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Effect of annealing treatment on structure of Ag doped ZnO films deposited by thermal evaporation method

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Abstract. The Ag doped ZnO films were prepared on sapphire substrates using simple thermal evaporation method. The effect of annealing treatment was investigated in detail. The results shows that the annealed Ag doped ZnO film has a prefer orientation along c-axis. The E_2 (high) mode in Raman spectra has a little blue shift which caused by crystal defects oxygen vacancies, meanwhile the compressive stress was exist in the film. After annealed, the intense of E_2 modes have great improvement which means the quality of the film was enhanced, meanwhile, the compressive stress released to some extent.

1. Introduction

Zinc oxide (ZnO) as a Ⅱ-Ⅵ semiconductor material, can be widely used in many fields, for instance nanogenerators [1-2], light-emitting diode (LED) [3-4], photodetectors [5], solar cells [6] and gas sensors etc [7-9]. As well known, because of the native defects such as interstitial zinc or oxygen vacancy ZnO expression n-type electrical conductivity, the application of ZnO based devices need both n-type and p-type ZnO. It is not easy to synthetise stable and reproduce p-type ZnO. Doping in ZnO with suitable elementary substance such as group Ⅴ(N,P,As and Sb), Group IB (Ag and Cu) can solve this problem efficiently [10]. Theoretical study has point out that based on its size and energy level, Ag can occupy the Zn site or interstitial to achieve p-type doping [11]. The studies also point out that Ag doping can adjust optical and electrical properties of ZnO thin films [12-14]. So it is necessary to synthesised stable and reproduceable Ag doped ZnO films [15-18].

Due to the different melting point, it is difficult to deposit Ag doped ZnO films (AZF), in this paper, we synthesised AZF using simple thermal evaporation method, and the effect of annealing treatment was studied by the image of scanning electron microscopy. Annealing treatment can improve the crystal quality to some extent; meanwhile it can make the dopant more effective.

2. Experiment

The AZF were deposited on sapphire substrates by thermal evaporation method. The substrate was cut into small pieces (1cm×1cm) then ultrasonically cleaned in acetone and ethanol for ten minutes, cleaning by deionized water repeatedly and subsequently dried in N_2 gas flow. The deposited process

was divided into three steps: First, the metal Ag was used as vapour source deposited on sapphire substrate by using vacuum coating equipment (DM-300B). Secondly, the Zn film was deposited on Ag film using the same equipment. Finally, the samples were put into a horizontal tube furnace for oxidize. The furnace was heated into 400℃ for 60 minutes under constant flow of oxygen (100sccm). The diagram was shown in Figure 1. After oxidation, the AZF were annealed at 700℃ in oxygen ambient with flow rate of 100 sccm for 40 minutes, and then the AZF before and after annealed were obtained. The crystal structure properties of the samples were evaluated by X-ray diffraction (XRD). Surface morphology was observed by scanning electron microscope (SEM) and the optical properties of AZF were carried out using Raman spectra.

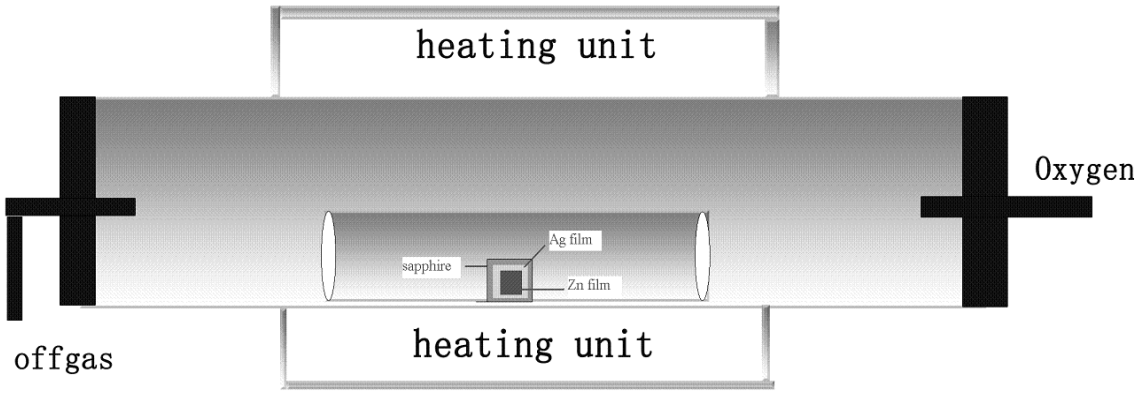

Figure 1. The illustration of experimental system.

3. Results and discussion

The surface morphology of Zn film marked as sample *a*, AZF heating at 400℃for 60 minutes marked as sample *b* and AZF annealed in oxygen for 40 minutes marked as sample *c* were shown in Figure 2a, b and c. The Zn film was composed of irregular pieces with many nanowires on the edge out of order. After oxidize sample *b* was composed of small grain arranged in order. There are also little small hole on the surface of the film, the amount of nanowires was reduced rapidly. As well known, the stand ZnO film was compact and normalizes, however due to Ag doping, there little changes in the surface ZnO film. When annealed in O_2, the film exhibit different feature: compact, regular grains mixed with little holes, only a few nanowires were found on the surface which indicates that after annealing treatment, the crystal quality have a great improvement.

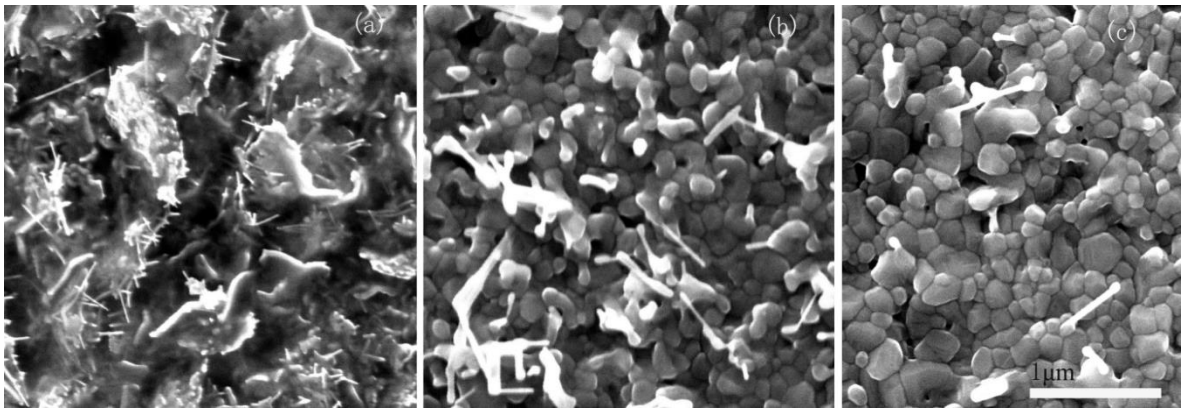

Figure 2. SEM image of Zn film(a); AZF heating at 400℃ for 60 minutes(b); AZF after annealed(c).

The XRD pattern of sample *b* and *c* were shown in Figure 3. There are seven peaks arrives at 31.63º, 34.33º, 36.18º, 62.75°, 65.08°, 72.57° and 78.18º respectively which corresponding to ZnO(100), (002), (101), (103), (200), (004) and (202) peak [19]. There are no phases caused by Ag oxides can be observed from the pattern. Among the seven peaks, ZnO (002) peak have a strong intense which means the sample have prefer orientation, the same orientation of c-axis which normal to the substrate. After annealing treatment, only ZnO (002) peak located at 33.95° with great intense could be found, this means the quality of the film have a great improvement. Compare with stand ZnO film (002) peak which located at 34.42º, both of the two samples have a slight shift to lower 2θ direction, this may be caused by the Ag doping, the exist of Ag atom affect the fabrication of ZnO film, this is consistent with SEM result. As we know the radius of Ag^{+} was 0.102nm bigger than the radius of Zn^{2+} which was 0.056nm[20], if Ag^{+}substitutes on Zn^{2+} sites, the 002 peak will shift to lower 2θ direction. The shift of sample *c* was bigger than sample *b*, which means after annealed more Ag^{+} was substitute Zn^{2+} sites[21], this may due to the annealing treatment, during the annealing process the Ag layer permeate into ZnO films, so the 002 peak shift more.

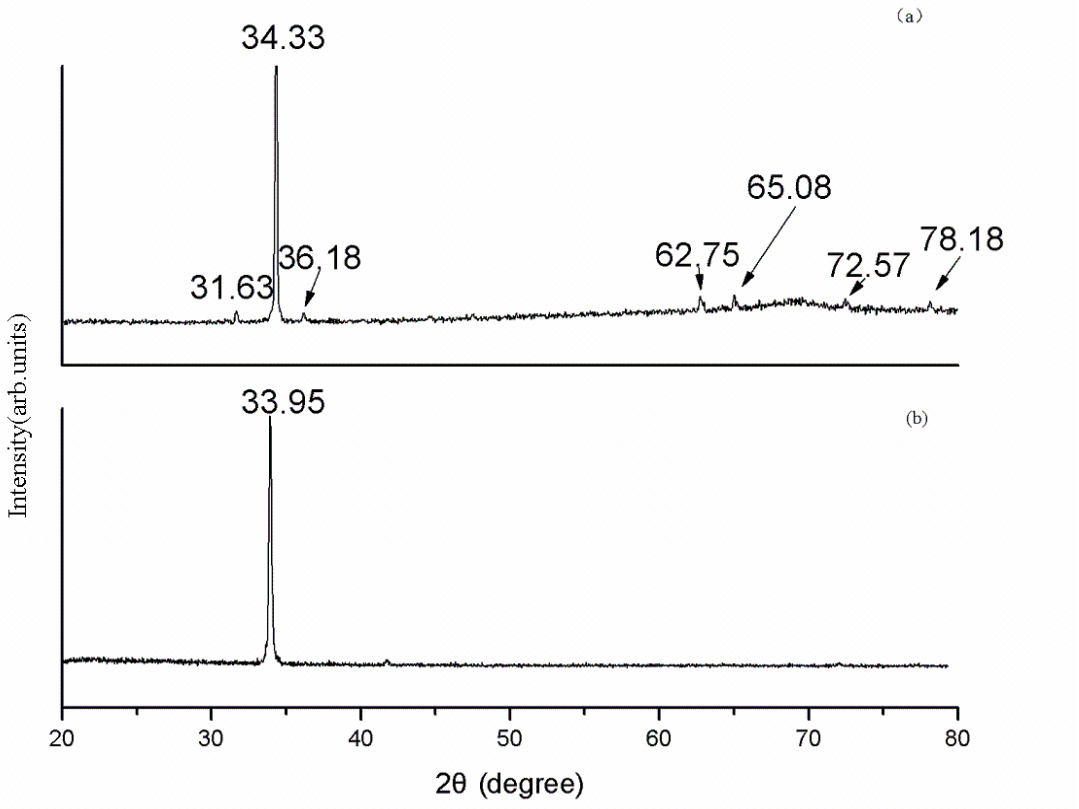

Figure 3. The XRD pattern of AZF before (a) and after (b) annealing.

Figure 4 shows the Raman spectrum of AZF before and after annealed. The six Raman active modes in ZnO crystal are $2E_1$, $2E_2$, $2A_1$. According to selection rules, only three of them can be observed from unpolarized Raman spectra which were E_2 (low), E_2 (high) and A_1 (LO). The Rman frequencies of the three modes were located at 101, 437 and 574 cm^{-1}, respective [22]. The E_2 (low) mode which associated with the vibration of the heavy Zn sublattice [23-25] and E_2(high) mode which associated with oxygen atoms appear at 96.03 cm^{-1} and 439.06 cm^{-1} could be clearly observed from Figure 4(a) respectively. The other six Raman peaks were from the sapphire substrate. Compare with stand ZnO, the E_2 (high) mode have slight shift to higher frequency direction, two reasons may be responsible. One is the crystal defect oxygen vacancies give rise to the lattice distortion, another one is

the sample was under compressive stress. Because of the sensitivity on stress, E_2 (high) mode always used to explain the situation of stress in films, under compressive stress the Raman frequency would have shift to higher direction [26]. After annealing treatment, the intense of the E_2 (low) and E_2 (high) modes enhance a lot, the intensity of E_2 modes have strong relationship with crystal quality, the great intense of E_2 modes indicated the perfect crystal quality [27].Compare with as deposited Ag doped ZnO film, the E_2 (high) mode showed 1.75 cm^{-1} red shift, which means the compressive stress in the film release to some extent. From Figure 4 we can deduce that the annealing treatment improve the crystal quality of the film and make the compressive stress released.

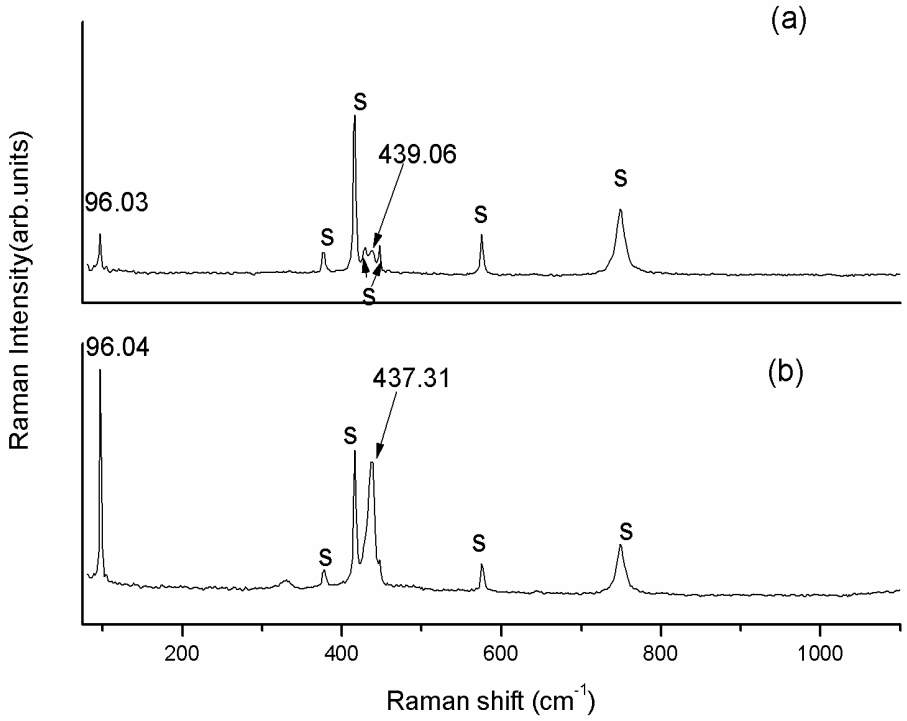

Figure 4. Raman spectra of AZF before(a) and after(b) annealing.

4. Conclusion

In summary, the Raman spectra of AZF before and after annealing treatment were deposited by simple thermal evaporation method on sapphire substrates. The effect of annealing treatment was investigated. The SEM image shows that after annealed the film was more compact, and the nanowires on the surface were reduced. The XRD results tell that the film was grown along c-axis and the Ag doping effect the fabrication of the film. Raman spectrum give information about the crystal quality, the film has perfect wurtzite structure and there was compressive stress in the film, after annealed, the stress was released to some extent.

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