IOP Conference Series: Materials Science and Engineering

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To cite this article: Aniruddh Bahadur Yadav *et al* 2015 *IOP Conf. Ser.: Mater. Sci. Eng.* **73** 012060

Study of post annealing effects on structural and optical properties of sol-gel derived ZnO thin films grown on n-Si substrate

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Abstract: Zinc oxide (ZnO) thin films were grown on n-type silicon (100) substrates by sol-gel spin coating technique. The prepared thin films were annealed in the presence of Ar at three different temperatures (at 450°C, 550°C and 650°C) to study the impact of annealing temperature on the structural and optical properties of the ZnO thin films. The structural, surface morphology and optical properties of the thin film were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) measurements respectively. The grown ZnO thin films are polycrystalline in nature with wurtzite hexagonal structure as evident from the XRD and SEM analyses. It further indicates that the crystalline size increases with increasing annealing temperature. The post annealing is also found to influence the optical properties in the terms of band gap energy of the ZnO thin films. The optical energy band gap was found to be decreased from 3.205 to 3.13eV as the annealing temperature is increased from 450°C to 650°C. However, our results concerning the growth of ZnO thin films on Si substrates suggest that there is an intermediate growth temperature allowing for the optimization of the ZnO film growth. The results of the study can be used as a guideline for growing ZnO thin films on n-Si substrates with a homogenous surface morphology, high surface to volume ratio and desired particle size, which are suited for optoelectronic/ gas sensing applications.

1. Introduction

The last decade has witnessed a dramatic development in the field of nanotechnology and nanoscience. The transparent thin films and nanostructures based different materials (e.g., Si, Carbon nanotube, GaN, ZnO) are becoming increasingly attractive for fabrication of optoelectronic and nano-electronic devices based on their thin films and nanostructures [1-3]. Among various nanostructured materials and their thin films, ZnO has drawn maximum attention of the researchers because of its important electrical, optical, magnetic and piezoelectric properties [4]. These properties have made way for many applications ranging from light emitting diodes, UV lasers, gas sensors, transparent field effect transistors, solar cells, piezoelectric nanogenerator and other optical coating applications [5]. Due to the various attractive properties for practical applications of ZnO films, there has been much attention paid on the fabrication of nanocryatalline ZnO thin films in recent years [6]. The ZnO thin film structural and its optical properties strongly depend on growth technique and growth condition.

Many different deposition techniques have already been reported. These include RF sputtering, metal organic chemical vapor deposition (MOCVD), sol–gel, spray pyrolysis, galvanic deposition technique, pulse laser deposition (PLD) and thermal evaporation method [7]. Among several techniques used to obtain high-quality undoped and doped ZnO thin films, the sol–gel processing still offers the possibility of preparing a small as well as large-area coating of ZnO thin films at low cost for technological applications. The main factors affecting the sol–gel film surface morphology and optical properties are dopant concentration, buffer layer on substrate, aging time of sol, the film's thickness and structure, and annealing treatment. Particularly, the annealing treatment is a significant factor to affect the sol–gel process [9]. Therefore, it is still necessary to study the effect of annealing temperature on the structure and optical properties of ZnO thin films. In this work, we deal with structural and optical properties of sol–gel derived nanocrytalline ZnO thin films. As a consequence, the influence of post annealing treatments on the structural surface morphology and optical properties will also be investigated.

2. Experiment

High-purity Zinc acetate dihydrate (Zn $(CH_3COO)_2{\cdot}2H_2O$) was used as starting materials; isopropanol was selected as a solvent, and diethanolamine ($C_4H_{11}NO_2$) was used as stabilizing agent for the fabrication of ZnO thin films by sol-gel technique. The concentration of zinc acetate was chosen to be 0.15mol and the resulting mixture was stirred for 3h at room temperature to yield a clear and homogeneous solution [9] to serve as the coating solution. The coating was usually made 24hr after the solution was prepared. The precursor solution was spin-coated onto n-Si (100) wafer for studying the effect of post annealing treatment on ZnO thin film. Silicon substrates were ultrasonically cleaned with acetone and methanol, then etched for 5 min in 2% HF water solution in order to remove the surface oxide, followed by de-ionized water and dried in vacuum before spin coating. Spin coating was performed at room temperature, with a rate of 1000 rpm for 15s and then of 2000 rpm for another 15s. After depositing by spin coating, the films were dried at 300°C for 10 min on a hotplate to evaporate the solvent and remove organic residuals. This process was repeated for five times to obtained the reasonable thickness of film (~250nm). The films were then inserted into a furnace and annealed in Ar at 450–650°C for 30mintues. The crystal structure and phases of the film were studied by X-ray diffraction (XRD). The surface morphology of ZnO thin films were studied by field emission scanning electron microscope (FSEM). The optical properties of the ZnO thin films were temperature analyzed by the photo luminous spectroscopy (PL). The electrical properties of the ZnO thin film were studied by the four point probe method.

3. Result and discussion

3.1*Crystal structure and surface morphology study*

The XRD patterns of nanocrystalline ZnO thin films deposited on n-Si (100) substrate by spin-coating technique annealed at different temperatures are shown in Figure 1. From Figure 1, (100), (002), (101), (102), (110) and (103) XRD peaks were observed, and it is concluded that all the films were polycrystalline with a hexagonal wurtzite structure and a random orientation, which generally occurs in the growth of ZnO thin films [9]. It is clear that the intensity of (002) peak gradually increases with the increasing annealing temperature from 450°C to 650°C, i.e., the increasing annealing temperature caused the crystallinity of ZnO to enhance. This indicated that the thin films had a high preferential oriented c-axis orientation perpendicular to the substrate surface. The crystallite size of the ZnO films ware calculated by using Scherer's formula [8]

$$D = \frac{.9\lambda}{\beta cos\theta} \quad (1)$$

where, λ is the wavelength of the X-ray, β is the observed angular full-width at half maximum (FWHM) intensity of each diffraction peak located at 2θ position and θ is the Bragg's diffraction angle.

IOP Conf. Series: Materials Science and Engineering **73** (2015) 012060 doi:10.1088/1757-899X/73/1/012060

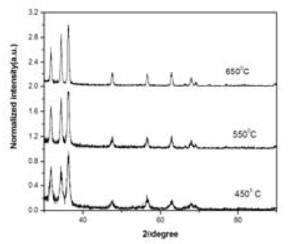

Figure.1: XRD image of ZnO thin films

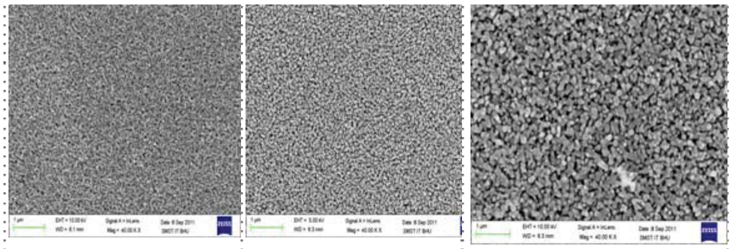

Figure.2: SEM image of ZnO thin films annealed at (a) 450^0C, (b) 550^0C (c) 650^0C temperature

The calculated values of the crystallite sizes ranged between 10 and 20nm. It was observed that crystallite size increased with increasing annealing temperature, which can be understood by considering the merging process induced from post annealing treatment on ZnO thin films. For ZnO nanoparticles, there are many dangling bonds related to the zinc of oxygen defects at the grain boundaries [6]. As a result, these defects are favourable to the merging process to form larger ZnO grains while increasing the annealing temperature

The surface morphology ZnO thin films were studied by field emission scanning electron microscopy (FESEM). Figure 2 shows the FESEM images of ZnO films annealed at various temperatures. The scanning electron microscopy result revealed that uniform ZnO nanoparticles were grown and grain sizes were found to be varied with annealing temperatures in close agreement with the XRD result. The film was granular in nature with good uniformity. Comparing the surface morphologies of ZnO thin films at the annealing temperatures of 450^0C, 550^oC and 650^oC, the grain size of the nanoparticles in the film was found to be increased with the post annealing temperature. In other words, the surface-to-volume ratio was found to be decreased with increased annealing temperature (450 to 650^0C). Since, the thin films with a larger surface-to-volume ratio could enhance the surface activity of the film thereby leading to a higher degree of UV absorption in the case of optical detection and gas adsorption in the case of gas sensing, the ZnO films at 450^0C has better suitability for both the gas sensing and optoelectronic applications than that of the films annealed at higher temperatures.

3.2. *Optical properties of thin film*

Room-temperature PL spectra of ZnO films annealed at various temperatures are shown in Figure 3. The PL spectra of ZnO thin films exhibit two emissions: a strong UV emission located at ~385nm and a weak broad emission band in the visible range. The UV emissions can be attributed to the near band edge emission and originate from the recombination of free excitons [7]. However, the wider spectrum in the visible band (500 to 650) can be attributed to electron transfer from the conduction band to the defect states in the forbidden band or between different defect levels in the forbidden band. Figure 3 further shows that the UV luminescence is degraded with increased annealing temperature which may be ascribed to excessive oxidized layers formed on the surface and the grain boundary of ZnO thin films after annealing in Ar [5]. Moreover, the UV emission is found to be red-shifted with increased temperature which is likely to be related to Burstein-Moss effect, [8] relaxation of tensile strain [4] and

increase in the grain size. The decrease in optical band gap energy is generally observed in the annealed direct-transition-type semiconductor films. Hong et al (2005) [10] observed an optical band gap shift of ZnO thin films from 3·31–3·26 eV after annealing, and attributed this shift to the increase in the ZnO grain size. Also, the shift of the energy gap was mainly due to both the quantum- size effect and the existence of an amorphous phase in the thin films. In our case, the band gap energy (E_g) value is found to be decreased from 3·205– 3·13eV with increasing annealing temperature from 450–650°C.

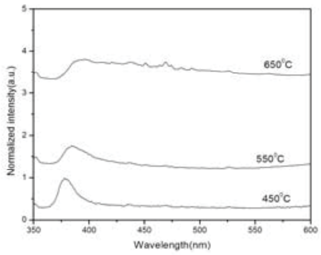

Figure.3 PL spectra of ZnO thin annealed at different temperature.

4. Conclusions

In summary, the effect of post annealing treatment on structural and optical properties of sol–gel derived ZnO films grown on n-Si (100) has been critically examined by XRD, SEM and PL measurements. All the films show polycrystalline hexagonal wurtzite structure ZnO with a high preferential *c*-axis orientation. Morphological and structural studies revealed that the annealing treatment improved crystal quality. The optical band gap energies have been found to be decreased from 3·205eV to 3·13eV as annealing temperature is increased from 450–650°C. The ZnO film at 450°C annealing temperature is observed to be having better suitability for gas sensing and optoelectronic applications than that at other two higher temperatures.

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