

CHEMICAL MODIFICATION OF SOME AMORPHOUS CHALCOGENIDE THIN FILMS

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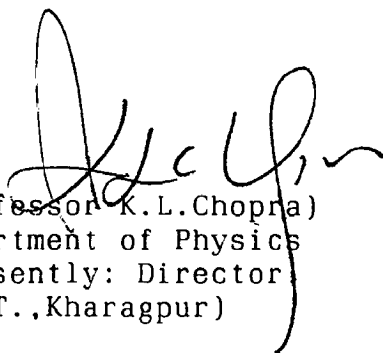


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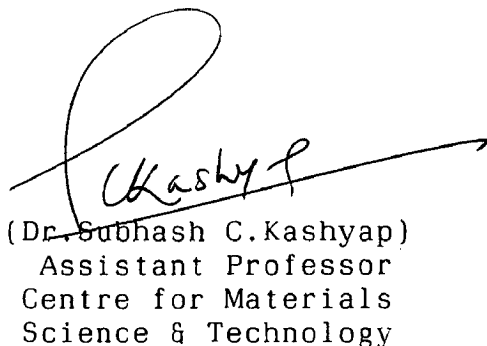
TO MY PARENTS

CERTIFICATE

We are satisfied that the Thesis entitled "Chemical Modification of Some Amorphous Chalcogenide Thin Films" presented by Sunil Kumar is worthy of consideration for the award of the Degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under our guidance and supervision, and that the results contained in it have not been submitted in part or full to any other university or institute for the award of any degree/diploma.



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ABSTRACT

The present work is centred round the chemical modification of amorphous thin films of $\text{Ge}_{20}\text{Se}_{80}$, As_2Se_3 and GeTe by incorporation of bismuth and oxygen. The preparation techniques for obtaining the films include thermal evaporation and activated reactive evaporation (ARE).

Both a- $\text{Ge}_{20}\text{Se}_{80}$ and a- As_2Se_3 are p-type semiconductors, each with a high value of optical absorption coefficient and a sharp absorption edge corresponding to an optical bandgap of about 2 eV. Thermally evaporated thin films of $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ ($x=2,4,10$) and $\text{As}_2\text{Se}_{3-x}\text{Bi}_x$ ($x=0.1, 0.2, 0.5$) have been systematically characterized for their compositional, electrical, optical and structural properties. The role of bismuth in these chalcogenide thin films has also been investigated. Furthermore, the feasibility of junction devices with these new materials has been established by making a Schottky barrier (between Bi metal and bismuth modified a- As_2Se_3) solar cell. Thin films of a-GeTe have been modified with oxygen impurity incorporated by using ARE.

The amorphous nature of the films is established by x-ray and electron diffraction studies. The concentration of different elements present in the films lies very close to that of the corresponding bulk alloys. Further, the Auger depth profile analysis revealed a uniform concentration of the modifier throughout the film thickness.

Incorporation of bismuth into a-Ge₂₀Se₈₀ and a-As₂Se₃ thin films has been observed to increase the electrical conductivity, σ , by several orders of magnitude. The enhancement of σ in case of a-GeTe upon modification by oxygen is small (only one order of magnitude). Bismuth modified films show n-type conduction (as confirmed by both the sign and the temperature dependence of the thermoelectric power) with Bi \geq 4 at.% whereas Bi contents in excess of 8 at.% are necessary to induce n-type conduction in the corresponding bulk glasses. Oxygen modified a-GeTe films, however, remain p-type.

An increased tailing of the band edges and a shift of the absorption edge towards lower energy occur as a result of bismuth addition to a-Ge₂₀Se₈₀ and a-As₂Se₃ films. Oxygen incorporation into a-GeTe, on the other hand, widens the optical gap. The correlation of the electrical and optical data suggests the existence of localized states at the conduction band edge due to the incorporation of impurities. The decrease of E_{σ} (electrical activation energy) being much larger than the decrease of half the optical gap, E_g^{opt} , indicates the unpinning of Fermi level with a shift towards the conduction band edge. This is corroborated by the x-ray photoelectron spectroscopy (XPS) results according to which bismuth atoms in the amorphous chalcogenide network are positively charged owing to an electronic charge transfer from Bi to Se atom. This Bi⁺ defects are responsible for the

reduction of C_3^+ (three-fold coordinated chalcogen atom) defects in the material and hence unpin the Fermi level leading to conductivity conversion and large increase in the electrical conductivity.

Low temperature diffusion of bismuth into a-As₂Se₃ films has been exploited for the first time to fabricate and characterize an all-thin film Schottky barrier solar cell (Bi/As₂Se₃:Bi). The n-type semiconductor (As₂Se₃:Bi) is obtained by thermally diffusing a part of the Schottky barrier metal (Bi) into p-type a-As₂Se₃ thin film. The remaining metal film forms the Schottky barrier with As₂Se₃:Bi layer. Typical open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) of the solar cell are 300 mV and 140 $\mu\text{A}/\text{cm}^2$, respectively. The temperature dependence of the diode ideality factor, n, and the reverse saturation current density, J_0 , suggests the dominance of tunneling via recombination states as the current transport mechanism for the device.

In conclusion, thin films of a-Ge₂₀Se_{80-x}Bi_x and a-As₂Se_{3-x}Bi_x have been made to exhibit n-type conduction with a concentration of bismuth nearly 4 at.% or above. The role of bismuth in the conversion of conductivity has been investigated. Low-temperature diffusion of bismuth into a-As₂Se₃ films has been exploited for fabricating a thin film Schottky barrier solar cell. The feasibility of modifying a-GeTe with a gaseous impurity (oxygen) has also been established.

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