PHOTO-OPTICAL CHANGES IN AMORPHOUS Ge-CHALCOGENIDE FILMS

By

S. Rajagopalan
Department of Physics

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THESIS SUPERVISOR:

Professor K.L. Chopra
Thin Film-Solid State Technology Cell
Department of Physics
Indian Institute of Technology, Delhi
New Delhi 110016, India

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S. Rajagopalan

(S. RAJAGOPALAN)

ABSTRACT

A quantitative study of photoinduced changes in the optical properties, photocontraction effect and photo- and electrochemical doping in Ge-X (X = Se, S, Te) films and the effect of replacing Se by S or Te in Se-Ge have been undertaken. It has been observed that these photoeffects can be enhanced significantly by varying the deposition conditions such as the angle and temperature of deposition. The compositional trends reveal that the glass forming tendency/ability, low density and average coordination and high bond ionicity in Se and S-rich chalcogenides are favourable physical conditions for the occurrence of large photoinduced transformations. Also, the electronic flexibility, set by the energy position and polarizability of the nonbonding lone-pair band, is essential. Further, the electron-phonon coupling seems to play an important role in the photostructural transformation.

There is a red-shift of the absorption edge (photodarkening) as well as a decrease in the slope of the Urbach tail, caused by band gap illumination. These photo-optical changes are enhanced in obliquely deposited films and the photoeffects are peaking at $x \sim 0.25$ in $Se_{1-x}Ge_x$ films. Annealing at T_g reverses the photoinduced changes to some extent and this reversible component is independent of angle of oblique deposition. It is noteworthy that ($\Delta n/n$) and ($\Delta k/k$) are positive and are peaking at the gap energy, suggesting creation/modification of gap states near the band edges by exposure.

Band gap irradiation causes a decrease in thickness in obliquely deposited films (photocontraction). The photocontraction is an irreversible effect; it is less in pre-annealed films and it is zero in well-annealed films. The spectral response and kinetics of exposure of photocontraction effect have been studied to know its origin. The associated changes in the topography and the columnar microstructure, observed by electron microscope reveal that a collapse (buckling) of the columns occure on contraction. Also, there exists a correlation between the value of photocontraction and the 'density deficit' in the films - both increasing with angle of deposition.

The electrochemical adsorption/doping and photodoping phenomena have been investigated in terms of changes in optical transmittance, and AES/XPS analysis. The composition, depth profile of various constituents and chemical shifts were obtained. TEM studies were carried out for structural characterization of the new phases of metal (Ag) in chalcogenides and also to detect the associated structural transformations in the films. It has been seen that, for small amount of adsorbed Ag, β-Ag_2Se is formed. As the Ag-content increases, precipitation of Ag clusters occurs and complexes/alloys like Ag-Ge-Se-O are formed. Electrochemical adsorption of Ag occurs by displacing Ge and it continues upto the substrate in 80^0-Se-Ge films.

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