Chapter 7
CONCLUSION
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7.1. Summary of the present work

This thesis is a record of study of the preparation and characterization of nanostructured copper oxide and titanium dioxide (TiO$_2$) films. Nanostructured copper oxide films were prepared by the oxidation of copper films deposited on glass substrates by thermal evaporation of metallic copper. From X-ray diffraction (XRD) and Gracing Incidence X-ray diffraction (GIXRD) studies, it was observed that the films oxidized at temperatures below 275°C were of Cu$_2$O phase while oxidation above 325°C produced pure CuO phase. Oxidation at temperatures between 275 and 325°C produced films of mixed Cu$_2$O and CuO phases. The oxidation temperature dependence of the phase change from Cu$_2$O to CuO phase was studied using Fourier Transform Infrared (FTIR) transmission spectra. High Resolution Transmission Electron Microscopy (HRTEM) images of the film samples annealed at 250 and 350 °C indicated the nanostructure of grains of the deposited films. Atomic Force Microscopy (AFM) images of the samples revealed that the surface of the films were nanoporous. XRD, HRTEM and AFM studies along with fractal analysis of the AFM images of the film samples revealed that the growth mechanism in the film consisted of the formation of nanograins as primary structure followed by the aggregation of nanograins as the secondary structure.

The UV-Visible and micro-Raman spectra of copper films oxidized at different temperatures were presented. UV-Visible spectra showed clear blue shift in the band gap values of the samples composed of pure Cu$_2$O and CuO phases and the blue shift in the band gap energy was attributed to quantum confinement effect. Resonant enhancement of intensities of Raman lines was observed in the micro-Raman spectra of films composed of Cu$_2$O phase when excited by 488 nm laser light. Resonance enhancement of the 150 and 211 cm$^{-1}$ Raman modes of Cu$_2$O showed the existence of electron-phonon coupling mediated by the Frohlich interaction in the samples composed of Cu$_2$O phase.
Nanocrystalline TiO$_2$ films of pure anatase phase were fabricated using RF magnetron sputtering followed by annealing. Transformation of amorphous as-deposited films into films of pure anatase phase with (004) preferred orientation was identified from GIXRD measurements. Grain size and crystalline perfection of the grains of the films were determined using HRTEM. AFM images of the samples revealed the evolution of morphological features on annealing. The surface porosity of the films resulting from the agglomeration of grains was estimated. Fractal analysis of AFM images was carried out using a post image processing software. The increase in the surface roughness of the films on annealing indicated a columnar growth due to ballistic agglomeration of nano-grains. From these observations, it was concluded that the deposited material showed a hierarchical structure having perfect nanocrystalline grains with anatase phase as the primary units and agglomerates of these units as the secondary structure.

UV-Visible and micro-Raman spectra of nanostructured TiO$_2$ film samples annealed at different temperatures were analyzed. The band gap values estimated from UV-Visible spectra of the nanostructured TiO$_2$ film samples in the present study were in good agreement with the reported band gap values of nanophase TiO$_2$. The present samples exhibit a blue shift in the band gap value compared to the band gap energy of bulk TiO$_2$ should be a result of quantum confinement effect in the nanosized crystalline grains of the samples. In the micro-Raman spectra of the samples, the strongest mode at 141 cm$^{-1}$ due to the vibrations of the anatase structure was well resolved which indicated that anatase phase with a long range order developed in the annealed films. The increased broadness of the 141 cm$^{-1}$ ($E_g$) Raman mode observed in the present study compared to the reported bulk values can be attributed to phonon confinement effect.

The absorption and photoluminescence properties of nanostructured TiO$_2$ films deposited by RF magnetron sputtering were studied. Photoluminescence spectroscopy results showed that post deposition annealing of a sputtered TiO$_2$ film can greatly influence its emission characteristics. The absorption properties of nanostructured TiO$_2$ thin films can be modified by the addition of ZnO. It is shown that the visible PL emission from anatase TiO$_2$ films by the addition of ZnO may be due to radiative recombination of impurity and defect trapped excitons.
7.2. Future scope

Nanostructured copper oxide and titanium dioxide films are technologically important materials with a wide range of applications. Two main avenues for future directions arise from the studies presented here. The first one is the extension of the present work to deepen our understanding of the properties of nanostructured copper oxide and titanium dioxide films. The second one is the application of nanostructured copper oxide and titanium dioxide films in various devices to study the performance of these films. Considering the nanostructure and tailored band gap energy, the prepared copper oxide films can be potentially used for harvesting solar energy in the visible range. The application of nanostructured TiO$_2$ films in the fabrication of Dye Sensitized Solar Cells (DSSC) is important. Composite films of TiO$_2$/Cu$_2$O can also be used in DSSC to enhance the visible light absorption. This new composite will provide a new way to take advantage of TiO$_2$ and make it function under visible light. Another application is the derivatization of the TiO$_2$ nanostructured film using organic molecules for the fabrication of electrochromic devices. More work is needed to study the emission properties of doped TiO$_2$ films. The changes in the visible light emission of the ZnO doped TiO$_2$ films can be studied by using various dopants at different concentrations.