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Effect of sputtering parameters on photoluminescence properties of Al doped ZnO films deposited on Si substrates

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Abstract

Al-doped ZnO (ZnO:Al) films were deposited on glass and Si substrates using radio frequency reactive magnetron sputtering technique. Crystal structure, surface morphology and optical properties of ZnO:Al films on the different substrates were studied. Subsequently, effects of sputtering parameters, such as the substrate temperature, annealing temperature, sputtering power and ratio of oxygen to argon gas flow, on photoluminescence (PL) properties of ZnO:Al films on Si substrates were systematically investigated. The results indicated that high substrate temperature will create more defects resulting in the Auger effect and then the quenching of the light emission in ZnO films. However, annealing treatment and appropriate sputtering power can improve light emission efficiencies. ZnO:Al thin films grown on Si substrates are very important for improving the efficiencies of optoelectronic devices fabricated utilizing ZnO/Si heterostructures.

Keywords: C. Optical properties; ZnO:Al thin films; Magnetron sputtering

1. Introduction

ZnO is a II–VI semiconductor with a wide and direct band gap (E_g ~3.37 eV at 300 K), excellent chemical and thermal stability, and specific electrical and optoelectronic property of having a large exciton binding energy (~60 meV) [1]. Such properties can be applied to transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, and thin film transistors [2,3]. Moreover, Al-doped ZnO (ZnO:Al) thin films have attracted a great deal of interest from suitable electrodes because ZnO thin films are more stable in a reductive ambient atmosphere [4]. Likovich et al. [5] investigated optically active surface defects in sputtered ZnO:Al films using scanning tunneling microscope cathodoluminescence (STM-CL). Banerjee et al. [6] reported optical properties of ZnO: Al films with various Al doping. Li et al. [7] study the effects of different substrates on the structural, electrical and optical properties of the ZnO:Al films. However, because the Al dopants typically have a large affinity with O atoms rather than Zn atoms during the growth process of the ZnO:Al films, faulted oxide results, which degrade the physical properties of the thin films. Generally, the electrical and optical properties of ZnO:Al films were improved by post-annealing treatment [8]. Our previous results have also indicated that intense blue emission of ZnO:Al can be obtained by appropriated Al doping or sputtering power [9]. In addition, ZnO:Al thin films grown on Si substrates are very important for improving the efficiencies of optoelectronic devices fabricated utilizing ZnO/Si heterostructures [10]. However, there have been only a few studies on the systematical effect of the sputtering parameters, such as the substrate temperature, annealing temperature, sputtering power and ratio of oxygen to argon gas flow, on the photoluminescence (PL) properties of Si substrates ZnO:Al films in detail.

In this paper, ZnO:Al thin films were deposited on glass and Si substrates using the radio frequency magnetron sputtering technique. The comparison of Si substrates ZnO:Al films with glass substrates ZnO:Al films and the effect of the sputtering power on the structural and optical properties of Si substrates ZnO:Al films were investigated. The crystal structures, surface morphology and optical properties of ZnO:Al thin films were investigated by X-ray diffraction (XRD) patterns, atomic force microscopy (AFM) images and PL spectra.

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2. Experiments

High-purity Zn target (99.999%, 60 mm in diameter), glass (Corning 7105) and p-Si (100) substrates were used in the experiments. The distance between target and substrate was 50 mm. Before loading into the radio frequency sputtering chamber, the Si substrates were ultrasonically cleaned with acetone and alcohol in sequence for 15 min, then dipped into the diluted hydrofluoric acid solution (5%) to remove a native oxide layer on them, and finally rinsed with distilled water and dried in nitrogen. The sputtering chamber was evacuated to 2×10^{-4} Pa prior to the introduction of the Ar and O_2 gas mixture. The Zn target was pre-sputtered in pure Ar for 10 min to remove surface contamination and maintain system stability. The reactant pressure was maintained at 1 Pa. To study the effects of sputtering parameters on the PL properties of ZnO:Al films deposited on Si substrates, different substrate temperature of room temperature (RT), 150, 250 and 350 °C, annealing temperature of 300, 450 and 600 °C, sputtering power of 50 W, 100 W, 150 W and 200 W, and ratio of oxygen to argon gas flow of 2:10, 6:10, 10:10 and 14:10 sccm have been used during the magnetron sputtering. ZnO:Al films deposited on glass substrates were deposited at substrate temperature of 150 °C, sputtering power of 100 W, the ratio of oxygen to argon gas flow of 6:10 sccm. ZnO:Al films deposited on glass and Si substrates were compared under the same sputtering conditions.

XRD patterns were studied by a D/Max-2400 X-ray diffractometer using the Cu Ka radiation with $\lambda=0.15406$ nm. AFM images were characterized by a SPM-9500 atomic force microscope. PL spectra were carried out by a LS-55 fluorescence spectrometer. The excitation source used in PL was a Xe laser operating at 325 nm. The emitting light from the sample was focused into the entrance slit of a monochromator. This was picked up by photomultiplier tube. All the optical measurements were performed in air at room temperature.

3. Results and discussions

Fig. 1 shows the XRD patterns of samples deposited on (a) glass and (b) Si substrates. Both strong (002) and very weak (004) peaks were observed for both samples. Meanwhile, there is also weak (100) diffraction peak in the Si-substrate ZnO:Al film. However, the intensity of (004) and (100) diffraction peaks was very weak compared with that of (002) diffraction peak, indicating a preferential *c*-axis orientation of the ZnO:Al films deposited. Park et al. [11] reported that highly *c*-axis oriented ZnO films can be applied to acoustic-wave devices. In addition, it was clear from Fig. 1 that both 2θ positions of the (002) diffraction peak were smaller than that of standard ZnO powder ($2\theta=34.42°$ [12]), and the diffraction angle of ZnO:Al (002) shifted to a lower angle compared with Si substrate ZnO:Al film.

The particle size of the films deposited on glass and Si substrates was 8.9 nm and 13.3 nm, respectively, which was calculated using the Scherrer equation [13]

$$D=\frac{0.9\lambda}{\beta\ \cos\ \theta} \tag{1}$$

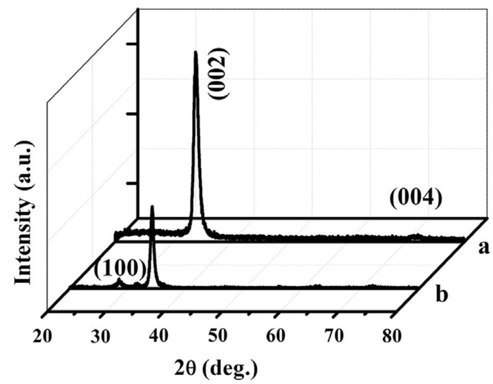

Fig. 1. XRD patterns of ZnO:Al deposited on (a) glass and (b) Si substrates.

where λ, θ and β are the X-ray wavelength (0.15406 nm), diffraction angle and FWHM of the ZnO:Al (002) peak, respectively.

The lattice constant c of the films deposited on glass and Si substrates, which could be calculated by Bragg formula, was 0.5302 and 0.5251 nm, respectively. It was found that all c values were larger than that of standard ZnO powder c_0, which is equal to 0.5206 nm [14], implying relaxation of the residual stress introduced in the films during the deposition process [15]. The calculation of the film stress is based on the biaxial strain model. The following formula is used, which is valid for wurtzite structure ZnO [16]:

$$\sigma=-233(c_0-c)/c_0\mathrm{Pa} \tag{2}$$

Where c is the lattice constant of ZnO:Al film, c_0 is the lattice constant of standard ZnO powder. According to Eq. (2), the sputtered ZnO:Al films exhibited compressive stress. And the compressive stress of the films deposited on glass and Si substrates was 4.30 and 2.01 Pa, respectively. These results, together with the full width at half maxima (FWHM) of the glass substrate ZnO (002) peaks increased, implying that the preferred orientation, lattice stress and particle size were influenced by different substrates.

Fig. 2 shows the morphology of ZnO:Al films deposited on (a) glass and (b) Si substrates. The images are obtained in contacting mode taken over a scale of $5\times5\ \mu m^2$. The root mean squares of the average surface roughnesses of ZnO:Al films deposited on glass and Si substrates are 6.571 nm and 5.210 nm, respectively. The relatively small surface roughness and large grain size growth might be ascribed to the smooth Si substrate surfaces.

Fig. 3 shows the PL spectra of samples deposited on (a) glass and (b) Si substrates. Three emission peaks (at 435 nm, 488 nm and 530 nm) were observed from the glass-substrate ZnO:Al film whose intensity became weak and the blue center at 435 nm red shifted to 449 nm when deposited on Si substrates under the same conditions. The blue peak occurred at about 435 nm whose corresponding phonon energy was about 2.86 eV. Thus according to Xu's results [17] the blue emission peak may be assigned to the electron transition from the electron transition from the Zn interstitial levels to the top of the valence band (2.9 eV).

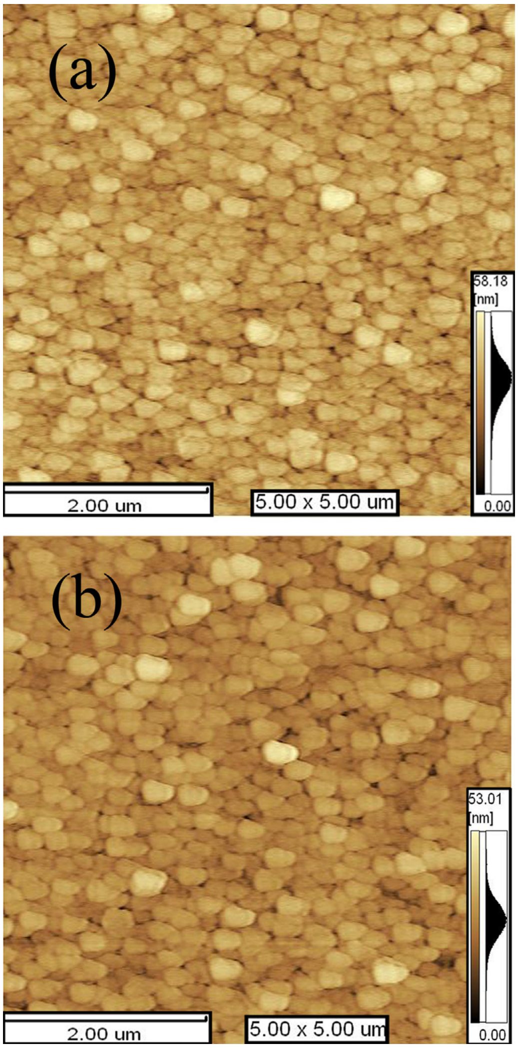

Fig. 2. AFM images of ZnO:Al deposited on (a) glass and (b) Si substrates.

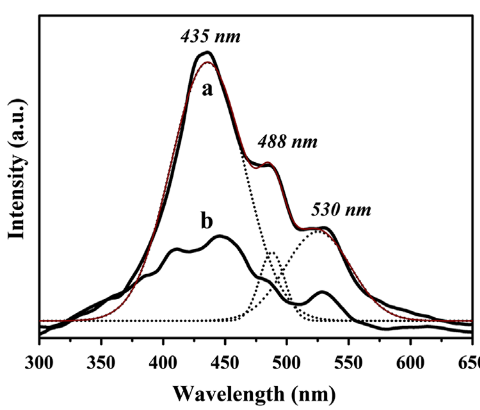

Fig. 3. PL spectra of samples deposited on (a) glass and (b) Si substrates.

However, as we mentioned above, ZnO:Al thin films grown on p-Si substrates are very important for improving the efficiencies of optoelectronic devices fabricated utilizing ZnO/Si heterostructures. In order to further investigate the optical properties of Si substrates ZnO:Al films, the effects of the substrate temperature, annealing temperature, sputtering power and ratio of oxygen to argon gas flow on the PL properties of Si substrates ZnO:Al films were studied.

Fig. 4 shows PL spectra of Si substrates ZnO:Al films at different substrate temperatures: (a) RT, (b) 150 °C, (c) 250 °C and (d) 350 °C. At a low substrate temperature (RT), PL spectrum exhibits a maximum blue peak at 440 nm whose intensity initially decreased (150 °C) and then increased (250 °C and 350 °C) as the substrate temperatures increased. The possible reason is that high substrate temperature will create more defects such as oxygen vacancies, more oxygen vacancies may cause a carrier concentration increase, thus resulting in the Auger effect and then the quenching of the light emission in ZnO films. In addition, peak at 408 nm red shift to 420 nm, while peak at 486 nm has almost no observable change with the increase of substrate temperature. Zhu et al. [18] observed near band edge (NBE) emission at around 390 nm (3.18 eV) when substrate temperature is 200 °C and no PL peaks are observed in other samples. In addition, in our experiment, it clearly shows that as the substrate temperature increase, one main emission center can be divided into three emission centers, which is important for creating a high-performing photoelectric devices.

Fig. 5 shows PL spectra of Si substrates ZnO:Al films at different annealing temperatures: (a) un-annealed, (b) 300 °C, (c) 450 °C and (d) 600 °C. A major emission peak located at 443 nm was observed from PL spectrum in un-annealed sample. It is clear

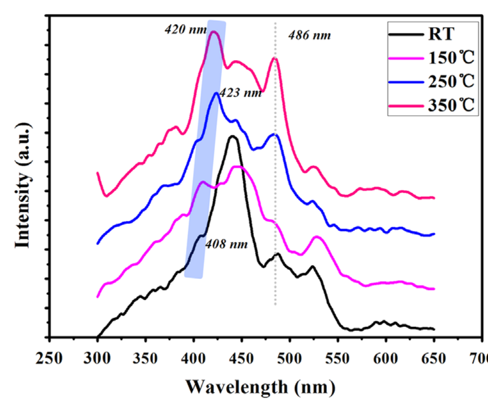

Fig. 4. PL spectra of Si substrates ZnO:Al films at different substrate temperatures.

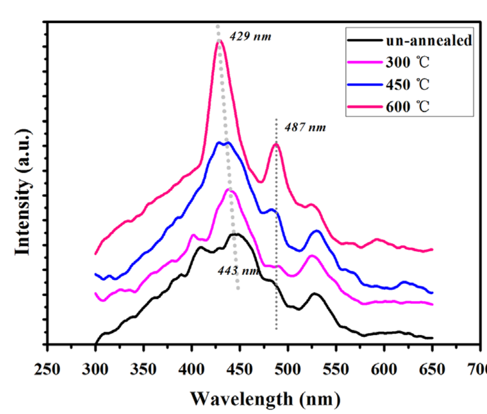

Fig. 5. PL spectra of Si substrates ZnO:Al films at different annealing temperatures.

that the intensity of the blue peak increases and blue center blue shifted continuously to 429 nm after annealing at 600 °C. According to our previous report [19,20], blue emission peak at 443 (2.8 eV) and 429 nm (2.9 eV) may be assigned to the electron transition from the Zn interstitial levels to both the Zn vacancies levels (2.6 eV) and the top of the valence band (2.9 eV). It was well known that with the increment of annealing temperature the oxygen vacancies and Zn interstitials will increase. Meanwhile, Zn vacancies will decrease due to charge equilibrium. So the blue shift of the blue peak from 443 nm (2.8 eV) to about 429 nm (2.9 eV) after annealing treatment is considered to be associated with the increment of Zn interstitials.

Fig. 6 shows PL spectra of Si substrates ZnO:Al films deposited at different sputtering power: (a) 50 W, (b) 100 W, (c) 150 W and (d) 200 W. Three main emission peaks located at 427 nm, 480 nm and 530 nm were observed from PL spectra whose intensity initially decreased (100 W) and then increased (150 W and 200 W) as the sputtering power increased. The most intense blue luminescence (427 nm) was obtained from a sample grown at 150 W. However, the position of emission peaks had almost no observable change when the sputtering power increased. It is noted that as the sputtering power is 100 W, peak at 427 nm disappears and there occur two emission peaks at 408 nm and 447 nm. This is different from previous report. Prabakar et al. [21] observed that PL spectra intensity increased markedly with the sputtering power.

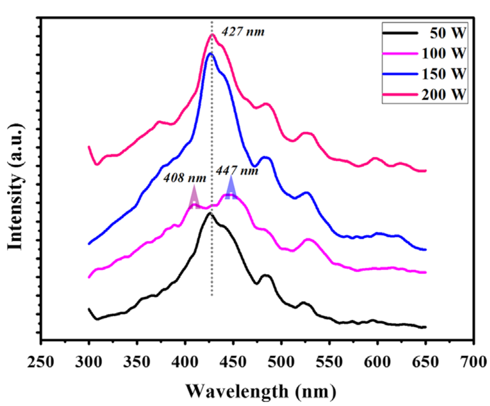

Fig. 6. PL spectra of Si substrates ZnO:Al films at different sputtering power.

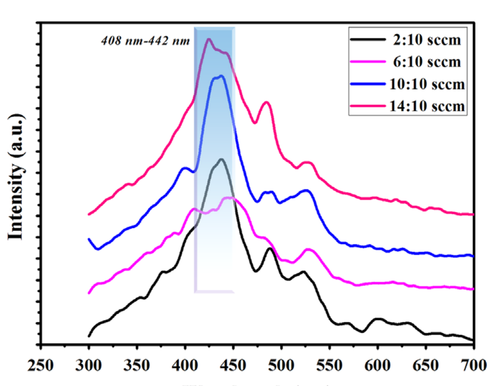

Fig. 7. PL spectra of Si substrates ZnO:Al films at different ratios of oxygen to argon gas flow.

Fig. 7 shows PL spectra of Si substrates ZnO:Al films at different ratios of oxygen to argon gas flow: (a) 2:10 sccm, (b) 6:10 sccm, (c) 10:10 sccm and (d) 14:10 sccm. A minimum PL band at 408–442 nm was obtained at 6:10 sccm, while at other ratios of oxygen to argon gas flow PL spectra shows a similar intensity. However, Hu et al. [22] found that the film with O_2: Ar = 0.4 had the highest luminescence efficiency.

Combined with above experimental results, we suggest that high substrate temperature will create more defects resulting in the Auger effect and then the quenching of the light emission in ZnO films. However, annealing treatment and appropriate sputtering power can improve light emission efficiencies. ZnO:Al thin films grown on Si substrates are very important for improving the efficiencies of optoelectronic devices fabricated utilizing ZnO/Si heterostructures.

4. Conclusions

ZnO:Al films were deposited on glass and Si substrates using radio frequency reactive magnetron sputtering technique. ZnO:Al films deposited on glass and Si substrates were compared under the same sputtering conditions. Three emission peaks (at 435 nm, 488 nm and 530 nm) were observed from the glass-substrate ZnO:Al film whose intensity became weak and the blue center at 435 nm red shifted to 449 nm when deposited on Si substrates under the same conditions. In order to further investigate the optical properties of Si substrates ZnO:Al films, the effects of the substrate temperature, annealing temperature, sputtering power and ratio of oxygen to argon gas flow on the PL properties of Si substrates ZnO:Al films were studied. The results indicated that the high substrate temperature will create more defects resulting in the Auger effect and then the quenching of the light emission in ZnO films. However, annealing treatment and appropriate sputtering power can improve light emission efficiencies. ZnO:Al thin films grown on Si substrates are very important for improving the efficiencies of optoelectronic devices fabricated utilizing ZnO/Si heterostructures.

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