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Effect of annealing on conductivity behavior of undoped zinc oxide prepared by rf magnetron sputtering

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Abstract

An undoped ZnO thin film with high resistivity was prepared by rf magnetron sputtering on the quartz substrates using a ZnO (99.999% pure) as target and high pure Ar as sputtering gas. Upon annealing in a temperature range from 513 to 923 K under 10^{-3} Pa, the conductive properties of the film change from high resistivity, to n-type, then to p-type and finally to n-type with increasing annealing temperature and the p-type ZnO film was fabricated near 863 K reproducibly. Temperature-dependent photoluminescence (PL) of the p-type ZnO shows a dominant PL band at 3.072 eV at low temperature, which is related to Zn vacancy (V_{Zn}) acceptor. The intensity of the 3.072 eV band decreases with increasing temperature, implying increment of amount of the hole induced by V_{Zn}. X-ray photoelectron spectroscopy (XPS) and room temperature PL measurements indicate that the undoped ZnO is Zn-rich and has oxygen vacancy (V_o) and interstitial Zn (Zn_i) donor defects. The amount of V_o and Zn_i donors changes with the annealing temperature. The intrinsic p-type conduction of the undoped ZnO film is ascribed to that the V_{Zn} acceptor concentration can compensate V_o and Zn_i donor concentration.

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Keywords: ZnO films; Annealing; Photoluminescence

1. Introduction

Zinc oxide (ZnO) is a direct wide band gap semiconductor with band gap of 3.37 eV and a free exciton binding energy of 60 meV at room temperature, so it is considered as an excellent material in optoelectronic device applications, such as ultraviolet light-emitting diode and laser diode [1]. However, the realization of p-type ZnO has far proven difficult due to its asymmetric doping limitations [2]. The successful fabrication of p-type ZnO films has been reported by several groups by doping nitrogen (N) [3,4], phosphorus (P) [5], arsenic (As) [6,7] and Li and coworkers [8] using different growth methods, such as pulsed laser deposition, molecular beam epitaxy, sputtering, metalorganic chemical vapor deposition, etc. A donor–acceptor codoping method has been also proposed to realize heavy p-type doping [9] and the experimental studies based on this concept have been performed [10,11]. Among these studies, several groups have reported p-type conductivity in ZnO samples. However, it is ambiguous for p-type doping mechanism and the stability as well as reproducibility of the p-type conductivity in ZnO is a main issue at present in this research field. Therefore, it is worthwhile to investigate the intrinsic p-type behavior of ZnO thin films before adopting any doping method.

There have been a few reports on undoped p-type ZnO [12–15]. Xiong et al. reported that the conductivity of ZnO films could depend on Ar/oxygen gas ratio during reactive sputtering and Ma et al. as well as Oh et al. produced intrinsic p-type conduction film by tuning the oxygen partial pressure. Recently, Zeng et al. reported the intrinsic p-type ZnO thin film by oxygen

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plasma growth. In all the above, the oxygen contents or partial pressures were optimized during the O-rich growing progress. However, under the O-rich condition, the concentration of acceptor defect, such as zinc vacancy (V_{Zn}) remains low due to their high formation enthalpies.

In this letter, a p-type undoped ZnO was prepared by rf magnetron sputtering and postannealing under 10^{-3} Pa, effects of annealing on the conductive properties of the undoped ZnO thin films were studied and mechanism of formation of the p-type undoped ZnO was discussed.

2. Experimental details

ZnO films were prepared on quartz substrates by rf magnetron sputtering. A ZnO disc with 99.999% purity was used as target. The chamber was evacuated below 5×10^{-4} Pa with a mechanical pump and a molecular pump firstly, and then filled with 99.999% pure Ar flow. The total flow rate was regulated to 45 sccm. The working pressure was kept at 1.0 Pa and the substrate temperature was 513 K. The sputtering power and time was 100 W and 2 h, respectively. The as-grown film thickness is about 600 nm. The as-grown ZnO film was annealed in a tube furnace for 1 h in the temperature range of 513–923 K under about 10^{-3} Pa. In order to prevent pollution, a quartz tube was inserted into the furnace and the film was placed in a quartz boat.

Structure of the films were characterized by X-ray diffraction (XRD) with Cu $K\alpha_1$ radiation ($\lambda = 0.15418$ nm). The chemical composition and bonding states of the films were analyzed by XPS with Al anode as an X-ray source. The ZnO films were sputtered for 30 min prior to XPS measurement. Hall effect measurements were carried out at room temperature using the van der Pauw configuration [16]. The insulating quartz assured that the measured electrical properties came from the ZnO thin films. Photoluminescence measurement was performed using a He–Cd laser with 325 nm line as excitation source in the temperature range between 82 and 302 K.

3. Results and discussions

Fig. 1 illustrates the X-ray diffraction patterns of the as-grown undoped ZnO film and the film annealed at 633, 703, 863 and 923 K under 10^{-3} Pa, respectively, indicating that all the ZnO films are of wurtzite structure. A strong (0 0 2) peak is observed in all patterns, implying that the ZnO films exhibit a preferred (0 0 1) orientation. The lattice constants of the films were calculated by using diffraction data of (1 0 3) and (0 0 4) peaks and plotted as a function of annealing temperature in Fig. 2. The lattice constants of the as-grown film are $a = 0.3261$ nm and $c = 0.5231$ nm, which are larger than a (0.3253 nm) and c (0.5209 nm) of bulk ZnO, respectively [17]. The difference in the lattice constants between as-grown ZnO film and bulk ZnO is $\Delta a = 0.0008$ nm and $\Delta c = 0.0022$ nm, respectively. Upon annealing, the lattice constants a and c decrease promptly at 633 K and then the lattice constant a increases gradually with increasing temperature but c has no apparent variety.

In order to understand the annealing temperature-dependent lattice constants, XPS measurement was performed for the as-grown and annealed ZnO films. Fig. 3 shows plots of Zn and O concentrations as well as difference between Zn and O concentration as a function of annealing temperature. It indicates that the Zn concentration is much larger than O concentration in the as-grown ZnO. Upon annealing at 633 K, the Zn concentration decreases greatly, while the O concentration increases sharply, as shown in Fig. 3, resulting in that Zn concentration is close to O concentration. Further increase in the annealing temperature, decrease of the Zn concentration and increase of O concentration become slowly and Zn/O ratio approaches to stoichiometry.

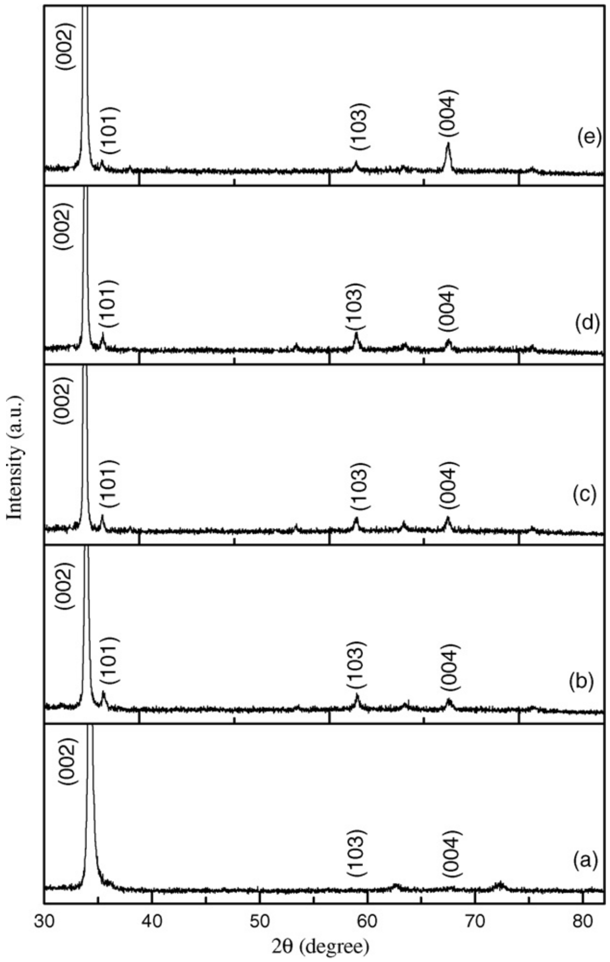

Fig. 1. XRD patterns of (a) the as-grown undoped ZnO film (513 K) and the films annealed at (b) 633, (c) 703, (d) 863 and (e) 923 K under 10^{-3} Pa, respectively.

It is well known that there are interstitial Zn (Zn_i) atoms in as-grown ZnO film, which usually locate between O^{2-} and Zn^{2+} layers, resulting in great increment of lattice constant c and gentle increase of lattice constant a. Combining the results of Figs. 2 and 3, it is deduced that the differences in lattice constants between the as-grown and bulk ZnO are attributed to existence of many Zn_i atoms in the as-grown ZnO film. Upon annealing at 633 K, the Zn_i atoms reduce greatly and Zn and O concentrations is near stoichiometry, leading to the decrease in lattice constants, sharply to near lattice constant of bulk ZnO. As annealing temperature rises further, as shown in Fig. 3, the Zn to O ratio decreases, which leads to increase of the lattice constants a and c due to which ionic radius of O is larger than that of ionic Zn. On the other hand, the amount of the Zn_i goes down as the annealing temperature rises, as shown in Fig. 4, which makes the lattice constant c decrease. Therefore, the lattice constant a increases with increasing annealing temperature when the annealing temperature is higher than 633 K, while the lattice constant c almost does not change, as shown in Fig. 2.

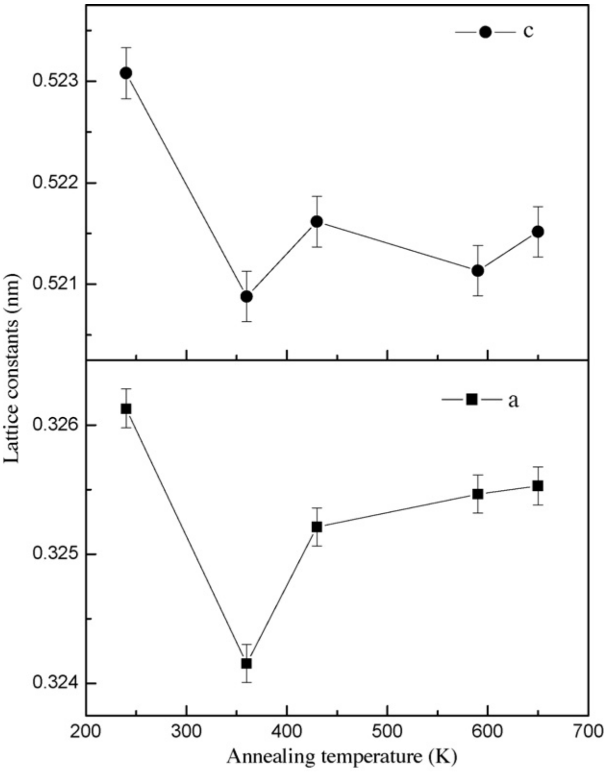

Fig. 2. The lattice constants of the undoped ZnO films vary as a function of annealing temperature.

Hall effect measurements were applied to characterize the electrical properties of the as-grown ZnO film and the film annealed at different temperature and the results are listed in Table 1. As shown in Table 1, the as-grown ZnO film shows insulating properties. With increasing annealing temperature, the conductivity of the film changed dramatically from insulator to weak n-type, to n-type, then to weak p-type, to p-type and finally changed back to n-type. A p-type undoped ZnO film was obtained at annealing temperature of about 863 K under 10^{-3} Pa reproducibly. It should be stressed that the p-type undoped ZnO can obtained under postannealing processing, that is different from results reported previously [12–15], which showed that the undoped p-type ZnO was realized in the rich oxygen growing conditions.

The X-ray photoelectron spectroscopy and photoluminescence measurement were carried out for explanation of the conductive mechanisms of the annealed undoped ZnO films. Fig. 3 shows the Zn and O concentrations in the as-grown ZnO film and the film annealed at 633 and 863 K calculated from the XPS measurements. The concentration of Zn decreased, while the concentration of O increased with increasing annealing temperature. Fig. 4 shows the Auger $ZnL_3M_{4.5}M_{4.5}$ spectra of the ZnO films annealed at 633 and 863 K, respectively. The two Auger peaks at 498.07 and 494.50 eV are attributed to the Zn–O bonds and the interstitial Zn (Zn_i), respectively. By fitting the zinc Auger peaks with Gaussian profile, the concentration of the (Zn_i) was estimated to be 15 at.% for the film annealed at 633 K and 8 at.% for the film annealed at 863 K, respectively, indicating that the concentration of Zn_i decreases with the increasing annealing temperature. Since the Zn_i in the ZnO film is a donor impurity, the decreasing of the Zn_i is favorable to the formation of the undoped p-type ZnO.

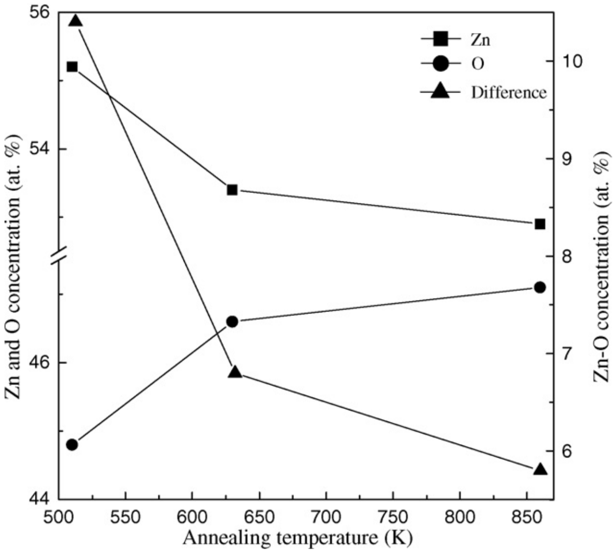

Fig. 3. A plot of the concentration of Zn and O in the undoped ZnO films as well as difference between Zn and O concentration vs. annealing temperature.

Fig. 5 shows the room temperature PL spectra of the as-grown and annealed ZnO films, presenting a near-band-edge (NBE) UV emissions at 378 nm (3.28 eV) and the broad emissions in visible region, the latter is ascribed to the transitions of the excited optical center from the deep level to the valence band, and the deep level is related to the intrinsic defects in the films [18]. It can be seen from Fig. 5 that the intensity of the orange emission

Table 1
Conduction type, resistivity, carrier concentration and carrier mobility of the undoped ZnO films annealed at different temperatures under 10^{-3} Pa

Temperature (K)	Type	Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} s^{-1}$)
513		Insulated		
633		Insulated		
703	n	3.66	7.8×10^{17}–4.3×10^{17}	4.23–2.32
773	n	5.92	2.1×10^{19}	0.06
	p	5.92	3.6×10^{18}–7.6×10^{17}	1.57–0.34
863	p	97.9	3.4×10^{16}–1.2×10^{16}	6.70–2.38
923	p	41.0	8.4×10^{17}	0.21
	n	41.2	1.9×10^{17}–1.7×10^{17}	1.03–0.88

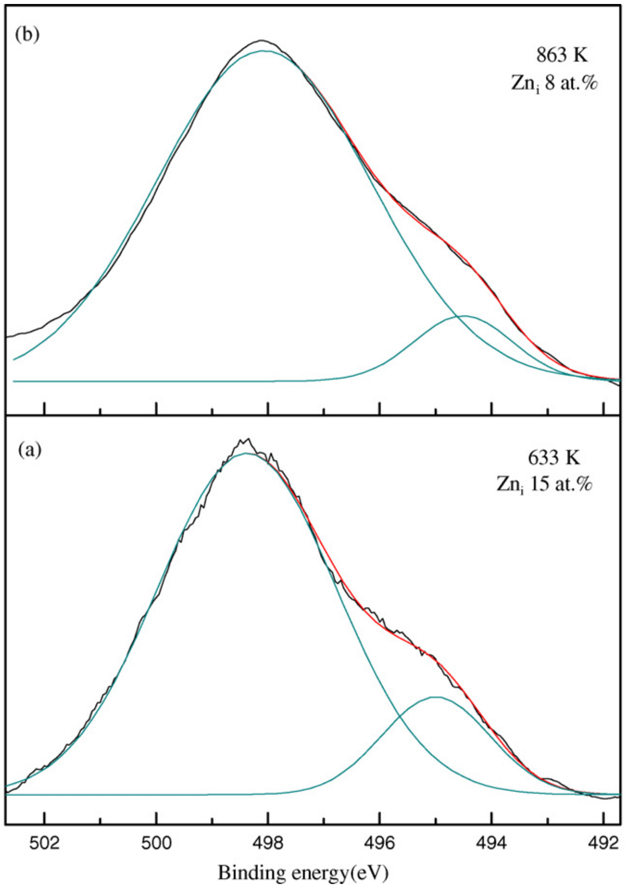

Fig. 4. ZnL$_3$M$_{4.5}$M$_{4.5}$ spectra of the undoped ZnO films annealed at (a) 633 and (b) 863 K under 10^{-3} Pa, respectively.

at around 602 nm (2.06 eV), which related to Zn$_i$ defects or Zn$_i$ complex [19], decreases with increasing annealing temperature, implying that the amount of the Zn$_i$ decrease with increasing annealing temperature, consistent with the XPS results. On the other hand, as Fig. 5 shows, a broad green emission at around 500–550 nm (2.48–2.25 eV) appears obviously at 863 K, which were assigned to the electron transition from conduction band to the single electron oxygen vacancy (V$_o^+$) level. The broad range of the green emission band is attributed to different local environments around the V$_o^+$ [20]. The intensity of the green emission increase with increasing annealing temperature, as shown in Fig. 5(e and f), implying that the amount of V$_o^+$ increases as annealing temperature rises.

To better understand the intrinsic p-type behavior, temperature-dependent PL measurement was performed. Fig. 6(a) illustrates 82 K PL spectrum for the p-type ZnO (annealed at 863 K) sample. We observed the strong emission at 3.072 eV dominated the PL spectra with the relative weak NBE emissions. The NBE emission at 3.367 eV was assigned to the D°X emission due to exciton bound to neutral donor [21,22]. The peak located at 3.350 eV is identified as the NBE emission of exciton bound to acceptor (A°X) [23]. The peak located at 3.312 eV might be identified as the first LO photon replica of the free exciton (1LO-FE$_A^{n=1}$) [23]. Other interesting peaks at 3.259 may be due to donor–acceptor pair transitions. For undoped ZnO

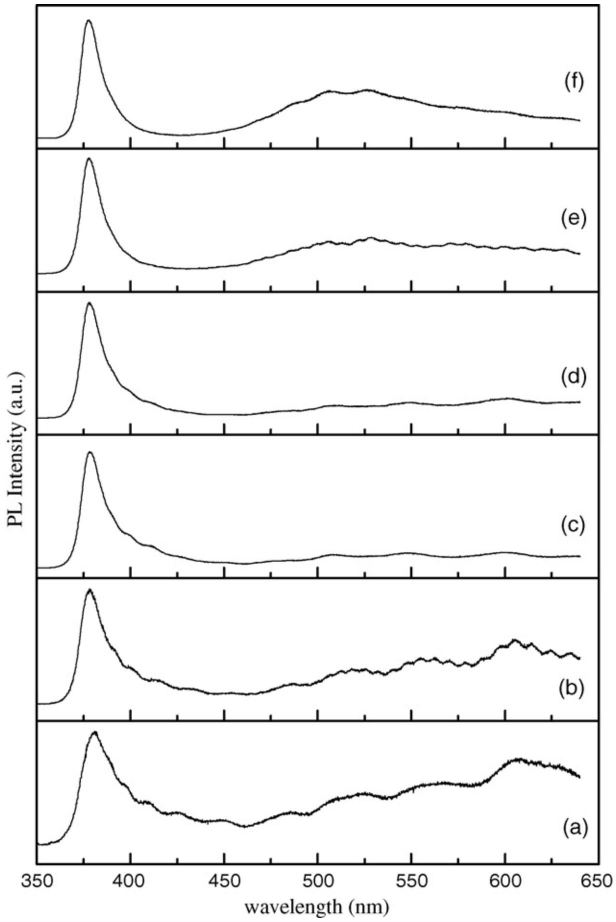

Fig. 5. Room-temperature PL spectra taken from (a) the as-grown undoped ZnO film (513 K) and the films annealed at (b) 633, (c) 703, (d) 773, (e) 863 and (f) 923 K under 10^{-3} Pa, respectively.

films, it is reasonable that the intensity of the A°X NBE emission is stronger than that of the D°X NBE emission because they are intrinsic p-type due to the presence of mass zinc vacancies. Our data suggest that the Zn vacancy (V$_{Zn}$) is responsible for the dominated emission at 3.072 eV [19,24] denoted as A band and Zn$_i$ is responsible for the 2.957 eV denoted as D band emerged at a temperature lower than 227 K.

Fig. 6(b) shows the temperature-dependent PL spectra of the p-type ZnO film obtained at 863 K, measured in the temperature range of 80–302 K. It indicates that the neutral bound excitons were decomposed into free exciton gradually with increasing temperature, so the bands in ultraviolet region come mainly from free exciton emission at high temperature [24]. Moreover, the intensity of the dominant V$_{Zn}$ emissions decreased with increasing measuring temperature, as shown in Fig. 6(b), implying that the amount of the ionized V$_{Zn}$ increased. Since V$_{Zn}$ is acceptor defect, the increment of the amount of the ionized V$_{Zn}$ means production of many holes in the undoped ZnO films. The holes can compensate electrons from intrinsic donors.

Based on the discussion mentioned above, it is deduced that there are native Zn$_i$ and V$_o^+$ donors and V$_{Zn}$ acceptor in the as-grown and annealed ZnO films and the conductive behavior of the undoped ZnO films is determined by competition between

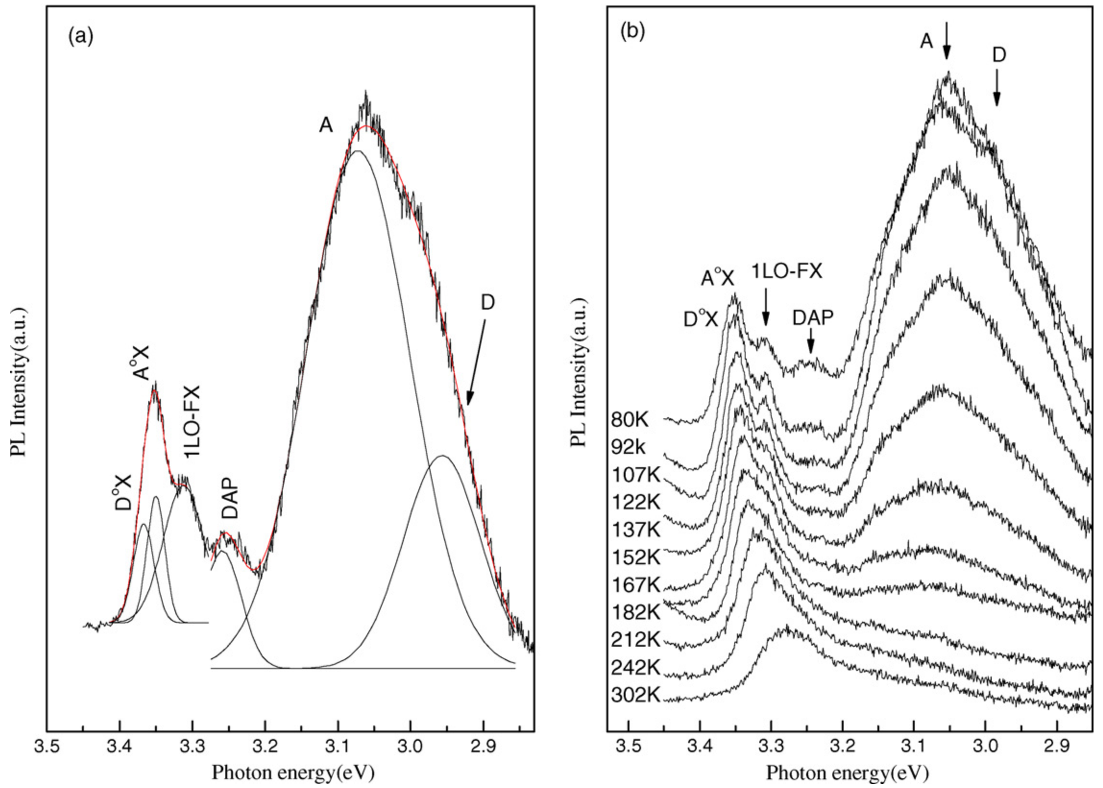

Fig. 6. Eighty-two Kelvin PL spectrum (a) and temperature-dependent PL spectra (b) of the undoped p-type ZnO film annealed for 1 h at 863 K under 10^{-3} Pa.

the Zn_i, V_o^+ and V_{Zn}. Electrons come mainly from Zn_i donors for the ZnO film obtained in the low annealing temperature range, but from V_o^+ donors for the ZnO film obtained in the high annealing temperature range. Since the concentration of the Zn_i decreases with increasing annealing temperature, while the V_o^+ appears at 773 K and its concentration begin to increase obviously with increasing annealing temperature from 863 K. Therefore, it is suggested that the amount of electrons decrease with increasing annealing temperature first and reach minimum near 863 K and then increase, so that the amount of the electrons in the 863 K-annealed ZnO may be not enough to compensate the holes generated from the ionized V_{Zn}, leading to formation of a p-type ZnO.

4. Conclusions

The insulating undoped ZnO films were deposited on a quartz substrate by using the magnetron sputtering technique with the high pure ZnO disc as the target and the high pure Ar as sputtering gas. It goes through a conductivity transformation from insulating, to n-type, weak p-type, p-type and finally n-type as annealed for 1 h in a temperature range of 513–923 K under 10^{-3} Pa. An undoped Zn-rich p-type ZnO film was produced reproducibly at annealing temperature of 863 K. There are native Zn_i and V_o^+ donors and V_{Zn} acceptor in the as-grown and annealed ZnO films and the amount of electrons may decrease with increasing annealing temperature first and reach minimum near 863 K and then increase. Formation of the p-type ZnO is attributed to that the amount of the electrons from the Zn_i and V_o^+ donors in the 863 K-annealed ZnO may be not enough to compensate the holes generated by ionized V_{Zn}.

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