Photocrystallization Effects in Chalcogenide Thin Films – A Review

Renu Tripathi

Dept. of Physics, Chhatrapati Shivaji Institute of Technology, Durg
Email: renutripathi@csitdurg.in

Abstract- Photo induced effects in Chalcogenide thin films are used in optical imaging .It is seen that the structure of chalcogenide thin film can be easily changed by light irradiation.Photocrystallization is one of the typical & drastic phenomena;which shows that in some cases light exposure enhances crystallization while in some cases it suppresses crystallization.

I. INTRODUCTION

Chalcogenide thin films exhibit a wide variety of photo induced phenomena that enable them to be used as optical imaging or storage media. They find application in high density information recording ,holography ,diffractive optics etc [1-5].Photo induced changes in chalcogenide thin films is the subject of systematic investigations with a view of better understanding the mechanism of the phenomena taking place in the films as well as its practical applications. Photo induced crystallization in chalcogenide glasses has been studied [6-9] by various researchers and it is shown that in some cases light exposure enhances thermal crystallization, while in some cases it suppresses crystallization. These mechanisms explained the photo effect in terms of intermolecular and intramolecular bond breaking and lattice distortion. Irreversible changes have also been explained in terms of bond breaking models. These changes are due to the transformations of the structural defect and they reflect on many related properties. The knowledge of the photo interaction in such films is a crucial point in understanding the basic mechanism and its technological applications.

The high conductivity in these glasses and the absence of ionic conduction in them led scientist to study the electrical & physiochemical properties. Further the advantage of preparing these glasses in thin film form makes them adaptable to integration with solid state technologies.

II. EXPERIMENTAL DETAILS

Chalcogenide glasses are prepared by quenching technique from the melt. This requires the prevention of nucleation and growth processes which are responsible for crystallization. This is achieved by rapid cooling of the melt. Thin film of these alloys were prepared by vacuum evaporation technique keeping the substrate at room temperature at a base pressure of 10^{-5} torr.Predeposited thick indium electrodes on well degassed glass substrate were used for electrical contact. The amorphous film where kept in the deposition chamber for 24 hours for the attainment of thermodynamic equilibrium as stressed by ablcowitz [10] in chalcogenide glasses.

Photocrystallization is studied in binary thin film of a $Se_{100-x}T_{ex}$ where (X=5, 10, 15, 20) by shining white light from a 200 W tungsten lamp at room temperature for different exposure times (30 min to 17 hours) in a vacuum of 10^{-3} Torr.It was found that photocrystallization is suppressed on addition of Te at 1000 concentration (X=5) however photocrystallization becomes more effective and predominant as compared to pure Se at higher concentration of Te.

TYPES OF PHOTOSTRUCURAL CHANGES

Chalcogenide glassy semiconductors exhibit a number of interesting changes when exposed to light having photon energy comparable to the band gap. Such changes can be structural, mechanical, and optical or chemical. These effects are of interest because of the information they yield on defects and metastable structural states in amorphous solids.

At least seven distinct photos induced structural or physio-chemical changes have been observed in amorphous chalcogenide, when sample in a suitable form are exposed to light or other irradiation, photo dissolution and light induced changes in local atomic configuration. These photo induced phenomena may be classified as reversible or irreversible in the sense that the system may partly revert to its initial state after some annealing treatment or recover completely on annealing at glass transition temperature (Tg)

A) Photo Vaporization – It is the photo oxidation reaction followed by thermal evaporation of the volatile oxidation product e.g. a As_2S_3 thin films.

B) Photo – Induced Morphological changes –

1) Photo volumetric changes – It has its origin in the changes in the macroscopic structure of chalcogenide thin films. That is in this morphology.

2) Photo contraction - In which volume of the substance changes and density becomes large due to light effect this property of chalcogenide is used in lithography

C)Photo-Polymerization – It has been found that thin films deposited by evaporation always contain some of the molecular species of which the vapour is composed e.g. a As_2S_3 molecular species one embedded in an amorphous As-Se network and illumination causes them to polymerize and combine with the network.

D) Photo Dissolution of Metals –

This is observed in 0.1-1 mm thick amorphous chalcogenide films. Illumination from either the chalcogenide or metallic side with light above or below band gap for the chalcogenide causes the metal to dissolve rapidly into the amorphous film and migrate through it.

E) Photo Crystallization:

When light of proper wavelength is absorbed a sharp increase in the free carrier concentration associated with the broken covalent bond occurs. This broken band weakens the metastability of the amorphous state and crystallization is enhanced at an accelerated rate, this is photocrystallization.

The photocrystallisation of amorphous is well known and was 1^{st} observed in a Se [11, 12].Photo induced crystallization in thermally evaporated $Ga_{15}Se_{81}Ag_4$ Chalcogenide,thin films has been studied [13].It was found that amount of crystalline phase increases with increasing illumination time & hopping conduction is taking place.

F) Photo induced changes in local Atomic Structure:

Photo induced reversible changes in local atomic structure are subtle effect which are induced by light of photon energy close to that of optical band gap,Eg of the chalcogenide glass. Amorphous As_2S_3 is the best known e.g. of the chalcogenide glass in which these structural effects are suggested to occur [14].The effects are reversible in that annealing restores the initial structure and property and in some cases the initial state can also be recovered by exposure to light where photon energy is less than that used to photo darken the samples.

III. RESULT & DISCUSSION

Photo Crystallization in chalcogenide glasses have been studied [11, 12, 15, 16] by various workers and showed that in some cases light expose enhance thermal crystallization while in some cases it suppresses the crystallization. Photocrystallization in a $Se_{100-x}T_x$ films was studied where X was varied from 0 to 25 while light from a 200 W tungsten lamp was used for light exposure which was done for different exposure times (30 min to 17 min).The measurement of dark conductivity & Photoconductivity were made after each cycle of light exposure. After each cycle of exposure, the sample was allowed to relax for 24h to avoid any residual photo current while measuring the temperature dependence of dark conductivity.

Temperature dependence of D.C. conductivity(s) was studied before and after exposing the films to white light for different exposure times. It was found that conductivity is thermally activated with a single activation energy(DE).No effect was observed after an exposure of 30 min.,However when the films are exposed to higher exposure times conductivity increases drastically .

Photoconductivity was also measured after each exposure to white light and was found that at higher exposure times photoconductivity increases drastically,similar to dark conductivity.The increase in photoconductivitymay be related to the change in band gap, optical absorption co-efficient on crystallization.

IV. CONCLUSION

The photo induced crystallization on evaporated $Se_{100-x}Te_x$ thin films studied. It was found that photo effect was suppressed on addition 5 at % of Te in a Se.However higher concentration of Te, photocrystallization increases as compared to pure a Se and these results are in agreement with the result obtained earlier using electron microscope techniques.

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