

Defect studies of thin ZnO films prepared by pulsed laser deposition

M Vlček¹, J Čížek¹, I Procházka¹, M Novotný², J Bulíř², J Lančok²,
W Anwand³, G Brauer³, J-P Mosnier⁴

¹Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2, 180 00 Praha 8, Czech Republic

²Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Praha, Czech Republic

³Institut für Strahlenphysik, Forschungszentrum Dresden-Rossendorf, 01314 Dresden, Germany

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

E-mail: vlcek@mbox.troja.mff.cuni.cz

Abstract. Thin ZnO films were grown by pulsed laser deposition on four different substrates: sapphire (0 0 0 1), MgO (1 0 0), fused silica and nanocrystalline synthetic diamond. Defect studies by slow positron implantation spectroscopy (SPIS) revealed significantly higher concentration of defects in the studied films when compared to a bulk ZnO single crystal. The concentration of defects in the films deposited on single crystal sapphire and MgO substrates is higher than in the films deposited on amorphous fused silica substrate and nanocrystalline synthetic diamond. Furthermore, the effect of deposition temperature on film quality was investigated in ZnO films deposited on synthetic diamond substrates. Defect studies performed by SPIS revealed that the concentration of defects firstly decreases with increasing deposition temperature, but at too high deposition temperatures it increases again. The lowest concentration of defects was found in the film deposited at 450°C.

1. 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 have been developed so far. In this work we employed pulsed laser deposition (PLD) [3] which enables the production of high-quality ZnO films at lower temperatures than other methods.

2. Experimental details

Samples were prepared in stainless-steel vacuum chamber with base pressure of 2×10^{-4} Pa. Deposition process was carried out using 266 nm frequency-quadrupled Nd:YAG laser providing 90 mJ pulses of 6 ns duration. High-purity ceramic ZnO target was ablated by laser light with fluence of 2.8 J cm^{-2} at distance of 55 mm from the substrate. Repetition rate of laser was set to 10 Hz and each sample was grown as a result of 5200 shots. Ambient atmosphere of 5N-pure oxygen at pressure of 10 Pa and 40 sccm flow rate was present during the film growth. These parameters are favorable for ZnO p-type doping in order to avoid compensation by oxygen



vacancies [4]. Four different substrates were used: sapphire (0 0 0 1), MgO (1 0 0) and fused silica (FS) supplied by MaTecK GmbH and nanocrystalline diamond (NCD) film on silicon (1 0 0) wafer. NCD films were prepared using plasma-enhanced linear antennas microwave CVD system [5]. Prior to deposition, the substrates except of NCD were baked out in vacuum at 950°C for 5 min to remove remaining surface contamination. ZnO thin films were deposited on sapphire, MgO and FS at 300°C and subsequently annealed in situ at 750°C in 10 Pa oxygen temperature. Another set of films was deposited on NCD at various temperatures. 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 slow positron implantation spectroscopy (SPIS) measurements.

SPIS studies were carried out using slow positron beam SPONSOR [6] with positron energy adjustable in the range from 30 eV to 36 keV. Doppler broadening (DB) of annihilation line was measured by high-purity germanium detector with resolution of 1.09(1) keV at 511 keV. DB was evaluated using the line shape S parameter. Central energy interval used for the calculation of the value of S parameter was selected so that S parameter for the reference ZnO bulk single crystal S_0 was close to 0.5, where it is most sensitive to changes in line shape of the annihilation peak. Actual value $S_0 = 0.5068(5)$ was calculated from the energy region 510.07-511.93 keV.

3. Results

XRD investigations revealed that ZnO films deposited on all substrates exhibit wurtzite structure. ZnO films deposited on single crystal substrates (MgO, sapphire) exhibit local epitaxy while films deposited on amorphous FS or NCD show (0 0 0 1) fiber texture with random lateral orientation of crystallites in the plane of substrate [7, 8]. Comparison of $S(E)$ curves, i.e. dependence of S parameter on positron implantation energy E , for ZnO films deposited on various substrates at 300°C is shown in figure 1(a).

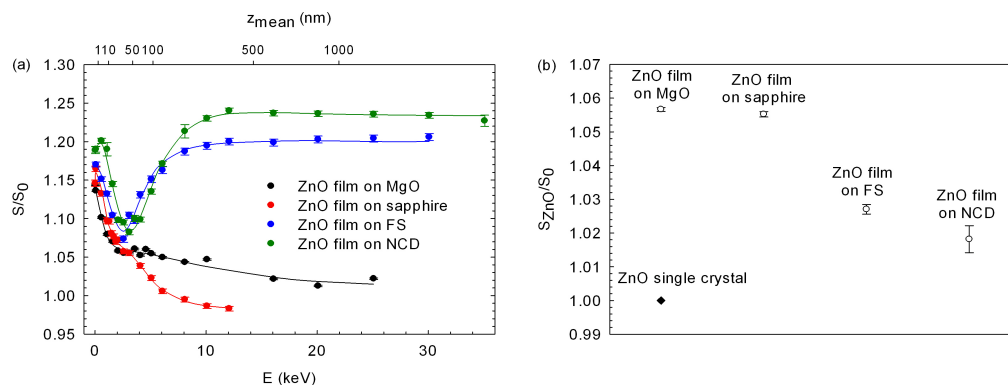


Figure 1. (a) $S(E)$ curves measured on ZnO films deposited on various substrates at 300°C. (b) Fitted S parameters for ZnO layers on various substrates and the reference ZnO crystal.

At the lowest energy $E = 0.03$ keV almost all positrons annihilate on the surface of ZnO films. With increasing energy positrons penetrate into the ZnO films and subsequently into the substrate. The largest fraction of positron annihilates in ZnO films at $E \sim 3$ keV. At energies $E > 20$ keV virtually all positrons annihilate in the substrate and measured S parameters approach bulk values for corresponding substrates. FS and NCD 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 [9] using two-layer model system (ZnO film and substrate). Fitted values for the S parameter and mean positron diffusion length L_+ for the ZnO model layer are shown in figures 1(b) and 2(a), respectively. Trapping rate K for positrons trapping at defects in ZnO films were calculated as $K = 1/\tau_B[(L_{+0}/L_+)^2 - 1]$, where L_+ is the positron diffusion length measured in the ZnO film, $L_{+0} = 280$ nm is the positron diffusion length in a perfect ZnO crystal obtained by theoretical calculations [10] and

$\tau_B = 154$ ps is the bulk positron lifetime in ZnO [11].

Trapping rates for films grown on different substrates and the reference ZnO crystal are compared in figure 2(b). The reference ZnO crystal exhibits positron diffusion length $L_+ = 59$ nm which is similar to the value reported by Uedono *et al* [12]. The fact that $L_+ < L_{+0}$ indicates that the hydrothermally grown crystal contains positron trapping defects. This was confirmed by positron lifetime spectroscopy [13, 14] and the defects were identified as Zn vacancies associated with H atoms [11].

S parameters and trapping rates for all ZnO films are higher than those in the ZnO crystal while the positron diffusion lengths are shorter. Thus, all ZnO films contain higher concentration of defects than the reference ZnO crystal. While ZnO films likely contain point defects similar to the reference ZnO crystal, additional types of defects may be present in polycrystalline 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. Moreover the concentration of defects in the ZnO films deposited on single crystal MgO and sapphire substrates is higher than in the films deposited on amorphous FS and NCD diamond substrates which is demonstrated by considerably higher S parameters, see figure 1(b). This is supported also by lower L_+ and higher K values for the films deposited on single crystalline substrates, see figure 2.

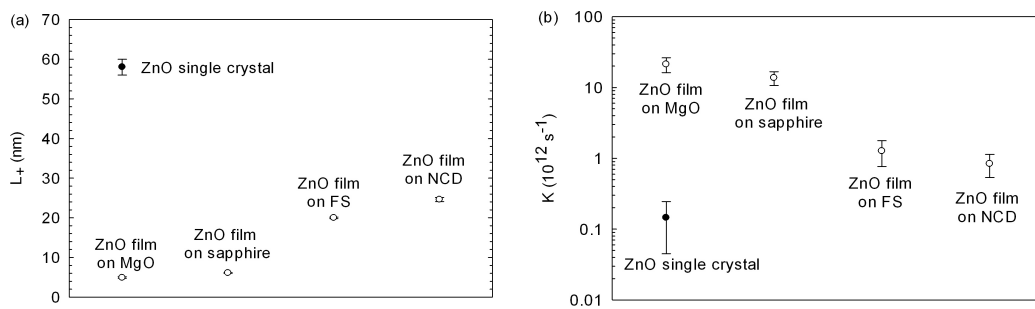


Figure 2. Comparison of parameters of ZnO films deposited on various substrates and reference ZnO single crystal: (a) mean positron diffusion length, (b) positron trapping rate.

Furthermore, the influence of deposition temperature on ZnO film properties was studied on films deposited on NCD substrate. Films at four different temperatures were deposited: room temperature, 300°C, 450°C and 600°C. Measured $S(E)$ curves are plotted in figure 3(a).

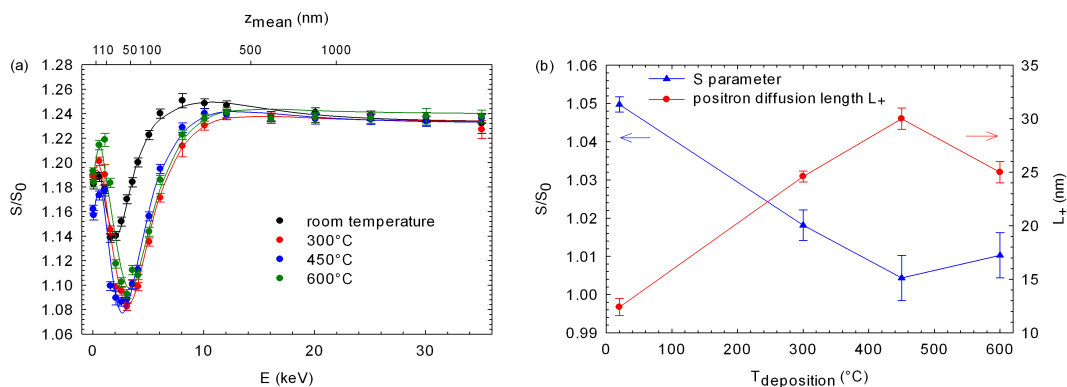


Figure 3. (a) $S(E)$ curves for ZnO films deposited at different temperatures on NCD. (b) Temperature dependence of the S parameter (blue triangles) and positron diffusion length (red circles) of ZnO layer deposited on NCD.

There is evident difference between the $S(E)$ curve of film deposited at room temperature and that of films deposited at elevated temperatures. Measured data were again analyzed by VEPFIT software and results are summarized in figure 3(b). ZnO film deposited at room temperature

exhibits the lowest diffusion length and therefore contains the highest concentration of defects. On the other hand, the highest positron diffusion length and lowest value of S parameter, indicating the lowest concentration of defects, were observed in film deposited at 450°C.

4. Discussion

XRD investigations [8] suggested that ZnO films grown on single crystal substrates (MgO, sapphire) exhibiting local epitaxy are of higher quality. Surprisingly, SPIS measurements revealed that these films have significantly higher concentration of defects than ZnO films deposited on FS and NCD. ZnO films deposited on single crystalline substrates exhibit well defined orientation with respect to the substrates. This inevitably results in formation of misfit dislocations compensating lattice mismatch between the substrate and ZnO layer while in the films deposited on FS and NCD the lattice mismatch is to some extent released by various orientation and tilting of the crystallites. Hence, SPIS measurements detect higher concentration of defects in film deposited on MgO and sapphire due to higher density of misfit dislocations.

Studies of ZnO films deposited on NC at various temperatures revealed that the film deposited at 450°C exhibits the lowest concentration of defects. Deposition at elevated temperatures increases chance of atoms to reach proper position in crystal lattice corresponding to the lowest interface energy. XRD investigations revealed that the mean size of crystallites increases with increasing temperature of deposition and therefore concentration of misfit defects at film-substrate interface increases as well. Minimum in temperature dependence of concentration of defects observed at 450°C is created as result of these antagonistic effects.

5. Conclusions

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

Influence of deposition temperature on properties of ZnO films deposited on NCD were investigated. The lowest concentration of defects was found in the film deposited at 450°C.

Acknowledgements

This work was supported by the Czech Science Agency (project P108/11/0958).

References

- [1] Bagnall D M, Chen Y F, Zhu Z, Yao T, Koyama S, Shen M and Goto T 1997 *Appl. Phys. Lett.* **70** 2230–2232
- [2] Hu J H and Gordon R G 1992 *J. Appl. Phys.* **71** 880–890
- [3] Vispute R D, Talyansky V, Trajanovic Z, Choopun S, Downes M, Sharma R P, Venkatesan T, Woods M C, Lareau R T, Jones K A and Iliadis A A 1997 *Appl. Phys. Lett.* **70** 2735–2737
- [4] O'Haire R, Meaney A, McGlynn E, Henry M O, Duclère J R and Mosnier J P 2006 *Superlattices Microstruct.* **39** 153 – 161
- [5] Fendrych F, Taylor A, Peksa L, Kratochvilova I, Vlcek J, Rezacova V, Petrak V, Kluiber Z, Fekete L, Liehr M and Nesladek M 2010 *J. Phys. D: Appl. Phys.* **43** 374018
- [6] Anwand W, Brauer G, Butterling M, Kissenger H R and Wagner A 2012 *Def. Diff. Forum* **331** 25
- [7] Novotný M, Čížek J, Kužel R, Bulř J, Lančok J, Connolly J, McCarthy E, Krishnamurthy S, Mosnier J P, Anwand W and Brauer G 2012 *J. Phys. D: Appl. Phys.* **45** 225101
- [8] Kužel R, Čížek J and Novotný M 2013 *Metall. Mater. Trans. A* **44A** 45–57
- [9] van Veen A, Schut H, Clement M, de Nijs J, Kruseman A and IJpma M 1995 *Appl. Surf. Sci.* **85** 216 – 224
- [10] Lukáč F, Čížek J, Procházka I, Melikhova O, Anwand W and Brauer G 2014 *Acta Phys. Pol., A* In press
- [11] Brauer G, Anwand W, Skorupa W, Kuriplach J, Melikhova O, Moisson C, von Wenckstern H, Schmidt H, Lorenz M and Grundmann M 2006 *Phys. Rev. B* **74** 045208
- [12] Uedono A, Koida T, Tsukazaki A, Kawasaki M, Chen Z Q, Chichibu S and Koinuma H 2003 *J. Appl. Phys.* **93** 2481
- [13] de la Cruz R M, Pareja R, González R, Boatner L A and Chen Y 1992 *Phys. Rev. B* **45**(12) 6581–6586
- [14] Tuomisto F, Ranki V, Saarinen K and Look D 2003 *Phys. Rev. Lett.* **91** 205502