3
Deposition of ZnO Thin Films

RF sputtered nano-crystalline ZnO thin films were deposited on Si substrate under various deposition conditions. Firstly, relative change in surface morphology and structural characterization with stress analysis have been studied for deposited ZnO thin films with various substrate temperature. In following section, effect of Ar: O_2 gases ratio on deposited thin films with variation of substrate temperature also studied. Surface morphologies and structural characterization with stress analysis also studied.

3.1 INTRODUCTION

In recent years, Zinc oxide thin film have been widely used and have drawn significant interest because of its promising properties like wide band gap of 3.37 eV at room temperature, large excitation binding energy of 60 meV, chemical stability, piezoelectric, nontoxic and strong tendency to deposit along c-axis [Znaidi, 2010; Ozgur *et al.*, 2005]. ZnO thin films are widely used in surface acoustic waves devices (SAW), light emitted diodes, photo-detectors and gas sensors etc. [Du *et al.,* 2007; Hwang *et al.,* 2007; Chen *et al.,* 2009; Suchea *et al.,* 2006]. Various thin film deposition techniques were used such as pulsed laser deposition (PLD), sputtering, molecular beam epitaxy, thermal evaporation, chemical vapor deposition (CVD), sol-gel, vacuum arc deposition etc. [Seshan, 2012; Lee and Park, 2003; Kern, 2012; Kumar *et al.,* 2015]. Crystallinity of ZnO thin film is one of the vital concern which effects commercial applications based on ZnO thin films. For reproducible and homogeneous growth of nano-crystalline thin films, RF sputtering is the most convenient method for ZnO thin films deposition. RF sputtering provides ability to deposit better film quality, nontoxic process and uniform film deposition throughout substrate even at low operating temperature [Ding *et al.,* 2010; Lu *et al.,* 2001]. It is reported that structural and optical properties along with surface morphology of deposited thin films are highly influenced by sputtering parameters, such as deposition pressure, RF power, gas ratio and operating temperature [Ismail and Abdullah, 2013; Chauhan *et al.,* 2014; Duygulu *et al.,* 2014; Kar *et al.,* 2010; Song, 2008; Zhu *et al.,* 2012]. In this chapter, complete understanding of fundamentals of nanostructured growth of thin film have been explained. Moreover, it's been reported earlier that good quality ZnO thin films are not possible to deposit on silicon substrate because of large lattice mismatch between ZnO and Silicon [Wang *et al.,* 2008; Karamdel *et al.,* 2012]. However, it is an essential requirement to achieve high quality ZnO thin films for integration of optical-electronics devices on large scale. In this chapter, High quality nano-crystalline ZnO thin film were deposited on silicon substrate with less defects and residual stress. In addition to these fundamental growth mechanisms for ZnO thin films, we will also study the effect of sputtering deposition parameters such as operating temperature and gas ratio (Ar/O_2 gas flow ratio) on structural, optical and surface morphology of ZnO thin films.

3.2 GROWTH MECHANISM OF THIN FILMS

Growth or deposition of nanostructure thin films has always been an important part to be studied since a century. Many deposition methods have been invented and improved till now for film growth by numerous researchers. Nano-structured thin film growth is deposited by "bottom –up" approach which requires fundamental understanding of thin film growth mechanism. Initial nucleation process and subsequent growth of nucleation sites on growth surfaces or

substrate always act as key aspect for growth of nanostructured thin films. Nucleation process always plays a significant role in the growth of thin film and has strong influence on crystallinity of deposited film. For selecting initial nuclei process, it is essential to know substrate and grown thin film depends on nucleation process and thermodynamic of adatoms on substrate [Ratsch and Venables, 2003; Reichet, 1998; Venables *et al*., 1984; Zhang and Lagally, 1997]. Figure 3.1 illustrates schematic diagram of three basic models for initial nucleation in nanostructure thin film deposition.

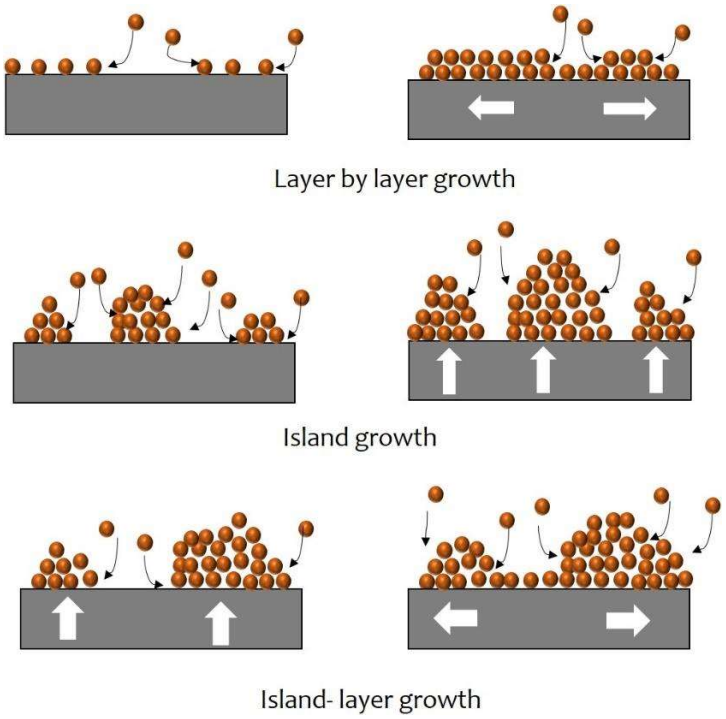

Figure 3.1: Schematic diagrams of three basic models for initial nucleation in thin film deposition

Three nucleation modes for nanostructure thin film growth mechanism are briefly described as [Cao, 2004; Vook, 1984]

(1) Island growth (Volmer-weber growth) described as three dimensional island growth. In this growth mechanism, growth species (adatom) are strongly bonded with each other in comparison to incoming particle-substrate interaction. This strong atom to atom interaction leads to formation of three dimensional islands or clusters throughout substrates. These island coalescing results in multilayer thin film growth.

(2) Layer by layer growth (Frank-van der Merwe growth) is a two dimensional growth mechanism for uniform thin film growth. In this nucleation mode, there is strong bonding between growth species and substrate in comparison to growth species (adatom) bonding with each other. This results in fully formed monolayer formation before occurrence of deposition of second layer.

(3) Island-layer growth (Stranski-Krastonov growth) mechanism is combined form of layer by layer growth and island growth mechanism. At first, monolayer of incoming species are formed on substrate and few layers are stacked up to deposit thin film. After certain level of deposition, growth species start three dimensional island growth for deposition

of nano-structure thin films. This kind of growth mechanism is highly unpredictable and typically develops a stressed nanostructure thin film.

The above mentioned growth mechanisms are applicable for single crystalline, polly-crystalline and amorphous deposition of nanostructured thin films. The Crystallinity of a thin film is strongly influenced by its growth condition and substrate on which it is grown. For deposition of highly crystalline thin films with stress free, highly crystalline substrate is required with close lattice match.

3.3 EFFECTS OF DEPOSITION PARAMETERS ON ZnO THIN FILMS

As we have discussed earlier, RF sputtering deposition parameters such as substrate temperature, gas flow, Ar: O_2 ratio during deposition, deposition pressure, RF power, target to substrate distance can be used as key methods to improve nano-crystalline thin film's structural, optical, electrical properties and surface morphology. By optimizing these deposition parameters, we can achieve highly crystalline ZnO thin films with minimum residual stress and less number of structural defects into grown thin films. Substrate temperature always plays a crucial role to improve film's quality and its crystallinity with optimized residual stress. Deposited ZnO thin film's structural and surface morphology is also highly tunable by substrate temperature as well as gas ratio of Ar/O_2. With different gas flow of Ar/O_2, stoichiometry of thin films as crystallinity and residual stress properties also changes.

3.3.1 Substrate Temperature Dependence

3.3.1.1 Experimental Setup

ZnO thin films (300-500 nm) were deposited on various substrate. 2-inch n-Si (100) wafer with resistivity 0.01-0.05 Ω cm were used to deposit thin films. Deposition parameters of ZnO thin films are shown in table 3.1. A 4-inch diameter ZnO target with 99.999% purity was used. The chamber was pumped by rotary pump and an additional turbo pump to maintain chamber base pressure of 1×10^{-6} mbar. During deposition process, RF power and chamber pressure were maintained at 150 W and 2×10^{-2} mbar, respectively. All thin film depositions were performed in presence of pure argon (99.99% purity) sputtering gas where its flow was maintained at 50 sccm. The gas flows were controlled by mass flow controllers (MFC). In sputtering chamber, target to substrate distance was kept constant of about 15 cm and substrate rotation was kept on during deposition. Thin film deposition duration was 2 hours. Cleaned substrates were loaded in sputtering chamber by using load-lock chamber to minimize contamination at room temperature. The sputtering target was pre-sputtered for 10-15 minutes in presence of dense plasma without removing target shatter to remove surface contamination of ZnO target. Substrate heater was used for constant heating during deposition. The effect of substrate temperature on structural and optical properties as well as surface morphology variation was studied to achieve highly crystalline ZnO by varying substrate temperature from room temperature RT to 100, 200, 300 and 400 ^{o}C, respectively.

Table 3.1 Deposition parameters of ZnO thin films deposited at different substrate temperatures

Substrate	n-Si (100)
Sputtering target	ZnO (99.999% purity)
Base pressure	1×10^{-6} mbar
Deposition pressure	2×10^{-2} mbar
Deposition time	2 hour
RF power	150 W
Sputtering gas	Argon (50 sccm)
Substrate temperature	RT, 100°C, 200°C, 300 °C, 400 °C
Target to substrate distance	15 cm

3.3.1.2 Structural Characterization

Structural characterization of deposited ZnO thin films on n-Si substarte were analyzed using X-ray diffraction technique. Figure 3.2 depicts X-ray diffraction (XRD) spectra for ZnO thin films deposited at various substrate temperature ranging from RT to 400°C. XRD diffraction patterns shows strong (0002) peak for all deposited substrate temperatures which indicates hexagonal wurtzite structure of ZnO thin films. As substrate temperature increases from RT to 400 °C, dominant peak (0002) intensity varies and changes full width half maxima (FWHM) and the peak position shifts towards higher 2θ angle. Minimum surface energy and rapid growth of crystallites nucleating along the (0002) plane is seen in wurtzite structured ZnO as compared to crystalline growth along other planes, which makes it a highly energy-stable structure. Hence, strong reflection along (0002) plane and crystal growth along c-axis is observed in wurtzite structure of ZnO [Chao *et al.*, 2016]

As operating temperature is raised from RT to 400 °C, we observed that (0002) diffraction peak angle shifts towards higher diffraction angle from 34.32° to 34.68° except at 100 °C substrate temperature, where peak shifts towards lower diffraction angle i.e. 34.28°. It is also observed that FWHM of (0002) peak is decreases from 0.327° to 0.26° as substrate temperature increases from RT to 400 °C. The narrowing of (0002) diffraction peak as FWHM decreases depicts increased crystallinity of ZnO thin film with increased operating temperature up to 400 °C.

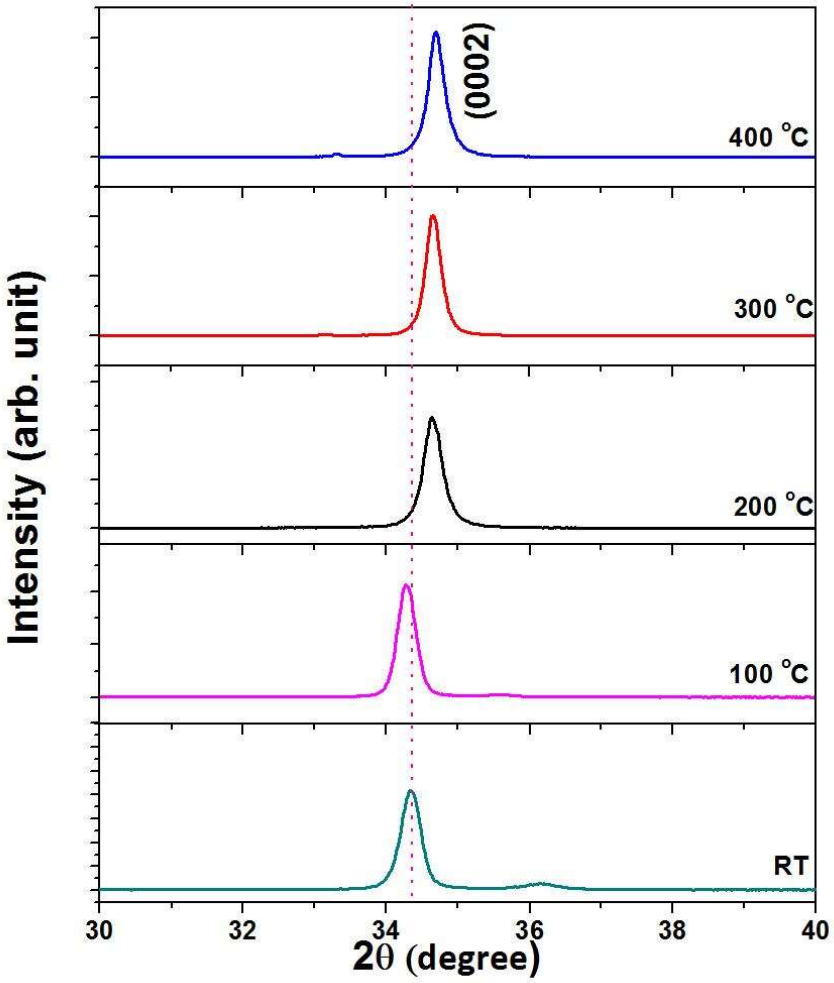

Figure 3.2: X-Ray diffraction spectra of ZnO thin film on n-Si substrate with growth temperature varying from RT to 400 °C, respectively.

These changes in crystallinity of thin films indicates that nucleation characteristics of ZnO thin films strongly depends on substrate temperature of deposited films and type of defects generated during deposition process. As operating temperature increases, adatoms such as zinc and oxygen species gain more energy. This process increases adatoms mobility on substrate which have tendency to move towards suitable lattice site by losing energy and act as a nuclei center for successive growth. As operating temperature further increases, more nuclei center enhances crystalline growth along c-axis and FWHM decreases. Cho, 2009 in [Cho, 2009], investigated effects of growth temperature on ZnO thin film by RF sputtering and showed improved crystallinity and decreased FWHM as growth temperature was increased up to 400 °C.

3.3.1.3 Stress Analysis

The change in FWHM and peak position of (0002) in X-ray diffraction spectra with growth temperature changing from RT to 400 °C is shown in Figure 3.3. As peak position shifts towards higher angle with increased substrate temperature, change in c-axis lattice parameter is observed. Two type of stresses are generated during deposition of thin film on substrate. Firstly, intrinsic stress is generated in ZnO thin film due to interstitial zinc and oxygen vacancies and secondly, residual stress is generated due to thermal expansion coefficient and lattice mismatch between ZnO and silicon substrate [Ozgur *et al.*, 2005]. Therefore, intrinsic stress may occur due to imperfection of crystallites (Zinc and oxygen adatoms) and thermal expansion coefficient mismatch between ZnO and substrate generates residual stress during deposition process [Ondo-Ndong *et al.*, 2003; Lee *et al.*, 2005]. Growth parameters such as substrate temperature, Argon/oxygen gas ratio, deposition pressure and RF power may tune intrinsic stress in ZnO thin films during deposition. It is observed that thermal stress contributes minor portion to the overall stress measured during deposition on substrate. Hence, the main cause of stress in to ZnO thin films is due to intrinsic stress generated during deposition process. There is shift in diffraction peak (0002) position towards higher angle due to biaxial tensile stress generation in deposited thin films at various temperature.

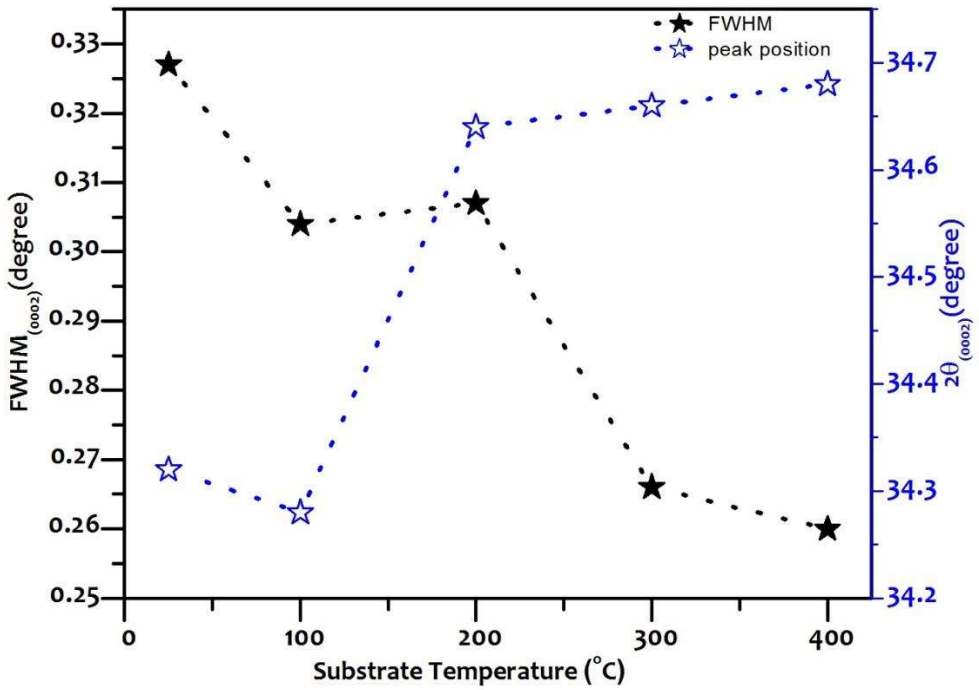

Figure 3.3: Variation of FWHM $_{(002)}$ and peak position $2\theta_{(0002)}$ (degree) with substrate temperature changing from RT to 400 °C.

It is observed that peak position is shifted towards lower 2θ angle from 34.32 to 34.28 at 100 ^{o}C. It may be at moderate operating temperature these adatoms could not get sufficient energy and creates nuclei centers which are not in stable energy state which may then cause high compressive stress in comparison to thin films deposited at room temperature. At high deposition temperature between 200-400 ^{o}C, adatom gets sufficient mobility on substrate and generates nuclei center for successive layer depositions which improves growth along c direction. This process improves crystallinity and generates biaxial tensile stress with decreased compressive stress as stoichiometric of Zn and Oxygen crystallite becomes unbalanced with increasing temperature up to 400 ^{o}C. Main cause of tensile stress development is due to lattice mismatch between Si and ZnO with the presence of oxygen vacancies (V_o) and Zinc interstitials vacancies in ZnO which also causes shift in diffraction peak towards higher angles [Panday *et al.,* 2013]. The biaxial in plane stress causes compression/elongation of the unit cell along c-axis.

The inter-plane spacing 'd' can be calculated using Bragg's diffraction law shown as [Rao *et al.,* 2009]:

$$2d\sin\theta_{(0002)} = n\lambda \tag{3.1}$$

Where θ represents peak position of (0002) peak, λ (0.15406 nm) represents X-ray wavelength and n=1 for inter-plane spacing calculation. As peak position is shifted due to biaxial stress, inter-plane spacing also varies accordingly.

By calculating the inter-plane spacing in hexagonal system, the c-axis lattice constant 'c' of ZnO thin films can be calculated using (hkl) as (0002) in following equation [Kunj and Sreenivas, 2016]

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + k^2 + hk}{a^2}\right) + \frac{l^2}{c^2} \tag{3.2}$$

Where h, k, l is miller indices and a, c are lattice constants along x, z direction. Lattice constant's value strongly depends on peak position of (0002) i.e. either blue shift or red shift. As (0002) peak shifts towards higher angle (blue shift) or towards lower side (red shift) with respect to bulk ZnO, it produces compression or elongation of unit cell along c-axis. In hexagonal wurtzite structures, residual stress is always perpendicular to film surfaces which originates because of c-axis strain generation due to various defects generation during film depositions. The stress along c-axis of the ZnO thin films is evaluated by [Singh *et al.,* 2010]

$$\sigma(\text{Pa}) = -233 \times 10^9 \left(\frac{c - c_0}{c_0}\right) \tag{3.3}$$

Where c is lattice constant of deposited film and c_0 is stress free lattice constant for ZnO powder i.e. 5.206 A^{o}. Calculated lattice constant and biaxial stress using (0002) peak position is given in Table 3.2. Negative sign of stress indicates elongation of lattice constant along c-axis and it leads to distortion of unit cell which generates compressive stress in deposited thin film. As (0002) peak shifts towards higher diffraction angle, it indicates compression of lattice constant in comparison to c_0 which causes tensile stress generation in deposited thin film. Reactive sputtering deposition conditions and sputtering ions bombardment may induce native defects and interstitials vacancies that leads towards biaxial compressive/tensile stress generation. In present work, biaxial stress generated during RF sputtering deposition strongly depends on deposition substrate temperature.

Table 3.2: List of calculated lattice constant (c) and Biaxial stress of ZnO thin film dependence on sputtering substrate temperature using (0002) Peak position

Substrate Temperature (°C)	2θ(°)	FWHM(°)	c(A°)	σ(GPa)
RT	34.32	0.327	5.225	-0.850
100	34.28	0.324	5.237	-1.387
200	34.64	0.307	5.179	1.20
300	34.66	0.266	5.176	1.342
400	34.68	0.260	5.173	1.477

It is observed that when ZnO film was deposited at RT, (0002) peak shifted towards lower side in comparison to bulk ZnO (0002) peak at 34.42° which indicates elongation of lattice constant along c-axis that generates in-plane compressive stress. At RT, induced compressive stress (-0.850 GPa) is minimum. Figure 3.4 shows dependence of lattice constant and biaxial stress on substrate temperature.

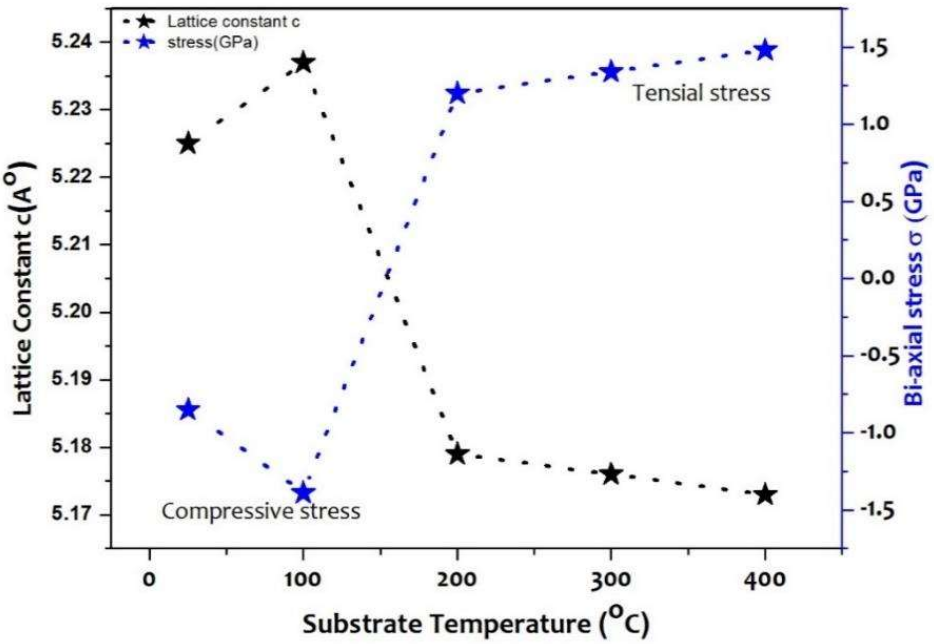

Figure 3.4: Linear relationship between lattice constant and biaxial stress on substrate temperature

It is clearly observed that as deposition temperature is altered towards higher temperature (400 °C), deposited adatoms gain more kinetic energy and comes in stable state by moving these adatom on substrate. By increasing temperature, it creates zinc interstitials and oxygen vacancies due to presence of non-stoichiometric oxygen in ZnO thin film. These defects generate biaxial tensile stress that increases with substrate temperature and exhibits decrease in lattice constant. As operating substrate temperate increases from RT to 100 °C, it is also observed that deposited film becomes highly compressive in nature with elongation of lattice constant. It is due to moderate operating temperature that sufficient energy is not transformed to deposited adatoms

so as to reach in stable state on substrate which eventually causes less stable nucleation formation. Because of these effects, deposited films are highly compressive in nature.

3.3.1.4 Surface Morphology

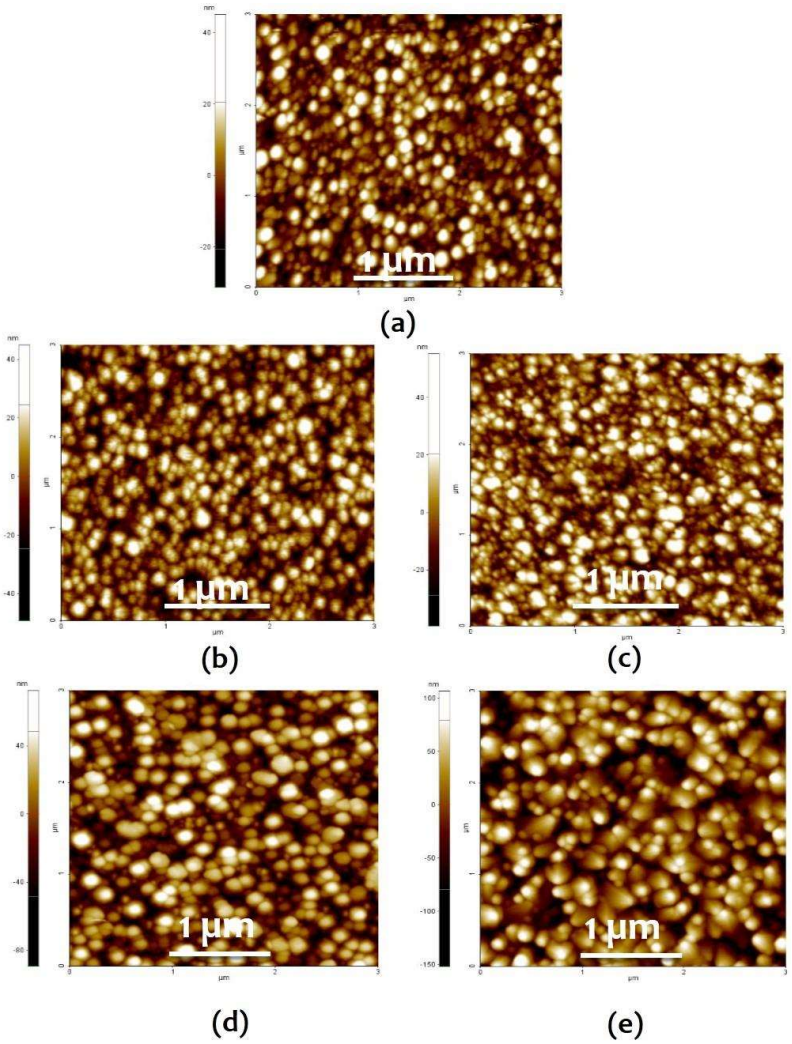

Figure 3.5: (a-e) AFM images of deposited nano-crystalline ZnO thin films at various growth substrate temperature varying from RT,100 °C, 200 °C, 300 °C and 400 °C, respectively

In this chapter, effect of substrate temperature on surface morphology of nano-crystalline ZnO thin films were studied using AFM and FESEM characterization. Figure 3.5 (a-e) shows AFM images (3×3 μm^2) of deposited nano-crystalline ZnO thin films at various growth substrate temperature ranging from RT to 400 ^oC. It is observed that deposited nano-crystalline ZnO thin films at RT substrate temperature shows uniform distribution of grain throughout substrate. Grains distribution is uniform and these grains are in spherical shape with diameter ~92.6 nm. These films show minimum RMS roughness i.e. 10.47 nm. As substrate temperature increases from RT to 400 ^oC, average grains distribution becomes denser on substrate and grain shape changes from spherical to trapezoidal shape with sharp peak tops. Average grain size also increases with increase in substrate temperature.

Figure 3.6 depicts variation of RMS roughness of nano-crystalline ZnO thin films with deposited substrate temperature ranging from RT to 400 °C. It is clearly observed that as deposition temperature increases from RT to 400 °C, RMS roughness increases from 10.47 nm to 40.63 nm. At higher deposition temperature, deposited adatoms at substrate surface gain sufficient energy which also increase its mobility on substrate. Because of higher mobility, adatoms moves towards appropriate lattice site for succeeding growth. Because of formation of suitable lattice sites, columnar growth is more dominating than spherical grains on ZnO thin films. These are the main reasons for increase in roughness as deposition temperature increases from RT to 400 °C.

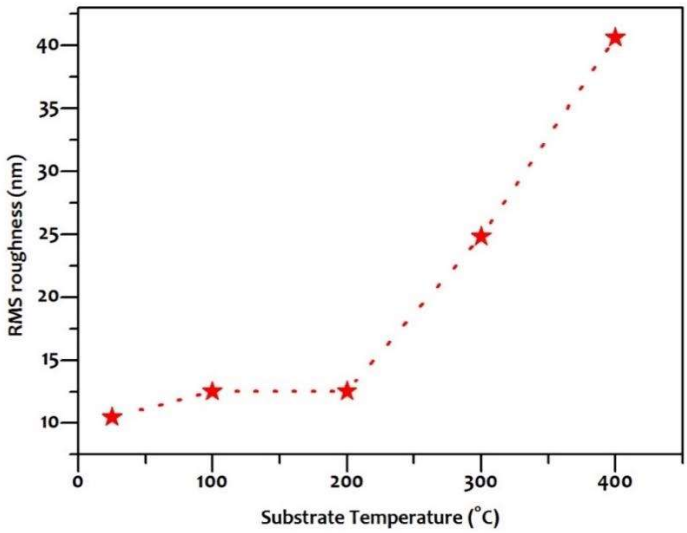

Figure 3.6: RMS roughness of deposited ZnO thin films as deposition temperature increases from RT to 400 °C

FESEM also shows similar surface morphology as we have already shown in AFM images. Figure 3.7 (a-d) shows top view of FESEM images of ZnO thin film as deposition temperature ranges from RT, 200 °C, 300 °C, 400 °C, respectively. FESEM also shows uniform spherical grain distribution of ZnO thin films at RT. As operating temperature increases from RT to 400 °C, average grain size increases as shown earlier in AFM images. Grown ZnO thin films becomes rougher at high deposition temperature in comparison to room temperature growth. Spherical shapes of ZnO grains are also converted into slightly pyramid shapes with increased average grain size.

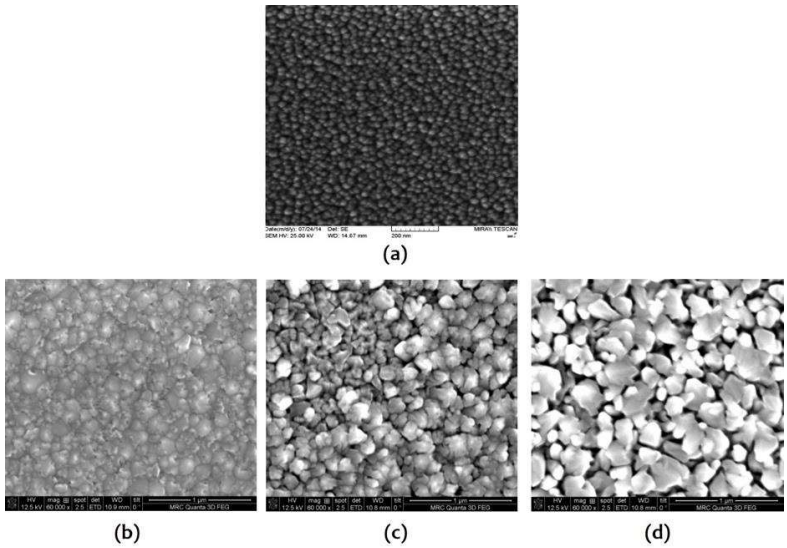

Figure 3.7: (a-d) Shows top view of FESEM images of ZnO thin films with various deposition temperature ranging from RT, 200 °C, 300 °C, 400 °C, respectively

3.3.1.5 Optical Characterization

Optical characterizations were performed using PL Photoluminescence. Figure 3.8 depicts room temperature PL spectra of ZnO thin film deposited at RT. PL spectra shows sharp peak at 383nm which is indexed near band emission (NBE) transitions and its optical band gap is approximately 3.23 eV. [30] It shows that the deposited thin film at room temperature are optically good. Normally, broad band emission region also appears in thin film PL spectra due to presence of structural defects formation during deposition. In this spectra, there is a slight peak of wide band spectra in range 450-600nm which indicates presence of few structural defects in thin film deposited at room temperature. These results resemble with earlier mentioned x-ray spectra exhibiting that deposition conditions induces minor compressive stress in ZnO thin film.

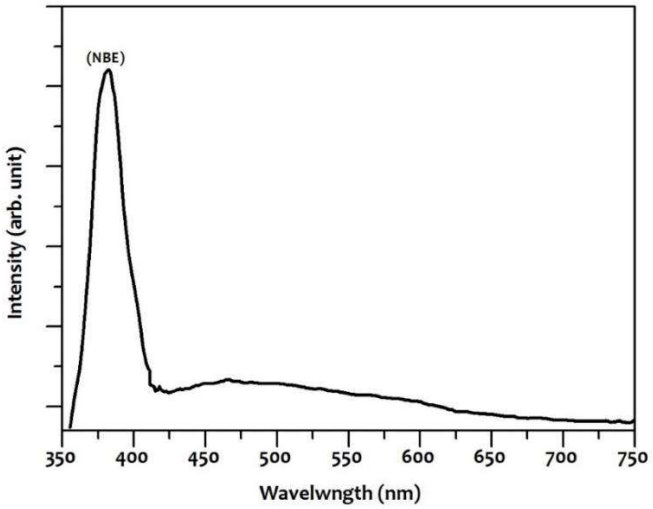

Figure 3.8: Room temperature PL characterization of ZnO thin film deposited at RT

3.3.2 Ar/O_2 Gas Ratio Dependence

3.3.2.1 Experimental Setup

In this section, relative study of effect of Ar/O_2 gas at various substrate temperature on deposited ZnO thin film is done. In the setup, ZnO thin film was deposited by RF sputtering system with gas flows of Ar/O_2 varying from 50/0, 35.5/5 and 28/11.5 sccm, respectively. For substrate temperatures varying between RT to 300 ^oC, ZnO thin films were deposited with variation in gas flow rates. The gas flow in sputtering chamber was maintained by mass flow controller. Remaining deposition parameter for ZnO thin films for various Ar/O_2 gas flows are shown in table 3.3.

Table 3.3: Deposition parameter of ZnO thin films deposited at different Ar/O_2 gas flows with different substrate temperature

Substrate	n-Si (100)
Sputtering target	ZnO (99.999% purity)
Base pressure	1×10^{-6} mbar
Deposition pressure	2×10^{-2} mbar
Deposition time	2 hour
RF power	150 W
Sputtering gas (Ar/O_2 gas flow rate)	50/0, 35.5/5, 28/11.5 sccm
Substrate temperature	RT, 100°C, 200°C, 300 °C
Target to substrate distance	15 cm

3.3.2.2 Structural Characterization and Stress Analysis

Effect of various Ar/O_2 gas flow rates (50/0, 35.5/5 and 28/11.5 sccm) on ZnO thin films at different substrate temperature ranging from RT to 300 ^oC were simultaneously studied using structural characterization. Figure 3.9 depicts (a) X-ray spectra of ZnO thin film deposited on n-Si, (b) shows relationship between FWHM and peak position and (c) gives lattice constant and Biaxial stress analysis with various Ar/O_2 gas flow rates at room temperature deposition. In XRD spectra, presence of strong peak (0002) depicts single crystalline, hexagonal wurtzite growth of ZnO thin films along c-axis at various Ar/O_2 gas flow. Effects of substrate temperature on crystallinity of ZnO thin films were discussed in earlier section. It is seen that increasing oxygen ratio during sputtering shows shift in (0002) towards lower 2θ angle and increase in FWHM. Increasing FWHM indicates decrease in crystallinity of deposited ZnO thin films.

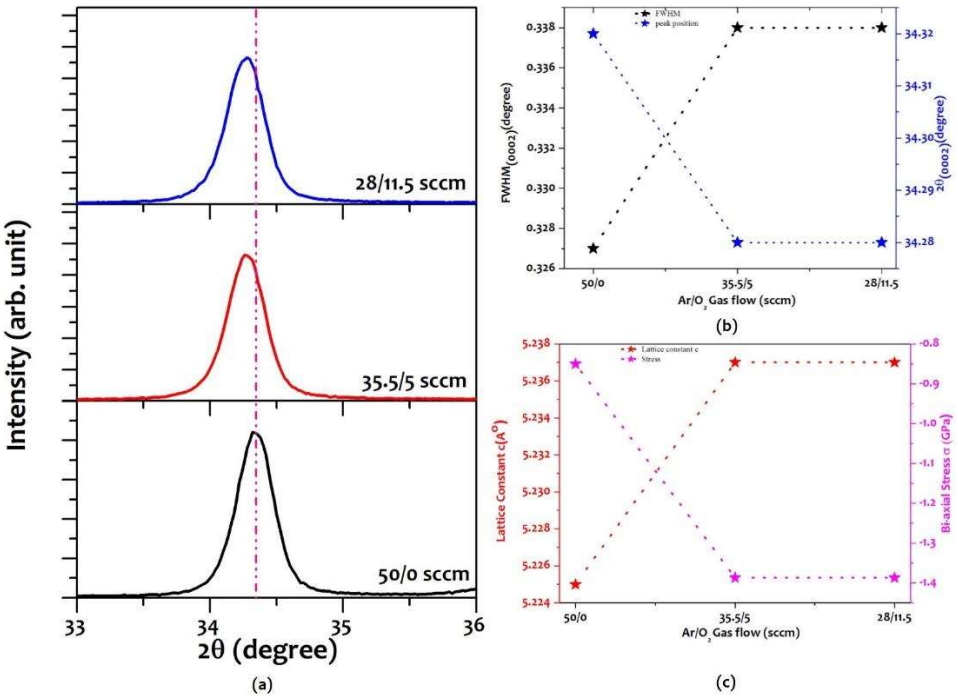

Figure 3.9: (a) X-Ray spectra of ZnO thin film deposited on n-Si, (b) Relationship between FWHM and peak position and (c) Lattice constant and biaxial stress analysis with various Ar/O_2 gas flow rates (50/0, 35.5/5 and 28/11.5 sccm) at room temperature deposition

It is also observed that as we increase oxygen ratio and decrease argon ratio, deposition rate of ZnO thin films slowed down in comparison to pure argon. Significant change in c-axis lattice parameter is also witnessed that strongly depends on (0002) peak position shifting driven by increasing oxygen gas ratio in sputtering [Singh *et al.*, 2007]. Our findings also illustrate that if oxygen flow rate is further increased above 35.5/5 sccm Ar/O_2, peak shifting and FWHM does not shows any further variation. This no change is due to the fact that ZnO target sputtering rates get saturated even if small amount of oxygen content is present in sputtering chamber. Ar/O_2 deposited ZnO thin film has higher lattice constant as compared to that of pure argon deposited ZnO thin film which indicates elongation of unit cells in c-axis direction. And this elongation of lattice constant generates intrinsic biaxial compressive stress in ZnO thin films deposited on n-si. As we have discussed earlier, generation of various defects such as zinc interstitials and oxygen vacancies causes in-plane biaxial stress generation in deposited film. As we increase Ar/O_2 gas flow rate from 50/0 sccm to 35.5/5 sccm, presence of oxygen in sputtering chamber slows down arrival of sputtered adatoms on substrate and reduces oxygen vacancies in grown films. Though, in-plane compressive stress may be due to the presence of other defects such as Zn_i, O_i etc. as (0002) shifts towards lower angle. In-plane compressive stress increases with low oxygen flow rate in sputtering chamber in comparison to pure argon gas flow. Earlier discussions show effects of deposition temperature on structural characterization. We have also performed Ar/O_2 gas flow rates variation for 100 ^oC, 200 ^oC and 300 ^oC. The change in structural characterization at temperatures 100 ^oC, 200 ^oC and 300 ^oC shows same kind of behavior as seen at room temperature. This same kind of behavior can be further explained by (a) X-ray spectra of ZnO thin film deposited on n-si, (b) relationship between FWHM and peak position and (c) lattice constant and bi axial stress analysis with various Ar/O_2 gas flow rates at 300 ^oC deposition in Figure 3.10.

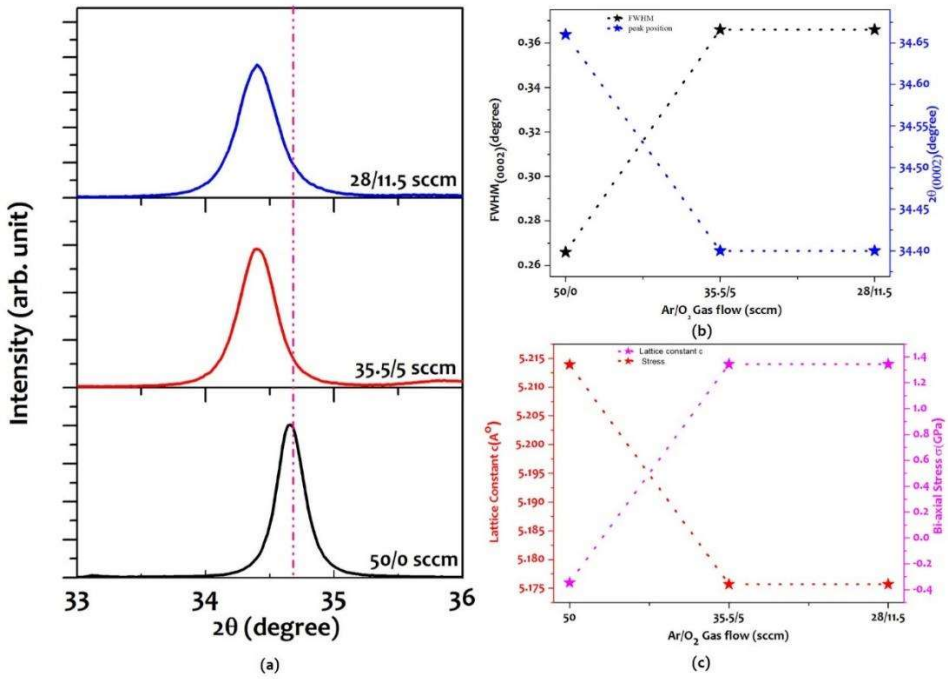

Figure 3.10: (a) X-Ray spectra of ZnO thin film deposited on n-Si, (b) Relationship between FWHM and peak position and (c) Lattice constant and biaxial stress analysis with various Ar/O_2 gas flow rates (50/0, 35.5/5 and 28/11.5 sccm) at 300 °C substrate deposition

ZnO thin films deposited in presence of pure argon at 300 °C shows high tensile stress as we have discussed in earlier section. At high deposition temperature and Ar/O_2 gas flow rates varying from 50/0 sccm to 35.5/5 sssm, deposited ZnO thin films shows transformation of tensile stress into compressive stress. This transformation of stress result in almost stress free ZnO thin film deposition in presence of oxygen at 300 °C as the value of compressive stress is insignificant. Table 3.4 gives calculated value to FWHM, lattice constant and in-plane stress analysis for deposited ZnO thin films at different Ar/O_2 gas flow rates at various substrate temperature.

Table 3.4: List of calculated lattice constant and biaxial stress of ZnO thin film dependency on various Ar/O_2 gas flow rates at different substrate temperature

Substrate temperature (°C)	**Ar/O_2 gas flow (sccm)**	**2θ (°)**	**FWHM(°)**	**c (A°)**	**σ (GPa)**
RT	50/0	34.32	0.327	5.225	-0.850
RT	35.5/5, 28/11.5	34.28	0.338	5.237	-1.387
100	50/0	34.28	0.304	5.237	-1.387
100	35.5/5, 28/11.5	34.26	0.329	5.235	-1.298
200	50/0	34.64	0.307	5.179	1.20
200	35.5/5, 28/11.5	34.26	0.328	5.235	-1.298
300	50/0	34.66	0.266	5.176	1.342
300	35.5/5, 28/11.5	34.40	0.366	5.214	-0.358

3.3.2.3 Surface Morphology

Surface morphological studies using AFM were also performed with various Ar/O_2 gas flow rates at different substrate temperature. Figure 3.11 (a-c) shows AFM images (3×3 μm^2) of deposited ZnO thin films at room temperature with Ar/O_2 gas flow rates varying from 50/0, 35.5/5 and 28/11.5 sccm, respectively. As we have discussed earlier, ZnO thin film deposited at room temperature in presence of pure argon shows uniform deposition of nano-crystalline grain distribution. It is clearly seen that in presence of pure argon, spherical grains are distributed throughout the substrate. As argon oxygen ratio changes from pure argon to Ar/O_2 gas flow rates of 35.5/5 and 28/11.5 sccm, grain distribution becomes denser with more smooth surfaces. At higher temperature of 100 °C, 200 °C and 300 °C, AFM images show same kind of change in surface morphology as it can be seen at RT with various Ar/O_2 gas flow rates. It is also observed that at low oxygen ratio, there is a slight increase in average grain size at each temperature. And with high oxygen ratio, average grain size decreases but is still higher than in pure argon deposition. Figure 3.12 (a-c) and Figure 3.13 (a-c) shows AFM images (3×3 μm^2) of deposited nano-crystalline ZnO thin films at 200 °C and 300 °C, respectively for Ar/O_2 gas flow rates being 50/0, 35.5/5 and 28/11.5 sccm, respectively.

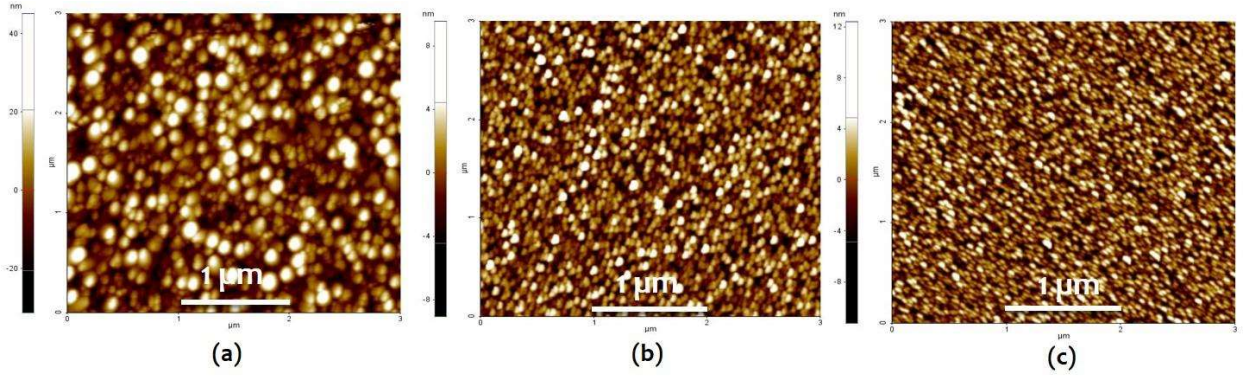

Figure 3.11: (a-c) Shows AFM images of deposited nano-crystalline ZnO thin films at room temperature for Ar/O_2 gas flow rates varying from 50/0, 35.5/5 and 28/11.5 sccm, respectively

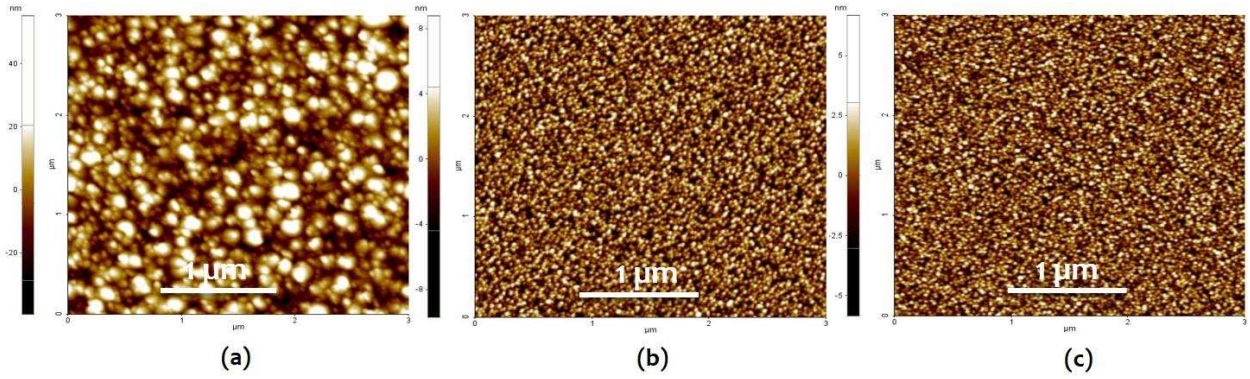

Figure 3.12: (a-c) Shows AFM images of ZnO thin films at 200 °C for Ar/O_2 gas flow rates of 50/0, 35.5/5 and 28/11.5 sccm, respectively

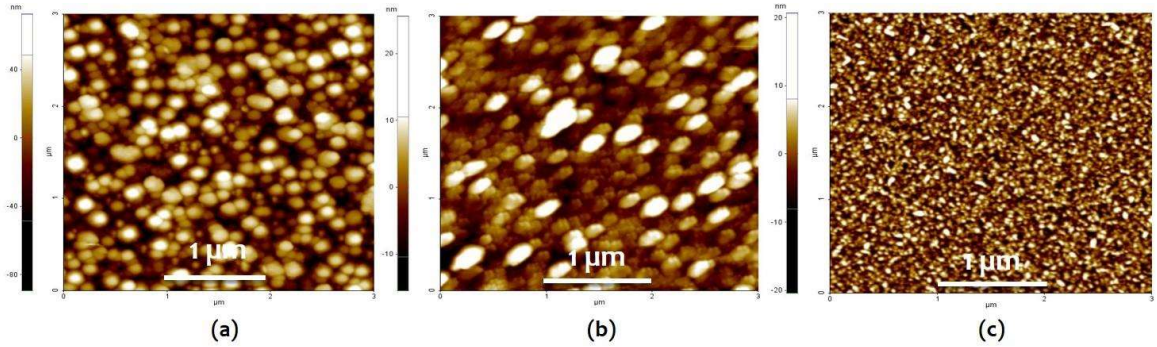

Figure 3.13: (a-c) Shows AFM images of ZnO thin films at 300 °C for Ar/O_2 gas flow rates of 50/0, 35.5/5 and 28/11.5 sccm, respectively

Figure 3.14 depicts change in RMS roughness with respect to change in Ar/O_2 gas flow rate at different substrate temperatures. It shows decrease in roughness with increasing oxygen flow rates during deposition. This change is due to excess of oxygen which decreases argon ions and results in less bombardment on deposited thin films. Oxidation of deposited thin films provides smoother surface and uniform grain distribution in comparison to pure argon deposition. At higher deposition temperature, we can achieve smoother films in argon/oxygen depositions as compared to pure argon depositions. At each deposition temperature, film roughness highly decreases in presence of oxygen than in pure argon gas depositions.

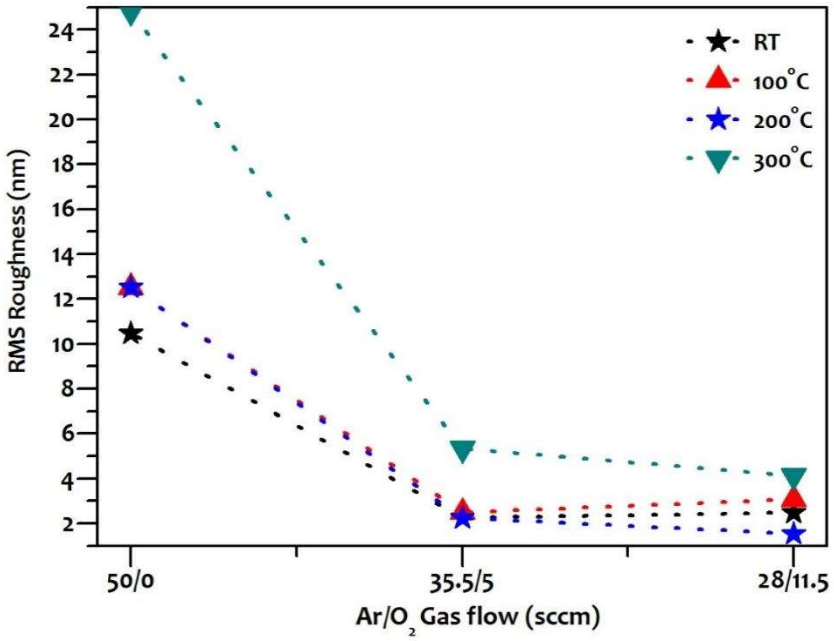

Figure 3.14: Variation of RMS roughness of deposited ZnO thin films with different Ar/O_2 gas flow rates at deposition temperature between RT to 300 °C.

3.4 CONCLUSION

In this chapter, nano-crystalline ZnO thin films were deposited on various substrate using RF sputtering technique. Structural characterization and surface morphology of deposited ZnO thin films were changed with different substrate temperature (RT to 400 °C) at different Ar/O_2

gas flow rates (50/0, 35.5/5 and 28/11.5 sccm). Deposited ZnO thin films were single crystalline, hexagonal wurtzite structure and grown along c-axis. The crystallinity of deposited ZnO thin films can be controlled by various deposition parameters. Investigation shows that increasing substrate temperature increases the crystallinity of ZnO thin film and decreases FWHM. And due to the presence of native defects, c-axis lattice constant decreases. Due to high temperature, (0002) peaks shifts towards higher angle and causes in-plane tensile stress in compression to ZnO thin film deposited at room temperature, where compressive stress is generated. Surface roughness increases as substrate deposition temperature is increased. ZnO thin film deposited at various temperatures and at different Ar/O_2 gas flow rates show uniform deposition of nano- crystalline grain distribution throughout the substrate. In presence of oxygen during deposition, crystallinity and roughness of deposited thin film decreases in comparison to pure argon deposition. Additionally, grain size also changes with change in Ar/O_2 gas flow rates.

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