

Deposition of ZnO Nanorods

ZnO nanorods are deposited on substrates using RF sputtering techniques at different deposition conditions. Initially, growth of ZnO nanorods over Si (100) substrate with substrate temperature variation have been studied followed by Structural characterization and surface morphology relative studies. In following section, effect of substrate variation on growth of ZnO nanorods with same deposition parameters and their growth variation have been studied using structural characterization and surface morphologies.

4.1 INTRODUCTION

1D nanostructures like tubes, rods and wires are currently in lime light due to their exclusive purpose in the field of nanotechnology. They have vast applications as building blocks in photonics, electronics and life science [Kim *et al.*, 2012; Xu and Wang, 2011; Shen and Chen, 2010]. Effect on electrical, thermal, thermo electrical and optical properties modified because of overall dimension and quantum confinement formed due to size reduction in 1D nanostructures [Xia *et al.*, 2003; Luo *et al.*, 2014]. 1-D nanostructure is best suited for gas sensing due to its high thermal stability and availability of larger surface area with large surface to volume ratio [Weng *et al.*, 2014]. Therefore, researchers are extensively focusing on different deposition schemes to deposit 1-D nanostructures of ZnO on the substrates like Si, GaN, ITO coated glass, Pt/Si, Sapphire etc. [Kim *et al.*, 2008; Kong and Cho, 2007; Chen *et al.*, 2010; Wu and Liu, 2002; Tak *et al.*, 2005; Park *et al.*, 2012]. Out of various schemes, growing ZnO nanorods on silicon substrate is the most preferred deposition scheme due to its low cost, availability of large single crystals and excellent substrate quality. Although, there are structural defects and in-plane stress in ZnO NRs due to mismatch between thermal coefficient of ZnO and Si [Wang *et al.*, 2008; Rusli *et al.*, 2012], high quality ZnO NRs can be deposited over silicon substrate after correcting these defects and stress by optimizing various deposition parameters.

Various physical vapor deposition methods such as metal organic chemical vapor deposition (MOCVD), pulse laser deposition (PLD), thermal evaporation, molecular beam epitaxy, sputtering etc. are used to grow ZnO nanostructures (nanorods, nanowire etc.) over various substrates [Montenegro *et al.*, 2012; Ajimsha *et al.*, 2010; Tu *et al.*, 2014; Tzou *et al.*, 2013; Nandi *et al.*, 201]. Amongst above stated methods, RF sputtering technique is best favored deposition method due to its cost effectiveness, non-toxic nature, even deposition with good hold of ZnO NRs over the substrate. RF sputtering also provides metal catalyst free deposition of ZnO NRs. Though RF sputtering is most popular thin film deposition technique, recently, good quality 1-D nanostructures are also deposited via buffer/catalyst layer on various substrates in RF sputtering [AbuDakka *et al.*, 2010; Song and Lim, 2007; Rosli *et al.*, 2014]. But, due to these catalytic supported growth, nanostructures are likely to get exposed to impurities, which might decrease the performance of the device [Venkatesh *et al.*, 2012]. Thus, catalyst free deposition of nanostructures is attained in RF sputtering. By varying RF sputtering deposition temperature, pressure, power and reactive gases, nanostructure's crystalline orientation, length, shape, density and morphology can be optimized [Venkatesh and Jeganathan, 2014].

This chapter illustrates RF sputtering technique used for deposition of ZnO NRs over several substrates and reveal modifications in ZnO NRs by altering numerous sputtering

parameters. Study also divulged that ZnO NR's growth, structural and surface morphology gets affected by substrates like ITO, Ge, Polyimide, Pt-Si and n-Si.

4.2 GROWTH MECHANISM OF ZnO NANOSTRUCTURES

1- D Nanostructure materials with obligatory size, shape, morphology, crystal structure and orientation along with chemical composition have major impact on its electrical and optical properties and are therefore, emerging materials in various sensing devices. Consequently, deposition of nanostructure with desired properties is of utmost priority in nanotechnology [Xia *et al.*, 2003; Al-Kaysi *et al.*, 2009]. Atoms, ions or molecules act as basic building blocks in 1-dimensional growth process. When these adatoms reaches at surface, aggregation of these adatoms forms a small cluster that act as a nuclei center. And through homogeneous nucleation, these nuclei centers act as seeds for more new adatoms on substrate for 1-D nanostructure growth.

For efficient nano-device fabrication, nanostructure material's key parameters for growth such as dimensions, morphology and uniformity should be in precise conditions. Bottom-up and top-down are two basic approaches for nanostructure fabrication. In bottom-up approach, nanostructures are deposited from the bottom in the form of atom by atom or cluster by cluster or molecule by molecule deposition. This approach is most commonly used for nanostructure deposition where spontaneous growth is attained using vapour-liquid-solid (VLS) technique and vapour-solid technique [Yi, 2012; Cao, 2004]. Here, growth techniques for nanostructure growth are elucidated. This chapter focuses on vapour-solid (VS) growth process as the research is carried out for ZnO NR's catalysis free deposition on various substrate using RF sputtering which is mainly governed by vapour-solid (VS) process.

4.2.1 Vapour-Liquid-Solid (VLS) Growth

In deposition of 1-dimensional nanostructure, various deposition technique use VLS growth mechanism where metal catalyst is used for spontaneous growth as nanomaterial growth essentially depends on metal catalyst regardless of substrate.

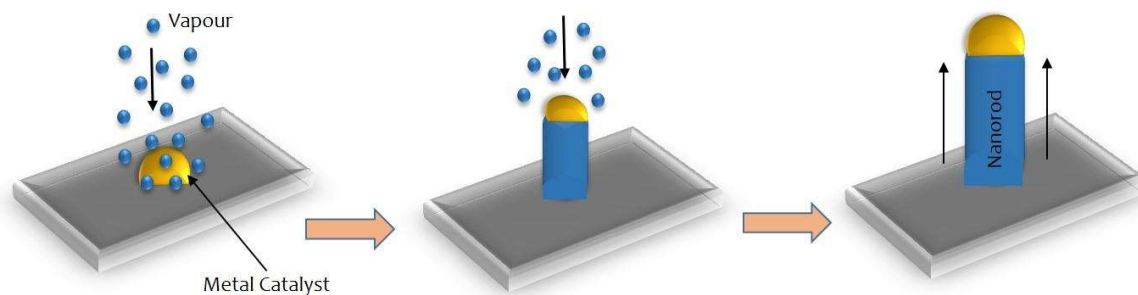


Figure 4.1: Schematic diagram of vapour-liquid-solid (VLS) process from initial nucleation to continuous growth

This process always delivers a controllable growth of nanostructure. Figure 4.1 shows illustration of vapour-liquid-solid process from nucleation to continuous growth, step by step process. Primarily, a thin layer of metal catalyst like Au, Pt, Fe etc. is deposited on substrate. At initial stage, metal catalyst segregates and forms metal nano droplets on substrate at desirable deposition conditions. When gaseous reactants react with nano-sized liquid droplets of metal, nucleation process is instigated. As more vapours arrive and reacts with nucleation center, they

get condensed and grow 1-D nanostructures like nanorods and nanowires. The dimension of these nanostructures strongly depends on the size of catalyst droplets. The grown nanorods or nanowires might grow from top or bottom of catalyst [Yi, 2012; Givargizov, 1975].

4.2.2 Vapour-Solid (VS) Growth

1-D nanostructures have been deposited on various substrates by different vapour phase deposition techniques using vapour-solid growth approach. No metal catalyst is used to grow nanostructures unlike in VLS growth process. Vapour species have been generated with the help of evaporation process and gaseous and chemical reactions occurring in deposition chamber. Figure 4.2 depicts schematic diagram of VS process from initial nucleation to continuous growth. After vapour generation, the vapours travels towards solid substrate, get condensed and forms various nucleation centers that further act as seed for additional deposition. Substrate temperature is kept lower than source material. Continuous deposition of vapour on these nuclei centers conclusively provides deposited 1-D nanostructures. Growth of these nanostructures also depends on supersaturation factor and by controlling it, nanorod or nanowire deposition is feasible irrespective of bulk crystal growth [Wang, N. *et al.*, 2008].

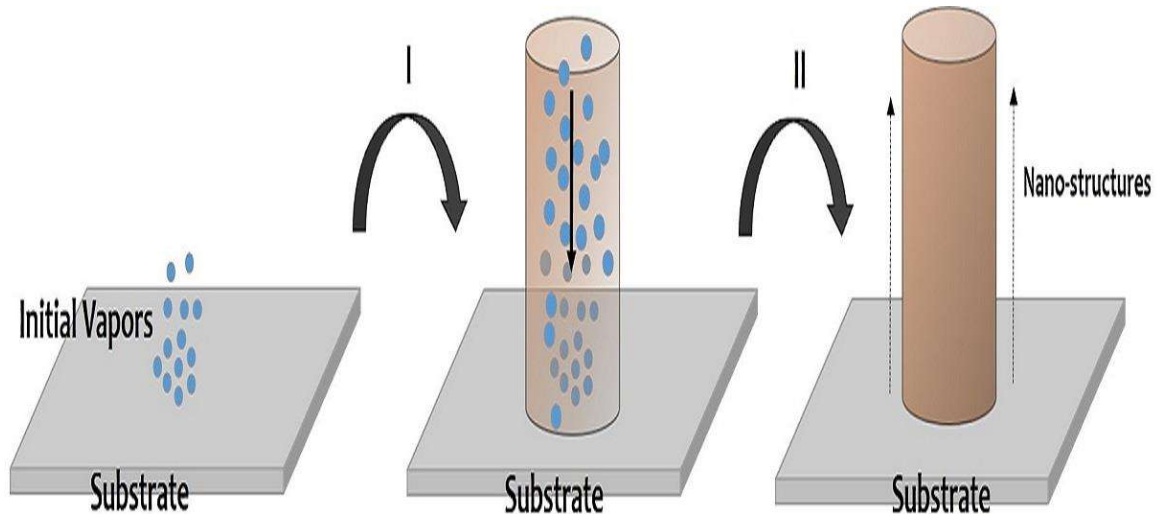


Figure 4.2: Schematic diagram of VS process from initial nucleation to continuous growth

In my PhD work, RF sputtering technique is used for well aligned ZnO nanorods deposition over various substrate using vapour-solid (VS) growth mechanism. Major advantage of this process is that it omits the probability of generation of undesired external impurities and yields catalyst free deposited ZnO NRs. And by using RF sputtering technique, material deposition is possible even at high melting point unlike thermal evaporation. It also provides good adhesion to these nanostructures over entire substrate with high vacuum environment avoids contamination and impurities in nanostructure deposition. During the process, high energetic charged Ar^+ particles discharges source materials in vacuum chamber. These adatoms initially moves towards the substrate to achieve stable state with minimum energy, forms island shape nanoparticles and act as nucleation center for subsequent growth of nanorods. Well aligned subsequent growth of ZnO nanorods on these seeds is observed due to high surface energy of these nucleation sites and anisotropic growth of columnar structure with self-shadow effects in comparison to flat surface [Venkatesh and Jeganathan, 2013]. Deposited nanorods growth can be controlled by varying few deposition parameters such as deposition temperature, deposition

pressure, gas flow rate and deposition time [Venkatesh *et al.*, 2013; Venkatesh and Jeganathan, 2014].

4.3 EFFECTS OF SPUTTERING DEPOSITION PARAMETERS

Well aligned ZnO nanostructures with high crystallinity and minimum number of native defects are required for efficient nanosensors with dependency on ZnO NRs electrical and optical properties. As studied in previous chapters, ZnO NRs growth with high crystallinity and less number of defects over various substrate can be achieved by optimizing key parameters of sputtering such as substrate temperature, RF power, argon: oxygen gas flow, deposition time, chamber pressure etc. Here, firstly, effect of substrate temperature variation on ZnO nanorods deposition over silicon substrate will be discussed. Secondly, relative change in crystallinity and surface morphology is also observed. Subsequently, effect of various substrates on structural and surface morphology during ZnO NRs deposition is also studied.

4.3.1 Substrate Temperature Dependency

4.3.1.1 Experimental Setup

Uniformly aligned ZnO nanorods are deposited over 2 inch n-Si (100) wafer using RF sputtering technique. High quality ZnO (99.999%) target is used in sputtering to avoid impurities in ZnO NRs. To further avoid contamination in chamber, ultra high vacuum is created with base pressure 1×10^{-6} mbar. n-Silicon substrate of resistivity $\sim 0.01-0.02$ ohm cm^{-1} is initially cleaned by chemical process and for further removal of oxides, 5% HF is used. Argon gas of 99.999% purity is used as sputtering gas with 60 sccm gas flow which gives constant chamber pressure of 2×10^{-2} mbar. During nanorods deposition, RF power, target to substrate distance and deposition time were 150 W, 14 cm and 2 hours, respectively. Sputtering target was pre-sputtered for 10-15 minutes to remove contamination from the target. And to study the change in structural properties and surface morphologies, substrate temperature was varied from 500°C to 600°C.

Table 4.1 Deposition parameters of well aligned ZnO NRs 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 (60 sccm)
Substrate temperature	500 °C, 600 °C
Target to substrate distance	14 cm

4.3.1.2 Structural Characterization

Structural characterization of ZnO NRs grown over silicon substrate have been characterized using X-Ray diffraction (XRD). The change in crystallinity is studied using XRD spectra for increasing substrate deposition temperature. Figure 4.3 depicts X-ray spectra of ZnO NRs for substrate temperature varying from 500 °C to 600 °C, respectively. A single peak of 0002 is observed at 34.64° which signifies that single crystalline ZnO NRs with hexagonal wurtzite structure are deposited [Liu *et al.*, 2004]. As cited in chapter 3, (0002) plane is the most stable energy plane as compared to other planes ($10\bar{1}1$, $10\bar{1}0$, $10\bar{1}2$ etc.) for wurtzite structure and as it contains minimum surface energy, rapid growth of crystallite is seen along (0002) plane and deposited ZnO nanorods are grown along c-axis. When substrate deposition temperature increases from 500 °C to 600 °C, crystallinity of ZnO NRs increases and full width half maxima (FWHM) decreases from 0.22° to 0.21° .

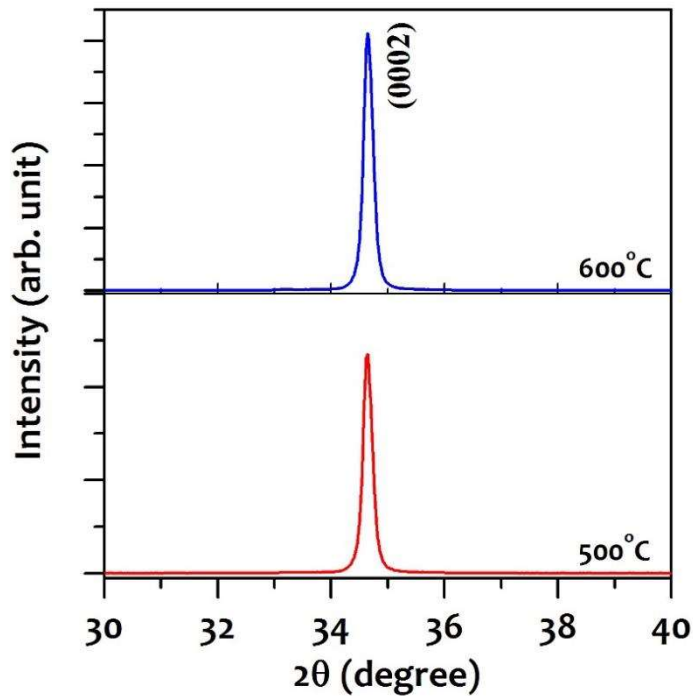


Figure 4.3: X-ray diffraction spectra of ZnO NRs on n-Si substrate with growth temperature varying from 500 °C to 600 °C

4.3.1.3 Surface Morphology

Surface morphology of ZnO nanorods was studied using FESEM and AFM characterization. Figure 4.4 shows top view and cross-sectional view of ZnO NRs grown over Si substrate with substrate temperature 500 °C and 600 °C, respectively. It is evident from FESEM images that deposited nanorods have been uniformly distributed throughout the substrate and are vertically aligned along c-axis. On increasing substrate temperature from 500 °C to 600 °C, diameter of nanorods increases from 48 nm to 58 nm. With increasing temperature density and height of nanorods also increases from $1.26 \times 10^{10} \text{ cm}^{-2}$ and 750 nm to $1.5 \times 10^{10} \text{ cm}^{-2}$ and 850 nm, respectively. It is also concluded that as substrate temperature increases, deposited adatoms get sufficient energy while moving on substrate which provide more adatoms for nucleation centers. Thus, migration length of these adatoms have an important role in growth of ZnO Nanorods which strongly depends on substrate temperature [Venkatesh *et al.*, 2013]. With sufficient high energy, these adatoms moves towards suitable lattice sites for successive growth and columnar growth along c-axis dominating as operating temperature increases. It may create more nucleation center of bigger diameter and as result, deposited nanorod's diameter as well as density increases. By increasing substrate temperature from RT to 600 °C with incremental steps of 100 °C, we were able to achieve deposition of vertically aligned ZnO NRs from nano-crystalline ZnO thin film. The change in surface morphology from deposited 2-D structure (nano-crystalline thin films) to 1-D nanostructure (NRs) is observed when operating temperature increases from lower range (RT to 400 °C) to higher range (500 °C- 600 °C). At particular temperature and pressure, adatoms can reach to the substrate with sufficient energy to form nuclei centers. By increasing temperature from 500 °C to 600 °C, migration length of these adatoms on substrate gets increased which further increases nanorods diameter and length.

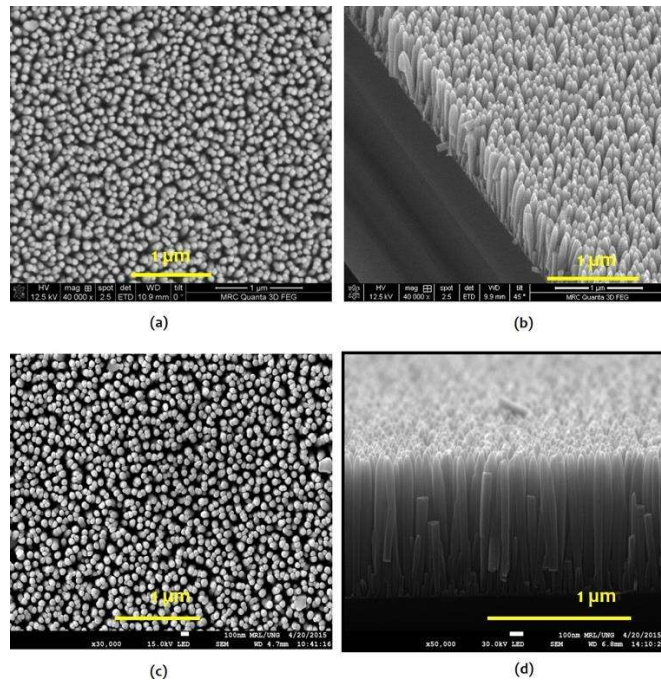


Figure 4.4: FESEM images with (a), (c) Top view and (b), (d) Cross-sectional view of ZnO NRs with substrate temperature varying from 500 °C to 600 °C

AFM characterization shows topography similar to FESEM characterization, which further validates uniform distribution of deposited ZnO NRs over entire substrate. Figure 4.5 shows AFM images with 2-D and 3-D view of ZnO NRs with substrate temperature ranging from 500 °C to 600 °C, respectively. These deposited nanorods were well aligned and uniformly distributed and by increasing substrate temperature from 500 °C to 600 °C, rms roughness decreases from 24.52 nm to 15.98 nm whereas diameter of nanorods increases as observed earlier in FESEM results. By increasing substrate temperature for deposition, increased ZnO nanorod's diameter provides more smooth surface. Thus, catalyst free growth of vertically aligned ZnO nanorods can be easily achieved on bare silicon.

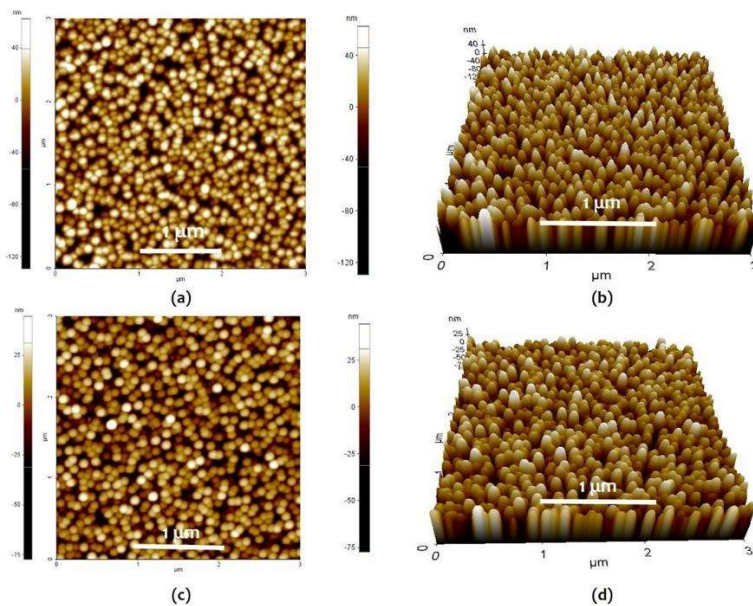


Figure 4.5: AFM images with (a), (c) 2-D view and (b), (d) 3-D view of ZnO NRs with substrate temperature varying from 500 °C to 600 °C

4.3.1.4 Optical Characterization

Optical characterization of ZnO nanorods were studied using raman spectroscopy. Raman spectra of ZnO NRs deposited at substrate temperature of 500 °C and 600 °C were recorded between 200 to 800 cm^{-1} as shown in figure 4.6. As ZnO has hexagonal wurtzite structure, there are three types of optical active phonon modes present in spectra viz. polar active mode (A_1), infrared active mode (E_1) and non-polar active mode ($E_2(\text{high})$) [Wu and Liu, 2002; Alim *et al.*, 2005]. Polar and infrared active phonon modes are further divided in to longitudinal-optical (LO) and transverse-optical (TO) modes at different frequencies. In raman spectra, after subtracting Si (100) substrate peak, a strong peak appears at 438 cm^{-1} that is corresponding to $E_2(\text{high})$ mode for both deposition temperatures of 500 °C and 600 °C. Thus, due to presence of $E_2(\text{high})$ peak, deposited ZnO NRs were highly crystalline in nature and had hexagonal wurtzite structure. One weak peak can also be observed at 582 cm^{-1} which signifies presence of E_1 (LO) phonon mode. In RF sputtering with high substrate temperature, some oxygen vacancies are generated in ZnO NRs crystal structure which is indicated by E_1 (LO) phonon mode in raman spectra.

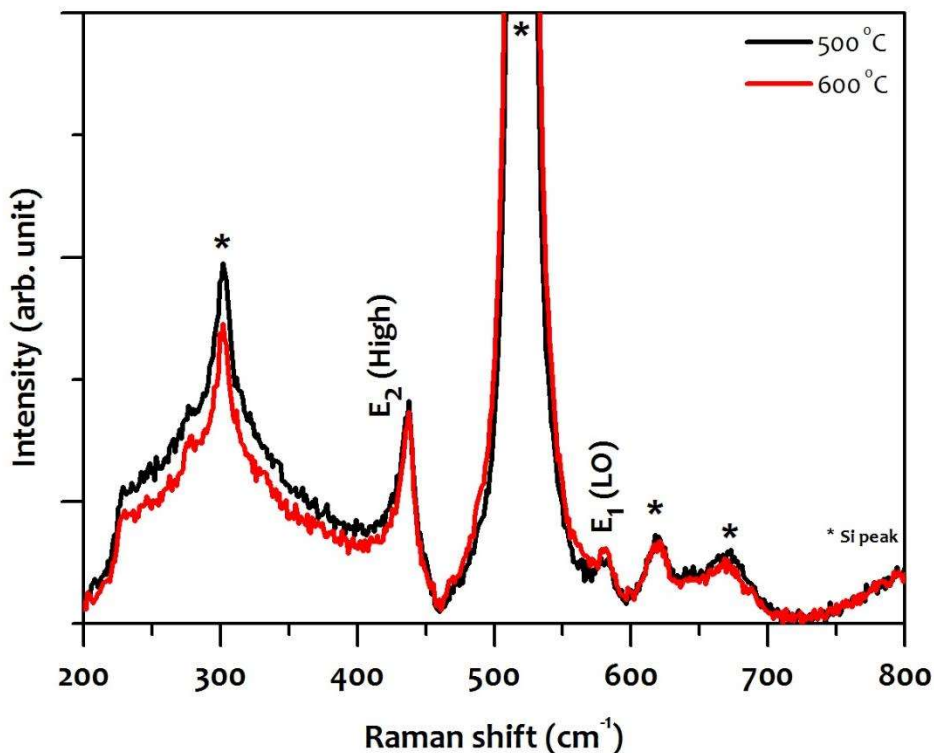


Figure 4.6: Raman spectra of ZnO NRs deposited at substrate temperature of 500 °C and 600 °C

4.3.2 Substrate Dependency

4.3.2.1 Experimental Setup

To understand the effect of various substrates on ZnO nanorod's growth, ZnO nanorods were deposited over substrates such as Si (100), Pt/Si (111), Ge, ITO coated glass and Polyimide flexible substrate, using RF sputtering at 500 °C and RT (for Polyimide flexible substrate) as operating temperature. Remaining deposition parameters were kept constant as mentioned in preceding sections. Table 4.2 shows deposition parameters of ZnO NRs deposited over various substrates.

Table 4.2: Deposition parameters ZnO NRs deposited over various substrates

Substrate	n-Si (100), Pt/Si (111), Ge, ITO coated glass, Polyimide flexible substrate
Sputtering target	ZnO (99.999% purity)
Base pressure	1×10^{-6} mbar
Deposition pressure	2×10^{-2} mbar
Deposition time	2 hours
RF power	150 W
Sputtering gas	Argon (60 sccm) for Si, Ge, Pt-Si, ITO coated Glass Ar:O ₂ (1:1) for Polyimide flexible substrate
Substrate temperature	500 °C for Si, Ge, Pt-Si, ITO coated Glass RT for Polyimide flexible substrate
Target to substrate distance	14 cm

4.3.2.2 Structural Characterization

For confirmation of Crystallinity of deposited ZnO NRs over various substrate, X-ray diffraction technique is applied. Figure 4.7 depicts X-ray diffraction spectra for ZnO nanorods grown over different substrates like (a) Pt-Si (111), (b) ITO coated glass, (c) Ge, (d) n-Si (100) and (e) Polyimide substrate, respectively. Few peaks with large intensity can be seen at 39.64° for Pt (111), 30.48° for ITO (222) and 27.17° for Ge (111) substrate planes [Gu *et al.*, 2009; Du *et al.*, 2014; Kang *et al.*, 2012]. By extracting these substrate peaks from XRD spectra, a strong diffraction peak of (0002) crystalline plane at 34.64° is observed that implies deposition of hexagonal wurtzite structure of ZnO NRs grown along c-axis. Highly crystalline nature of nanorods is further validated by full width half maxima (FWHM) width. When substrate is varied from n-Si (100), Pt-Si (111), Ge and ITO coated glass, FWHM increases from 0.21° , 0.27° , 0.28° and 0.29° , which indicates decreased crystallinity of ZnO NRs in comparison to Si substrate. Although, there is large lattice and thermal mismatch between ZnO-Si and ZnO-Pt/Si (17%), ZnO NRs shows high crystallinity [Hur *et al.*, 2006; Jeong *et al.*, 2003]. ITO also has minimum (3%) lattice mismatch with ZnO, due to which, deposited ZnO nanorods shows crystalline nature [Lupan *et al.*, 2010 A]. For easy application in electronics, crystalline growth of ZnO NRs along c-axis is highly required, for which, ZnO NRs were grown on polyimide substrate at RT in presence of Oxygen: Argon (1:1) gases. Figure 4.7 (e) shows XRD spectra of ZnO NRs grown over polyimide substrate. The spectra show strong peak at 34.4° with an extra peak at 36.2° which corresponds to (0002) and (101) crystalline planes. These deposited ZnO NRs shows polycrystalline nature with (0002) peak FWHM~ 0.37° and are grown along [0001] direction on flexible substrate. Due to the presence of oxygen during deposition, deposition rate and crystallinity of ZnO NRs is reduced in comparison to presence of pure argon.

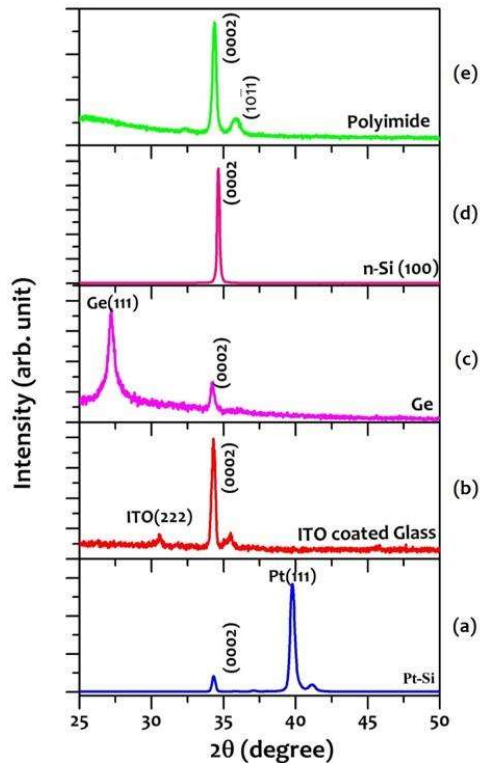


Figure 4.7: X-Ray diffraction spectra for ZnO nanorods grown over substrates - (a) Pt-Si (111), (b) ITO coated glass, (c) Ge, (d) n-Si (100) and (e) Polyimide, respectively

4.3.2.3 Surface morphology

To further understand effect of substrate variation on ZnO NRs deposition, surface morphology has been studied using FESEM images. The surface roughness has been calculated by AFM XEI software. Figure 4.8 shows top view FESEM images of ZnO NRs grown over (a) n-Si, (b) Ge, (c) ITO coated Glass, (d) Pt-Si (111) and (e) Polyimide substrate, respectively. ZnO NRs are deposited over various substrate without using catalyst or buffer layer, which helped getting uniformly distributed ZnO NRs over entire substrate. Nanorods were vertically aligned with homogenous distribution of almost uniform diameter and length. Although, larger lattice mismatch between ZnO and substrate can cause residual stress and degrade the quality. But, as 1-D nanostructures have smaller footprints in comparison to thin films, there is no significant effect of lattice mismatch on quality of nanostructures. Hence, high quality self-assemble ZnO NRs with uniform diameters can be accomplished over larger lattice mismatches substrate such as Si (100) and Ge. ITO coated substrate has minimum lattice mismatch of around 3% between two neighboring (O-O) atoms [Lupan *et al.*, 2010 A]. But, roughness of ITO and Pt-Si substrate is greater than bare Si due to which, dense distribution of ZnO NRs is reflected in comparison to NRs grown at silicon substrate. These deposited nanorods have average diameter of 36.6 nm, 41.6 nm, 45 nm and 48nm for substrate Pt-Si, Ge, ITO coated glass and n-Si (100), respectively.

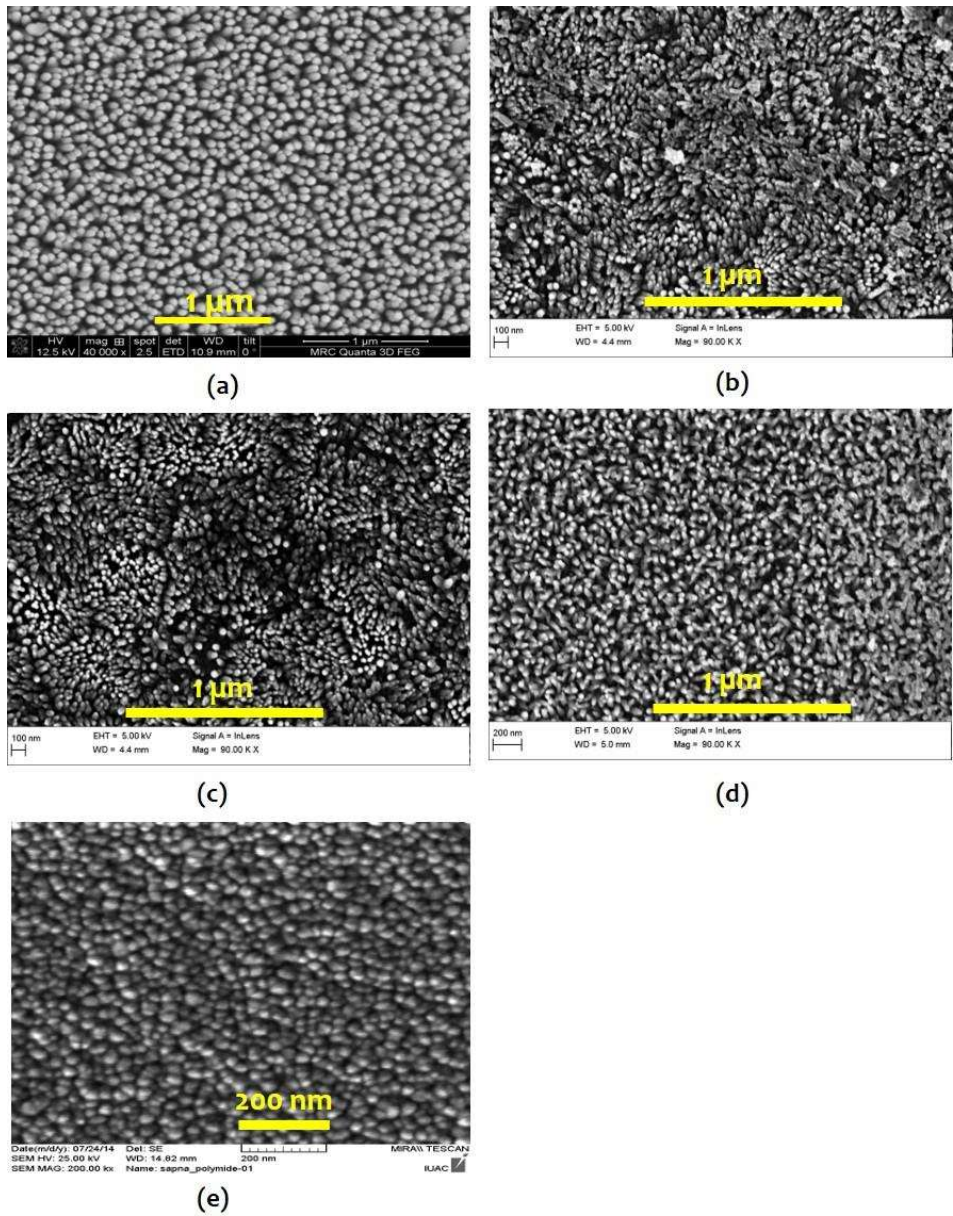


Figure 4.8: Top view FESEM images of ZnO NRs grown over (a) n-Si, (b) Ge, (c) ITO Coated glass, (d) Pt-Si (111) and (e) Polyimide substrate, respectively

Density of NRs also increases over other substrates in comparison to bare Si. As roughness of Pt-Si and ITO coated glass surface is higher than silicon, increasing adatoms creates additional nucleation centers because rough surface causes initial loss of energy of adatoms in comparison to smoother surface. Thus, high density of nanorods with small diameters are deposited over entire Pt-Si and ITO coated glass substrates. During deposition, growth of nanorods was stimulated by migration of adatoms with sufficient energy along nanorods walls which then added to the top of these nanorods [Venkatesh and Jeganathan, 2013]. If sufficient adatoms are unable to reach at the tip of nanorods, the circular tip of nanorods alters to needle tip. This process implies that because of high surface roughness, ZnO nanorod's tip changes from circular to needle form as substrate changes from Si to ITO coated glass, Pt-Si and Ge. For RT deposition of ZnO NRs over flexible substrate, FESEM images with 45 degree tilted view of ZnO NRs is shown in figure 4.8 (e). The deposited nanorods were vertically aligned with 25 nm average diameter and ~300 nm height. The depositions were carried out in presence of Ar: O₂ (1:1) and RT as substrate temperature which reduces deposition rate due to which, average height of nanorods also gets reduced as adatoms are unable to attain sufficient energy to reach at the top of nanorods

which ultimately reduces average height and average diameter. In case of Si substrate deposition at room temperature, nano-crystalline thin film was deposited. Added roughness of Polyimide substrate leads to generation of nuclei centers of constant diameter through adatoms, which further enhances ZnO nanorods growth even at RT.

4.4 CONCLUSION

RF sputtering system was used to deposit vertically aligned ZnO nanorods with uniform distribution throughout substrate. To improve the quality of deposited nanorods and reduce impurities, catalytic or buffer layer free substrates were used for deposition using VS method. By altering RF sputtering temperature and substrate material, diameter and density of nanorods were tuned. By optimizing substrate temperature and deposition pressure, morphology of deposited nano-crystalline thin films is changed into self-assembled, uniformly distributed ZnO NRs.

For deposition of ZnO NRs on Si substrate, substrate temperature was varied from 500 °C to 600 °C that changed nanorod's diameter from 48nm to 58 nm. And by increasing substrate temperature, density and height of these nanorods were changed from $1.26 \times 10^{10} \text{ cm}^{-2}$ and 750 nm to $1.5 \times 10^{10} \text{ cm}^{-2}$ and 850 nm, respectively. Furthermore, improvement in its crystallinity was observed by increasing operating temperature from 500 °C to 600 °C. In addition, morphology of ZnO NRs was witnessed by varying substrate material. Even these deposited nanorods show denser nanorods with 36.5nm, 41.5 and 45 nm diameters for Pt-Si, Ge and ITO coated glass in comparison to Si substrate at 500 °C. Surface roughness is one of many other parameters such as surface free energy, wettability and contact angle which may plays important role in the growth of ZnO nanorods over various substrates.

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