Effects of thermal treatment on structure, surface microstructure and optical properties of nitrogen-ion irradiated nanoparticle thin films

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Abstract

In this paper, we studied the effects of ion irradiation and annealing treatment on the ZnO thin films. ZnO thin films were first prepared on sapphire substrate by rf-magnetron sputtering technique, followed by nitrogen ion irradiation and annealing treatment. The crystallographic properties, surface morphology and optical properties changed after nitrogen ion irradiation and annealing treatment, which were investigated by X-ray diffraction, scanning electron microscopy and absorption spectroscopy.

Keywords: Rf-magnetron sputtering, Ion irradiation, X-ray diffraction, transmittance.

1. Introduction

Oxide semiconductor metal nanocomposites, have received great research interest in recent years due to their size-dependent electrical and optical properties, which made these nano-sized materials have potential in energy storage and fluidic sensors [1], optoelectronics [2] and photo catalysis [3]. Because of its wide band gap (3.3 eV), higher transparency in the visible region and large exciton binding energy (60 meV), ZnO is widely used in transparent electronics, UV light emitting devices, invisible field effect transistors and other optical applications [4-6]. The properties of the ZnO nanoparticles depended on the microstructures of the materials, containing crystalline density, crystal size and aspect ratio [7]. Currently, various methods including laser ablation in liquid [3], magnetron sputtering [4-5], thermal evaporation [8], sol-gel technique [9], ion irradiation [2], etc. have been reported for the preparation and modification of ZnO nanostructures. Ion irradiation technique has been widely used for doping in semiconductor yield because it introduces impurity concentrations in selected areas and controlled depths below the surface as well as provides accurate dose control. However, the irradiation process produces undesirable lattice disorder, which can affect the structural and optical electrical properties of the semiconductor. Post irradiation annealing is required to both recover the structure and activate the dopants.

P-type and n-type semiconductor can be obtained from ZnO with different dopants. Group V elements such as N, P and As are used for p-type ZnO [10-11]. Recently, non-metal doped ZnO could effectively improve the light absorption in the

visible light activity. Nitrogen has been considered as the potential dopant due to its similarity to oxygen (electronic structure and similar ionic radius), low ionization energy, ease to handle and source abundance [12]. Much experimental work reported about N-doping ZnO films enables the fabrication of transparent conductive devices [13-14]. Many studies on the growth of high quality ZnO thin films have used c-plane sapphire as a substrate because of its high crystallinity and low cost [15].

In this work, doped ZnO thin films on sapphire substrate have been achieved by radio-frequency (rf) magnetron sputtering, ion irradiation and annealing treatment at different temperatures. The effect of nitrogen ion irradiation and annealing at different temperatures on the microstructural and optical properties of the doped ZnO nanoparticle thin films were investigated in detail.

2. Materials and methods

Doped ZnO thin films were deposited on seven virgin (0001) oriented sapphire substrates using rf-magnetron sputtering in a mixture of O₂ (content of 6.25%) and Ar (purity, 99.999%). A doped ZnO ceramic target (Er/Yb/ZnO=1:4:95) with a 3-inch diameter and 0.24-inch thickness was used. The distance between the target and the substrates was 4.7 inches. To remove the surface contamination, the substrates were dipped in acetone, rinsed with a large amount of de-ionized water and dried in air before deposition. The substrates were then placed in a chamber where the deposition was performed for 2 hours under 4.3×10^{-4} Pa evacuation and an rf power of 120 W at room temperature.

Table 1. Continuation annealing treatment conditions of the samples in air.

No irradiation	N ⁺ irradiation	Annealing condition (for 30min)
S1	S11	At room temperature
S2	S21	100°C
S3	S31	200°C
S4	S41	300°C
S5	S51	400°C
S6	S61	500°C

Afterwards, samples S11-S61 were irradiated with 90 keV nitrogen ions at a fluence of 1×10^{15} ions/cm² at room temperature. The current intensity of the beams is less than 100 μ A and the sample temperature of the sample surface below 100 °C during the irradiation. Samples S2-S6 and S21-S61 were thermally annealed at different temperatures as shown in Table 1. A resultant ZnO thin films thickness of 349 nm was achieved which was estimated using the Filmetrics F20. The nitrogen-ion irradiation was simulated using the Stopping and Range of Ions in Matter (SRIM) 2013 software. The structural characterization was performed by X-ray diffraction (XRD) using Cu K α radiation with a Rigaku RINT-2500VHF. Scanning electron microscopy (SEM) imaging on a Hitachi S-4800 was performed to analyze the sizes and surfaces of the obtained samples. The chemical compositions of the samples were also analyzed with a field emission scanning electron microscope equipped with energy-dispersive spectroscopy (EDS). The absorption spectra of the nanoparticle thin

films were measured with an UV-Vis spectrometer with a wavelength range of 200-800 nm.

3. Results and discussion

Fig. 1. Electronic, nuclear energy deposition and atom distributions simulated by the SRIM 2013 program. The inset shows the schematic of the thin film heterostructure and normal incidence of ions.

The simulated atom distribution profile and the stopping power profiles of the incoming nitrogen ions and the schematics of the thin film heterostructure and ion-irradiation are shown in Fig. 1. The density of ZnO and Al₂O₃ are 3.2 g/cm³, 5.606 g/cm³, respectively. The displacement thresholds energy of zinc and oxygen are both 57 eV [16], 18 eV for aluminium and 76 eV for oxygen [17]. During the ion irradiation process, the incident nitrogen ions lose energy through elastic collisions (nuclear stopping power) and inelastic collisions (electron stopping power). The nuclear energy loss process dominant in the low energy regime results in a decrease in the physical density [18]. As a result of the collisions between electrons and ions at high ion fluence such as those used in our study, the electronic excitations are known

to cause breaking of chemical bonds [19-20]. The range of 90 keV nitrogen ion into the doped ZnO thin films is approximately 576 nm; therefore, the incoming ions are expected to pass through the film (about 349 nm thick), as shown in Fig. 1.

Fig. 2 presents the XRD patterns of 12 samples, which were in good agreement with the standard JCPDS Card of ZnO (No. 36-1451). To reduce the influence of the substrate, we removed the XRD patterns of the Al_2O_3 substrate. The samples exhibit well defined reflection corresponding to (0002) plane of the wurtzite structure of ZnO nanoparticles thin film indicating the films with the c-axis normal to the substrate [1]. The full width at half maximum (FWHM) and intensities values of these (0002) peaks changed with different thermal annealing treatment (as shown in Table 2), and the markedly diminished (0002) peaks of these samples indicate deterioration of the nanoparticle film crystallinity and an increase of defects especially after N-ions irradiation. Annealing resulted in the shifting of (0002) diffraction peaks, suggesting the presence of compressive stress in the annealed films.

Fig. 2 XRD pattern of the obtained films showing the (0002) ZnO peaks. Short dash dot line are the samples S1-S6, straight line are samples S11-S61, the dot line is the 2θ for S1 and the short dash line is the 2θ for S11.

The lattice constant a and c of the wurtzite structure have been determined by the following formula [22]:

$$d_{hkl}^2 = \left(\frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \right)^{-1} \quad (1)$$

where d is the interplanar space and h, k, l are miller indices. For (0002) peak h, k, l are 0, 0, and 2 respectively. The calculated lattice constant c is given in Table 2. It clearly shows that c values decreased after N-ion irradiation and increasing annealing temperature.

To obtain detailed structural information, the average crystallite size was calculated from the FWHM of the (0002) diffraction peak according to the Debye-Scherrer equation [23]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where D is the crystallite size, k is a constant of 0.89, λ is the X-ray wavelength (0.15406 nm), β is FWHM, and θ is the Bragg angle of the (0002) peak. The variations are shown in Table 2.

Table 2 Bragg angle, 2θ , d-spacing, d , lattice constant, c , FWHM, β , calculated average size and transmittances for all samples.

Sample	2θ (deg)	d (Å)	c (Å)	β (deg)	D (nm)	T (%)
S1	33.938	2.639	5.277	0.925	8.884	82.6
S2	33.982	2.636	5.271	0.896	9.173	78.9
S3	34.068	2.630	5.259	0.849	9.683	81.6
S4	34.133	2.624	5.248	0.803	10.239	75.9
S5	34.414	2.603	5.207	0.702	11.721	80.4
S6	34.435	2.602	5.203	0.700	11.755	82.1
S11	34.306	2.611	5.223	0.748	10.997	81.5

S21	34.327	2.610	5.221	0.728	11.299	73.1
S31	34.326	2.610	5.220	0.713	11.538	81.4
S41	34.305	2.611	5.223	0.699	11.768	71.6
S51	34.478	2.599	5.199	0.666	12.357	82.7
S61	34.543	2.594	5.189	0.669	12.304	82.4

As we can see from Fig. 2, after nitrogen ion irradiation, the (0002) peak shifted to the large angle range, which demonstrated that nitrogen have entered into the lattices of ZnO and the d-spacing has decreased. The (0002) peak of S11 became sharper and narrower than that of S1, this result reveals the increase of nanoparticles size and the improvement of crystallinity, which possibly means the occupation of the irradiated nitrogen ion in the oxygen vacancies can improve the crystallinity of doped ZnO nanoparticle thin films. This result is also supported by SEM images as shown in Fig. 3. The decrease of FWHM (as shown in table 2) indicates that compressive stress have developed in the film, which means nitrogen irradiation did not cause any changes in wurtzite phase structure of ZnO but the lattice dislocation improvement of S11 crystallite quality [24]. The ionic radius of N^+ (0.146 nm) is larger than that of O^+ (0.138 nm), thus the shorter Zn-N bond formation induces the change in the lattice constant [12]. This result indicates that the nitrogen atoms maybe incorporation in the ZnO crystal lattice structure at oxygen sites, which improves the crystallite quality by reducing the defect concentration [25]. Generally, it is clear that the FWHM of the (0002) peaks decreases and the crystallite size increases with increasing annealing temperature. It is shown that the annealing treatment can promote the nucleation and growth of the crystallite as well as improve the crystallite quality of the samples.

Figs. 3(a) and 3(b) shows the SEM images of samples S1 and S11. S1 show a rather rough surface with many pores, On the contrary, a smoother surface profile is obtained for S11. Nitrogen ions filled the pores and occupied the oxygen vacancies of the thin films, which improved the crystallinity of the samples. This result supports the XRD results, which shows relatively strong intensity of the (0002) peak. The EDS pattern in Fig. 3(c) shows that the nanoparticles are composed of zinc, oxygen, erbium, ytterbium, carbon and nitrogen elements without additional impurities.

Fig. 3 SEM images of samples (a) S1 and (b) S11. (c) EDS pattern of S11.

Fig. 4 depicts the SEM images of samples S2-S6 and S21-S61. All samples show spherical shaped particles displaying grain-like morphologies. After 300°C annealing treatment, the particles are no longer spherical and fused together into a strip nanoparticle until 500°C annealing for non-irradiated ZnO thin films. The magnified SEM images of S21-S41, as shown in Figs. 4(a)-4(c), respectively, indicate that the particles are more perfectly spherical and uniform in size distribution. However, a small amount of nanoparticles burst after 200°C annealing. When the annealing

temperature increases, the size of the nanoparticles grows quickly and they are no longer perfectly spherical, as shown in Fig. 4(d). As we can see from Fig. 4(e), most nanoparticles burst, the mixture of spherical and quadrilateral type morphology can be observed. Higher thermal annealing caused great damage for doped ZnO nanoparticle thin film, which leads to the (0002) diffraction peak shift for samples S51 and S61 in XRD pattern. The average sizes of the nanoparticles are about 10, 22, 31, 45, 47, 18, 26, 32, 40 and 61 nm for samples S2, S3, S4, S5, S6, S21, S31, S41, S51 and S61, respectively.

Fig. 4 SEM images of samples (A) S2, (a) S21, (B) S3, (b) S31, (C) S4, (c) S41, (D) S5, (d) S51, (E) S6 and (e) S61.

To better understand the optical properties, we tested the UV-Vis absorbance. The changes in the light transmittance characteristics of twelve samples are shown in Fig. 5. The transmittances are approximately 71.6%-82.7% in the visible region for twelve samples, as shown in Table 2. All spectra showed a sharp absorption edges in the wavelength region at about 375 nm. The transmittance of S1-S6 decreased slightly about 0.5%~6.7% in the visible region, and it is believed that annealing treatment led to a significant increase in the carrier concentration for ZnO thin films. Similar result was founded by Q. H. You et al. who attributed this phenomenon to the increase of free carrier absorption [26]. From the inset of Fig. 5, we can see that with the increase of annealing temperatures, the optical absorption edge exhibited a slight red-shift, which was attributed to the increase of nanoparticles size of the film [27]. This phenomenon can be seen clearly in Fig. 6, which shows the relationship between the absorption coefficient and the photon energy.

Using the absorption data the band gap was estimated by Tauc's relationship [28]:

$$\alpha h\nu = A_0(h\nu - E_g)^{\frac{1}{2}} \quad (3)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, and A_0 is a constant. The absorption coefficient α is obtained by using the relationship:

$$\alpha = -\left(\frac{1}{d}\right) \ln T \quad (4)$$

where T is the transmittance and d is the thickness of the film. The E_g values of the thin films were determined by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus $h\nu$ to the energy axis, as shown in the inset in Fig. 6. After nitrogen ion

irradiation, the optical band gap has a blue-shift of 0.03 eV. This phenomenon is believed to be the shift in the variation of the carrier mobility with respect to the heavy doping of nitrogen in the doped ZnO film [29]. With the increase of annealing temperature, the absorption edges have a red-shift. When the annealing temperature is 500°C, the red-shift for S61 is approximately 0.17 eV.

The E_g is related to several factors such as the nanoparticles size, stress, doping, defects and carrier concentration in material [30-31]. Furthermore, with increasing annealing temperature, the red-shift of absorption edges should be related to the increase of nanoparticles size, the compressive stress and the occupation of the irradiated nitrogen ion in the oxygen vacancies which lead to the decrease of the carrier concentration in the conduction band [32-33]. On the other hand, the band gap narrowing of ZnO nanoparticles with increasing annealing temperature is probably due to the Burstein-Moss effects [34].

Fig. 5 Transmittance spectra of all samples. The inset shows the absorption spectra in the region of 340-400 nm.

Fig. 6 (1) Plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for the twelve samples. (b) The value of the optical band gap when $(\alpha h\nu)^2 = 0$.

4. Conclusion

In summary, doped ZnO thin films were grown on sapphire substrates using rf-magnetron sputtering after nitrogen ion irradiation, the size of the ZnO nanoparticles increased, which improves the crystallite quality of the samples. The XRD and SEM patterns demonstrate that the size of ZnO nanoparticles increased with increasing annealing temperature. The absorption spectra changed after ion irradiation and annealing treatment. Nitrogen ion irradiation and annealing treatment resulted in structural and optical changes of the doped ZnO thin films.

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