Effect of substrate temperature on the structure and optical properties of ZnO thin films deposited by reactive rf magnetron sputtering

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Abstract

Zinc Oxide films were deposited on quartz substrates by reactive rf magnetron sputtering of zinc target. The effect of substrate temperature on the crystallinity and band edge luminescence has been studied. The films deposited at 300 °C exhibited the strongest c-axis orientation. AFM and Raman studies indicated that the films deposited at 600 °C possess better overall crystallinity with reduction of optically active defects, leading to strong and narrow PL emission.

Keywords: ZnO; rf magnetron sputtering; Microstructure; Optical properties

1. Introduction

ZnO is a versatile, wide band gap semiconductor with large exciton binding energy (60 meV) and interesting piezoelectric and ferroelectric properties. Its high chemical and thermal stability and abundance make it an attractive material for a wide variety of applications, such as, UV emitters and detectors, SAW devices, gas sensors and transparent conducting electrodes [1]. Several growth techniques, such as, spray pyrolysis, sputtering, pulsed laser deposition, MBE and MOCVD have been extensively used for the deposition of un-doped and doped ZnO films, among which, sputtering has been the most widely used. Most of this work has been reviewed in Refs. [1] and [2]. High quality epitaxial films of un-doped ZnO have usually been deposited on single crystalline substrates, such as sapphire by MBE [3,4], MOCVD [5,6], PLD [7,8] and sputtering [9–11]. However, reports of sputtering of ZnO films on amorphous substrates such as quartz and glass with properties comparable to those of epitaxial films are limited [12–14]. In this work, we report the sputtering of un-doped ZnO films of high optical quality deposited on fused quartz substrates. In particular, the effect of substrate temperature on the crystallinity and band edge luminescence has been studied.

2. Experimental details

ZnO films were deposited on quartz substrates by reactive rf magnetron sputtering. A 99.9% pure Zn target of 3-in diameter was used. The target to substrate distance was 55 mm. The base pressure was 1×10\textsuperscript{−5} mbar. The flow rates of argon (24 sccm) and oxygen (6 sccm) were controlled by mass flow controllers. Deposition was carried out at a working pressure of 10\textsuperscript{−2} mbar, after pre-sputtering with argon for 10 min. The sputtering power was maintained at 400 W during deposition. The depositions were carried out in the temperature range of room temperature to 600 °C.

X-ray diffraction (XRD) studies were performed with a PANalytical X’Pert PRO powder diffractometer using Cu K\textsubscript{α} radiation. Specular transmittance (\(T\)) and reflectance (\(R\)) measurements at normal incidence were carried out with a PerkinElmer Lambda-950 UV/Visible spectrophotometer. Photoluminescence (PL) measurements were carried out at room temperature using a 325 nm He–Cd laser and a JOBIN YVON HR-460 monochromator. Raman spectra of the films were recorded at room temperature in back scattering geometry, using JOBIN YVON HORIBA HR-800 instrument equipped with a 20 mW Ar\textsuperscript{2} laser (514.5 nm). Ambios XP-2 surface
profilometer was used for thickness measurements. AFM studies were carried out in contact mode with silicon nitride probes using Digital Instruments Nanoscope IV Multimode SPM.

3. Results and discussion

The growth rate of films increased from $\sim 1.0 \, \mu\text{m/h}$ at room temperature, to $\sim 1.4 \, \mu\text{m/h}$ at 100 °C and remained unchanged at higher substrate temperatures. All the films were approximately of the same thickness (600±50 nm). XRD patterns of typical ZnO films are shown in Fig. 1. The films deposited at room temperature and 100 °C showed a strong peak at $2\theta \sim 34^\circ$ and a weak peak $\sim 72^\circ$, which were identified respectively as (0002) and (0004) reflections of hexagonal ZnO, indicating, a strong c-axis orientation of crystallites. However, the films deposited in the temperature range of 150–250 °C (a typical case of 200 °C is shown in Fig. 1) exhibited multiple reflections (as indexed in Fig. 1), though with a dominant (0002) peak. Interestingly, the films deposited at 300 °C and higher temperatures, again showed peaks corresponding to only (0002) and (0004) reflections. The intensity variation of (0002) peak with substrate temperature shown in Fig. 1 also reveals an interesting pattern. The film deposited at 300 °C exhibited (0002) peak intensity, nearly 40–60 times that from the films deposited at lower temperatures. At higher temperatures, the intensity decreases gradually but remains within the same order of magnitude.

The enhancement of c-axis orientation with increasing substrate temperature above 100 °C is attributed to increase in surface diffusion of the adsorbed species and is in tune with most of the earlier studies [1,2]. The unusual reduction in the extent of c-axis orientation at intermediate temperatures and its subsequent enhancement at higher temperatures seen in the present work, has been reported earlier in sputtered ZnO films [15]. There are also a few reports on ZnO films deposited by sputtering [12,16] and MOCVD [17], showing a strong c-axis preferred orientation near room temperature followed by its reduction with increase in substrate temperature to the range 150–300 °C. The present results also show that the film deposited at 300 °C is of the highest quality in terms of c-axis orientation of crystallites. The marginal decrease in intensity of (0002) peak seen at higher substrate temperatures has not been reported earlier and is attributed to mis-orientation of (0002) planes with substrate surface.

A comprehensive understanding of the processes leading to c-axis orientation over the complete range of substrate temperatures, which is required to explain all the above features, seems to be lacking. Recently, Kajikawa [18] has extensively reviewed and analyzed the complex dependence of c-axis preferred orientation in sputtered ZnO films on processes such as, preferential nucleation, preferential crystallization,
sticking, surface diffusion and grain growth and concluded that the validity of each process under given experimental conditions cannot be ensured, due to lack of reliable data on sticking coefficients and surface diffusivities.

Fig. 1 also reveals shifts in the positions of (0002) and (0004) peaks, with substrate temperature. The position of (0002) peak shifts monotonically from 34.18° for the film deposited at room temperature to 34.44° for the film deposited at 400 °C, the later being quite close to the corresponding value of 34.467° for bulk ZnO (JCPDS file No. 75-1526). The position of the (0002) peak remains unchanged for the films deposited at higher substrate temperatures. The lattice constant $c$ was obtained from the position of the (0002) peak for all the films, and was used to estimate the strain ($\varepsilon$) in the films along $c$-axis given by, $\varepsilon = (c_{\text{film}} - c_{\text{bulk}})/c_{\text{bulk}}$. Fig. 2(a) shows the variation of strain with substrate temperature. The film deposited at room temperature showed the maximum compressive strain ($\sim 8 \times 10^{-3}$), which decreased monotonically to nearly zero at $\sim 400$ °C. The expected thermal strain introduced by differences in thermal expansion coefficients of the film ($\alpha_{\text{ZnO}} = 4 \times 10^{-6}$ K$^{-1}$) and quartz substrate ($\alpha_{\text{quartz}} = 0.5 \times 10^{-6}$ K$^{-1}$) at a substrate temperature of 300 °C is $\sim 10^{-3}$ and is expected to be lesser at lower substrate temperatures. The higher values of strain ($2 - 8 \times 10^{-3}$) in the films deposited below 400 °C and its decrease with increasing substrate temperature indicate that thermal stress does not contribute significantly to the observed strain. Further, the amorphous nature of quartz substrate rules out strain due to lattice mismatch. Hence the compressive strain in the films deposited below 400 °C is not attributed to extrinsic stress but is considered intrinsic to the growth process. It has been reported in the case of ZnO films that O$^-$ ions formed at the target have sufficient energies to bombard the growing film and cause implantation or displacement of surface atoms deeper into the film, resulting in compressive strain [19]. The decrease in strain at higher substrate temperatures is attributed to annealing effects and consequent reduction in defects.

The FWHM of (0002) peak was used to estimate the crystallite size along $c$-axis (growth direction) by Scherrer’s relation. The variation of crystallite size with substrate temperature is shown in Fig. 2(b). It is seen that in the films deposited up to 100 °C, the crystallite size along the growth direction is $\sim 100$ nm. A noticeable decrease is seen in crystallite size for films deposited in the temperature range of 150–250 °C, which had earlier exhibited reduced $c$-axis...
preferred orientation. However, at substrate temperature of 300 °C, the crystallite size increases to \(\sim 80\) nm and remains practically unchanged till \(\sim 600\) °C, whence a slight increase to \(\sim 110\) nm is noticed.

Typical AFM images of the films are shown in Fig. 3. Fig. 3(a) shows surface features of uniform lateral size of 50–70 nm for room temperature deposited film. In contrast, the film deposited at 200 °C shows a mixture of small (40–80 nm) and large (150–200 nm) surface features (Fig. 3(b)). However, the film deposited at 300 °C again shows uniform features similar to the room temperature deposited films, but with larger size of 60–100 nm (Fig. 3(c)). The film deposited at 600 °C, shows distinctly different surface morphology, as large features of \(\sim 250\) nm along with smaller features of 60–100 nm are seen. The increase in the lateral size of morphological features with substrate temperature is attributed to the increase in lateral size of crystallites.

Fig. 4 shows the Raman spectra of ZnO films along with that of quartz substrate. The ZnO film deposited at room temperature shows two very broad peaks centered \(\sim 398\) cm\(^{-1}\) and \(\sim 569\) cm\(^{-1}\). The broad peak \(\sim 398\) cm\(^{-1}\) is attributed to a combination of \(A_1(\text{TO})\) and \(E_1(\text{TO})\) modes [20,21]. The appearance of LO modes has been attributed to the presence of oxygen defects and zinc interstitials [22]. These observations, including the weak \(E_2\)-high mode as a shoulder, indicate the presence of structural defects, misorientation of (0002) planes and disorder in the film [22–24], in spite of its \(c\)-axis preferred orientation, seen in the XRD pattern. The film deposited at 300 °C shows an enhancement of \(E_2\)-high intensity, though a broad band of TO modes is still seen. The increase in the prominence of \(E_2\)-high peak corroborates well with the significant improvement in \(c\)-axis orientation of the film.

Interestingly, the film deposited at 600 °C shows only an intense \(E_2\)-high peak along with weak \(A_1(\text{LO})\) mode \(\sim 575\) cm\(^{-1}\), which is characteristic of strong \(c\)-axis orientation [1,21]. The reduction in intensity as well as shift of LO modes to higher frequencies seen in this film, are attributed to decrease in point defects [21]. The decrease in defects correlates well with the increase in crystallite size and decrease in stress, leading to overall improvement in crystallinity of the film deposited at 600 °C. It is interesting to note that such features are seen in the films deposited at 600 °C, which shows a lesser degree of \(c\)-axis orientation, as compared to that deposited at 300 °C.

Typical specular \(R\) and \(T\) spectra of the films are shown in Fig. 5(a). All the films exhibit high transmittance in the visible region, limited by 10–15% reflectance. The sharp fall in transmittance below 400 nm is due to the onset of fundamental peak \(\sim 569\) cm\(^{-1}\) is assigned to a combination of \(A_1(\text{LO})\) and \(E_1(\text{LO})\) modes [20,21]. The appearance of LO modes has been attributed to the presence of oxygen defects and zinc interstitials [22]. These observations, including the weak \(E_2\)-high mode as a shoulder, indicate the presence of structural defects, misorientation of (0002) planes and disorder in the film [22–24], in spite of its \(c\)-axis preferred orientation, seen in the XRD pattern. The film deposited at 300 °C shows an enhancement of \(E_2\)-high intensity, though a broad band of TO modes is still seen. The increase in the prominence of \(E_2\)-high peak corroborates well with the significant improvement in \(c\)-axis orientation of the film.

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Fig. 6. PL spectra of ZnO films deposited at different substrate temperatures.
absorption of ZnO. Absorption coefficient ($\alpha$) was obtained from specular $R$ and $T$ data and thickness ($d$) of the films, using the expression,

$$T(\lambda) = (1 - R(\lambda))^2 e^{-\alpha(\lambda)d}$$

for a self supporting film, with high absorption and low reflectance. The corresponding plots of $\alpha^2$ vs. $h\nu$ are shown in Fig. 5(b), from which, the direct band gap of the films has been estimated. The band gaps for all the films are $\sim 3.30$ eV, which agrees well with bulk band gap of ZnO. It is however observed that with the increase in substrate temperature, the $\alpha^2$ vs. $h\nu$ plots become sharper, indicating a reduction of defects in the films. The presence of optically active defects in films deposited at room temperature and 300 °C is evident from the relatively enhanced sub-band gap absorption in the films.

Fig. 6 shows room temperature PL spectra of the films. All the films show strong emission $\sim 377$ nm, attributed to near band edge UV luminescence of ZnO [25]. Weak and broad bands are seen in green–yellow region, which are known to arise from oxygen defects and zinc interstitials [1,26]. The intensity of band edge luminescence is found to increase with substrate temperature, accompanied by narrowing of the peak, as reported earlier for sputter deposited ZnO films on Si [27]. The PL spectrum of the ZnO film deposited at 600 °C showed a high intensity band edge emission with FWHM of 102 meV. This value of PL peak width is comparable to reported values for ZnO films deposited by MBE [3], MOVPE [25] and PLD [26] on single crystalline substrates. The PL results are in line with optical absorption, which indicate reduction of optically active defects in the films deposited at 600 °C. It may be noted that the most intense and narrow PL emission does not come from the ZnO film deposited at 300 °C, which exhibited strongest $c$-axis orientation. The improved band edge luminescence of the film deposited at 600 °C is attributed to its better overall crystallinity resulting from reduction of strain and defects as well as improvement in crystallite size (both lateral and along growth direction) as indicated by the structural studies presented above and supported by Raman spectra.

4. Conclusions

ZnO thin films of high optical quality have been deposited on quartz substrates by reactive sputtering. Though XRD studies showed the strongest $c$-axis orientation for the films deposited at 300 °C, AFM and Raman studies indicated that the films deposited at 600 °C possess better overall crystallinity resulting from reduction of strain and defects and improvement in crystallite size. As a consequence of reduction in optically active defects, the ZnO film deposited at 600 °C showed a high intensity band edge luminescence with FWHM of $\sim 102$ meV, which is comparable to the reported values for films deposited on single crystalline substrates.

Acknowledgements

The financial support from MHRD (Govt. of India) for this work is gratefully acknowledged. Sukhvinder Singh is thankful to CSIR, New Delhi (India) for Senior Research Fellowship. FIST (Physics)-IRCC central SPM Facility and CRNTS of IIT Bombay are respectively acknowledged, for providing AFM and Raman facilities.

References