ABSTRACT

Nanomaterials are defined as the material having at least one dimension in nanometer range, i.e., 1-100 nm regime. Nanomaterials having their low dimensionality show size dependant properties, which are different from those of the atomic and bulk counterparts, enabling them to tune for a wide-range of applications. Nanomaterials exist in different dimensionalities, such as, zero-dimensional (0D): quantum dots, nanoparticles; one-dimensional (1D): nanorods, nanotubes, nanowires, nanobelts; two-dimensional (2D): quantum well, nanoplates, thin films etc. depending upon their controlled growth synthesis. Owing to different physical as well as chemical properties, they can play important roles for the fabrication of nanoscale electronic, optoelectronic, electrochemical, and electromechanical devices. So far, various attempts have been made to synthesize metals in the, semiconductors, oxides and other materials in nanocrystalline form due to their outstanding applications. The present work focused on some important semiconducting metal chalcogenides, such as, CdS, ZnS, CuS and MoS_2 with their different dimensional nanostructures. They have various applications in numerous fields, such as in photo thermal conversion, in solar cell devices, coatings for microwave shields in the form of thin films, optical filters, room temperature ammonia gas sensors etc.

In the present work, copper sulfide nanocrystals in the form of nanowires (1D), nanorods (1D) and some complex structure (flower-like morphology) has been synthesized with simple and new approaches and characterized. CuS nanowires have been synthesized by hydro/solvothermal method using Cu-dithiooxamide complex as a single-source precursor and the effect of reaction temperature, duration and solvents (solvothermal treatment) on the 1D growth and formation of copper sulfide has been investigated. A plausible reaction mechanism has been proposed to understand the chemistry behind the hydrothermal treatment, which is supported by the FTIR analysis and the nature of the complex has also been discussed. The nanowires have diameter of 40-80 nm and length up to few microns, which at high reaction temperature transformed to microrods of diameter of 1-2 μm and length up to 10 μm. Moreover, the pyrolyzed product of Cu-DTO complex at 680 ± 5 °C shows the formation of porous microbelts

having 10 μm in width and several micrometers in length. The structural, morphological and optical properties of products have also been investigated. CuS nanorods with length of 60-100 nm and 20-40 nm in diameter have also synthesized via simple wet chemical method by *in-situ* source-template interface reaction (ISTIR), where water and CS_2 are used as oil-water system and the reaction occurs at the interface of this oil-water system. The CS_2 droplets are employed as both reaction precursor as well as architecture template and facilitate the growth of CuS nanorods and nanoparticles depending upon the reaction condition. A possible reaction mechanism has been proposed to understand the growth of nanorods and the reaction has been carried out at different temperatures. On increasing the reaction temperature, the size of nanorods was found to be decreased and at high reaction temperature only nanoparticles of 30-70 nm diameter was observed. Moreover, nanorods and nanoparicles both are observed to have twinned structure and discussed in light of defects introduced during the growth process. The optical properties of products also have been discussed in detail. In recent years, synthesis of copper sulfide with complex structures (dendritic, flake-type or flower-like morphology) has also been attracted lots of interests. Therefore, synthesis of copper sulfide with flower-like morphology has been carried out by solvothermal means while using ethylenediamine as the solvent. The growth path as well as reaction mechanism during the formation of flower-like morphology has also been investigated. The products have been studied and characterized at different reaction durations. It is observed that ethylenediamine plays very important role on the growth as well as formation of flower-like morphology of copper sulfide. The detailed optical properties also have been carried out.

Thin films are categorized as the 2D nanomaterials and properties of thin film often differ significantly from those of bulk due to their very high surface area to volume ratio. Several techniques have been used for depositing thin films. In the present study, chemical bath deposition process has been used due to its simplicity, efficiency, cost effectiveness and reproduction ability. The deposition of CdS thin films have been carried out due to its extensive application in solar cells and opto-electric device fabrication. CdS thin films has been deposited on a glass substrate using tartaric acid as complexing agent, $CdCl_2{\cdot}2H_2O$ and thiourea as precursors at 60 °C maintaining the pH range in between 10 and 11. The deposited films are of much better quality in terms of thickness, uniformity and adherence to the surface compared to that obtained by using ammonia as a complexing agent. *In-situ* Sn doping of CdS thin film has also been carried out by CBD technique using the same complexing agent. The annealing effect as well as the doping effect on pure CdS thin film has been investigated. X-ray diffraction patterns of pure CdS films are of polytype in nature, i.e., the XRD peaks are correspond to mixture of hexagonal as well as cubic structure but after doping a tendency to adopt predominantly cubic phase have been observed. The microstructural parameters (crystallite size, lattice distortion and dislocations, strain etc.) have been calculated to determine the defects in the films introduced on doping. The purity as well as composition of films has been analyzed by EDX and XPS analysis. The films are nanocrystalline as the size of the grain particles ranges from 40-80 nm, observed from SEM and TEM analysis and the surface nature of films have also been examined by AFM analysis. The change in optical properties of CdS thin films on annealing and doping has also been investigated. The electrical resistivity of films is found to be decreased significantly on doping. However, the application of CdS thin films has been limited due to its hazard nature of using as CdS layer in solar cells. ZnS is found to be most suitable for use as the substitution of CdS thin films. Therefore, keeping this in mind, we also focused our work on the deposition of ZnS thin film using tartaric acid as complexing agent by CBD method at 80 °C. The annealing effect on pure ZnS thin films also has been investigated. Since the films are very thin, multiple depositions have been carried out to get structural informations from XRD analysis. The structure of deposited ZnS thin films is of hexagonal in nature, although the XRD of doped films was not possible to analyze due the thinness of doped ZnS thin film. The particle size ZnS thin film is of 20-70 nm in diameter and characterized by SEM and TEM and the surface nature by AFM analysis. The effect of copper doping on ZnS film under the same reaction condition has also been studied. A detailed investigation towards the change in optical properties of annealed as well as doped film has also been carried out. The room temperature electrical resistivity of ZnS thin film decreased after doping and the temperature dependence of electrical conductivity confirms the semiconductor nature of films. Owing to layered-type of structure, MoS_2 shows very good lubricating and tribological properties and is one of the very promising material for the solar cell and photovoltaic applications. MoS_2 thin film has been deposited on glass/quartz substrate from a single-source precursor, ammonium tetrathiomolybdate, by CBD technique at the temperature of 60 °C. The film was found to be poorly crystalline in nature having some oxide contamination. The EDX and XPS analysis shows the formation of non-stoichiometric films with small sulfur deficiency after annealing. The microstructural parameters of films after annealing at different temperatures have been investigated. On increasing the annealing temperature, crystallite size increases and the microstrain values fall significantly. Additionally, dislocation density decreases after annealing as the films becomes more aligned on introducing thermal energy. The morphology of the MoS_2 film has been studied by SEM analysis. The band gap values of MoS_2 thin films before and after annealing have also been calculated from the optical spectra.

Keywords: Nanomaterial, thin film, semiconductor, metal sulfide, hydrothermal/solvothermal, chemical bath deposition, structure, morphology, optical property, electrical property.