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Violet luminescence emitted from Ag-nanocluster doped ZnO thin films grown on fused quartz substrates by pulsed laser deposition

Songqing Zhao, Yueliang Zhou*, Kun Zhao, Zhen Liu, Peng Han, Shufang Wang, Wenfeng Xiang, Zhenghao Chen, Huibin Lü, Bolin Cheng, Guozhen Yang

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, PR China

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Abstract

Silver nanocluster doped ZnO thin films were fabricated on fused quartz substrates at different temperatures by pulsed laser deposition (PLD) using a silver-ZnO mosaic target. X-ray diffraction (XRD) measurements showed that ZnO and doped silver nanoclusters crystallized with preferred *c*-axis orientation. Scanning electron microscopic (SEM) images of the sample fabricated at 450 °C and the X-ray photoelectron spectroscopy (XPS) showed the radius of the silver clusters to be about 3–16 nm. Under 266 nm laser excitation, the photoluminescence (PL) spectra exhibited a peak at 414–420 nm for silver nanocluster doped ZnO thin films deposited at different temperatures. Through the investigation of the energy level of the defects in ZnO thin films, the energy levels of the zinc vacancy (V_{zn}, $E_{V_{zn}} = 3.03$l eV) and the interstitial zinc atom (Zn_i, $E_{Zn_i} = 2.95$ eV) were found to be consistent with the peak wavelengths of 414 and 420 nm. We suggest that this violet emission originates from an electronic transition between the interstitial-zinc level and the valence band, or between the bottom of the conduction band and the V_{Zn}level.

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Keywords: Nanocluster; Violet luminescence; Ag; Interstitial zinc; Zinc vacancy

1. Introduction

ZnO, a wide band-gap (3.37 eV) compound semiconductor, is considered as a promising material for blue and ultraviolet diode lasers along with GaN and its related compounds [1]. More importantly, its exciton binding energy is about 60 meV, which is much larger than the thermal energy at room temperature and that of ZnS (22 meV) and GaN (25 meV) [2]. So many researchers have attempted to investigate the emitting properties of ZnO films, including doped and undoped ones, in order to improve the efficiency of emission [3,4] or to understand the physical mechanisms behind the luminescence [5,6]. ZnO exhibits three major luminescences including ultraviolet (UV), green and red emissions [7,8]. It is known that the UV emission is due to the direct recombination of the excitations, while the green and the red emission are still controversial because of the complicated microscopic defects in ZnO. Xu et al. [6] calculated the energy levels of defects in ZnO thin film by a full-potential linear muffin-tin orbit method, suggesting that the violet is a possible emission from ZnO.

Due to its attractive feature of the stoichiometric deposition from target to thin film and easy control of the species and amounts of the doping elements by using different targets, pulse laser deposition (PLD) is proven to be the most rapid and efficient tool for fabrication of high-quality multi-component thin films, and widely used in fabricating metal oxide thin films and related materials [9]. Recently, metal nanoparticle doped oxide films were shown to exhibit fascinating properties such as large nonlinearity, photocatalysis, etc [10,11]. In this article we applied an Ag–ZnO mosaic target [12] to obtain the Ag-nanocluster doped ZnO thin films by PLD. An interesting phenomenon

*Corresponding author. Tel.: +86 10 8264 8108.
E-mail addresses: ylzhou@aphy.iphy.ac.cn (Y. Zhou), kzhao@aphy.iphy.ac.cn (K. Zhao).

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in our experiment was that only the violet luminescence centered from 414 nm (3.03 eV) to 420 nm (2.95 eV) was observed instead of the traditional 375 nm (3.35 eV) and 550 nm (2.25 eV). We suggested that this phenomenon was due to the point defects of zinc vacancies and interstitial zinc atoms induced by doped Ag clusters.

2. Experimental details

The films were prepared on fused quartz substrates by PLD. A KrF excimer laser (wavelength: 248 nm, pulse width: 30 ns, energy density: 1 J/cm^2) was used for ablation of a ZnO mosaic target ($\frac{1}{4}$ area of the target was uniformly covered with high-purity silver slices in the shape of a sector). In our experiments, the repetitive frequency of the laser was 4 Hz, the O_2 pressure was 5×10^{-4} Pa, and the temperature of the substrates varied from 350 to 550 °C. All the samples were cooled to room temperature under a O_2 pressure of 5×10^{-4} Pa in the chamber.

The crystal structures and the composition analysis were performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The photoluminescence (PL) measurement was examined by the excitation of a quadruple Nd:YAG laser (wavelength 266 nm) at the output power of 10 mW. All the spectra were taken at room temperature in air by using a collecting quartz lens whose focus was on the slit of a spectrometer.

3. Results and discussion

Fig. 1 shows XRD patterns of ZnO thin films fabricated at different temperatures, confirming a single-phase structure of ZnO with (0 0 2) preferred orientation. The Ag (1 1 1) peak appears at about 38° with the full-width at half-maximum (FWHM) of 0.645°, 0.899° and 1.103° at 350, 450, and 550 °C, respectively. As shown in Fig. 2, the Ag nanoclusters uniformly appear in the SEM image, and the largest three clusters are denoted by 18.2, 16.2 and 14.2 nm. The average size of the clusters in this image is about 5–9 nm, close to the estimated value by the Scherrer function, $D = 0.89\lambda/\mathrm{FWHM}\cos\theta$, inserting $\theta = 19°$. Simultaneously, electron energy loss spectroscopy (EELS) analysis shows that the doped amount of silver is about 3.12%, 5.23% and 6.75% (atomic ratio of Zn/Ag) at 350, 450 and 550 °C, respectively.

Fig. 3 gives the XPS spectra of Ag 3d of our Ag nanocluster doped ZnO films at 350, 450 and 550 °C fabrication temperature. A peak at 368.2 eV is observed, which is due to Ag^0 3d. The combined use of XRD, SEM and XPS allows us to elucidate that the silver doped into the ZnO films is in the form of nanoclusters.

Fig. 4 shows the PL spectra of Ag-cluster doped ZnO thin film grown at different temperatures (350, 450 and

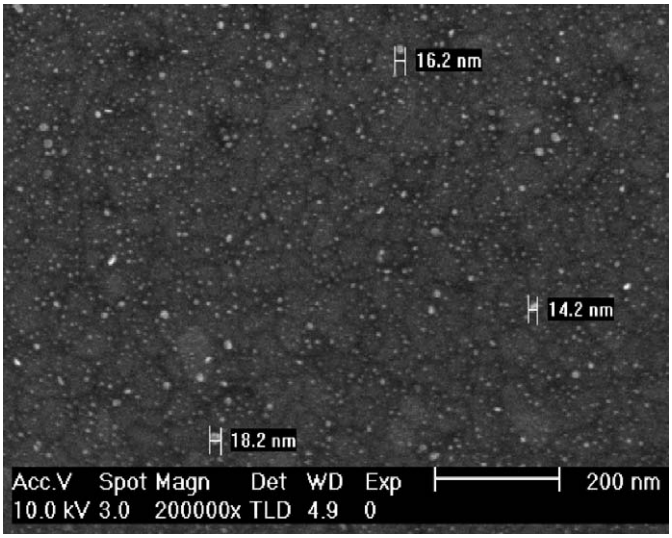

Fig. 2. SEM image of Ag-cluster doped ZnO thin film at 450 °C.

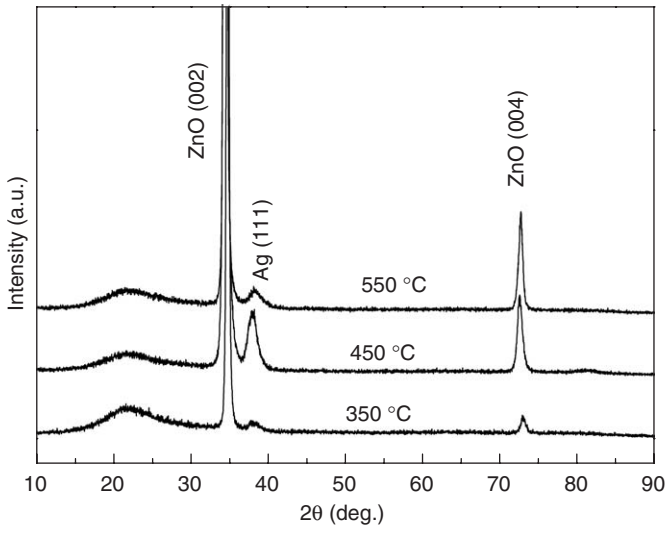

Fig. 1. XRD patterns of ZnO thin films prepared at different temperatures (350, 450 and 550 °C) on fused quartz substrates.

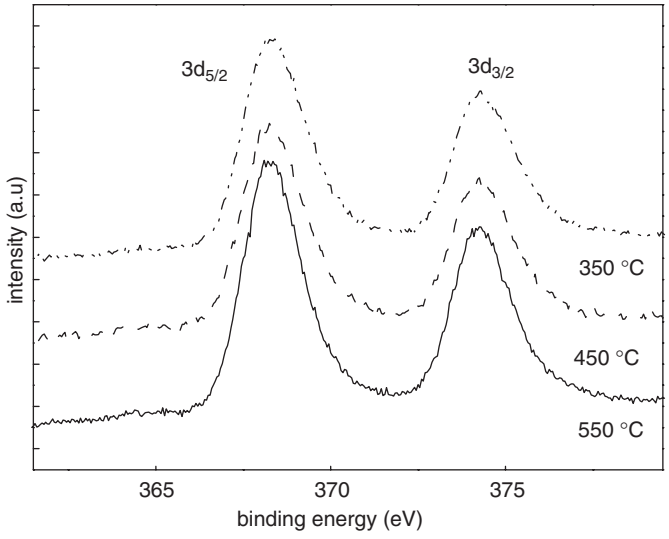

Fig. 3. XPS spectra of Ag-cluster doped ZnO thin films at different substrate temperatures.

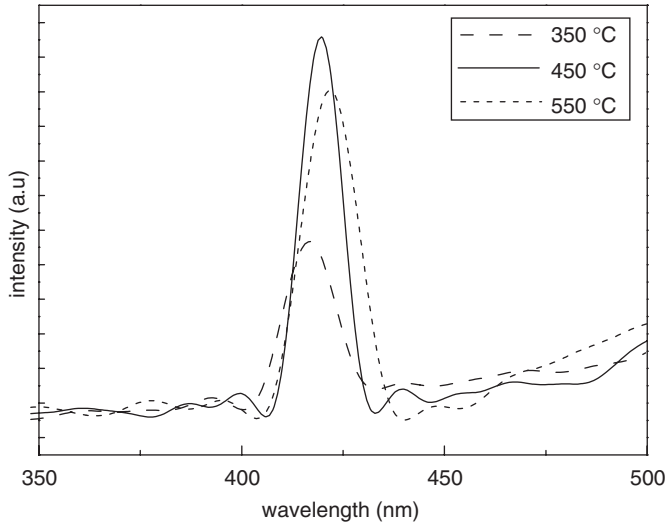

Fig. 4. PL spectra of Ag-cluster doped ZnO thin films at different substrate temperatures.

550 °C). All the PL spectra of the samples have only one violet luminescence peak centered at 414–420 nm. Jin et al. [13] first reported the observation of violet luminescence emitted from ZnO thin films grown on sapphire by PLD under 1.33×10^{-1} Pa oxygen pressure. It is well known that the defects in ZnO film include oxygen vacancy (V_O), zinc vacancy (V_{Zn}), interstitial zinc (Zn_i), interstitial oxygen (O_i) and anti-site oxygen (O_{Zn}) [5]. Fig. 5 presents the energy levels of defects in ZnO thin film, calculated by the full-potential linear muffin-tin orbit method [6]. The energy intervals, 3.03 and 2.95 eV, are exactly consistent with the emission peaks at 414 and 420 nm. The violet luminescence is probably due to the radiative defects Zn_i and V_{Zn} related to the interface traps existing at the grain boundaries between silver nanoclusters and ZnO grains, and emitted from the radiative transition between this level and the valence band or the conduction band. For our PLD deposition at 5×10^{-4} Pa, the resulting ZnO thin film with silver particles may have more grain boundary defects Zn_i and V_{Zn}, which greatly enhances the intensity of the violet luminescence. In addition, an apparent red shift of the emission peaks occurs with the increase of fabrication temperature. This phenomenon means that the radiative center may move from zinc interstitial atom to zinc vacancy, and the mechanism of this shift is still not clear at the present time.

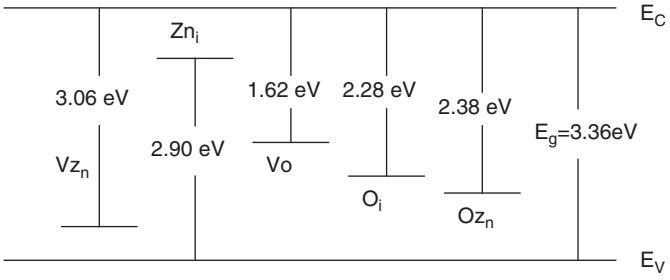

Fig. 5. Energy levels of the intrinsic defects in ZnO thin films.

4. Conclusion

In summary, Ag-nanocluster doped ZnO films were fabricated on fused quartz substrates at different temperatures by PLD. The structure and the luminescence properties were measured by XRD, SEM, XPS and PL. Violet luminescence centered at 414–420 nm (3.03–2.95 eV) was observed, which was thought to be emitted from the grain boundaries of the silver particles and the oxygen-deficient ZnO film. The zinc vacancies (V_{Zn}) and interstitial zinc atoms (Zn_i) induced by Ag-doping are suggested to be responsible for the violet luminescence emission.

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