, all ZnO films contain higher concentration of defects than the reference ZnO single crystal. They likely contain point defects similar to the reference ZnO single crystal. However, additional type of defects may be present in polycrystalline thin films: (i) misfit dislocations compensating the lattice mismatch between the film and the substrate and (ii) open-volume defects at grain boundaries or crystallite interfaces. Trapping rate *K* which is directly proportional to the concentration of defects is substantially higher in ZnO films deposited on single crystal MgO and sapphire substrates than on amorphous fused silica and nanocrystalline diamond.



S parameter for the ZnO samples



Positron diffusion length for ZnO samples



Positron trapping rate calculated by Eq (1)

Conclusions

ZnO films deposited on single crystal MgO and sapphire substrates exhibit significantly higher concentration of defects than films deposited on amorphous fused silica and nanocrystalline diamond substrates due to presence of misfit dislocations at film-substrate interface.

Influence of deposition temperature on properties of ZnO films deposited on nanocrystalline diamond were investigated. Lowest concentration of defects was found in the film deposited at 450°C.

Samples

PLD process parameters:

- 266 nm frequency-quadrupled Nd:YAG laser
- 90 mJ pulses of 6 ns duration
- Laser light fluence of 2.8 J.cm^{-2}
- High-purity ceramic ZnO target at distance of 55 mm from the substrate
- Repetition rate 10 Hz, 5200 shots
- Atmosphere of 5N-pure oxygen at pressure of 10 Pa and 40 sccm flow rate
- Final film thickness 40-80 nm

Four different substrates were used:

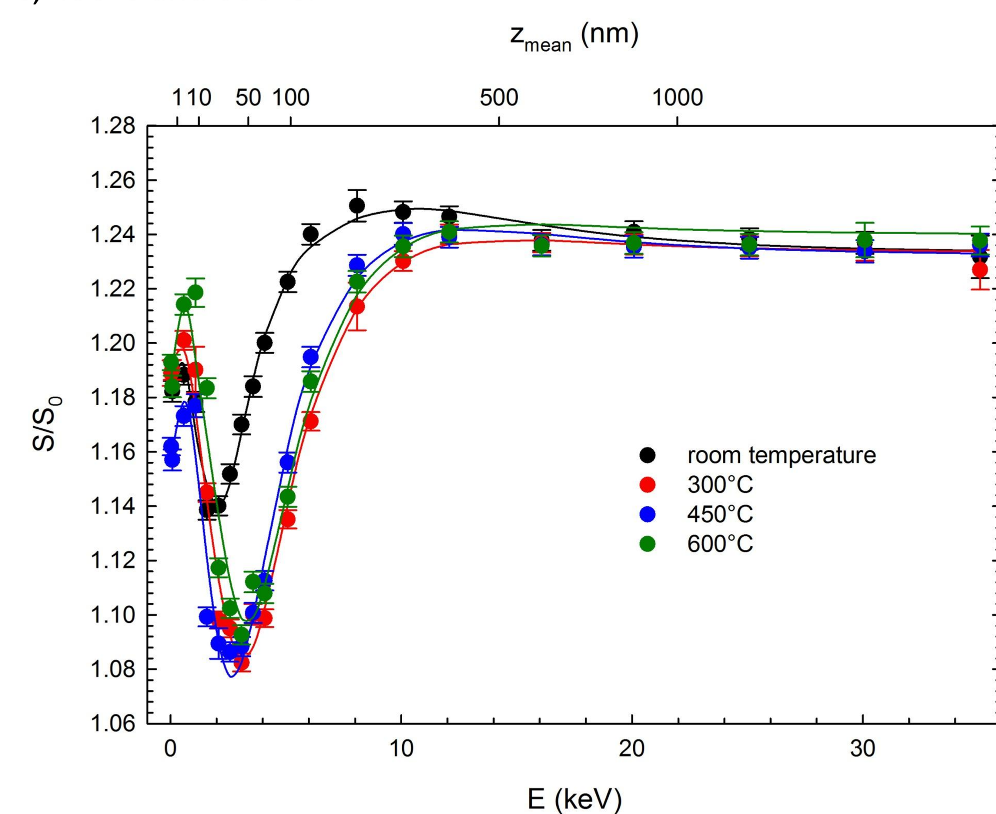
- sapphire (0 0 0 1)
- MgO (1 0 0)
- fused silica
- nanocrystalline synthetic diamond

ZnO thin films were deposited on baked out (950°C/5 min) sapphire (0 0 0 1), MgO (1 0 0) and fused silica at 300°C and subsequently annealed in situ at 750°C in 10 Pa oxygen temperature. ZnO films on nanocrystalline diamond were deposited at room temperature, 300°C, 450°C and 600°C. No baking out of substrate or annealing of ZnO films were performed in this case.

Bulk ZnO (0 0 0 1) single crystal, supplied by MaTecK GmbH, with O-terminated surface grown by hydrothermal method was used as reference material for SPIS measurements.

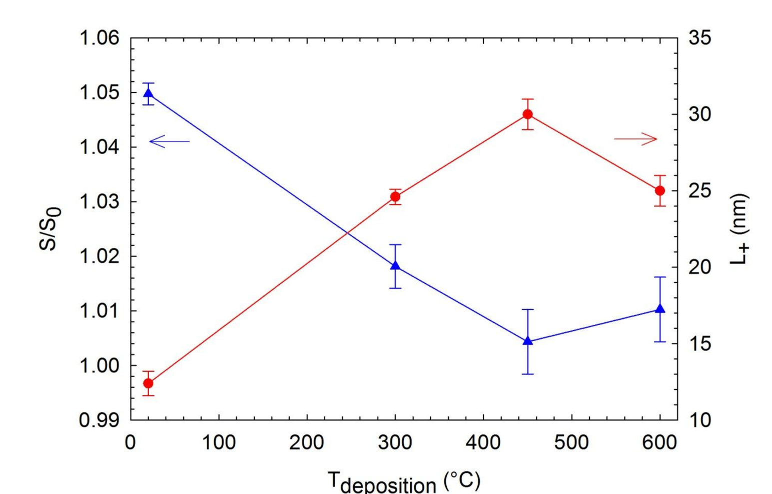
Results (2)

Influence of deposition temperature on ZnO film properties was studied on films deposited on nanocrystalline diamond substrate. Films at four different temperatures were deposited: room temperature, 300°C, 450°C and 600°C.



S(E) curves of ZnO films deposited on nanocrystalline diamond at various temperatures

There is a striking difference between *S(E)* curve of the film deposited at room temperature and those of the films deposited at elevated temperatures. Measured data were analyzed by VEPFIT software package [5] using two-layer model system to obtain values of *S* parameter and diffusion length L_+ of ZnO films. ZnO film deposited at room temperature exhibits the lowest positron diffusion length and therefore contains the highest concentration of defects. The highest positron diffusion length and the lowest value of S parameter were observed in film deposited 450°C.



Fitted values of *S* parameter and diffusion length

Discussion

XRD investigations suggest that ZnO films grown on single crystal substrates (MgO, sapphire) exhibiting local epitaxy are of higher quality [4]. Surprisingly, SPIS measurements revealed that these films have significantly higher concentration of defects than ZnO films deposited on amorphous fused silica and nanocrystalline diamond. Although individual crystallites are better defined in films grown on MgO and sapphire, lattice mismatch between substrates and ZnO film inevitably results in presence of misfit dislocations. Hence, SPIS measurements detect higher concentration of defects in film deposited on MgO and sapphire due to presence of misfit dislocations.

Studies of ZnO films deposited on nanocrystalline diamond at various temperatures revealed that lowest concentration of defects is in the film deposited at 450°C. One could expect that deposition at elevated temperatures increases chance of atoms to reach proper position in crystal lattice. On the other hand, crystallite growth occurs at high temperatures and therefore concentration of misfit defects at film-substrate interface increases. Minimum in temperature dependence of concentration of defects observed at 450°C is created as result of these antagonistic effects.

References

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This work was supported by the Czech Science Foundation (project P108/11/0958) and by the grant SVV-2013-267303.