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Origin of stress in radio frequency magnetron sputtered zinc oxide thin films

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Highly *c*-axis oriented ZnO thin films have been deposited on silicon substrates by planar rf magnetron sputtering under varying pressure (10–50 mTorr) and oxygen percentage (50–100%) in the reactive gas (Ar + O₂) mixture. The as-grown films were found to be stressed over a wide range from -1×10^{11} to -2×10^8 dyne/cm² that in turn depends strongly on the processing conditions, and the film becomes stress free at a unique combination of sputtering pressure and reactive gas composition. Raman spectroscopy and photoluminescence (PL) analyses identified the origin of stress as lattice distortion due to defects introduced in the ZnO thin film. FTIR study reveals that Zn-O bond becomes stronger with the increase in oxygen fraction in the reactive gas mixture. The lattice distortion or stress depends on the type of defects introduced during deposition. PL spectra show the formation of a shoulder in band emission with an increase in the processing pressure and are related to the presence of stress. The ratio of band emission to defect emission decreases with the increase in oxygen percentage from 50 to 100%. The studies show a correlation of stress with the structural, vibrational, and photoluminescence properties of the ZnO thin film. The systematic study of the stress will help in the fabrication of efficient devices based on ZnO film. © 2011 American Institute of Physics. [doi:10.1063/1.3552928]

I. INTRODUCTION

Zinc oxide (ZnO), a wide bandgap (3.4 eV), II — VI compound semiconductor, has a stable wurtzite structure with lattice constant, $a = 3.2498$ Å and $c = 5.20661$ Å.¹ The *c*-axis oriented ZnO thin films have attracted intensive research effort in the both basic and applied research because of their unique properties and multifunctional applications such as transparent electronics,² ultraviolet photodetectors,³ piezoelectric devices,⁴ chemical sensors,^{5,6} biosensors,⁷ and spintronics.^{8,9} In most of these applications, the presence of stress in the ZnO thin films has been identified as a critical parameter that affects its functional properties thereby degrading the device performance. Various deposition techniques are being used to grow ZnO thin films, and each technique has its own advantages and disadvantages.¹ Rf magnetron sputtering is found to be the most suitable technique due to better control over stoichiometry and deposition of uniform films.^{1–4}

Extensive work on the structural and optical properties of highly *c*-axis oriented ZnO thin films prepared by rf sputtering has been reported, showing these properties to depend strongly on the processing conditions.^{10–19} However, there are few reports on the effect of stress on the structural, optical, and electrical properties of the ZnO films^{10–12}. The optimization of sputtering pressure and oxygen content in the reactive gas is important for the growth of stress free ZnO films.^{13–19} The lattice distortion or presence of stress in the

films depends on the type of defects introduced during processing. The systematic studies of these defects will assist in the realization of efficient functional devices based on ZnO films. However, no report is available toward understanding the origin of stress in ZnO thin films especially using sensitive characterization tools such as Raman spectroscopy and photoluminescence spectroscopy. In the present work, efforts have been made toward a systematic study on the origin of stress in rf sputtered ZnO thin films. The ZnO thin films were deposited by varying processing pressure and reactive gas composition and studied using various characterization tools. The unique combination of sputtering pressure and oxygen content in the reactive gas was identified for the growth of stress free ZnO thin films.

II. EXPERIMENTAL PROCEDURES

ZnO films (1.0 μm thick) were deposited on silicon (100) substrates by rf magnetron sputtering unit using a 6 in diameter zinc metal target with the typical processing conditions as reported earlier¹⁹ at different growth pressures (10–50 mTorr) and oxygen percentages (50–100%) in a reactive gas mixture (O₂ + Ar) at room temperature. It may be noted that the native oxide layer from Si surface has not been removed prior to deposition of ZnO. The zinc target was pre-sputtered for 30 min using a shutter in pure argon ambient. The structural properties of films were studied using Philips PW 1130 X-ray diffractometer (XRD) using Cu Kα radiation. The surface morphology of the films was investigated with a JEOL JSM-840 scanning electron microscope (SEM). Fourier transform infrared (FTIR) spectroscopy was used in

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transmission mode to confirm the formation of Zn-O bond. ZnO films were also deposited on transparent KBr pellets (1.2 cm diameter) under similar processing conditions for IR studies. Vibrational phonon studies on deposited films were performed using a Raman spectroscopy (Renishaw Invia Raman Microscope) using 514 nm laser radiation as the excitation source. Photoluminescence (PL) studies were performed using excitation with 325 nm radiation from a He—Cd laser and analyzed using 0.5 m spectrometer (SpectraPro 2500i), at 13 K.

III. RESULTS AND DISCUSSION

A. Structural properties

ZnO films deposited on silicon substrates were found to be uniform, transparent, and strongly adherent. Figure 1 shows the XRD pattern of ZnO thin films deposited at 20 mTorr sputtering pressure and under varying oxygen percentage (50–100%). Only the reflection corresponding to (002) plane of wurtzite structure was observed in the XRD pattern for all prepared films, indicating the growth in a preferred orientation along the *c* axis normal to the Si substrate.

The (002) reflection for ZnO thin film grown at 20 mTorr pressure and 100% oxygen was observed at Bragg's angle, 2θ 33.99° (Fig. 1), which is lower than the reported value (34.42°) for bulk ZnO. The deviation in the 2θ value is generally associated with the presence of stress in the film.¹¹ Therefore lower value of 2θ indicates that residual stress is present in the ZnO film grown in 100% oxygen ambient. The position of the (002) XRD reflection was found to depend strongly on both the processing oxygen composition (Fig. 1) and sputtering pressure (Table I). With a decrease in oxygen percentage from 100 to 50% in reactive gas mix, the position

TABLE I. Stress in ZnO thin film grown at varying sputtering pressure and O₂ percentages. Pressures are in mTorr.

Sputtering Pressure → Oxygen percentage (%) ↓	10	20	25	30	40	50
	Stress ($\times 10^{10}$ dyne/cm ²)					
100	−10.432	−5.577	−3.702	−2.151	−0.432	−2.340
80	−7.453	−4.143	−1.866	−0.347	−1.944	−3.956
60	−5.145	−2.412	−0.208	−1.023	−3.497	−5.532
50	−3.018	−0.020	−1.089	−2.920	−4.979	−6.916

of (002) reflection for ZnO film approaches that of the bulk value. The deviation in the position of (002) XRD peak from the bulk value was found to be minimum at a particular processing pressure and increases for films deposited at other pressures.

The average grain size of the ZnO films is estimated from the full width at half maximum, (FWHM) of the (002) XRD peak using the well-known Scherrer's formula, after subtracting the instrumental broadening corresponding to Si peak from the observed FWHM.¹¹ The estimated values of grain size for all ZnO films in this work are in the range of 25–50 nm.¹⁹ The SEM images of the surface of ZnO thin films grown at 20 mTorr sputtering pressure and different oxygen percentages are shown in Fig. 2. The obtained values of grain size were found to be in well agreement with the SEM images. The grain size of the deposited film was found to increase with a decrease in the processing oxygen percentage, as shown in Fig. 2, and was also found to increase with increasing sputtering pressure. The increase in grain size may be due to the extensive collisions between the sputter species at higher pressure, where atoms have enough time to coalesce together and form bigger crystallites on the substrate surface. Similarly, reduction in the processing oxygen content at fixed sputtering pressure results in an increase in the grain size. This clearly indicates that the influence of overall sputtering pressure on grain size does not apply to the change due to variation in oxygen percentage. Similar results have been reported on glass also.¹⁹

The residual stress, σ , in the as-grown ZnO thin films was evaluated using the estimated value of lattice constant, *c*, obtained from XRD data and is listed in Table I as a function of sputtering pressure and oxygen percentage.¹³ A significant amount of stress was still present in the film deposited at 10 mTorr due to extensive bombardment of energetic particles on film surface. The negative sign of stress (Table I) indicates that the lattice constant, *c*, of as-grown ZnO films is elongated as compared to that of single crystal, and the unit cells are under compressive stress.^{11,19} The increase in sputtering pressure was found to reduce the stress, and ultimately ZnO thin films become almost stress free at an optimum value of processing pressure (Table I). Similar variation in stress was observed for the ZnO film prepared under varying oxygen percentages at a fixed sputtering pressure. It was identified that unique combinations of the sputtering pressure and oxygen percentages are required to produce ZnO thin films with minimal stress. It may be noted

FIG. 1. (Color online) XRD spectra of ZnO thin films deposited on silicon substrates at 20 mTorr and varying oxygen percentages (50–100%).

FIG. 2. SEM images of ZnO thin films deposited at 20 mTorr pressure and different oxygen percentages (a) 100%, (b) 80%, (c) 60%, and (d) 50%.

that a slight change in the value of stress was observed in the present study in comparison to previous work on glass substrates. However, the variation in the stress with processing conditions was found to be similar. The deviation in the value of stress may be due to change in the substrate.

The processing of ZnO thin films under reactive ($O_2 + Ar$) atmosphere at low sputtering pressure (10 mTorr) may induce native defects at the interstitial site or grain boundaries due to extensive bombardment on the surface of the substrate, resulting in the elongation of unit cell along the c axis, thereby giving higher value of stress. However, when ZnO films were processed with reduced oxygen percentage (100–50%), the concentration of interstitial oxygen decreases resulting in reduction in stress from $(-10.4 \text{ to } -3.0) \times 10^{10} \text{ dyne/cm}^2$ (Table I). Furthermore, increase in collision between the energetic species in the sputtering chamber with increasing processing pressure may also restrict the incorporation of oxygen at interstitial sites or grain boundaries. This is further supported by our data where higher processing pressure is required to obtain stress free ZnO film under oxygen rich environment. At high sputtering pressure (50 mTorr), the stress in ZnO film was found to increase from $(-2.3 \text{ to } -6.9) \times 10^{10} \text{ dyne/cm}^2$ with a decrease in processing oxygen percentage (Table I). The adatom surface mobility is reported to be less at higher deposition rate,²⁰ therefore films grown under low oxygen content and high sputtering pressure have higher residual stress. The increase in oxygen percentage at higher sputtering pressure reduces the deposition rate, and therefore the sputtered species have enough time to arrange themselves on the substrate surface resulting in a decrease in stress in the deposited ZnO film.

B. Vibrational properties

ZnO crystallizes in the hexagonal wurzite structure, which belongs to the space group C_{6v}^4 . The group theory predicts the phonon modes corresponding to the $2E_2$, $2E_1$, $2A_1$, and $2B_1$ symmetries.^{21,22} The two B_1 symmetry modes are both Raman and IR inactive. The two E_2 modes [$E_2(\text{high})$, $E_2(\text{low})$] are nonpolar modes and are Raman active only. The low frequency E_2 mode is associated with the vibration of the heavy Zn sub-lattice, while the high frequency E_2 mode involves only the oxygen atoms. Both A_1 and E_1 modes are polar and split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active. The A_1 phonon vibration is polarized parallel to the c axis while the E_1 phonon is polarized perpendicular to the c axis.

1. Infrared spectroscopy

FTIR spectra of ZnO thin films, as shown in Fig. 3, show a strong absorption band in the region $400\text{--}440 \text{ cm}^{-1}$ corresponding to the $E_1(\text{TO})$ mode, which is in agreement with earlier reports for ZnO films and bulk confirming the formation of Zn-O bond.^{22–24} A continuous shift in the absorption band toward higher frequency was observed with a decrease in oxygen percentage in the reactive gas mixture at a fixed sputtering pressure of 20 mTorr. No significant shift in the position of $E_1(\text{TO})$ mode was observed (Fig. 4) in the FTIR spectra of ZnO films grown with increasing sputtering pressure and at fixed oxygen percentage (50%). The frequency of absorption mode depends on the relative masses of the constituent atoms, force constants of the

FIG. 3. (Color online) FTIR spectra for ZnO films deposited at 20 mTorr and different oxygen percentages.

bonds, and relative arrangement of the atoms. The bond energy is calculated using the $E_1(\text{TO})$ mode, and a decrease in its value from $(8.44 \text{ to } 8.08) \times 10^{-21}$ kJ/mol was observed for the ZnO films prepared with decreasing oxygen percentage from 100 to 50% at a fixed sputtering pressure of 20 mTorr.²⁵ However, the variation in bond energy was found to be consistent for all pressures. The higher value of bond energy obtained for ZnO thin film deposited under 100% oxygen ambient implies that more energy is required for the transition from the ground state to the first excited state.²⁵

The ratio of the population in the conduction band (N_{upper}) to the valence band (N_{lower}) is calculated from the estimated bond energy.²⁵ An increase from 13.0 to 14.2% in the number of transitions from ground state to the excited state was observed in the films prepared under decreasing oxygen percentage from 100 to 50%. The observed decrease in transitions was attributed to the fact that the oxygen is a strong electron acceptor; thereby more electrons from the conduction band are being captured by the excess interstitial

oxygen in the ZnO film prepared under high oxygen percentage. With the decrease in oxygen percentage in the gas mixture, one weak absorption mode at 567 cm^{-1} corresponding to $A_1(\text{LO})$, starts appearing, indicating more crystallites are aligned along the c axis.²⁶

2. Raman spectroscopy

Room temperature Raman spectroscopy studies on ZnO thin films deposited on Si substrate were carried out under backward scattering configuration with incident light normal to the sample surface. Figures 5 and 6 show the Raman spectra of ZnO thin films deposited under different processing pressure and oxygen percentage. The phonon modes observed at around 300, 500, 610, and 670 cm^{-1} in the Raman spectra (Figs. 5 and 6) are attributed to Si substrate. Raman modes are observed at around 437, 574, and 583 cm^{-1} for all ZnO films and assigned to $E_2(\text{high})$, $A_1(\text{LO})$, and $E_1(\text{LO})$ modes, respectively.^{21,22,27,28}

$E_2(\text{high})$ is the characteristic mode of ZnO wurtzite phase at around 437 cm^{-1} and is associated with oxygen atoms.²³ The position of $E_2(\text{high})$ optical mode in ZnO thin films grown with 50% O_2 and 50% Ar was found to be in agreement with the corresponding value 438 cm^{-1} reported for bulk ZnO.²¹ A shift in the $E_2(\text{high})$ phonon mode toward higher frequency from 437 to 447 cm^{-1} was observed in the Raman spectra (Fig. 5) of ZnO thin films grown with increasing oxygen percentage from 50% to 100% at a fixed sputtering pressure of 20 mTorr. The observed blueshift in the $E_2(\text{high})$ Raman mode indicates the presence of compressive stress in the deposited ZnO thin films²⁹ and stress becomes minimal in the films grown at 20 mTorr sputtering pressure in 50% oxygen and 50% argon ambient. A weak and broad optical mode was observed at around $570 \text{ to } 590 \text{ cm}^{-1}$ in the Raman spectra of all as-grown ZnO thin films that is attributed to $E_1(\text{LO})$ phonon mode (Figs. 5 and 6). It may be noted from Fig. 5 that the $A_1(\text{LO})$ and $E_1(\text{LO})$ phonon modes merge and the Raman intensity increases with the increase in oxygen percentage in the sputtering gas. The presence of an

FIG. 4. (Color online) FTIR spectra for ZnO films deposited at 50% oxygen under varying pressure (20–50 mTorr).

FIG. 5. (Color online) Raman spectra for ZnO films deposited at 20 mTorr under various oxygen percentages (100–50%).

FIG. 6. (Color online) Raman spectra for ZnO films deposited under 50% oxygen ambient at varying sputtering pressure (10–50 mTorr).

electric field can induce scattering by Raman inactive optical phonons and is due to the change in lattice symmetry.²⁶ The electric field induced Raman scattering was observed for the LO phonon scattering and therefore the observed optical mode at around $570\text{--}590\text{ cm}^{-1}$ is directly related to the presence of a built-in electric field.²⁶

The ratio of the intensity of $A_1(\text{LO})$ to $E_1(\text{LO})$ phonon mode increases with the increase in the sputtering pressure from 20 to 50 mTorr in 50% oxygen ambient (Fig. 6). However, at lower sputtering pressure (10 mTorr), the ratio of intensity of $A_1(\text{LO})$ to $E_1(\text{LO})$ mode decreases, indicating an increase in the intensity of $E_1(\text{LO})$ phonon mode. The $E_1(\text{LO})$ mode is related to oxygen vacancies that results in residual stress in the ZnO thin films deposited at low sputtering pressure.

C. Photoluminescence studies

PL measurements are important to extract the information related to the optical emissions and the quality of the deposited films. Two emission bands are generally observed in the PL spectra of ZnO, an intense and sharp band at around 380 nm corresponding to the near bandedge (NBE) emission due to free excitons³⁰ and a broad band emission at longer wavelength that is attributed to the presence of native defects, nonstoichiometry, and crystal imperfections.²³ The most referred defects in ZnO are zinc interstitials (Zn_i), zinc vacancies (V_{Zn}), oxygen vacancies (V_o), oxygen interstitials (O_i), and oxygen antisites (O_{Zn}). V_o and Zn_i contribute as shallow donor states and V_{Zn} , O_i , and O_{Zn} as deep level acceptor states in the forbidden gap.

Figure 7 shows the PL spectra recorded at 13 K for ZnO thin films deposited under different oxygen percentages at a fixed sputtering pressure (20 mTorr). The NBE peak becomes sharper for the ZnO thin films deposited with decreasing oxygen percentage (100–50%), indicating an improvement in the quality of as-deposited ZnO thin films. A blueshift in the NBE peak is observed with decreasing oxygen percentage (Fig. 7) and is in agreement with an earlier

report on the variation of bandgap of ZnO with oxygen percentage in the gas mixture.¹⁹

The PL spectra of ZnO thin films deposited under 100% oxygen exhibit the orange emission at around 2.0 eV (Fig. 7), which is associated with the presence of interstitial oxygen. A blueshift in the deep emission peak was observed (Fig. 7) with a decrease in the oxygen percentage, indicating the presence of antisite oxygen defects.³¹ The observed green emission (2.5 eV) from the ZnO thin film deposited under 60% oxygen and 40% argon is attributed to the presence of oxygen vacancies.²³ However, no significant deep emission was observed in the PL spectra of ZnO films grown in 50% oxygen ambient at 20 mTorr, indicating reduction in radiative defects or impurities. The observed result is in accordance with the XRD studies discussed earlier, where a highly c axis oriented and stress-free ZnO film was obtained at 20 mTorr and 50% oxygen.

The PL spectra of ZnO thin films deposited in 50% oxygen ambient and at different sputtering pressure (10–50 mTorr) are shown in Fig. 8. A strong emission at around 2.5 eV was observed in the ZnO film grown at 10 mTorr and is attributed to oxygen vacancies.^{21,23} It may also be noted that a large amount of stress is present in the film deposited at 10 mTorr due to extensive bombardment of energetic sputtered particles on the film surface. However, a ZnO film grown at higher pressure (>10 mTorr) exhibits a strong NBE peak, and no deep defect emission was observed (Fig. 8). A shoulder near the NBE peak starts appearing with an increase in the sputtering pressure and becomes prominent at higher growth pressure (50 mTorr), where the film is found to be highly stressed. At higher sputtering pressure, the collisions between the sputtered species are very high. The kinetic energy of zinc particles is reduced as a result of collisions

FIG. 7. (Color online) PL spectra recorded at 13 K for ZnO films deposited at 20 mTorr and varying oxygen percentages from 100 to 50%.

FIG. 8. (Color online) PL spectra recorded at 13 K for ZnO films deposited in 50% oxygen percentage and at different pressures (10–50 mTorr)

with oxygen molecules. This is expected to result in a decrease in the concentration of Zn in as-grown thin films, resulting in excess zinc vacancies (V_{Zn}). The shoulder near the NBE is at about 3.1 eV, and this energy level corresponds to the electronic transition from the conduction band to the acceptor energy level of V_{Zn} .³² Thus with the increase in sputtering pressure, zinc vacancies are expected to increase in the deposited film, resulting in the presence of a shoulder (3.1 eV) near NBE. A narrow and sharp NBE peak observed at 20 mTorr processing pressure indicates that ZnO thin film of good quality with preferred *c*-axis orientation and minimal stress can be obtained.

III. CONCLUSION

ZnO thin films having stress over the wide range (-1×10^{11} to -2×10^8 dyne/cm²) have been deposited by rf sputtering under varying processing pressure and oxygen percentages in the reactive gas mixture. The films deposited under a unique combination of sputtering pressure and oxygen percentage in the reactive gas mixture results in minimal stress. The vibrational and photoluminescence studies indicate a correlation between the native defects and the stress in the film. The shift in E_2 (high) optical phonon mode is due to the presence of stress in the film. A shift in the deep defect emission peak toward higher energy shows a continuous change in the nature of defects introduced in the ZnO thin films with varying oxygen percentage in the reactive gas mixture. Stress free and highly *c*-axis oriented ZnO thin films without any lattice distortion was obtained at 50% oxygen and 20 mTorr pressure, where a sharp NBE peak was observed, without shift in the E_2 (high) optical phonon modes and (002) XRD peak from the values of bulk ZnO.

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