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Defects in zinc oxide grown by pulsed laser deposition

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ABSTRACT

ZnO films are grown on c-plane sapphire using the pulsed laser deposition method. Systematic studies on the effects of annealing are performed to understand the thermal evolutions of the defects in the films. Particular attention is paid to the discussions of the ZnO/sapphire interface thermal stability, the Zn-vacancy related defects having different microstructures, the origins of the green luminescence (~2.4–2.5 eV) and the near band edge (NBE) emission at 3.23 eV.

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1. Introduction

Zinc oxide is a semiconductor having a direct band gap of 3.3 eV at 300 K and a large exciton binding energy of ~60 meV. It has received extensive attention because of its potential in a variety of applications including ultra-violet (UV) optoelectronics, photovoltaics, sensors, and spintronics etc [1]. As compared to GaN, which is more maturely developed for optoelectronic device applications, ZnO has the advantage of its large exciton binding energy (~60 meV). Excitons in ZnO are thermally stable at room temperature, thus enabling intense near band edge (NBE) exciton emission and low threshold lasing at room temperature [2].

Despite its potential in fabricating UV optoelectronic devices with good performance, the realization of practical ZnO-based devices is hindered by the asymmetric p-type doping difficulty of ZnO [1,3,4]. Defects in ZnO play a crucial role in determining the electrical, optical and magnetic properties of the material and thus the devices. However, the knowledge of defects in ZnO is far from complete [5].

The present paper reports our recent work on studying the defects in ZnO films grown by the pulsed laser deposition (PLD) method using a comprehensive spectroscopic approach. These include a summary of our recently published works in Refs. [6] and [7], as well as some unpublished new results of the research in progress.

2. Experimental

Undoped ZnO films having thickness of 300 nm were grown on c-sapphire substrate using the PLD method and a ZnO target with purity of 99.999%. To obtain comprehensive results, the films were grown with different substrate temperatures (T_{sub}=300 and 600 °C) and oxygen pressures ($P(O_2)$=0, 1.3 and 5 Pa) systematically. Cu-doped ZnO samples were also grown on c-sapphire with T_{sub}=600 °C and $P(O_2)$=0 using a ZnO:CuO target with a weight ratio of 99%:1%. Isochronal annealing was performed in Ar atmosphere for 40 min with two approaches being adopted, namely (i) with another piece of ZnO placed on top to protect the sample surface during the annealing, and (ii) the sample being annealed is exposed to the Ar atmosphere without coverage. To obtain a comprehensive picture of the defects in the samples, a multi-spectroscopic approach was adopted to characterize the samples. These included X-ray diffraction (XRD), atomic force microscopy (AFM), high resolution transmission electron

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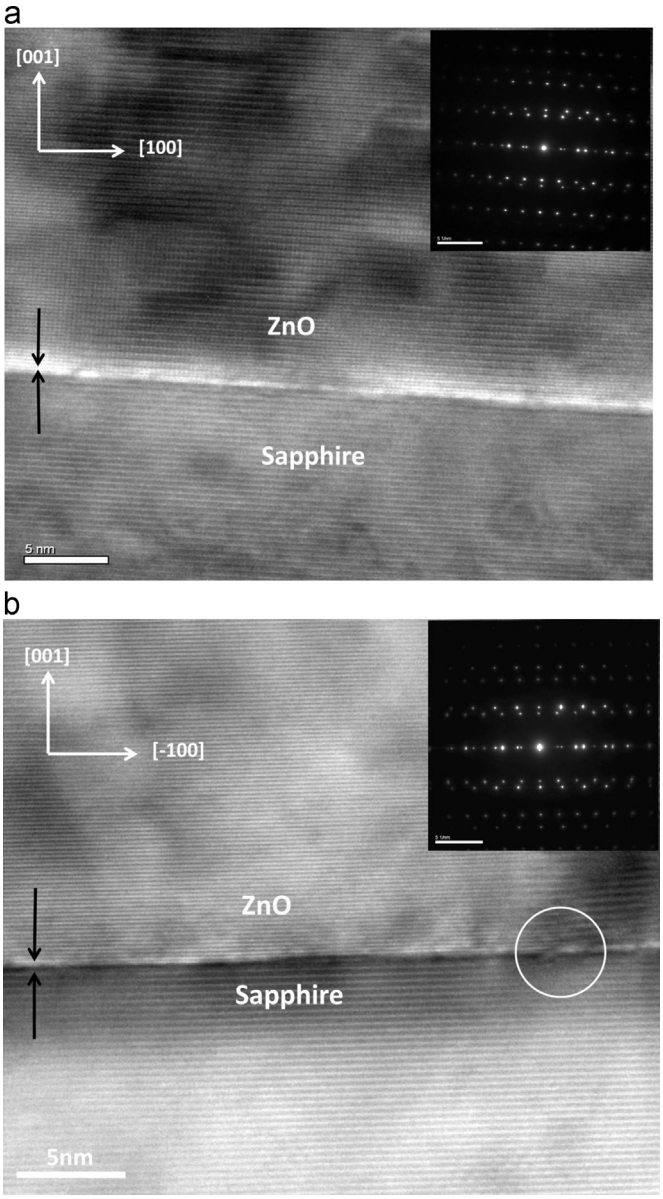

Fig. 1. (a) The cross-sectional HRTEM image at the film/substrate interface (dark arrows) for the undoped ZnO/sapphire sample annealed at 750 °C without covering the surface. The inset shows the electron diffraction pattern from the film-substrate interface; (b) The cross-sectional HRTEM image at the film/substrate interface for the undoped ZnO/sapphire sample annealed at 750 °C with covering the surface. The corresponding diffraction pattern from film-substrate interface is presented in the inset. The undoped samples are grown at T_{sub}=600 °C without oxygen.

microscopy (HRTEM), secondary ion mass spectroscopy (SIMS), photoluminescence (PL), and positron annihilation spectroscopy (PAS). We have studied the effect of whether the sample surface was covered by another piece of ZnO. Experimental detail concerning the growth, post-growth annealing and the spectroscopic characterizations are given in Refs. [6] and [7].

3. Results and discussion

The ZnO films exhibit only the (002) and (004) peaks in the XRD spectra. The films have electron concentrations of 1×10^{18}–2×10^{19} cm^{-3} and the mobility varies from 25 to 95 $cm^2\,V^{-1}\,s^{-1}$ depending on T_{sub} and P(O_2) during growth, as well as the post-growth annealing temperature [6].

Atomic force microscopy (AFM) studies [6] showed that the surface roughness of the as-grown undoped film grown without oxygen is 1.97 nm. The surface morphology upon annealing at 900 °C is dependent on whether the sample surface is covered during annealing. The uncovered annealing introduces surface damage and the surface roughness increases to 3.37 nm. For the covered annealing, the surface roughness is improved to 0.82 nm.

Whether the sample surface is covered during annealing also influences the thermal stability of the ZnO/sapphire interface. The HRTEM images of the undoped samples grown at T_{sub}=600 °C and $P(O_2)$=0 Pa upon annealing at 750 °C without and with the cover are shown in Fig. 1(a) and (b) respectively. The HRTEM image of the sample annealed without coverage (Fig. 1(a)) shows perfect ZnO growth along (002) plane and the interface to be atomically sharp (parallel lattice fringes can be seen even very close to the interface) without any interfacial reactions and inter-diffusion. The film/substrate shows clear continuity without bending and wrinkling of the lattice fringes. The diffraction pattern from film-substrate interface (inset of Fig.1(a)) shows perfect epitaxial growth and the absence of spots apart from those belonging to the film and substrate. The native ZnO film also demonstrates some image contrast (dark and white regions) revealing non-uniform density distribution due to introduction of some intrinsic defects after annealing. Similarly Fig.1(b) demonstrates a cross-sectional HRTEM image at the film/substrate interface for the sample annealed with cover. The image shows perfect ZnO growth along the (002) plane but the film/substrate interface is not atomically sharp as that observed in the previous case. We can see atomically thick and crumpled film/substrate interface and clear discontinuity at some localized region (marked by circle). This discontinuity may possibly arise because of localized interfacial reactions due to Zn out-diffusion into the substrate. Moreover, the native ZnO thin film show less image contrast indicating more uniform density distribution due to suppression of intrinsic defects but at the expense of deterioration of film/substrate interface.

The Zn and Al profiles obtained by secondary ion mass spectroscopy (SIMS) of the undoped ZnO samples annealed at 900 °C with and without coverage are shown in Fig. 2(a) and (b). The figures show that the Zn out-diffusion of the sample annealed with cover is more extensive than that without the cover, which agrees with the speculation made in the last paragraph that the discontinuity observed in the HRTEM image of the interface is due to Zn out-diffusion, which would be enhanced by the coverage during the annealing. The out-diffusion of Zn at the interface could lead to the formation of Zn-vacancy related defects. The Al out-diffusion is similar for the two samples annealed with and without the coverage.

Low temperature (LT) PL study was carried out to study the defects in ZnO samples annealed at different temperatures with coverage [7]. Broad defect emissions peaking at 2.2 eV–2.5 eV are found in the low temperature (10 K) PL spectra of the undoped samples, with the peak positions and shapes depending on the growth parameters and the subsequent annealing temperature. However, irrespective of the initial growth parameter, after post-growth annealing at 900 °C with the surface covered, all the undoped samples exhibit an identical green luminescence having the same peak position (2.47 eV) and shape (see the normalized spectra in the insert of Fig. 3(a)). The defect emissions of the samples annealed at temperatures lower than 900 °C originate from more than one defect. The relative compositions of the defects are dependent on the annealing temperature and the initial growth conditions, and thus so are the shape and the peak of the resultant defect emission spectra. After the 900 °C annealing, all the samples irrespective of the initial growth condition exhibit the same GL peaking at 2.47 eV (GL-2.47 eV), which is interpreted as that the GL originates from a single type of defect and that the

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