A STUDY OF MICROSTRUCTURE AND PHOTO-THERMAL TRANSPORT OF AMORPHOUS SELENIUM

THESIS

Submitted for Partial Fulfillment
of M. Sc. Degree in Physics

By

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1987

TO

SOUL OF MY WIFE

PROF. DR. M.F. KOTKATA

MY FRIENDS STONE GROUP

بسم الله الرحمن الرحيم

ACKNOWLEDGEMENTS

The author would like to thank Professor Dr. A.H. Mousa, Head of Physics Department, Faculty of Science, Ain Shams University, for his encouragement and providing the necessary facilities.

The author wishes to express his sincere thanks and gratitude to Professor Dr. M.F. Kotkata, for suggesting the point of research, close supervision and valuable guidance throughout the course of this work.

Special thanks are also to Professor Dr. M.H. El-Fouly (N.C.R.R.T.) and Professor Dr. A.A. El-Shazly (Faculty of Education) for their generous offer in allowing the author to use the coating unite and the spectrophotometer in their research laboratories.

Great thanks are due to Professor Dr. N. Barakat and Dr. F.M. Motowe.

Finally, my thanks are due to my colleagues in the Semiconductor Research Laboratory of the Physics Department, Faculty of Science, Ain Shams Univereity, for kind cooperation in various ways.

CONTENTS

SUMMARY

The study of optical properties is a good and accurate method to identify the structural properties of the materials. In this respect, amorphous selenium films having different thicknesses, in the range of 320-515 nm, were prepared by the rapid thermal evaporation technique. X-ray diffraction and differential thermal analysis were used to identity the amorphous structural nature of the prepared films. The spectral distribution curves of the transmittance (T) and the reflectance (R) have been recorded for the prepared selenium films using both spectrophotometer (Model Varian Cary) and specially constructed temperature-controlled optical system. The latter gave very promised data for the distribution curves, mainly in the spectrum of the absorption range (400-720 nm).

The spectrophotometric method of Hadley's is applied to calculate the refractive (n) and absorption (k) indices from the experimental data of T and R using the computer facilities in our research laboratories of semiconductors.

Calculations of the optical energy gap E_g^{opt}, from the incident photon energy dependence of the absorption coefficient, display a small decrease of E_g^{opt} with the increase of selenium film thickness. The rate of decrease is mounted to be 5×10^{-4} ev/nm. The observed values of E_g^{opt} (1.73-1.82 ev) for amorphous selenium films (320-515 nm) corroborate the

the results obtained by other investigators.

The continuous variation of the optical parameters (T, R, n and k) during the amorphous to crystalline transitions of selenium films, which has not yet been reported, has been studied in the present work. This study has been done at different isotherms in the temperature range of 70-120^{o}C during the incident of isoenergetic photons of 1.8 ev on selenium films of thickness 450 nm. The amorphous-crystalline transition passes via three different time-dependent stages. The last stage is characterized by a limiting constant value depending on annealing temperature and indicating the completion of the transition process. The reflection micrographs taken for the last stage declar different morphology of crystallization at the different temperatures of annealing. The morphology of the films corresponds to different absorption coefficients lie in the range of $5x10^{5}$ cm^{-1}.

Also, the isothermal time-dependence of the fractional volume has been calculated from the functions T,R,n,k=f(t). These data have been used to calculate the kinetic parameters (m and k) of the transition process and hence the activation energy of crystallization. The latter is mounted to be 1.3 ev in the temperature range of 70-120^{o}C. Moreover, the optical energy gap of the crystallized selenium films shared a decrease of about 56%.

INTRODUCTION

INTRODUCTION

The information on physical properties of new class of semiconductors is paralleled by the creation of ideas concerning their possible practical use. Some of these ideas have already been realized in various devices, used successfully in the present day technological applications. These include solar cells, electrophotography, switching, electronic and optical memories, image sensors scanners, thin film transistors, vidicons, large-area displays and/or table computers.

Localized gap states play a fundamental role in determining the electronic and optical properties of amorphous semiconductors, and in particular chalcogenide glasses. Most of the early theories of amorphous chalcogenides did not take into account the presence of lone pair (Lp) orbitals on the chalcogen atoms. In Se for example, two electrons are needed to complete the valency requirements, thus making Se-two-fold coordinated in covalently bonded glasses. The consequence of this in a simple model, has been represented by Kastner(1). He suggests that an As-Se alloy, for example, will have three bands associated with the bonding (σ), non-bonding (Lp) and antibonding (σ^*) orbitals. He places the Lp states between σ and σ^* bands which imply that the optical gap for such lone pair semiconductor involves transitions from the Lp to the σ^* states.

A crucial problem is the nature and origin of the discrete localized states. As suggested earlier, they are presumably associated with specific defect states such as missing As or Se atoms (e.g. As_2Se_3) leaving "dangling" (i.e. unsatisfied) bonds, Fig. (1). The situation must be more complex, however, because dangling bonds with single unpaired electron would be expected to show spin paramagnetism and electron-spin-resonance (E.S.R.), an enhanced optical absorption near the absorption edge and a conductivity varying as $\log\sigma\alpha(1/T)^{1/4}$ at low temperatures. None of these features is observed in chalcogenide glasses even though the experimental densities of the discrete levels are often high ($\gtrsim 10^{18}$ cm^{-3})(2). Thus, although one can envisage the origin of the localized defect states general terms, it is much more difficult to provide theoretical basis.

Interest of switching phenomena is observed in the elemental selenium, either crystal or amorphous form(3,4). Also, reports of switching in liquid selenium(5-8) have considerably extend the range of the phenomena, and the work reported by Armitage and Champness(9) on solid amorphous selenium extends the temperature range still further.

Although amorphous selenium can be obtained by quenching the liquid, various electrical measurements have been made on evaporated films. This is because of the commercial applications of selenium in thin-film form to rectifiers, photocells, the vidicon and xerography.

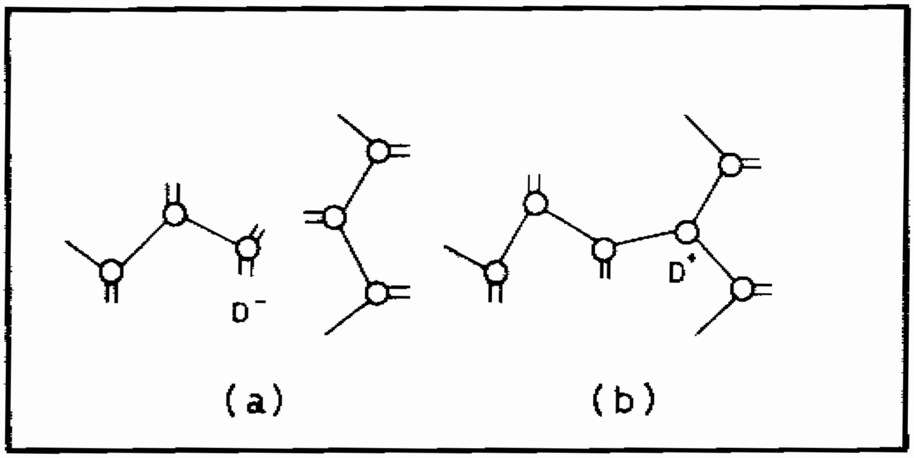

Fig.(1) Bonding configurations of D^+ and D^- defects in two-fold coordinated chalcogenide glasses, showing lone-pair and bonding p-electrons. For further details of the theory, see Refs.(1,2,62).

The discharge of selenium (or selenium alloy) film in the electrostatic copying process known as xerography (Fig. 2) involves the creation of electron-hole pairs by optical absorption in a thin layer at the surface, and their subsequent separation under the action of an electric field. The photoconductive selenium layer is typically charged up about + 1000 V by passing under a corona discharge. Ions generated by the corona discharge migrate towards the photoreceptor surface where they are discharged, the charge being trapped at the surface. A charge of the opposite polarity is induced on the surface of the conductive substrate on which the selenium layer is deposited, establishing an electric field across the selenium layer. In the imagining step, the photoconductor is exposed to light and the photogenerated electrical carriers discharge the photoreceptor in the bright region of the image. If the photoconducting selenium film crystallizes, it losses its insulating properties and its ability to hold electrical charge and becomes useless for xerographic purposes(10).

Selenyi(11) observed that light enhances the crystallization of amorphous selenium at lower temperature. Changes with illumination in the morphology and growth rate of selenium crystals grown from the vapour phase have been observed and ascribed to thermal effects(12). An increase in the growth velocity of individual Se crystallites under irradiation by a neon light at 130°C has also been reported(13).

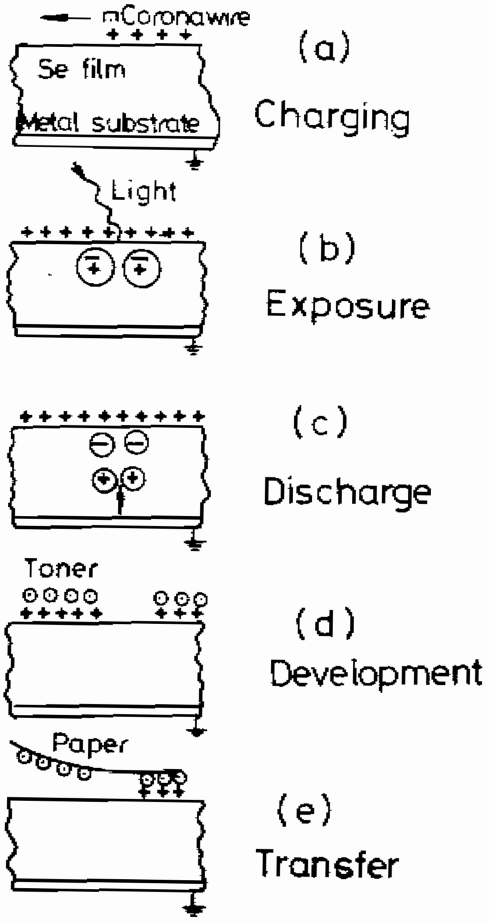

Fig.(2) The xerographic process. (a) the photoconducting film is charged positively by a corona discharge induced from a wire, held at high potential, which is moved parallel to the top surface, (b) the document to be copied is imaged on to the film. Electron-hole pairs are created in the film by strongly absorbed photons reflected from light areas on the document, (c) under the action of the electric field, the holes drift towards the metal substrate; the electrons move in the opposite direction to neutralize the positive surface charge, (d) negatively charged "toner" particles (carbon black dispersed in low melting plastic) are cascaded on to the surface, adhering to those areas of the film that have not been discharged, (e) the toner is transferred to paper with the aid of a second corona discharge. The paper is removed and the image made permanently by heating.

C.C

In the work of Dresner and Stringfellow(14), 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(15) 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(16). This thermal erasure process can also be accomplished through the use of laser beam(17). This effect is used to write holograms(18,19).

Amorphous selenium thin films can be prepared by rapid condensation of selenium vapour in vacuum(14,20-23). In amorphous films, it is known that there is no long-range periodicity of the atomic arrangements, and the local environment surrounding the atoms is ordinarily different from that in the case of crystalline material. The bond lengths, the bond angles and the local configuration are normally all optimised in a crystalline solid whereas in an amorphous solid the bond angles are ordinarily different from the optimum values(24,25). Since the bond angles depend on the preparation conditions of the film, the structure of the