Defect studies of ZnO films prepared by pulsed laser deposition on various substrates

O. Melikhova[1], J. Čížek[1], I. Procházka[1], R. Kužel[1], M. Novotný[2], J. Bulíř[2], J. Lančok[2], W. Anwand[3], G. Brauer[3], J. Connolly[4], E. McCarthy[4], S. Krishnamurthy[4], J.-P. Mosnier[4]

Introduction

Externally-pumped lasing observed in epitaxial ZnO films stimulated a great interest in the preparation of high-quality ZnO films [1]. Pulsed laser deposition (PLD) enables the production of high-quality ZnO films at lower temperatures than other methods, due to high energy of the ablated particles in the laser-produced plasma plume [2]. The quality of films deposited by PLD is influenced by laser fluence, substrate temperature, the atmosphere in the deposition chamber, and also by the type of substrate. In the present work, we aim to clarify the role played by the substrate. To this end we have carried out structural investigations of very thin ZnO films, deposited by PLD under identical conditions, on MgO (100), sapphire (0001) and fused silica (FS) substrates, respectively. We selected these substrates because of their different crystallographic structure; MgO crystallizes in a rocksalt structure in contrast to the hexagonal lattice of sapphire and the amorphous phase of FS.

Experimental

• ZnO films were deposited by PLD using a frequency-quadrupled Nd:YAG laser providing 90 mJ of 266 nm laser light in 6 ns pulses at the repetition rate of 10 Hz, ablating an ultra-high purity ZnO ceramic target with a fluence on target of 2.8 Jcm^{-2}. Polished sapphire (0001), MgO (100) and FS substrates baked out in vacuum at 950ºC were used for depositions. The ZnO films were grown in an oxygen atmosphere at a pressure of 10 Pa, with a substrate temperature of Ts = 300ºC as a result of 5,200 laser shots. A hydrothermally-grown bulk ZnO (0001) single crystal with an O-terminated surface supplied by MaTecK GmbH was used as a reference material in SPIS investigations.

•XRD studies were performed with an X'Pert MRD diffractometer using Cu-K$_\alpha$ radiation. SPIS investigations were performed using a slow positron beam, SPONSOR [3], with the energy of incident positrons adjustable in the range from 0.03 to 36 keV. Doppler broadening (DB) of the annihilation photopeak was measured by a HPGe detector with an energy resolution of (1.09 ± 0.01) keV at 511 keV. Evaluation of DB was performed using the line shape parameters S and W. The central energy region for the calculation of S was chosen as $|E - m_0c^2| < 0.93$ keV and all the S parameters are normalized to the bulk value S_0 = 0.5068(5) determined in the reference ZnO crystal. The energy ranges 508.21-509.00 keV and 513.00-513.79 keV were used for calculation of the W parameter. All the W parameters were normalized to the reference value of the bulk ZnO crystal W_0 = 0.1039(7).

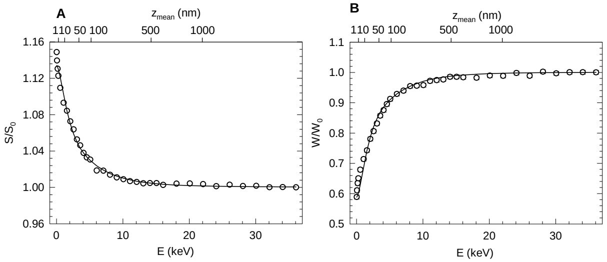

Figure 1 *The dependence of the S (A) and W (B) parameters on the positron energy E for the reference ZnO (0001) single crystal. The mean positron penetration depth z_{mean} is shown on the upper horizontal axis. The solid line shows the model curve calculated by VEPFIT.*

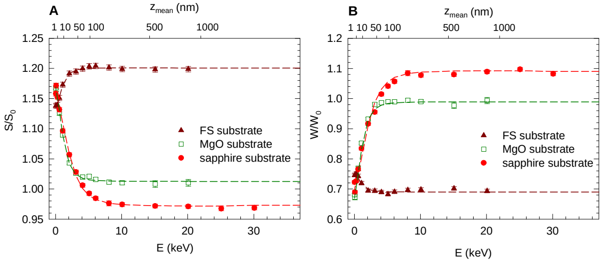

Figure 2 *Dependence of the S (A) and W (B) parameters on positron energy for bare substrates. The mean positron penetration depth z_{mean} is shown on the upper horizontal axis. The dashed lines show the model curves calculated by VEPFIT for bare substrates.*

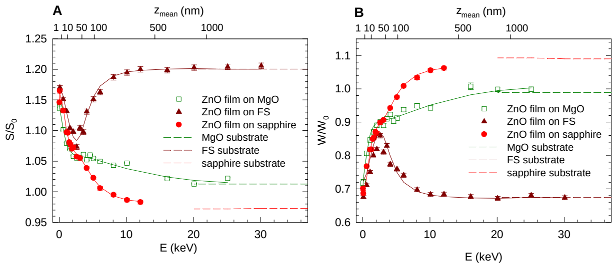

Figure 3 *Dependence of the S (A) and W (B) parameters on positron energy for ZnO films. The mean positron penetration depth z_{mean} is shown on the upper horizontal axis. The dashed and solid lines show the model curves calculated by VEPFIT for bare substrates and ZnO films, respectively.*

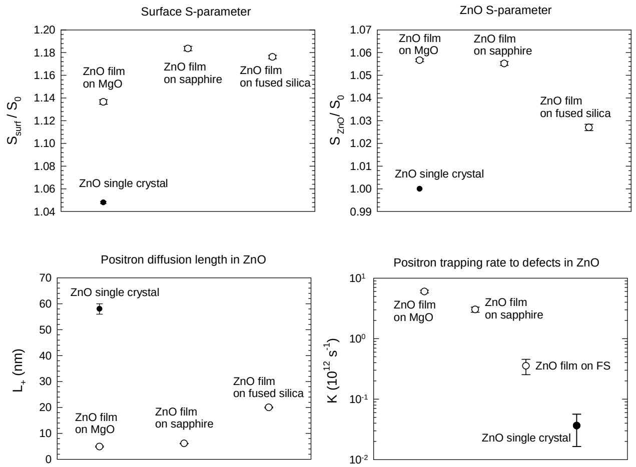

Figure 4 *Positron parameters obtained from fitting of S(E) curves: The surface S parameter, the S parameter for ZnO layer, the estimated positron diffusion length and positron trapping rate to defects in ZnO films and the reference crystal.*

Table 1 *Properties of ZnO films deposited on MgO (100), sapphire (0001) and FS substrates: the film thickness calculated from measurement of optical reflectance and transmittance (t_{OPT}), determined from XRD reflectivity curves (t_{XRD}) and estimated by SPIS (t_{SPIS}); the mean crystallite size estimated by SEM (d_{SEM}); the lattice parameters a, c determined by XRD; the stress σ determined by XRD; the S parameter for the ZnO layer S_{ZnO}; the mean positron diffusion length L_+ and the surface value of the S parameter S_{surf}. Errors expressed in the order of the last significant digit are shown in parenthesis.*

Substrate	MgO (100)	Sapphire (0001)	Fused silica
t_{OPT} (nm)	81(3)	41(3)	75(3)
t_{XRD} (nm)	76(2)	48(2)	75(2)
t_{SPIS} (nm)	80(2)	45(3)	76(1)
d_{SEM} (nm)	30-100	25-70	20-50
a (nm)	0.3249(1)	0.3258(1)	0.32569(7)
c (nm)	0.52087(3)	0.5207(7)	0.5195(2)
σ (GPa)	14(2)	≈ 0	0.9(1)
S_{ZnO}	1.0566(6)	1.0552(8)	1.027(1)
L_+ (nm)	4.9(2)	6.9(1)	21.0(4)
S_{surf}	1.137(8)	1.184(8)	1.176(8)

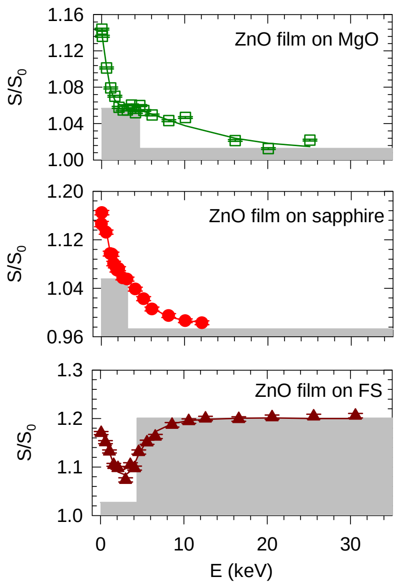

Figure 5 *Layered model of ZnO films on various substrates. Each layer is represented by a box with thickness corresponding to the layer depth and height which equals to the S parameter for the layer. The experimental S(E) curves are plotted in the figure for comparison.*

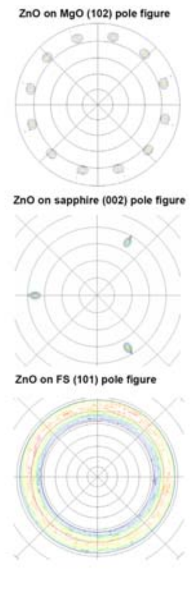

Figure 6 *Results of texture measurements: (1) 102 pole figure measured on ZnO film deposited on MgO substrate (axis divided by 45°- φ, 18° - ψ); (2) part of the pole figure for 002 reflection measured on ZnO film deposited on sapphire substrate (axis divided by 45° - φ, 10° - ψ); (3) Part of 101 pole figure measured on ZnO film deposited on FS substrate (axis divided by 45° - φ, 10° - ψ).*

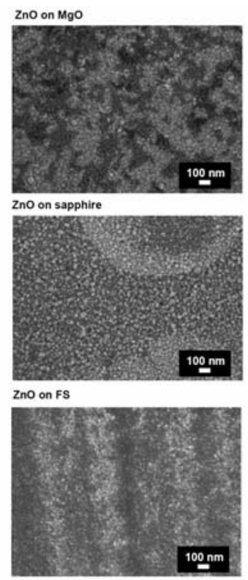

Figure 7 *SEM micrographs of ZnO film deposited on MgO (100) substrates, sapphire (0001) and FS.*

Conclusions

- Very thin ZnO films deposited by PLD on various substrates were characterized.
- All films exhibit higher concentrations of open volume defects than a bulk ZnO single crystal.
- The ZnO films deposited on the single crystalline substrates (MgO, sapphire) exhibit a higher concentration of defects than film deposited on an amorphous FS substrate. This is most probably due to a higher density of misfit dislocations, which compensate for the lattice mismatch between the film and the substrate.

Acknowledgement

This work was supported by the Czech Science agency (project P108/11/0958), by the Ministry of Education, Youths and Sports of the Czech Republic (project MEB101102) and by the Deutscher Akademischer Austauschdienst DAAD (project 50755628).

References

[1] Bagnall B M, Chen Y F, Zhu Z, Yao T, Koyama S, Shen M Y and Goto T 1997 Appl. Phys. Lett. 70 2230

[2] Hu W S, Liu Z G, Sun J, Zhu S N, Xu Q Q, Feng D and Ji Z M 1997 J. Phys. Chem. Sol. 58 853

[3] Anwand W, Kissener H R and Brauer G 1995 Acta Physica Polonica A 88 7

Affiliations

[1] Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2, CZ-180 00 Prague 8, Czech Republic

[2] Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague, Czech Republic

[3] Institut für Strahlenphysik, Helmholtz-Zentrum Dresden-Rossendorf, Postfach 510119, D-01314, Dresden, Germany

[4] National Centre for Plasma Science and Technology, School of Physical Sciences, Glasnevin, Dublin 9, Ireland