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Morphological and Optical Characterization of Post-annealed ZnO Films prepared by Sol-Gel Method

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Transparent zinc oxide (ZnO) films have been prepared by sol –gel method using spin coating method on quartz glass from 0.5M zinc acetate 2-methoxyethonal solution, and using monoethanolamine(MEA) as stabilizer. The as-prepared samples were heat-treated at 550°C for 90min in air, oxygen and vacuum ambient, respectively. XRD patterns show that the prepared samples exhibit wurtzite structure, the sample annealed in O_2 has best crystalline quality and biggest degree of preferential orientation of (002) plane, and the sample annealed in vacuum nearly has no preferential orientation. It can be found from AFM images that surface roughness of the three films are: Vacuum > air > O_2. The sample annealed in O_2 has rod-like and uniform particles, the sample annealed in air with ball-like particles and sample heat treated under vacuum ambient with ball-like uniform particles. PL analysis tells that vacuum atmosphere leads to more oxygen vacancy (VO) and zinc excess, however annealed in O_2 can decrease the oxygen vacancy (VO) and zinc excess obviously. The band gap of prepared ZnO films is about 3.3eV from PL spectra. Through analyze the UV-Vis result, it can be found that the surface morphology does influence the absorptance. Generally speaking, the annealed ambient influences the intrinsic defect and extrinsic defect, and then influence the properties of prepared ZnO films.

Key words: Znic oxide film, Sol-gel method, post anneal, atmosphere.

1. INTRODUCTION

In recent ten years, much effort has been devoted to study on ZnO film due to its potential optoelectronic applications, such as short-wavelength lasers, light-emitting diodes[1] and varistors[2]. The excellent optoelectronic properties of ZnO film attribute to its wide direct band gap (~3.4eV) and large exciton binding energy (60meV, compared with GaN, ~25meV)[3]. Molecular-beam epitaxy (MBE)[4], pulsed-laser deposition (PLD)[5], chemical vapor deposition[6,7] and sputtering[8,9] are the most commonly used techniques for ZnO preparation. While these method have disadvantages of a relative low deposition rate and a high cost for equipment. Recently, sol-gel method which is considered to be a flexible, a low cost and a flexible method have been published to prepare ZnO film[10]. Such as, very recently, Cao et al[11] have co-doped N and In into ZnO film by sol-gel method, and yielded a P-type ZnO.

Ohyama et al[12] have found that the electrical conductivity of ZnO is due to intrinsic defect and extrinsic defect such as oxygen vacancies and zinc excess, and achieved the lowest resistivity value (6.5×10-3Ω·cm) by a post-heat-treatment in nitrogen atmosphere. K. Ogata et al[13] have observed that the N_2 atmosphere benefit the formation of electron carrier, however oxygen vacancies and zinc excess can be decreased by using O_2 atmosphere and lead to stronger PL. The reducing atmosphere has been used to modify the morphology of ZnO film[14]. But these studies almost during a doping, the report about the influence of atmosphere on the pure ZnO film is very few, especially, the effect of vacuum atmosphere and to the ZnO films prepared by so-gel method. In this work, the transparent insulating fused quartz glass was used as a substrate to eliminate the influence of the conducting substrates. The effect of post-annealing atmosphere (O_2, air, vacuum) on the properties of ZnO film has been investigated by sol-gel method using spin coating.

2. EXPERIMENTAL

Using Zinc acetate 2-hydrate (Zn(CH3COO)2·2H2O), 2-methoxyethanol and monoethanolamine(MEA) as zinc source, solvent and stabilizer, respectively. The concentration of Zinc acetate was 0.5M, and the molar ratio of Zn and MEA was maintained 1:1.The mixed solution was prepared at room temperature. Then it was stirred at 60°C for 1h to yield a clear and homogeneous solution. After the solution was cooled to room temperature, it was coated on quartz glass substrate at 3000rpm for 30S. The precursor films were heated at 250°C for 10min to remove the solvent and organic residuals. The coating and heating process repeated for 3 times. The prepared films were then annealed at 550°C

for 1.5h in the atmosphere of O_2(sample A), air(sample B) and vacuum(sample C), respectively.

The crystallization and preferential orientation of the prepared samples were identified by X-ray diffraction (XRD; RINT 2000, Rigaku), the surface morphology and particle shape were observed by atomic force microscope (AFM, JSPM-5200TM, JEOL), The optical properties of prepared samples were investigated by photo- luminescence spectra (PL, SPEX 1702/04 spectrometer, excited by a 325nm He-Cd laser) and UV-Vis spectra (V-570, JASCO) at room temperature.

3. RESULTS AND DISCUSSION

3.1. X-ray pattern

The prepared three samples have been analyzed by XRD method, and the results are shown in Fig. 1. It is observed that the samples A and B exhibit wurtzite structure with strong preferential orientation of the (002) plane and without other peak. The sample C also exhibits wurtzite structure but the preferential orientation is not obvious and we can observe other two peaks. The sample A has best crystalline quality and biggest degree of preferential orientation. This should be due to the pure O_2 decreases the oxygen vacancies[15].

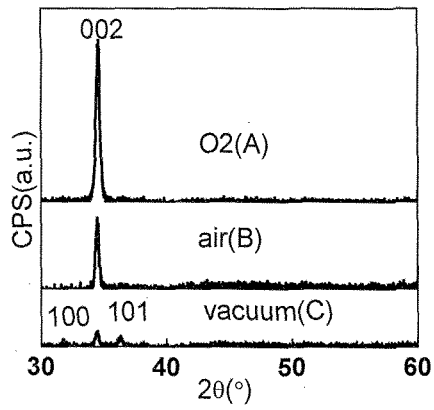

Fig. 1 XRD patterns of samples prepared in ambient of O_2, air and vacuum

3.2. AFM images.

AFM images of the three samples are shown in Fig. 2. It can be found that, in scanned area, the surface roughness of sample A, B and C is 49nm, 53nm and 78nm, respectively. The surface of the sample A is smoothest, and that of sample C is roughest. On the surface of the sample C, there are several ridges. So, the surface can be smoothed by using O_2 ambient. The differences among particles of the three samples maybe attribute to the influence of oxide. Pure O_2 ambient should benefit the ZnO particles grow along the <001> direction, so the particles of sample A are rod-like and uniform. The length and width of the particle is about 100nm and 40nm. The particles of sample B are ball-like and not uniform, the particle size is ranged from about 30nm to about 80nm. In Vacuum, as exist little oxygen, the growth rate in all direction almost the same. So the particles of sample C were ball-like and very uniform. The particle size is about 30nm. And this result almost agrees with that of XRD

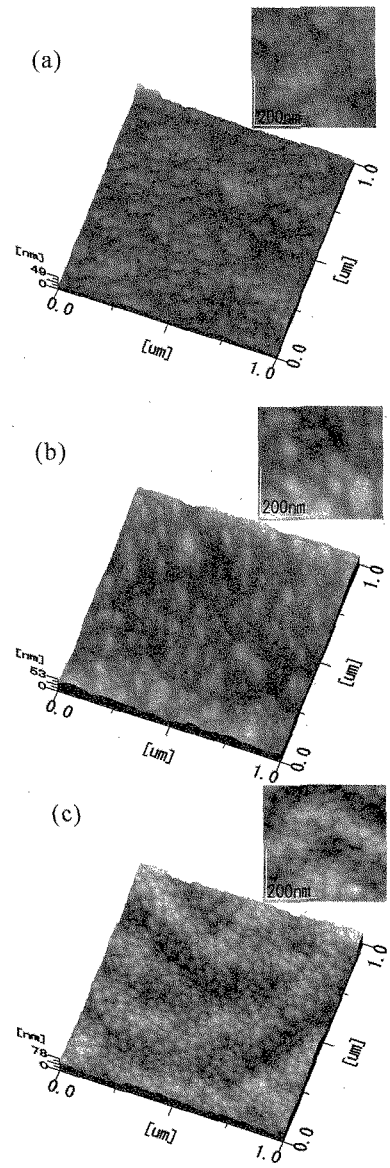

Fig. 2 AFM images of ZnO films: (a) sample A, O_2, (b) sample B, Air, (3) sample C, Vacuum.

3.3. Optical properties.

PL and UV-Vis measurement have been used to investigate the optical properties of the three samples, and the PL spectra and UV-Vis spectra have been shown in Fig. 3 and 4, respectively.

From Fig. 3, it can be found that there is a broad peak centered around 505nm (2.37eV) extending from the blue into the green range for all samples, several authors have suggested that oxygen vacancy (VO) is responsible for the broad green band[16,17]. The sample under post -annealing in vacuum yields a strongest peak around 505nm, which should mean highest concentration of oxygen vacancies. For the sample annealed in O_2 yields a weakest peak, which should means lowest concentration of oxygen vacancies. So this peak is confirmed to be attributed to oxygen vacancy. There appears a sharp peak at about 385nm (3.22eV) has appeared only for sample C. This peak also has been found by other researchers, and it is a donor-acceptor-pair (DAP) transition, but the chemical

identity of the acceptor is unknown[18]. For sample A and B, this transition does not occur. The sample C much more oxygen vacancy (VO) and zinc excess than other two samples. So the transition should attribute to the oxygen vacancy (VO) or zinc excess, also maybe the result of cooperating. For all the samples, there is a peak at about 375nm (3.3eV), it should due to the band gap of ZnO.

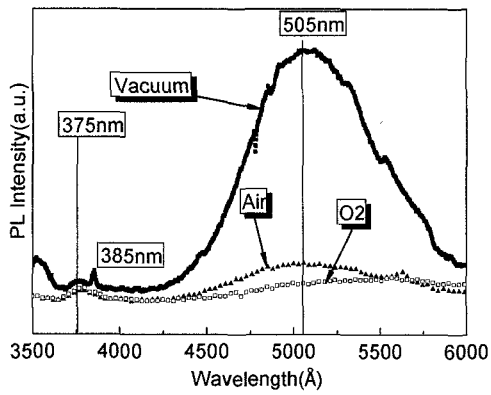

Fig. 3 PL spectra of samples post-annealed in O_2, air and vacuum.

UV-Vis absorptance spectra are shown in Fig. 4. The absorptance of sample treated in vacuum in both UV and vis range is best, and that of sample treated in O_2 is weakest. These absorptance spectra are calculated from reflectance and transmittance. Usually, the scattering occurred from the rough surface is not considered in the reflection and transmittance. AFM images show the roughness of the three samples are sample C > B > A, so the difference observed in the absorptance spectra for three samples maybe attribute to the roughness of the surface. All the three samples have a sharp absorptance edge at about 380nm (3.24eV). Compare with 3.3eV from PL, it is a bit smaller, maybe due to the scattering influence. In Fig. 4, every curve has a peak centered at about 360nm (3.41eV).Sans et al[19] have reported that the peak at 3.41 eV corresponding to the B-exciton, may be with a small contribution of the A exciton in the low energy tail.

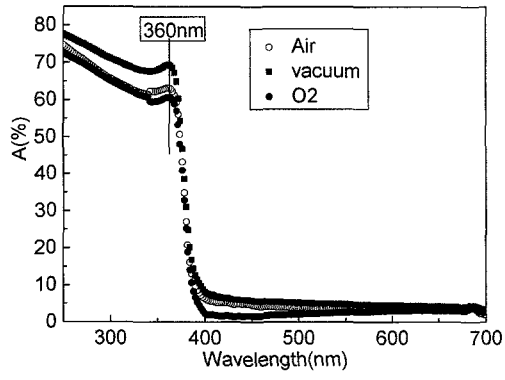

Fig. 4 UV-Vis spectra of samples post-annealed in O_2, air and vacuum

4. CONCLUSION

ZnO films have been prepared by sol-gel method using spin coating, and post annealed in the atmosphere of O_2, air and vacuum, respectively. The prepared samples exhibit wurtzite structure. Atmosphere does influence the growth of the ZnO film. The sample that annealed in O_2 shows best crystalline quality and biggest degree of preferential orientation of (002) plane, and yield rod-like uniform particles. The sample annealed in air with preferential orientation of (002) plane and ball-like particles. The sample annealed in vacuum nearly has no preferential orientation with ball-like uniform particles. The surface roughness of the three films are Vacuum > air > O_2, and the difference surface morphology maybe affect the UV-Vis absorptance. The band gap of prepared ZnO film is about 3.3eV from PL spectra. Vacuum ambient leads to much more oxygen vacancy (VO) and zinc excess which may be responsible for the broad transition around about 505nm (2.37eV) and sharp transition centered at about 385nm.

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