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Effects of annealing on excitonic properties of sputtered ZnO films at room temperature

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ZnO films have been deposited on quartz glasses by RF magnetron sputtering. The optical and structural properties of the ZnO films were studied. It was found that annealing the ZnO films in oxygen dramatically improved the optical properties. Excitonic absorption features were observed in the annealed ZnO films at room temperature. The excitonic absorption peaks were deconvoluted to three peaks, A-, B- and C-excitons resonance peaks. The stress inside the ZnO films changes those resonance peaks positions.

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1. Introduction

ZnO is a wide-bandgap II-VI semiconductor with a large exciton binding energy of about 60 meV. The large exciton binding energy makes excitons stable even above room temperature and ensures the applications of ZnO in exciton-related optoelectronic devices at room temperature or even higher[1,2]. Usually, the recombination processes of excitons are found in ZnO film with high optical quality, grown by MBE[3] or MOCVD[4] on sapphire substrates, for exciton is a sensitive indicator of material quality[5]. However, there has been considerable interest in the growth of high-quality ZnO on glass or SiO_2/Si substrates because of its low cost and potential for the integration of ZnO-based devices with other Si-based devices. The quality of ZnO films is not only determined by the growth process, but also by postdeposition treatment conditions. Postannealing treatment, when carried out in suitable conditions, is a conventional and effective technique to reduce intrinsic defects and to improve the quality of ZnO film [6-9].

A study on the postannealing to improve the quality of ZnO films deposited by radio frequency (RF) magnetron sputtering should be a subject of great interest and need an extensive research, in view of the popularity and convenience of the RF magnetron sputtering to grow ZnO thin films. In this study, we deposited the ZnO films on the quartz glasses substrates using the RF magnetron sputtering and investigated the effect of annealing process on the structural and optical properties of the ZnO thin films.

2. Experimental procedure

The ZnO films were deposited on the quartz glasses substrates by RF magnetron sputtering using a ZnO target (99.99%) in mixture gas of Ar (99.99%) and O_2 (99.99%) with Ar/O_2 ratio of 2:3. During film deposition, the RF power was 100W and the total pressure was maintained at 1Pa. Substrate temperature was kept at 300℃. The sputtering time was 20 minutes. Some samples were annealed in a quartz tube furnace at three different temperatures: 500, 700 and 900℃and these samples were labeled as T1, T2, and T3, respectively. Accordingly, the asgrown sample is labeled as T0. When the furnace was heated to each selected temperature, the sample was put into the quartz tube and held at the temperature for 60 minutes, and then the furnace was cooled to room temperature. During the samples annealing, O_2 (99.99%) gas was flowing into the quartz tube with flow rate of 1000 sccm. The crystal structures properties of the films were investigated by using a Panalytical X-pert x-ray diffractometer (XRD) in θ-2θ configuration with a monochromatic Cu Kα (λ = 0:15406 nm) radiation. The transmission spectra of the samples were measured with a Varian Cary-300 spectrophotometer within the range from 300 nm to 800 nm at room temperature in air.

3. Results and discussion

The transmission spectra at room temperature for the sample T0 and T3 are shown in Fig.1. The interference fringes in the transmission before the absorption edge are

due to the interference between the air/ZnO/glass interfaces. The uniform nature of the transmission spectrum indicates that light is not being scattered by a rough surface morphology or inhomogeneous interfaces. The room temperature absorption edge of the annealed films is quite distinct as compared with the as grown film. In the inset the exciton resonance is visible and it is apparent that the signal to noise ratio for the transmission spectrum is good.

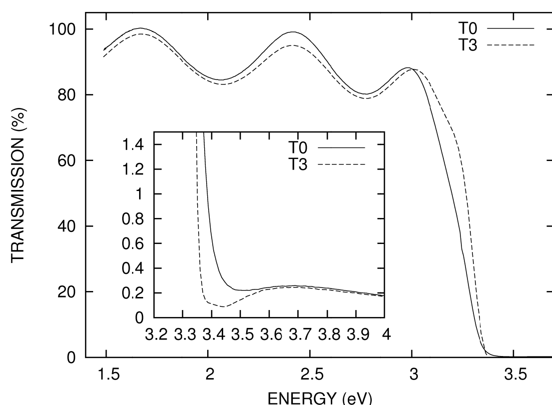

Fig. 1. Transmission spectra of the samples: T0 and T3.

The calculated absorption coefficients for the annealed and unannealed films at room temperature are shown in Fig.2. The optical absorption coefficient α is defined by the transmission spectra[10]. At room temperature, a clear excitonic absorption peak is observed at about 3.3 eV. Excitonic absorption peak has been found by Makino et al. for undoped-ZnO epilayers grown by the Laser-Molecular -Beam-Epitaxy(L-MBE) method on lattice -matched $ScAlMgO_4$ substrates[11]. Muth et al. and Tang et al. also reported a similar excitonic absorption peak for ZnO films that were grown on sapphire substrates using PLD[5] and L-MBE[12]. However, there has been no report on observation of room temperature excitonic absorption from ZnO films grown on glass by RF magnetron sputtering. The presence of room temperature exciton absorption peaks is a good indication that our samples have high optical quality.

The broad asymmetric shape of the excitons absorption peaks at room temperature may be attributed to the coupling of A-, B- and C-excitons resonance[5,13]. The absorption spectra from sample T2 and T3 were fitted using Gaussian approximations in MATLAB^{TM}. Three Gaussian peaks were required to deconvolute the measured excitons absorption spectrum by varying the amplitude and peak position. The deconvoluted peaks are A-, B- and C-excitons peaks, as shown in Figs.3 and Fig.4, respectively. The peak positions are shown in Table 1, as compared with the value given in reference[5].

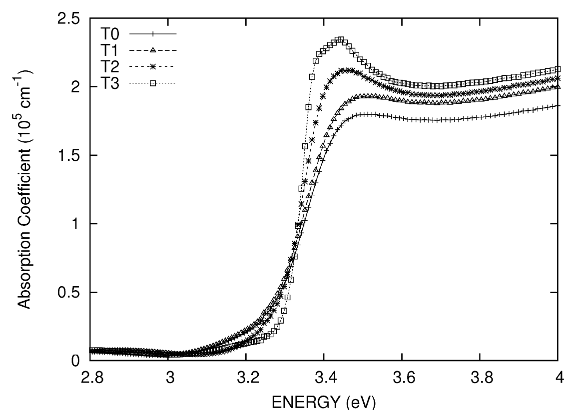

Fig.2. Absorption coefficient and excitonic structure for annealed and unannealed samples at room temperature.

Table 1. Exciton position and the compressive stress for the annealed samples.

	A-	B-	C-exciton	Stress(10^{10}dyn/cm^2)
T2	3.33	3.40	3.59	0.65
T3	3.36	3.41	3.54	0.82
Ref.5	3.40	3.45	3.55	-

There is a difference of the peaks positions for the A-, B- and C-exciton between our sample and the reference [5]. This difference may come from the strain inside the ZnO films[14]. The magnitude of strain generated between the ZnO films and the substrate can be experimentally estimated by determining the lattice constants with an X-ray diffraction technique. The XRD patterns of the asgrown and annealed ZnO films are shown in Fig. 5. The as-grown films are highly c-axis orientation. Its XRD pattern shows a strong ZnO (002) diffraction peak at around 34.4°, which characterizes the hexagonal wurtzite structure of ZnO crystal, and a weak ZnO (103) diffraction peak. The other samples also show a strong ZnO (002) diffraction peak. As the annealing temperature increase, so does the intensity of the (002) diffraction peak, which indicated the ZnO crystal grains grow up during the annealing. Annealing also intensifies the c-axis preferred orientation for the film by the recrystallinity process, so sample T3 only show a sharp (002) diffraction peaks.

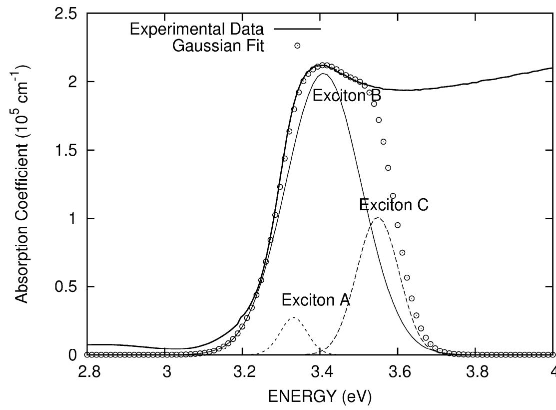

Fig.3. Gaussian fit for room temperature excitons absorption peaks of ZnO thin films annealed at temperatures 700℃.

The shift of the diffraction peak position from it powder value (34.42°) is mainly associated with tensile strain produced within the film and the substrate. The peak positions of all films are larger than the powder value, indicating that films are in a state of stress with compressive components parallel to c axis. The strain is given by $(c_0-c)/c_0$, where c is the lattice constant obtained from the strong(002) reflection

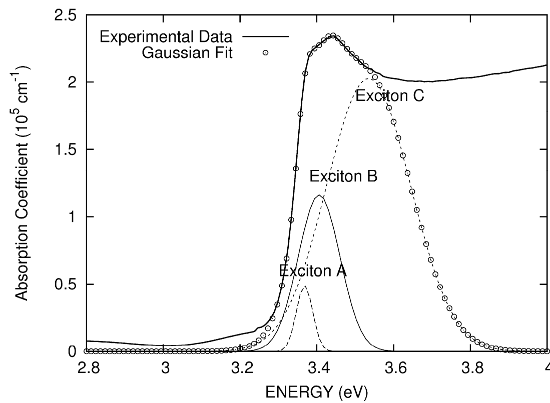

Fig. 4. Gaussian fit for room temperature excitons absorption peaks of ZnO thin films annealed at temperatures 900℃.

in the x-ray diffractometer and the corresponding value for power ZnO, c_0, is 5.205Å. The stress in the plane of the film is[15]

$$\sigma = [2C_{13} - C_{33}(C_{11} + C_{12}) / C_{13}](c - c_0) / c_0 \qquad (1)$$

The values of the stiffness constants for ZnO are C_{11} = 2.097^{12}*dyn*/*cm*^{2}, C_{12} = 1.211^{12}*dyn*/*cm*^{2}, C_{13}=1.051^{12}*dyn*/*cm*^{2} and C_{33}= 2.109^{12}*dyn*/*cm*^{2} [16]. The value of the stress is given in Table 1. The stress is much less than the value given by reference[17] and [18]. The lower stress in our films makes the perfection crystallites of ZnO during growth. Some author have proposed the dependence of the exciton peaks position with strain at room temperature [19-21], but this relation can not explain the diversity of the exciton peaks positions in our samples. More detailed investigations about the diversity of the peaks positions are under way in our group.

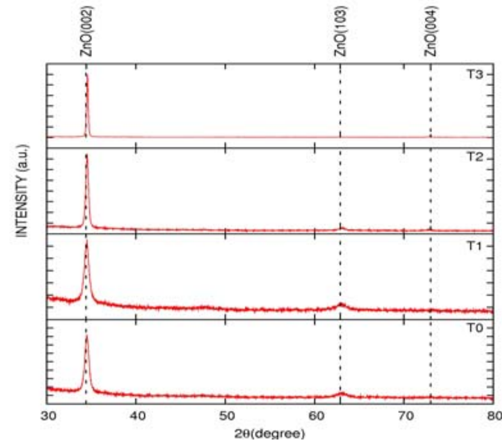

Fig. 5. XRD line profile.

4. Conclusions

In conclusion, transmission measurements and absorption spectra were used to investigate the excitonic structure of high quality ZnO films grown on glass substrates by RF magnetron sputtering. It was found that the excitonic structure was useful in investigating and quantifying the effects of annealing on the quality of ZnO films. The postdeposition annealing in oxygen improved the excitonic features in ZnO films. These results indicate that RF magnetron sputtering and postdeposition annealing are viable techniques to produce high quality ZnO films for optical devices.

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