

Effect of Nitridation and Pre-Growth Annealing of the Sapphire Substrate on the Quality of Zinc Oxide Thin Films Grown by RF-Magnetron Sputtering

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ZnO has attracted much attention due to its wide bandgap (3.2 eV) and high exciton binding energy of 60 meV. These properties make ZnO a highly desirable material for high frequency devices that can work in harsh environment. We have grown ZnO thin films at different temperatures ranging from 100 °C to 500 °C. We have observed that surface roughness is first decreased with the increase in the growth temperature but then by further increasing the growth temperature beyond 300 °C, results in increased surface roughness of the grown samples, whereas grain size of the samples increases with the increase in the growth temperature. Crystalline quality of the films is also improved with the increase in the growth temperature but then degrades by further increase beyond 200 °C. We achieved the highest Hall mobility for the ZnO sample grown at 200 °C. The optimum growth condition of ZnO thin films on sapphire (0001) in our RF/DC magnetron-sputtering unit were achieved for the films grown at 200 °C. Subsequently, we performed pre-growth treatment to the sapphire substrate then grew ZnO films at 200 °C. Pre-growth treatment involved heating the substrate at 500 °C for about half an hour and then etching the sapphire surface with nitrogen plasma. We have observed that pre-growth heating and nitridation of the sapphire substrate results in bigger grain size whereas no improvement was observed in the crystallinity of the film.

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1. Introduction

ZnO has attracted much attention due to its interesting optical, electrical and piezoelectric properties. ZnO can potentially be used for electronic and optoelectronic applications including gas sensing, transparent conductors for touch screen windows, renewable energy, and spintronics [1–3]. ZnO has a band gap of 3.2 eV and exciton binding energy of ≈ 60 meV, which is much higher than room temperature thermal energy of ≈ 25 meV that makes it attractive material for short wavelength and transparent electronics [4–9]. ZnO also has an edge over competing wide band gap semiconductors e.g. GaN that has an exciton binding energy of only ≈ 24 meV. Moreover, both constituent elements of ZnO are abundantly available in nature and are environmental friendly that makes it attractive for consumer applications.

ZnO films have been grown at different substrates including glass, quartz, silicon and sapphire but most commonly sapphire(0001) is used as substrate to grow ZnO films. Intrinsically grown ZnO is *n*-type semiconductor due to oxygen vacancies and Zn interstitials [2, 10]. The quality of the grown film can be improved by choosing appropriate substrate and pre-growth treatment of the substrate. For example, GaN has traditionally been grown on sapphire (0001) substrate but before the growth es-

pecially in MBE process, sapphire substrate is heated and nitridated before the growth of GaN film. It has been reported that pre-heating of sapphire makes sapphire surface atomically clean that results in the smooth growth of the thin film. Nitridation of sapphire surface results in the formation of thin layer of AlN [11–13]. Lattice mismatch between GaN and AlN is much smaller as compared to the mismatch between GaN and sapphire [14–16]. Therefore, nitridation of sapphire results in less stacking fault defects in GaN film and atomically smoother growth. This make pre-treatment of sapphire an essential element for GaN thin film growth.

Similar to GaN, ZnO ($a = 3.2495$ Å) has also large lattice mismatch with sapphire ($a = 4.758$ Å). This lattice mismatch results in strained layers that result in high defect densities. These defects in turn effect the crystallinity, electrical, and optical properties of the films. In order to achieve good quality smooth films and to control the properties of the ZnO thin film, it is important to study the effect of different growth parameters like substrate temperature and pre-treatment of the substrate on the properties of the grown ZnO films.

Here we report the growth of ZnO thin films by radio frequency magnetron sputtering on sapphire(0001) substrate at different growth conditions and found the best growth temperature that results in highly crystalline and smooth films. In the next step we grew ZnO films on pre-heated and nitridated substrate and study the effect of substrate treatment on the properties of the film.

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2. Experiment

ZnO thin films were grown in RF/DC magnetron sputtering unit on sapphire (0001) substrate at different growth temperatures. First, the substrates were ultrasonically cleaned for five minutes in acetone and then five minutes in isopropanol. After sonication, the substrates were left in air to dry until all the solvent was evaporated. Then the substrates were introduced into the RF/DC magnetron sputtering chamber. The chamber was evacuated to a pressure of about 1.6×10^{-6} mbar. Ar gas (99.99% pure) was introduced in the chamber at a flow rate of 2sccm (standard cubic centimeters per minute). Then RF plasma was turned on with a plasma power of 150W. The substrate temperature was set to desired growth temperature and was set into rotation at 6RPM for uniform film growth. The growth was started by sputtering 99.9% pure ZnO target. During the growth the chamber pressure was $\approx 8.5 \times 10^{-3}$ mbar. Average thickness of our ZnO films were about 100 nm. We grew five samples (H1, H4, H5, H6, and H7) at 100, 200, 300, 400, and 500 °C respectively.

After the growth samples were taken out of the chamber and surface morphology of the samples were studied by atomic force microscopy (AFM) using non-contact or tapping mode of Veeco Innova diSPM. Crystallinity of the samples were studied by X-ray diffractometer (Shimadzu XRD-6000 diffractometer) using Cu K_{α} radiations of wavelength 1.548 Å. Finally, electronic properties of the films were studied by four probe Van der Pauw method at room temperature using ECOPIA HMS 3000 Hall effect system. Another sample H2O was grown on a pre-heated and nitridated sapphire (0001) substrate. Before starting the sputtering, the substrate temperature was raised to 500 °C and kept at this temperature for about 30minutes. Then Argon and Nitrogen gases were introduced in the chamber at a flow rate of 20sccm and 10sccm respectively. Finally DC etching plasma was turned on at 100% etching power for about 15 minutes. Subsequently, etching plasma was turned off and the sample temperature was brought down to the growth temperature, N₂ flow was stopped and Ar flow was reduced to 2 sccm for ZnO thin film growth. Rest of the growth and characterization procedure is similar to what has been described above for samples H1 and H4-H7.

3. Results and discussions

Surface morphology, grain size and surface roughness of the grown films were studied by AFM. Shown in Fig. 1(a–e) are the AFM images of the samples (H1, H4, H5, H6, and H7).

AFM images shown in Fig.1 reveal that the surface morphology of all the ZnO films grown on sapphire substrate exhibit grain like 3D features. It is evident from the AFM images that grain size increases with the increase in the growth temperature especially when the growth temperature is above 300 °C. This is because higher growth temperature results in increased energy of

TABLE I

Thin films growth temperatures, AFM surface roughness and grain size of the films from AFM images.

Sample	Growth temp. [°C]	Surface rough. [nm]	Grain size (AFM) [nm]
H1	100	9	8
H4	200	3	7
H5	300	3	9
H6	400	7	12
H7	500	17	17

species (Zn, O, ZnO) that fall on the surface and have bigger diffusion length. The increased diffusion length of the new species will allow them to move around on the surface and attach to already nucleated sites, which in turn results in the bigger grain sizes. A summary of the lateral grain sizes of the samples is given in Table I.

It was observe that surface roughness first decreased with the increase in the growth temperature and then started to increase at higher growth temperatures.

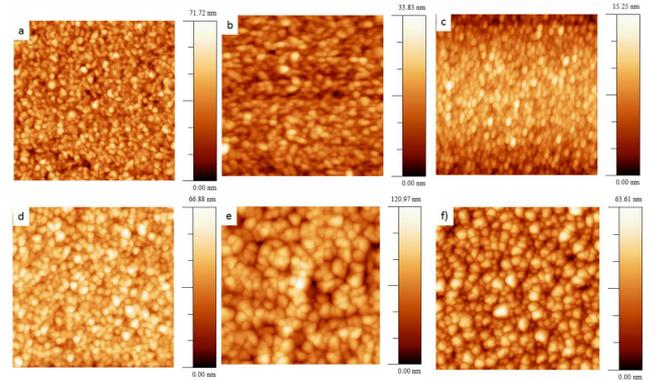


Fig. 1. AFM images of a) H1, b) H4, c) H5, d) H6, e) H7, and f) H2O ZnO films.

Show in Fig. 1(a) is the AFM image of sample H1 grown at 100 °C, this sample has an average grain size of ≈ 8 nm and root mean square (rms) surface roughness of about 9nm. Shown in Fig. 1(b) is the AFM image of sample H4 grown at 200 °C, that has an average grain size of about 7nm and rms surface roughness of about 3nm. Both the grain size and rms surface roughness has been decreased compared to sample H1 that was grown at 100 °C. Shown in Fig 1(c) is the AFM image of sample H5 grown at 300 °C, the grain size for this sample has been increased to 9nm whereas there is little change in the rms surface roughness compared to sample H4. Shown in Fig. 1(d) is the AFM image of sample H6 grown at 400 °C, the grain size has been further increased to 12nm and rms surface roughness has also been increased to 7nm. Shown in Fig1(e) is the AFM image of sample H7 grown at 500 °C. The surface morphology of H7 is quite different from the previous samples; here both rms surface roughness and grain size have been in-

creased. RMS roughness of H7 surface is about 17nm and average grain size is about 17nm. This indicates that at this temperature the surface diffusion length has been greatly increased resulting in the bigger grain sizes. At higher growth temperatures ($> 300^{\circ}\text{C}$) the grain size is increasing that results in more three dimensional growth which leads to higher rms surface roughness. Shown in Fig. 2 are the X-ray diffraction results of the ZnO films. The XRD spectrum of H1 sample consists of a major ZnO (002) peak at 34.48° with two small peaks at 31.82° and 36.08° corresponding to ZnO(100) and ZnO(101) respectively. Full width at half maximum (FWHM) of major ZnO(002) peak is about 0.92 degrees. The XRD spectrum of H4 sample is comparatively different from XRD spectrum of H1, it contains only ZnO(002) peak at 34.58° with no other secondary phases present in the spectrum. Moreover, the FWHM of ZnO(002) peak is 0.72° that is approximately 21% narrower compared to the ZnO(002) peak in H1 sample, which is an indication of better crystallinity. X-ray diffraction spectrum of H5 sample also contains only ZnO(002) peak at 34.64° degree but the intensity of this peak is relatively smaller compared to the ZnO(002) peak of H4 sample.

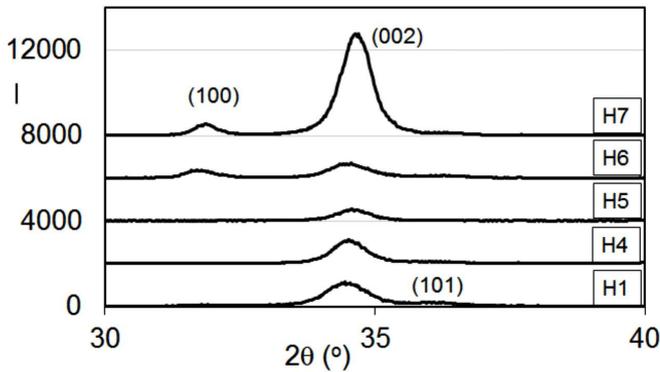


Fig. 2. XRD spectra of H1, H4, H5, H6 and H7 samples.

As well as the FWHM of ZnO(002) peak of H5 sample is 0.96° which is about 33% wider compared to the corresponding peak in H4 sample. This indicates that H4 exhibits better crystallinity compared to samples H1 and H5. The XRD spectrum of H6 contains ZnO(002) peak at 34.55° along with ZnO(100) and ZnO(101) peaks. The intensity of ZnO(100) has increased considerably as compared to sample H1. The FWHM value of the ZnO(002) peak for H6 sample is 0.88 degrees. The XRD spectrum of sample H7 consists of ZnO(002) peak at 34.7° along with a strong peak at 31.8° corresponding to ZnO(100) peak. The FWHM value of ZnO(002) peak is 0.7 degrees. Although FWHM of ZnO(002) H7 is comparable to sample H4 but there is a strong presence of secondary phases in H7 sample. XRD analyses of all the samples indicate that best growth temperature of ZnO on sapphire for our system is 200°C .

Hall effect measurements were performed on ZnO samples to investigate the carrier concentration and mobility

of our samples. The carrier concentration and mobility of our samples are given in Table II. We can readily see that our samples are *n*-type and the carrier concentration of our samples increase with the increase in the growth temperature. This is expected because *n*-type characteristic of intrinsically grown ZnO samples is attributed to oxygen vacancies and Zn interstitials [2, 10] It is expected that more oxygen atoms/molecules would desorb from the film at higher growth temperatures.

Some of the samples (H1, H4, H5) show *p*-type carrier concentration, we believe this is erroneous because it has been reported that less conductive or insulating samples give erroneous results for Hall effect or Van der Pauw measurements [19]. We achieve the best thin film growth with single phase and good crystallinity and the highest mobility at a growth temperature of 200°C .

TABLE II

Hall effect data of ZnO films.

Sample	Growth temp. [$^{\circ}\text{C}$]	Carrier conc. [cm^{-3}]	Carrier type	μ [cm^2/Vs]
H1	100	1.9×10^{13}	<i>p</i> -type	50
H4	200	1.5×10^{12}	<i>p</i> -type	439
H5	300	2.9×10^{12}	<i>p</i> -type	23
H6	400	2.0×10^{15}	<i>n</i> -type	9
H7	500	8.8×10^{16}	<i>n</i> -type	2
H2O	200	3.8×10^{13}	<i>n</i> -type	60

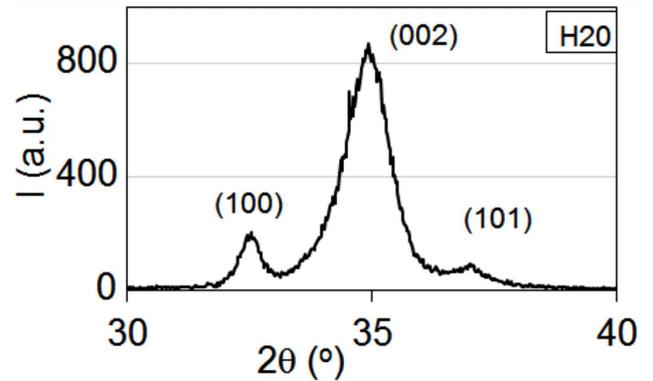


Fig. 3. XRD spectrum of H₂O ZnO sample grown on treated substrate.

After determining the optimal growth condition in our system, we grew another film (H2O) at 200°C but first treated the sapphire(0001) substrate by pre-heating and nitridation.

Shown in Fig.1(f) is the AFM image of the H2O sample that has an average grain size of ≈ 10 nm and RMS roughness of 9 nm. This indicates that pre-heating and nitridation has resulted in considerable surface smoothness of the sapphire substrate that would result in relatively bigger grain size of ZnO compared to the sample grown at 200°C without the pre-growth treatment of the substrate. ZnO species deposited on a relatively

smoother sapphire substrate would have greater diffusion length that would result in increased grain size.

Shown in Fig.3 is the XRD spectrum of the H₂O sample, it can be seen that ZnO was grown preferably along (002) direction but still there are a couple of small peaks along (100) and (101) direction, which indicates little improvement in the crystallinity of the sample due to pre-heating and nitridation of the substrate. Hall effect measurements were performed and it was found that carrier concentration of the H₂O sample is *n*-type and is about $3.8 \times 10^{13} \text{ cm}^{-3}$.

4. Conclusion

Zinc Oxide samples were grown at different growth temperatures ranging from 100 °C to 500 °C by RF/DC magnetron sputtering. We have observed that surface roughness of the grown films is first improved with the increase in the growth temperature but then by further increasing the growth temperature beyond 300 °C results in increased surface roughness. Whereas grain size as estimated from the AFM images increases with the increase in the growth temperatures. Crystalline quality of the films is also improved with the increase in the growth temperature but then degrades by further increasing beyond 200 °C. We achieved the highest Hall mobility for the sample grown at 200 °C that is an indication of comparatively less defects compared to the samples grown at other temperatures. The optimum growth condition of ZnO thin films on sapphire (0001) in our RF/DC magnetron sputtering unit were achieved for the films grown at 200 °C. Pre-growth treatment to the sapphire substrate was performed for a sample grown at 200 °C by heating the substrate at 500 °C for about half an hour and then etching the sapphire surface with nitrogen plasma. It was observed that pre-growth heating and nitridation of the sapphire substrate resulted in larger grain size due to initial smoother substrate surface whereas no improvement was observed in the crystallinity of the film.

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