STUDY OF CRYSTALLIZATION OF SOME AMORPHOUS SEMICONDUCTORS

THESIS

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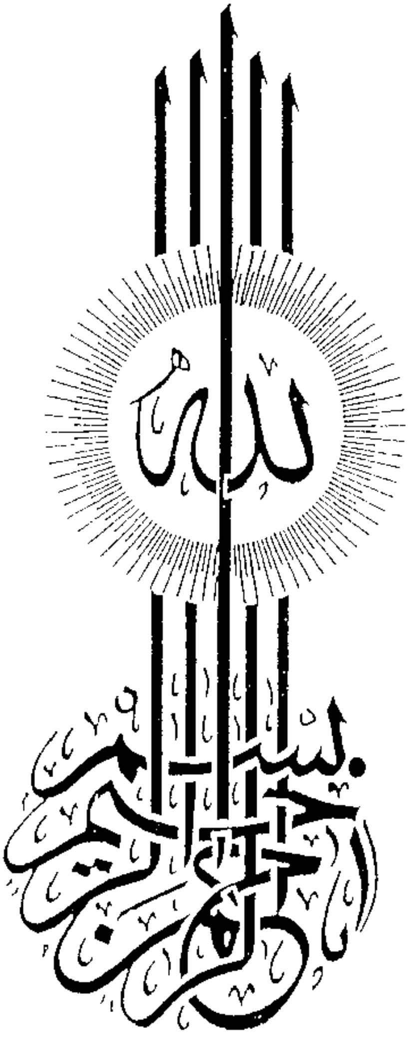
بسم الله الرحمن الرحيم

Ms. Fatma Mahmoud Mohamed Ayad attented and completed successfully, the following graduate courses offered by the Physics Department, as partial fulfilment of the requirements for the M.Sc. degree, during the academic year 1974/1975 :

(1) Special Courses :

- i- Transport theory.
- ii- Imperifictions of Solids.

(2) General Courses :

- i- Numerical Analysis.
- ii- Electronics.
- iii- Computer Science.

(3) Arbitrary Courses :

- i- Laser Applications.
- ii- Physics of Metals.
- iii- Physics of Polymers.

(4) German Language.

CONTENTS

ABSTRACT

This thesis is concerned with studying the effect of photo-illumination on surface crystallization of amorphous Se doped with 4.26 % S in the temperature range of 98–144°C. The change in the electrical conductivity during the isothermal transformation was used to investigate the crystallization kinetics in light of recent concepts of crystallization in organic polymers applying Avrami theory. Two distinct approaches had been applied to interpret the results namely; Odelevsky and Landauer approaches. Odelevsky approach considers σ as characteristic property of the double phase system while Landauer approaches consider log σ as characteristic property.

The main results can be summarized as follows :

1- Kinetic calculations on basis of log σ indicates that crystallization under purely thermal effects proceeds as one process with single Avrami exponent n decreasing monotonically from 1.24 to 1.08 with increasing temperature (98–132°C). The crystallization rate constant K increases by 31 % in the same range. This process corresponds to 29.29 K.Cal/mole for the activation energy of crystallization.

2- On basis of σ the values of n show that at temperatures above 120°C transformation proceeds through two stages of primary and secondary crystallization processes. The former has $n_1 > 2$ while the second has $n_2 \simeq 1$, similar to that for the single process of log σ representation, suggesting that the growth is ristricted to one direction only. The rate constant K_2 is higher than K_1 indicating a faster secondary process. The activation energy of the first process ($< 120°C$) is 27.5 K.Cal/mole equal to that for the second stage (120-132°C).

3- Illumination makes the first process as reflected from log σ representation more decleared. The values of n_1 (for σ and log σ representation) are greater than their correspondings for the nonilluminated sample revealing an intensive of nuclei through photo-nucleation.

INTRODUCTION

Solids which do not meet the criterian of a long-range periodically repeated pattern of atoms are known as non-crystalline or amorphous solids . A distinctive class of such solids is glasses which can be obtained by quenching from the melt. To electrical conduction they may be classified as metallic, semiconducting, or insulating glasses. That is, upon melting, semiconductors either retain their semiconducting properties (Se, Te, Zn Te, Pb Te) or become metallic (Ge, Si, Al Sb, Ga Sb, In As, In Sb) where the metallic character is similar to that of liquid mercury(1). Melting is accompanied by abrupt changes in the mass density, electrical and thermal conductivities, thermoelectric power, and magnitic susceptibility. The changes in mass density are a few persent and negative (as in Se, Te, and the tellurides) or positive (as in Ge, Si, and the II-V compounds). In the first group of materials, melting is accompanied by the formation of molecular or chain-like structures, while in the second group a destruction of the covalent bonds in a structure with the closer packing prevails.

Semiconducting glasses in whose composition enter S, Se or Te are known as chalcogenides. It was the Leningrad school under Kolomiets(2) that begins the work of studying the electrical properties of chalcogenide glasses. A property established by this school is that their electrical conductivity is less sensitive to impurities than that for the crystalline form. That is, the familiar shallow donors and acceptors of crystalline semiconductors do not seem to exist. Also, it has been suggested, theoretically, that impurities should not affect the electronic conductivity of non-crystalline semiconductors(3,4). However, there are some exceptions of that rule; e.g. elements of group I(5) and oxygen(6) may change the conductivity by as much as six orders of magnitude. The response of conductivity to impurities may be one major difference between crystalline and non-crystalline semiconductors of similar compositions, and has the result that the conductivity increases by many orders of magnitude upon crystallization. It may be the reason why chalcogenides switches show a memory effect(7,8). Some attempts have been made to explain these switching properties of chalcogenide glasses on the basis of thermally induced structural transformations in glasses(9).

Transformation from non-crystalline to crystalline states is accompanied by remarkable changes in various phisco-chemical properties(10). The determination of the changes of a certain property may be useful for qualitative investigation of such phase transformations. Of these are, density measurements(11,12), optical measurements(13-15), electrical(16) and thermal(17) conductivities, X-ray diffraction(18-20), magnetic susceptibility measurements(21,22), electron microscope spectroscopy(23-25) as well as ESR spectroscopy(26).

The unique potential for changes in the optical and electrical properties resulting from phase transformation is of great scientific and technological interest. Numerous studies on optical properties are found in the literatures. For example; changes in the optical absorption(13), refractive index(14), and absorption edge(15) have been reported.

The electrical properties, in particular dc conductivity, may also be used to follow the amorphous-crystalline phase transformation. This may be mainly due to the big variation in the conductivity during the crystallization process, e.g. 10^6 times for pure Se(16), beside the ease with which this technique can be followed. It has been shown that the dc conductivity represents an experimental parameter to account for phase transformation, particularly for Se and Se-like structure materials(27-30).

The use of conductivity-structure characterization for a proper description of the volume fraction which has crystallized depends on the specific regimes of phase transformation. This, in turn, may validated by considering a power or logarithmic conductivity dependence(27).

Chalcogenide glasses are known to posses high ability to crystallize. Such crystallization can be, however, induced either through purely thermal or through a combination of elevated temperature and light effects. The disorder - order transformation, achieved by isothermal annealing, takes place through processes of nucleation and crystal growth(31); small crystallites form and grow Transformation kinetics can be adequately described as for many polymers by Avrami equation which relating the extent of crystallinity to exposure time during isothermal annealing.

Recently there has been much interest in the growth of spherulites in bulk polymers(32). These objects are the principal site of the crystallization in a number of highly crystallizable linear polymers. Attention is directed mainly to polymers that may be represented as systems of flexible linear chains which can in time achieve a high degree of crystallinity.

Spherulites in bulk polymers grow outward from a nucleation center that is frequently of a heterogeneous character. The radial growth of a spherulite is commonly the result of the formation of stacks of bladelike lamellas that grow outward from the nucleation center.

Lauritzen and Hoffman(33,34) have developed in great detail a theory for the growth of polymeric (chain) materials. Their theory accounts for the experimental observations that polymeric materials grow with a lameller morphology, having a lamellar thickness that decreases with decreasing temperature. The lamellar thickness (of the order of 100 A°) is much smaller than the molecular length, with the molecules being chain folded within the lamellas.

Recently, Crystal(35) has applied the Hoffman Lauritzen(34) theory of polymer crystallization to study the crystallization of amorphous Se using dynamic density measurements .

Selenyi(36) observed that light enhances the crystallization of amorphous Se at lower temperature. Changes with illumination in the morphology and growth rate of Se crystals grown from the vapour phase have been observed and ascribed to thermal effects(37). An increase in the growth velocity of individual Se crystallites under irradiation by a neon light at 130°C has also been reported(38). In the work of Dresner and Stringfellow(39), they demonstrated that the increase of the crystal growth rate by light results from the production of hole-electron pairs in the vitreous Se and that the growth is controlled by the flux of holes towards the crystal boundary. Moreover, Ovshinsky and Klose(40) have shown that the number of nuclei can be greatly increased by light (photonucleation), especially in films sensitized by the incorporation of certain crystals. The nuclei can then be developed through subsequent grain growth either thermally or in combination with light.

The material which has been crystallized under light irradiation can be returned to its initial amorphous state through heating and quenching cycle(10). This thermal erasure process can also be accomplished through the use of a laser beam(41). This effect is used to wirte holograms(42,43).

Recently Kim and Turnbull(44) have studied the thermal- and photo-induced crystallization of amorphous Se. They observe a fast thermal crystallization rate in pure Se and conclude that impurities play an important role when photo-enhanced effects are observed.

The aim of this thesis is to study the effect of incident photons on the amorphous-crystalline transformations of Se doped with 4.26 % S using electrical conductivity technique. The continuous recording for the changes of electrical conductivity will be used to find a quantitative data on percent crystallization conducted at different isotherms between T_g and T_m in absence and persence of photo-illumination. This is achieved by considering either of the two electrical conductivity-content dependence; power and logarithmic. The obtained results will be analyzed and correlated with the present concepts of Avrami equation for the transformation kinetics of organic polymers.