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Topic: Study of the Physical Properties of Nanostructured Chalcogenide Based Compound Semiconductors

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Findings

Due to the energy crisis and environmental pollution, society immediately needs high efficiency clean energy to replace the traditional fossil energy. The two prominent solutions to fight against the problem of energy shortage are the use of photovoltaics and thermoelectric devices. The chalcogenide materials are considered as chameleon compounds which are beneficial in both crystalline and amorphous forms. The exciting applications of chalcogenide include solar cells, thermoelectric devices, phase change memory (PCM) devices, photoelectrochemical water splitting for the generation of hydrogen and batteries. So due to their innumerable applications, it is essential to understand their physical properties in order to effectively use these materials in various energy harvesting devices. Chalcogenide materials being better known as chameleon compounds constitute an important class of semiconductor materials with a wide variety of applications both in amorphous and crystalline form. The study of chalcogenide glasses and crystalline metal chalcogenides in nanostructured form will enhance and revolutionise the various areas of applications of chalcogenide materials.

The present research work investigated the possibility of engineering various physical properties especially structural, morphological, optical and electrical properties by doping isoelectronic S in SeTe and Te in Sb_2Se_3 films, deposition of S doped SeTe, Te doped Sb_2Se_3 and Sb_2Te_3 films on different glass substrates and finally tailoring the physical properties of Sb_2Te_3 thin films by SHI irradiation. Major findings are summarized in this chapter.

Thin films of sulphur (S) incorporated SeTe with the chemical composition of $Se_{80}Te_{20-x}S_x$ ($x=0, 5, 10, 15$, indicate the weight percentage of sulphur incorporated) were deposited via vacuum evaporation technique. S incorporation in the SeTe alloy led to a reduction in the glass transition temperature from 333 K to 314 K. The investigated films were amorphous in nature with a thickness of ~ 250 nm. In comparison to pure selenium telluride (SeTe) film, the electrical conductivity exhibited an enhancement up to 10 wt % sulphur doping above which a decrease in electrical conductivity was apparent owing to microstructural porosity and enhanced bandgap. It is inferred that reduced grain size and dense morphology led to a higher value of absorption coefficient as well as enhancement in the electrical conductivity. Interestingly, Te replacement with S results in a monotonic increase in bandgap from 1.81 to 2.60 eV and a reduction in absorption coefficient. The trend of the observed bandgap for the S incorporated samples is consistent with the Kastner and single oscillator models. Moreover, bandgap tuning to 1.92 eV from 1.81 eV by S doping in SeTe with improved conductivity in comparison to pure SeTe unveils the importance of S incorporation in optimizing the performance of the optoelectronic devices. The obtained optical bandgap value of 1.91 eV with spherical and dense microstructure without cracks and pinholes leading to enhanced conductivity for the S (5%) doped SeTe thin films can be useful for the photovoltaic and photoelectrochemical (PEC) applications. Furthermore, it is important to note that the S incorporation into SeTe alloy resulted in a decrease in glass transition temperature (T_g) and increase in glass forming ability (GFA) and also tunes the characteristic temperatures of the SeTe alloy that may be useful in phase-change memory (PCM) devices.

Sb_2Se_3 and Te doped Sb_2Se_3 films of ~ 250 nm film thickness were deposited through facile thermal evaporation technique from the bulk material synthesized via melt quenching

technique. Thermogravimetric analysis of the pure and Te doped Sb_2Se_3 alloy in bulk form indicate decomposition of the alloys with the rise in temperature from 303 K to 673 K. X-ray diffraction pattern revealed single-crystalline orthorhombic phase stabilization of as prepared alloys in bulk as well as in the annealed thin film form. Phase formation is also evident in the Raman spectra from the appearance of two peaks at $\sim 189 \text{ cm}^{-1}$ and 210 cm^{-1} which are ascribed to Sb_2Se_3 Ag mode. The absorbance spectra of as annealed pure Sb_2Se_3 and Te incorporated Sb_2Se_3 films show significant reduction with Te doping due to an increase in the optical bandgap. The DC conductivity of as annealed Sb_2Se_3 and Te doped Sb_2Se_3 films recorded in the range from 308 K (room temperature) to 392 K show a decrease in DC conductivity and activation energy with the insertion of Te in the Sb_2Se_3 system reflecting Te doping induces structural changes as well as defect passivation. Interestingly, the DC conductivity is in the range of $\sim 10^{-7} \Omega^{-1}\text{cm}^{-1}$ at 308 K, which is higher than the previously reported conductivity of Sb_2Se_3 films and is prominently attributed to thermally assisted processes. The as annealed pure Sb_2Se_3 films show a higher value of optical conductivity than the CdTe films. Presently, the preferred orientation of grains, deep level defects and surface oxidation in Sb_2Se_3 thin films are pressing issues that hinder their scope in device applications. Herein this study brings fore a strategy to overcome these issues by doping Te in Sb_2Se_3 thin films and hence it is a step forward towards the replacement of environmentally toxic CdTe based devices. It is well-established fact that the solar cell efficiency of Sb_2Se_3 is close to 10% which still lags behind that of CIGSe and CdTe based solar cells. To improve their efficiency for above 10%, Sb_2Se_3 solar cells face challenges of effective p-type doping, reduction of defects and orientation of grains. Herein, Te doping has proved to be efficient doping for Sb_2Se_3 thin films. The composition with lower content of Te doping (0.04%) is highly desirable due to its bandgap of 1.60 eV, dense microstructure without cracks and pinholes, good conductivity, passivated defects and oriented grains.

This study focuses on the 200 MeV Ag ion irradiation effect at various ion fluences on the structural, optical and thermoelectric properties of antimony telluride (Sb_2Te_3) thin films. The Sb_2Te_3 thin films were deposited via vacuum thermal evaporation technique from the bulk alloy synthesized by melt quenching method. Ag ion irradiation led to preferential orientation of crystals along the [104] direction. The ion irradiation led to a reduction in optical bandgap from 1.37 eV for pristine to 1.14 eV for irradiated samples ascribed to the structural modifications. The value of the Seebeck coefficient decreases with the increase in ion fluences (1×10^{10} and 1×10^{12} ions/cm²) owing to variation in carrier concentration determined from the Hall measurements and the value of the Seebeck coefficient of the pristine film (457 $\mu\text{K}/\text{V}$ at 313 K) is higher than the previously reported value. The optimal bandgap and high Seebeck coefficient values can be highly desirable for thermoelectric and photovoltaic applications. The antimony telluride belongs to the family of topological insulating materials that have contributions due to bulk and surface states. Samples with dominant surface states possess higher S values.