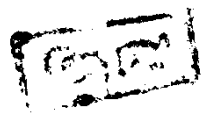
Thermal Transformation and Physical Properties of Amorphous Se-I Semiconductors

THESIS

Submitted in Partial Fulfilment of Master Degree of *Physics*



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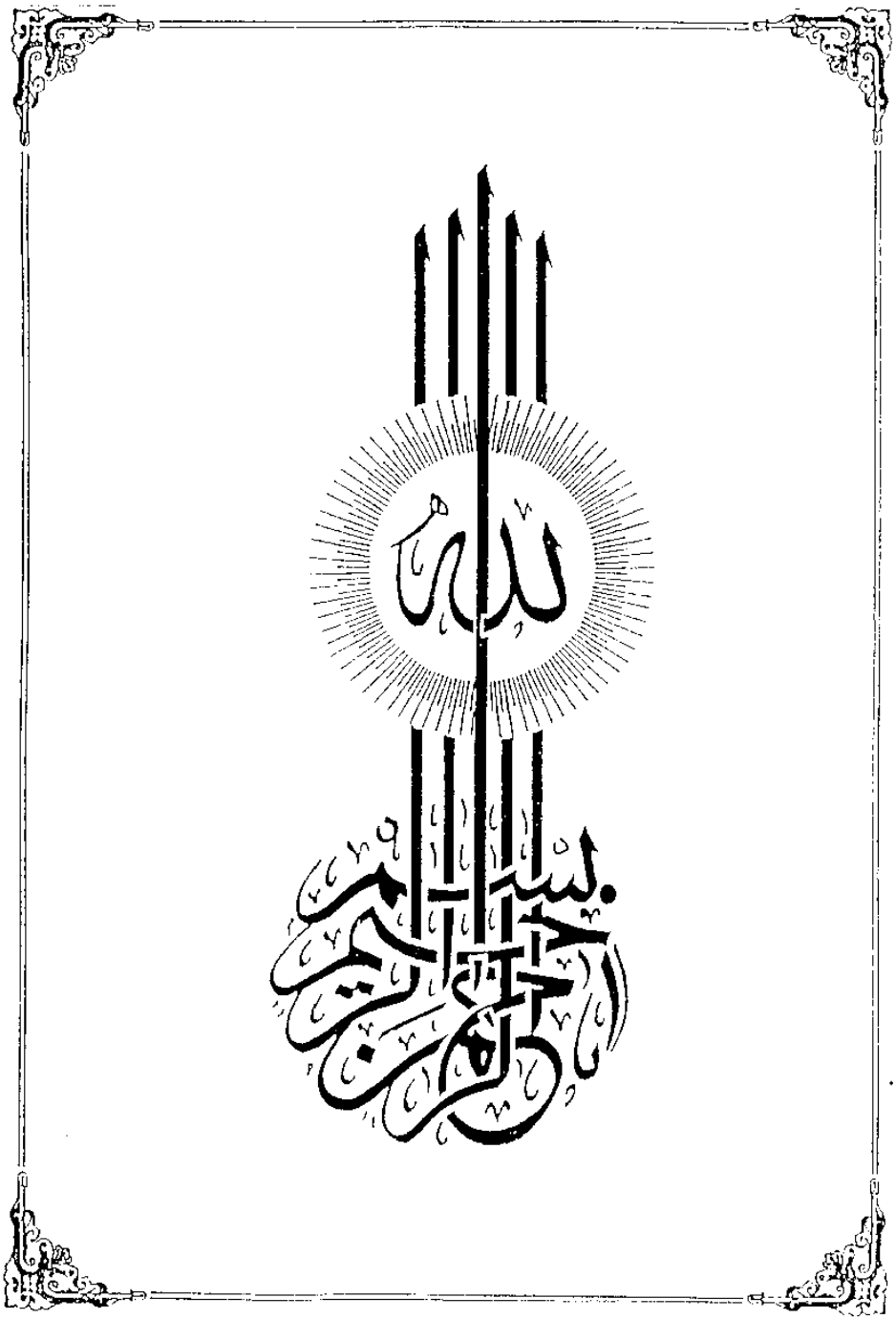

ABSTRACT

Amorphous samples of pure Se (99.999%) and I-Se alloys (with different iodine content) were prepared in sealed pyrex tubes under vacuum (10^{-4}Torr) by direct quenching from the melt. Isothermal phase transformations were carried out at different temperatures ranging between 95-145°C in absence and presence of light illumination from mercury arc. The dc electrical conductivity was measured continuously during isothermal annealing to monitor the possible transformations. Kinetic study was carried out on the basis of Avermi's equation in conjunction with different models for the conductivity of binary mixture. The kinetic results were interpreted in terms of the current theories of Se crystallization.

The main results can be summarized in the following:

1) Addition of small amount of(I)(~1.01 at%) to Se leads to a large enhancement (about 500%) in both nucleation and growth rates at relatively low temperatures (95°C). This enhancement decreases by temperature and completely bleaches above 120°C where thermal effects predominate. Also,Increasing (I)content leads to a decrease in these rate enhancement.
2) For I-Se alloys, light plays no important role in the rate of the process attributed to formation of germ

nuclei (e.g. for nonilluminated ISe_{95} the time for this process at $110^{o}C$ =18 min. and for illuminated case =19 min.); it only decrease the rate of a process related to the growth of individual crystallites and their linkings (e.g. for nonilluminated ISe_{95} time = 8 min. and for illuminated ISe_{95} = 16 min. at $110^{o}C$).

3) The kinetics of these transformations as reflected by the dc electrical conductivity show that crystallization of Se and I-Se alloys can proceeds through two different processes. A primary process is of lower n-values (Avrami-exponent) (1.2 — 1.5) and of higher rate (10^{-6} - 10^{-3}) and of activation energy compares favorably with that for chain folding mechanism ($\sim$ 19.1 Kcal/mol). The secondary process is of higher n-values (2 — 4) and of lower rate(10^{-13} — 10^{-7}) and corresponds to activation energy more than either I-Se or Se-Se bonds,which may suggest that it may involve bond breaking.

4) Regarding the activation energy, light has no effect on energy values during the primary process. Light causes increase in energy values during the secondary process, which may suggests the possibility of optically activated bond breaking and negatively affecting the crystal growth.

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INTRODUCTION

An amorphous solid, from the thermodynamic viewpoints, is in a nonequilibrium state. Its structure and bond configuration are therefore not fixed but can be changed, sometimes reversibly, not only by thermal treatment but also by light irradiation. This fundamental difference based on the thermodynamics between amorphous and crystalline solids makes the subject of amorphous semiconductor more interesting[1].

Numerous chalcogenide glasses based on Se or Te were investigated by our group and various studies on thermal and optical transformations were reported[2]. Kinetic studies for isothermal phase transformation, either in absence or presence of light illumination, have been presented using the electrical conductivity as an experimental parameter to monitor these transformations. Different models for the electrical conductivity of binary mixtures were used to express the conductivity of amorphous-crystalline mixtures.

Iodine, from one hand,has been shown to posses an active effect on the structure of liquid Se and,therefore, on its crystallization tendency[3]. Photo-induced optical and structural changes,from the other hand, have been observed in various kinds of chalcogenide glasses. The

key elements of these are the chalcogen, S and/or Se[4].

The light-induced changes in amorphous chalcogenides are ranging from relatively subtle effects involving minor atomic rearrangement (e.g. photo-darkening) to more substantial atomic and molecular reconfigurations which cause a variety of physical and chemical changes (e.g. photocrystallization)[5]. These effects are of interest because of the information they yield on defects and metastable structural states in amorphous solids, and because they are mostly unique to the amorphous state. Reviews of photo-induced phenomena in amorphous chalcogenides , have pointed out that the mechanism responsible for these changes are not yet fully understood[6].

It is the objective of this the is to present a study on isothermal phase transformation of Se doped with low I content (1-2%) in presence and absence of light illumination. Kinetic study of these transformations will be presented,where the dc electrical conductivity is being used to monitor these transformations.

THE STRUCTURE OF SELENIUM, IODINE AND IODINE SELENIUM ALLOYS

I.1- Structure of Selenium :

I.1.1 *liquid Selenium :*

The solubility of vitreous Selenium (Se) in Carbon disulfide was measured by Briegleb[7]. He conclude that vitreous Se is heterogeneous, since part of the sample went into the solution extremely quickly and the reminder took longer time to dissolve. Briegleb explain his results on the basis that vitreous Se composed of two separate molecular species, Se' and Se''. However, he was suggested that Se' and Se'' are existed in equilibrium. The fact of matter is that, Briegleb reasoned, upon rapid quenching, the liquid Se has a little time to adjust any dynamic equilibrium before the molecules were frozen into position. Hence the relative amount of the species present in vitreous Se is the same as in the heated liquid Se.

Briegleb data, at any temperature was interpreted as representing the percentage of small rings present in liquid Se at that temperature. The similarity between vitreous Se at room temperature and liquid Se at 230 and 430 $^{\circ}C$ was confirmed by X-ray diffraction technique[8].

Buschert[9] has been used the X-ray reflection technique as a structure characterization for liquid Se at

235 and 310 °C. The obtained redial distribution curves, after proper correction, gives two atoms in the first coordination sphere of a typical Se atom, each separated from the central atom by distance of 2.36Å. This implies a chain structure since only one constituent is involved. One of the problem, However, is that in using the X-ray reflection technique and Fourier analysis, we cannot differentiate between an open-ended chain structure and a closed ring structure.

Richter and Herre[10] was used the X-ray scattering and Fourier analysis of the data to yield radial distribution curves. They were studied two temperature ranges (270-300°C) and (400-430°C). In the lower temperature range the atomic distance was 2.32Å and in the higher was 2.33Å. They were found, in both temperature range, two atom in the first coordination sphere and suggested that liquid Se was composed of chains with an extensively ordered parallel arrangement, a quite considerable portion of Se_6 rings, and small crystalline regions having the usual trigonal Se lattice.

Harrison[11] had to investigate the effect of pressure (up to 4 kbars) on the viscosity of liquid Se. He showed that the pressure has a little effect on the ring-chain equilibrium.

Harrison have to calculate what he referred to as "number-average chain length" in liquid Se as a function of temperature; e.g. 800 at 220°C. Actually, he calculated what should be referred to as the "number-average degree of polymerization", which is the chain length of the polymer expressed in unites of Se_8[12]. Therefore,the number-average chain length would be 6.4 $x10^3$atoms at 220°C.

Eisenberg and Tobolsky[13] presented a theoretical analysis based on a model relates the number-average degree of polymerization in Se to enthalpies and entropies involved in the equilibrium reactions between Se_8 rings, Se_8 diradicals and $(Se_8)_n$ chain. They found that it is necessary to accept the experimental data of Briegleb[7]. Their published data felt to be reasonably valid estimations[12].

I.1.2 *The amorphous allotropes of Solid Selenium :*

All the noncrystalline forms of Se are considered under the general classification of amorphous Se. They are red, black amorphous and vitreous Se :

Red and Black amorphous Se;

Red amorphous Se can be prepared either by chemical reduction from aqueous solution of selenium

acid[14];

$$H_2SeO_3 + N_2H_4 \longrightarrow Se_{\downarrow} + 3H_2O + N_2$$

$$H_2SeO_3 + 2SO_3 \longrightarrow Se_{\downarrow} + 2H_2SO_4$$

or by condensation from the vapor phase at high temperature [15].

The Se-Se bond distance, for the chemically precipitated modification, was on the average 2.33Å, and the coordination number of a typical Se atom was about 2.4[8].

The Se molecule has a chain-like structure as suggests by a coordination number 2, but the redial distribution diagram cannot distinguish between an open-ended chain and a closed ring structures. Richter et al[8] suggested that chemically precipitated red amorphous Se was composed of long spiral chains.

As red amorphous Se is readily soluble in Carbon disulfide, it might be composed of ring molecules[7]. During chemical precipitation Se forms chains, and with subsequent digestion many of these chains evolve into rings. This suggestion implies that the chemically

precipitated powder is a mixture of chains and predominantly rings[14].

When red Se is slowly heated, an endothermic heat effect occurs within the sample, and the power turns black[14]. The resulting powder is the selenium modification that is commonly referred to as black amorphous Se and both the color change and the endothermic heat effect are reversible.

The onset of the transition was reported to occur at 37°C[16], and the heat of transition was suggested to be 0.09 K cal/g.atom[17]. Other work[18] has indicated a heat of transition of 0.107±0.009 K cal/g.atom with a transition temperature of 53.0±0.5°C.

From X-ray diffraction experiments, it was shown that black Se powder is amorphous[16,18]. Also it has been suggested that the endothermic transition observed might be due to a cleavage of ring molecules[16]. A suggestion was made[14] that black Se not be considered as a separate allotropic modification, but rather as a transition type between red amorphous Se and trigonal Se. However, the red to black amorphous Se transition appears to be well-defined and characterized thermodynamically. So it seems logical to consider black amorphous Se as a separate modification[12].

Vitreous Selenium;

Vitreous or glassy Se is prepared by the quenching of molten Se. It is generally accepted that some of the physical properties (density, elastic constant, etc.) of the quenching material are dependent of the temperature of the molten Se prior to quenching[19], and its thermal pretreatment[20].

Krebs and Schultze-gebhardt[21] suggested that vitreous Se is composed solely of rings of both high and low molecular weight. They reported a coordination number of 2.1 for a typical selenium atom in the vitreous material. This value of 2.1 has been corroborated by a number of investigators and a theoretical value of 2.07 was calculated[22]. A Raman spectrum of vitreous Se has indicated the presence of both ring and chains[23].

In El-Mously work[20], using the electrical conductivity and activation energy of conduction of heat-treated Se (60-700°C for 1-100 h), he could explained his data in terms of the presence of different allotropic forms.

For Se heat-treated at high temperature two different amorphous states were recognized ($\sigma = 10^{-14}$