

ABSTRACT

Selection of a semiconductor material with appropriate band gap is essential for specific (opto)electronic applications. Moreover, it is necessary to use earth-abundant and environment friendly materials that are easy to manufacture using cost-effective synthesis techniques onto a range of substrates. However, electronic structure and optoelectronic properties of these semiconductors are found to be highly sensitive to their overall microstructure, which in turn depend on the synthesis route as well as process parameters used for their fabrication. Moreover, choice of deposition technique plays an important role in designing efficient and cost-effective devices. It is also equally important to understand the surface and interface physics in terms of their variation in the surface microstructure and electronic structure along with bulk optoelectronic properties as these films are always present in a stack structure (consisting of multiple layers), thereby influencing the electrical properties of the next layers and thus the entire device. To this end, Al-doped ZnO (AZO) as a transparent conductor (TC) and Cu_{2-x}S as an absorber are investigated in this thesis. AZO is one of the most studied *n*-type TC because of its low cost, less toxicity, stability in hydrogen plasma, higher optical transmittance in visible range and lower electrical resistivity, hence, finding broader applications in technological domains, such as, thin film solar cells, touch-sensitive panels, light-emitting diodes, liquid crystal displays, organic electroluminescent and electrochromic devices. Similarly, Cu_2S is a promising low-cost, non-toxic *p*-type semiconductor with an optical band gap of 1.21 eV, which is in the optimum range for various applications, such as, photovoltaic, thermoelectric, gas sensor and optical filter. The optoelectronic properties of Cu_{2-x}S are highly sensitive to its stoichiometry, where a change in *x* (in the range of $0 \leq x \leq 1$) corresponds to distinct crystalline phases enabling significant variation in the optoelectronic properties (i.e., electrical resistivity of 0.8 $\Omega\text{-cm}$ for Cu_2S , 1×10^{-3} $\Omega\text{-cm}$ for $\text{Cu}_{1.8}\text{S}$ and 1×10^{-4} $\Omega\text{-cm}$ for CuS and optical band gap of 1.1-1.3 eV for Cu_2S , 1.5 eV for $\text{Cu}_{1.8}\text{S}$ and ~ 2.0 eV for CuS). Thus, a systematic interrelation between electronic structure, microstructure and optoelectronic properties of these materials with respect to the various synthesis methods and

process parameters is very important to get optimized quality for specific application.

In this PhD project, AZO and Cu_{2-x}S thin films are deposited on ultrasonically cleaned (1 cm \times 1 cm) soda lime glass (SLG) substrates by varying the process parameters (i.e., substrate temperature (T_s) and deposition time (t)) in radio frequency (RF) magnetron sputtering. Additionally, Cu_{2-x}S (with x being 0, 0.25 and 1.0) microtubes are synthesized by thermally dissociating the self-sacrificed $\text{Cu}(\text{tu})\text{Cl}\cdot 0.5\text{H}_2\text{O}$ template and by varying the concentration of the reducing agent (Na_2SO_3) from 0 to 1.7 mmol in solution chemical route. In addition to above, Cu_{2-x}S films of varying stoichiometry are prepared by dissolving appropriate concentration of Cu and CuS particles in binary thiol-amine alkahest solvent mixture through molecular solution approach. Then a range of experimental techniques, such as, X-ray diffractometer (XRD), field emission scanning electron microscope (FESEM), energy dispersive spectroscopy (EDS), atomic force microscope (AFM), transmission electron microscope (TEM), UV-Vis-NIR spectrophotometer, Hall effect measurement system (HEMS), X-ray photoelectron spectroscopy (XPS), conductive atomic force microscopy/spectroscopy (C-AFM/C-AFS), scanning tunnelling microscopy/spectroscopy (STM/STS) are used to understand the overall electronic structure, microstructure and optoelectronic properties of these materials.

The work on the AZO films addresses the relation between microstructure and optoelectronic properties of these films by varying process conditions (i.e., varying T_s from 303 to 673 K and t from 15 to 120 mins) in RF magnetron sputtering. Here, 242 nm thick AZO film deposited at 623K T_s for 60 mins and at 50 W RF power is found to show the most oriented crystallite growth and best optoelectronic properties (i.e., the average transmittance in the visible range (T) = 91%, electrical resistivity (ρ) = $9.38 \times 10^{-4} \Omega\text{-cm}$, carrier concentration (n_e) = $4.09 \times 10^{20} \text{ cm}^{-3}$, carrier mobility (μ_e) = $16.28 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Furthermore, C-AFM is used to study the nanoscale surface conductivity of AZO thin films deposited onto SLG substrates by varying T_s from 303 K to 673 K for 60 mins. The obtained local surface electrical conductivity values are found to be influenced by their bulk electrical resistivity, surface topography and tip geometry. Further, the average (local) surface conductivity from the film surface is found to increase with

increasing T_s from 303 K to 623 K, beyond which they decrease until 673 K. Additionally, the variation in the local surface electrical heterogeneity within and also for a thickening AZO film is studied using the C-AFM/C-AFS technique. To this end, these films were deposited by varying the t from 15 to 120 mins by RF magnetron sputtering. The local surface electrical heterogeneity was found to be strongly dependent on the overall microstructure of the film grown at a particular deposition time. XPS and TEM-EDS are used to discern the distribution of the chemical constituents over these film surfaces. This study correlates the presence of a large amount of chemisorbed oxygen and/or segregated Al_xO_y at the grain boundaries associated with relatively non-uniform and/or rough films to the overall lower surface current values. Subsequently, a uniformly thick AZO film with a homogenous microstructure grown at an optimum deposition time is found to have the least amount of chemisorbed oxygen along with an effective distribution of Al doping on the film surface, leading to an increase in the overall surface current. This higher surface current is then found to increase the surface electrical heterogeneity of the film due to increased difference between a defect and defect-free region, contrary for a non-uniform and/or rough film.

Next, a simple, cost-effective thermolysis route to produce single phase, stoichiometric, hollow $Cu_{2-x}S$ microtubes of varied composition by using $Cu(tu)Cl \cdot 0.5H_2O$ as a self-sacrificed template is devised. Here, the concentration of the reducing agent (i.e., Na_2SO_3) is precisely controlled to obtain these $Cu_{2-x}S$ microtubes, which are confirmed by using XRD, EDX and FESEM. The optical absorption as well as the optical band gap of these compounds are found to be strongly influenced by its composition. Finally, the mechanism of formation of these precisely controlled compounds and direct impact of the shape of the self-sacrificed template on the ultimate tubular morphology of $Cu_{2-x}S$ is discussed. Moreover, to study copper deficiency induced varying electronic structure and optoelectronic properties of $Cu_{2-x}S$ thin films, here varying composition of $Cu_{2-x}S$ (i.e., Cu_2S , $Cu_{1.96}S$, $Cu_{1.8}S$, $Cu_{1.8}S + Cu_{1.6}S$ and CuS) films are grown here by using a low temperature molecular solution based deposition method, following which a wide range of characterization tools were used to understand their microstructure, electronic structure and optoelectronic properties. The hole concentration of these films are found to vary from $3.32 \times 10^{19} \text{ cm}^{-3}$ to 2.54×10^{22}

cm^{-3} as Cu_{2-x}S composition changes from Cu_2S to CuS . This is because of the induced Cu deficiency in Cu_{2-x}S films with decreasing Cu/S-molar ratio, which reduced the Cu *d*-band width in the valence band, thus pushing the Fermi level deep into the valence band. This leads the optical and transport gap to increase from 1.36 eV to 2.23 eV and 1.31 eV to 2.02 eV respectively with increasing copper deficiencies from Cu_2S to CuS . Moreover, in this work, both the valence and conduction band edge positions are found to shift negatively with increasing Cu deficiency in these films. Finally, this thesis addresses the influence of film thickness on the microstructure, electronic structure and optoelectronic properties of Cu_2S films. To this end, thickening Cu_2S films are deposited on the SLG substrate by varying *t* from 60 to 420 mins at room temperature (303 K) using RF magnetron sputtering. Following which a range of experimental techniques are used to characterize these films. Though films deposited at *t* of 60 to 360 mins are found to have pure Cu_2S phase, additional $\text{Cu}_{1.8}\text{S}$ phase is detected for the film deposited at 420 mins. The valence state of Cu is found to be +1 in all these films, though the binding energy positions of the core level 2p electrons are found to shift systematically and is correlated to the thickness induced compositional changes in these films. Sulfur is found to exist in two valence states in all these films; S^{-2} bound with Cu_2S and elemental or non-stoichiometric S^{-n} , the overall $\text{S}^{-n}/\text{S}^{-2}$ ratio being found to reduce with increasing film-thickness. This microstructural adjustment in the thickening film is found to alter the electronic structure and optoelectronic properties of these films, measured using XPS, STM/STS, UV-Vis-NIR spectrophotometer and HEMS. In the end, principle behind the microstructure alteration of this thickening film is proposed.

Chapter 2

Microstructure and optoelectronic properties of Al-doped ZnO films deposited by varying process conditions in radio frequency magnetron sputtering

Abstract

In this study, a correlation between microstructure and optoelectronic properties of Al-doped ZnO (AZO) films deposited by varying process conditions in radio frequency (RF) magnetron sputtering is established. To this end, AZO films are deposited on soda lime glass substrates by varying two important process parameters, such as, substrate temperature (T_s) from 303 K to 673 K and deposition time (t) from 15 to 120 mins via RF magnetron sputtering. A range of experimental techniques, such as, atomic force microscopy (AFM), grazing incident X-ray diffractometer (GIXRD), field emission scanning electron microscopy (FESEM), Hall effect measurements system (HEMS) and UV-Vis-NIR spectrophotometry, are used to understand the overall microstructure and optoelectronic properties of these films. All the films are found to grow in ZnO hexagonal wurtzite structure with strong (002) orientation of the crystallites, along with an average transmittance of 84 – 93 % in the visible range. However, the electrical properties of these films are found to show a strong dependence on T_s and t . Here, 242 nm thick AZO film deposited at 623K T_s for 60 mins and at 50 W RF power is found to show the most oriented crystallite growth and best optoelectronic properties (i.e., the average transmittance in the visible range (T) = 91%, electrical resistivity (ρ) = 9.38×10^{-4} Ω -cm, carrier concentration (n_e) = 4.09×10^{20} cm^{-3} , carrier mobility (μ_e) = $16.28 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

Chapter 3

Interpreting the Conductive Atomic Force Microscopy measured inhomogeneous nanoscale surface electrical properties of Al-doped ZnO films

Abstract

In this work, conductive atomic force microscopy (C-AFM) is used to study the inhomogeneous surface electrical conductivity of Al-doped ZnO (AZO) thin films at a nanoscale dimension. To this end, AZO films were deposited onto the soda lime glass substrates at substrate temperature (T_s) varying from 303 K to 673 K in RF magnetron sputtering. The obtained local surface electrical conductivity values are found to be influenced by their bulk electrical resistivity, surface topography and tip geometry. Further, the average (local) surface conductivity from the film surface is found to increase with increasing T_s from 303 K to 623 K, beyond which they decrease until 673 K.

Chapter 4

Microstructure influenced variation in the local surface electrical heterogeneity in thickening Al-doped ZnO films: Evidence using conductive atomic force microscope

Abstract

In this study, variation in the local surface electrical heterogeneity within and also for a thickening Al-doped ZnO film is studied using the conductive atomic force microscopy/spectroscopy (C-AFM/C-AFS) technique. To this end, these films were deposited by varying the deposition time from 15 to 120 mins by RF magnetron sputtering. The local surface electrical heterogeneity was found to be strongly dependent on the overall microstructure of the film grown at a particular deposition time. X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy-Energy Dispersive Spectroscopy (TEM-EDS) were used to discern the distribution of the chemical constituents over these film surfaces. This study correlates the presence of a large amount of chemisorbed oxygen and/or segregated Al_xO_y at the grain boundaries associated with relatively non-uniform and/or rough films to the overall lower surface current values. Subsequently, a uniformly thick AZO film with a homogenous microstructure grown at an optimum deposition time is found to have the least amount of chemisorbed oxygen along with an effective distribution of Al doping on the film surface, leading to an increase in the overall surface current. This higher surface current is then found to increase the surface electrical heterogeneity of the film due to increased difference between a defect and defect-free region, contrary for a non-uniform and/or rough film.

Chapter 5

Role of reducing agent and self-sacrificed copper-thiourea complex in the synthesis of precisely controlled Cu_{2-x}S microtubes

Abstract

In this study, a simple, cost-effective thermolysis route to produce single phase, stoichiometric, hollow Cu_{2-x}S microtubes of varied composition by using $\text{Cu}(\text{tu})\text{Cl}\cdot 0.5\text{H}_2\text{O}$ as a self-sacrificed template is devised. Here, the concentration of the reducing agent (i.e., Na_2SO_3) is precisely controlled to obtain these Cu_{2-x}S microtubes, which are confirmed by using XRD, EDX and FESEM. The optical absorption as well as the optical band gap of these compounds are found to be strongly influenced by its composition. Finally, the mechanism of formation of these precisely controlled compounds and direct impact of the shape of the self-sacrificed template on the ultimate tubular morphology of Cu_{2-x}S is discussed.

Chapter 6

Copper deficiency induced varying electronic structure and optoelectronic properties of Cu_{2-x}S thin films

Abstract

Copper sulfide (Cu_{2-x}S) is a class of low-cost, environment friendly *p*-type semiconductor, where electronic structure and the thus induced optoelectronic properties can be significantly varied through the creation of copper deficiency. To this end, varying composition of Cu_{2-x}S (i.e., Cu_2S , $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{1.8}\text{S}+\text{Cu}_{1.6}\text{S}$ and CuS) films were grown here by using a low temperature molecular solution based deposition method, following which a wide range of characterization tools were used to understand their microstructure, electronic structure and optoelectronic properties. The hole concentration of these films are found to vary from $3.32 \times 10^{19} \text{ cm}^{-3}$ to $2.54 \times 10^{22} \text{ cm}^{-3}$ as Cu_{2-x}S composition changes from Cu_2S to CuS . This is because of the induced Cu deficiency in Cu_{2-x}S films with decreasing Cu/S-molar ratio, which reduced the Cu *d*-band width in the valence band, thus pushing the Fermi level deep into the valence band. This leads the optical and transport gap to increase from 1.36 eV to 2.23 eV and 1.31 eV to 2.02 eV respectively with increasing copper deficiencies from Cu_2S to CuS . Moreover, in this work, both the valence and conduction band edge positions are found to shift negatively with increasing Cu deficiency in these films.

Chapter 7

Thickness induced microstructure, electronic structure and optoelectronic properties of Cu₂S films deposited by radio frequency magnetron sputtering

Abstract

This study addresses the influence of film thickness on the microstructure, electronic structure and optoelectronic properties of Cu₂S films. To this end, thickening Cu₂S films are deposited on the soda lime glass substrate by varying deposition time (t) from 60 to 420 mins at room temperature (303 K) using radio frequency (RF) magnetron sputtering. A range of experimental techniques, such as, X-ray diffractometry (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), UV-Vis-NIR spectrophotometry, scanning tunnelling microscopy/spectroscopy (STM/STS), X-ray photoelectron spectroscopy (XPS) and Hall effect measurement system (HEMS) are then used to characterize these films. Though films deposited at t of 60 to 360 mins are found to have pure Cu₂S phase, additional Cu_{1.8}S phase is detected for the film deposited at 420 mins. The valence state of Cu is found to be +1 in all these films, though the binding energy positions of the core level 2p electrons are found to shift systematically and is correlated to the thickness induced compositional changes in these films. Sulphur is found to exist in two valence states in all these films; S⁻² bound with Cu₂S and elemental or non-stoichiometric S⁻ⁿ, the overall S⁻ⁿ/S⁻² ratio being found to reduce with increasing film-thickness. This microstructural adjustment in the thickening film is found to alter the electronic structure and optoelectronic properties of these films, measured using XPS, STM/STS, UV-Vis-NIR spectrophotometer and HEMS. In the end, principle behind the microstructure alteration of this thickening film is proposed.