Chapter 5

Conclusion and Future Scope

5.1 Introduction

The primary objective of this thesis is to investigate some performance characteristics of p-Si(bulk)/n-TiO_2 and p-SiNWs/n-TiO_2 thin film (TF) based nanostructured heterojunction ultraviolet (UV) photodiodes fabricated by using two low-cost deposition techniques namely the Sol-gel (SG) and Electron Beam Evaporation (EBE) for n-TiO_2, without using any buffer layer. We have considered the Si substrate based TiO_2 TF heterojunction devices due to their possibility of integration with the well-matured Si based IC technology for the designing of Si based future generation smart UV photodetectors. Since the properties of the nanostructured devices are highly process dependent, we have considered four individual p-Si/n-TiO_2 heterojunction photodiodes: (i) The first two devices are fabricated by depositing n-TiO_2 TFs on the bulk p-Si <100> substrates by two different low-cost and low-temperature deposition techniques namely EBE and SG techniques; (ii) The other two are p-SiNWs and n-TiO_2 based core-shell heterojunction diodes fabricated by depositing the n-TiO_2 TFs (by the same EBE and SG methods) on p-SiNWs synthesized by the Electroless Metal Deposition and Etching (EMDE) of the p-Si <100> substrates. The major findings and observations presented in the previous chapters of the thesis are summarized in this chapter as described in the following.

5.2 Chapter-Wise Summary of Major Contributions

Chapter-1 introduces the fundamental concepts of the nanomaterials and devices related to the present thesis. The properties of TiO_2 TFs and Silicon Nanowires (SiNWs) are discussed with their potential applications. Various approaches for the fabrication of different nanostructures as well as their characterization techniques have been discussed. A detailed literature survey is carried out on the fabrication and characterizations of Si/TiO_2 based nanostructured heterojunction devices. Some important state-of-the-art works reported on the SiNWs and TiO_2 fabrication techniques, TiO_2 TF characterizations, electrical characteristics of bulk and nanostructured Si/TiO_2 based heterojunctions, and temperature-dependent performance of Si/TiO_2 heterojunctions have also been examined. Based on the literature survey, the scopes of the thesis have been outlined at the end of this chapter.

Chapter-2 presents a comparative study of the fabrication and characterization of two p-Si(bulk)/n-TiO_2 TFs heterojunction UV photodiodes. In one device, the n-TiO_2 TF has been deposited on bulk p-Si substrates by the EBE method while other device uses the n-TiO_2 TF using the SG with spin coating method. The structural, electrical and optical properties of the two types of TiO_2 TFs as well as their corresponding heterojunction devices have been investigated in a systematic manner. Selected key points of Chapter-2 can be given below:

- ❖ The anatase phase SG solution was synthesized at room temperature using titanium tetraisopropoxide which was processed for TiO_2 TF deposition using spin coating method.
- ❖ The surface morphology and other characterizations have confirmed high surface quality of the TiO_2 films grown by both the deposition techniques. However, SG

based TiO_2 TFs are found to have smaller nano-roughness, grain size and grain length than those of the EBE based films.

- ❖ Both the EBE and SG deposition techniques under consideration are found to be suitable for the uniform deposition of TiO_2 TFs over a wide area having nanocrystalline surface and enable us to make TiO_2 TFs on p-Si <100> with the dominant "anatase phase" having <101> diffraction peak and "tetragonal crystal structure" confirmed by HRSEM, AFM images and XRD spectra analysis.
- ❖ Experimental and theoretical values of reflectance and transmittance parameters of both the samples are in good agreement with min. Goodness of Fit >85 %. The TiO_2 TFs are transparent in nature to the visible light.
- ❖ The UV-Vis measurements provide band gap energies of the EBE and SG based TiO_2 TFs as ~3.1 eV and ~3.3 eV, respectively.
- ❖ The room temperature PL emission spectra of both the EBE and SG based TiO_2 TFs show strong emissions in UV region and weak emissions in visible region.
- ❖ Energy band diagram analysis shows that the current flowing across the n-TiO_2/p-Si heterojunction device can be determined predominantly by the "flow of electrons" from n-TiO_2 to p-Si side.
- ❖ The as-fabricated n-TiO_2/p-Si heterojunctions using EBE and SG based TiO_2 TFs have excellent rectifying and UV detection characteristics with respective rectification ratio of ~65 and ~18240 and the respective contrast ratio of ~14.9 and ~56704 at 10 V bias.
- ❖ The barrier height, ideality factor, responsivity, photoconductive gain, specific detectivity and resistance-area product measured for the EBE (SG) based heterojunction photodiodes under consideration are respectively given by ~0.7383 eV (~0.8105 eV), ~3.1466 (~3.8388), ~0.693 A/W (~1.25 A/W), ~2.35, 8.62×10^{10}

mHz$^{1/2}$W^{-1} (~4.24, 1.62×10^{11} mHz$^{1/2}$W^{-1}) and ~132.88 Ω.m^2 (~20639.16 Ω.m^2) at 10 V bias voltage. Clearly, the heterojunction diodes under investigation in Chapter-2 are promising device for UV detection applications.

- ❖ The transient response time was measured and compared between the SG and EBE based heterojunctions. The SG based device shows faster response and recovery time than those of the EBE based heterojunction photodiodes.
- ❖ The barrier height, specific detectivity, external quantum efficiency and area-resistance product of the SG based p-Si(bulk)/n-TiO_2 TF heterojunction photodiodes are observed to be larger than their corresponding values of the EBE based photodiodes. The enhancement of about ~223.74 times in the rectification ratio, ~6445 times in the contrast ratio (at -5.2 V), about two times enhancement in the responsivity imply that the SG based p-Si/n-TiO_2 TF heterojunction UV photodetectors have superior properties over the EBE based heterojunction UV photodiodes under study.

Chapter-3 investigates the temperature-dependent I-V (say, I-V-T) characteristics of the two types of p-Si/n-TiO_2 heterojunction devices fabricated and characterized in Chapter-2. The effects of temperature on various parameters such as barrier height, ideality factor, and reverse-saturation current of the heterojunction diodes have been examined for a wide temperature range of ~303 K to 453 K. Many of the device parameters show unrealistic values due to the non-ideal heterojunction interface which is well-known as the *Barrier Height Inhomogeneity* (BHI) phenomenon in the Schottky junction devices. The BHI has been modelled by assuming a Gaussian distributed barrier height at the heterojunction in the similar manner as considered for the Schottky junction diodes. The I-V-T analysis has been carried out for determining the Richardson constant of the TiO_2 TFs possibly for the first time in this thesis. Some of the important points of present chapter can be listed below:

- The estimated value of the zero-bias mean barrier height $(\phi_{B0,\mathrm{m}})$ at T ~0 K at the p-Si(bulk)/n-TiO_2 heterojunction is increased from an unrealistic value of ~0.21 eV to ~1.68 eV for EBE based heterojunction whereas it is increased from ~0.31 eV to ~1.69 eV for the SG based device after taking the BHI phenomenon at the heterojunction interface into consideration. As per the Anderson's model, the finally estimated values after considering the BHI phenomenon are nearly equal to its theoretical value of the difference between the work functions of Si and TiO_2 at the heterojunction interface.
- As mentioned earlier, we have reported the estimation of the Richardson constant for TiO_2 TFs from the analysis of I-V-T characteristics of p-Si(bulk)/n-TiO_2 heterojunctions possibly for the first time in the present thesis. The estimated values of the Richardson constant for EBE and SG based heterojunction devices are ~9.604×10^{-8} $Acm^{-2}K^{-2}$ and ~6.1712×10^{-7} $Acm^{-2}K^{-2}$, respectively when the effect of BHI is neglected.
- Note that the theoretically predicted value of the Richardson constant for TiO_2 is ~1200 $Acm^{-2}K^{-2}$. Thus, the estimated values of the Richardson constant without taking BHI phenomenon at the heterointerface into consideration are completely erroneous and unrealistic too.
- The estimated values of the Richardson constant are changed from the unrealistic value of ~9.604×10^{-8} $Acm^{-2}K^{-2}$ to the practical value of ~1332 $Acm^{-2}K^{-2}$ for EBE based TiO_2 film and from ~6.1712×10^{-7} $Acm^{-2}K^{-2}$ to ~1265 $Acm^{-2}K^{-2}$ for the SG based TiO_2 film after the effect of BHI is taken into consideration.

- The estimated value of the modified Richardson constant (A^{**}) for the SG based TiO_2 film is closer to its theoretical value than the EBE based TiO_2 film. Thus, the quality of SG based TiO_2 film appears to be better than the EBE based film in the present study.

Chapter-4 reports the fabrication, characterization, and UV detection applications of p-SiNW/n-TiO_2 heterojunction diodes. We have grown the single crystalline p-SiNW arrays by Electroless Metal Deposition and Etching (EMDE) of the bulk p-Si substrate. Then TiO_2 TFs have been grown on the p-SiNW arrays using EBE and SG methods as considered in Chapter-2 for forming the p-SiNWs/n-TiO_2 core-shell heterojunction photodiodes. Detailed structural, optical and electrical properties of p-SiNWs capped n-TiO_2 heterostructures have been analyzed by using various analytical instruments such as HRSEM, AFM, XRD, EDAX, Raman, PL, and Semiconductor device parameter analyzer. Key observations of the present chapter are summarized below:

- An in-house developed low-cost and low-temperature metal (Ag)-induced chemical etching, known as the EMDE method, is proposed for the fabrication of high-quality vertically aligned SiNW arrays uniformly distributed over a large area of p-Si substrate. The possible growth mechanism of SiNW arrays have also been discussed.
- In this work, n-type TiO_2 poly-crystalline TFs have been deposited on the vertically-aligned p-SiNW arrays by the EBE and SG methods without using any additional buffer layer.
- The HRSEM and AFM measurements show the diameters of the p-SiNWs lying in the range of ~100–500 nm and ~620–800 nm before and after the TiO_2 TFs deposition on the NWs.

- The crystallography study shows that the as-deposited TiO_2 films (annealed at 550 °C) are of anatase phase in nature with tetragonal crystal system for both the EBE and SG based films.
- The PL spectra shows a dominant emission peak at ~420 nm in both types of TiO_2 under study. It is attributed to the oxygen related defect emission and the near band edge emission of the anatase phase based n-TiO_2 TFs. A weak emission peak is also observed in the visible region. The dual PL peaks may imply the possibility of application of the device for dual band photodiode applications. Under similar measurement conditions, the EBE based TiO_2 film offers higher emission intensity of the peaks as compared to the corresponding peaks for the SG based samples.
- The as-fabricated EBE based p-SiNWs/n-TiO_2 heterojunction photodiode shows rectifying behavior with a rectification ratio of ~519.82 at (12 V), Ideality factor *(η)* ~5.498, reverse saturation current ~24.836, and effective barrier height ~0.7924 eV. The values of Contrast Ratio, Responsivity, External Quantum Efficiency and Detectivity have been estimated to be ~113.82, ~0.234 A/W, ~79.33 % and ~8.66×10^{11} $mHz^{1/2}W^{-1}$, respectively at -11 V bias.
- The as-fabricated SG based p-SiNWs/n-TiO_2 heterojunction photodiode shows rectifying behavior with a rectification ratio of ~673.259 (at 12 V), ideality factor *(η)* ~6.627, reverse saturation current ~4.167V and effective barrier height ~0.8379 eV. The values of Contrast Ratio, Responsivity, Gain, and Detectivity have been estimated to ~1212.63, ~6.341 A/W, ~21.543 and ~2.055×10^{11} $mHz^{1/2}W^{-1}$, respectively at -11 V bias.
- The photodiode performance parameters of the p-SiNWs/n-TiO_2 core-shell heterojunction photodiodes appear to be promising for the present day's Si based nanoelectronic and optoelectronic applications.

- The EMDE based SiNWs coated p-Si substrate shows an optical reflectance of <0.3 % over a wide range of wavelengths starting from the UV to visible regions (~400 nm to ~1100 nm) which is negligible as compared to reflectance of more than 50 % and 30 % in the UV and visible regions, respectively, of the bulk p-Si substrates. Thus, the as-fabricated SiNWs can be used as an excellent antireflection coating material in Si solar cells and other Si based photodetectors.
- The measured high frequency (at 1 MHz) room-temperature C-V characteristics of the heterojunction diodes under investigation have been analyzed for estimating the electron concentration in the n-TiO_2 films, barrier height, and built-in potential of the diodes.
- Based on the Anderson's model, we have discussed the carrier transport phenomenon with the help of the energy band diagrams for p-SiNWs/n-TiO_2 heterojunction diodes under bias, dark and illuminated conditions.
- The p-SiNWs/n-TiO_2 TFs based core-shell heterojunction photodiodes show better UV detection properties over the p-Si(bulk)/n-TiO_2 TF heterojunction photodiodes considered in Chapter-2.
- For UV detection applications the SG based devices will be preferred over the EBE based heterojunction diodes for their simpler and cost effective fabrication.

5.3 Future Scopes of Research in the Related Area

Since research is an endless process, no research work is truly complete in all facets. Thus, there are always some limitations and scopes in the works presented in any thesis. We would like to suggest some future scopes of research related to the works presented in this thesis as listed below:

- In future, different n-TiO_2 nanostructures may be grown with and without a seed layer on the p-Si substrates for investigating the performance of different types of p-Si/n-TiO_2 heterojunction diodes for optical and gas sensing applications.
- The study of photoresponse characteristics as a function of wavelengths of the heterojunction diodes under study is missing in the present thesis. This can be taken as a future work.
- The gas sensing properties of the heterojunctions considered in this thesis may be investigated.
- Attempt may be made to develope doped p-type TiO_2 TFs on n-Si and n-SiNWs for fabricating n-Si(bulk)/p-TiO_2 and n-SiNWs/p-TiO_2 TF heterojunction diodes. The structural, electrical and optical characteristics of the proposed devices may also be carried out.
- Fabrication and characterization of TiO_2 nanostructure based devices on flexible polymer substrates can be explored.