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Amorphous Semiconductors Characteristics and Their Modern Application

A Thesis Submitted for the award of the degree of philosophy (Ph.D.)

$\mathbf{B}\mathbf{y}$

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Cairo 2013



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Acknowledgment

I would like to express my gratitude to Prof. Dr. Abdelhalim Zekry, professor of Electronics and Communications Engineering Department, Faculty of Engineering Ain Shams University for guidance, assistance and encouragement during the period the work undertaken in this thesis.

I would like to express my sincere appreciation to Associate Prof. Hatem.Hassan. Amer, Solid State Department, National Center for Radiation, Atomic Energy Authority for suggesting the point of research carried out in this thesis, supervision, interesting discussion, continuous and comprehensive follow up during all phases of carrying out this work.

I would like to express my gratitude to Prof. Dr. Sayed Mohamed Sayed Elarabi, Engineering and Scientific Instrument Department, Nuclear Research Center, Atomic Energy Authority for guidance, assistance and encouragement during the period the work undertaken in this thesis.

I would like to thank Dr.Karima Ezz El-Din Mohamed Ghareeb, Metallurgy Dep., Nuclear Research Center, Atomic Energy Authority for her Kind help concerning obtaining necessary reference papers of this work and analysis the resultes.

I am also greatly indebted to Prof. Dr. L.F. Foad Fikri, Atomic Energy Authority for her advice and encouragement.

I would like to express my gratitude to faculty staff at Ain Shams for its financial, technical and time support.

I would like to thank all staff and members of solid state and Electrons Accelerator department, NCRRT, AEA, for help and support.

Thanks are also due to personal and staff of Engineering and Scientific department, NRC, AEA, for the facilities offered during realizing this thesis.

My family unlimited and continued encouragement was actually the true and real support which pushed me up to finish my work and complete this thesis, so I could not say better than" God Bless Them".

Abstract

Chalcogenide glasses are a recognized group of inorganic glassy materials which always contain one or more of the chalcogenide elements S, Se or Te but not O, in conjuction with more electro positive elements as As, Sb, etc.

Chalcogenide glasses are generally less robust, more weakly bonded materials than oxide glasses. Glasses were prepared from Sb, Se, Bi and In elements with purity 99.999%. These glasses are reactive at high temperature with oxygen. Therefore, synthesis was accomplished in evacuated clean silica tubes. The tubes were washed by distilled water, and then dried in a furnace whose temperature was about 100°C.

The weighted materials were introduced into the cleaned silica tubes and then evacuated to about 10⁻⁴ torr and sealed. The sealed tubes were placed inside the furnace and the temperature of the furnace was raised gradually up to 900°C within 1 hour and kept constant for 10 hours. Moreover, shaking of the constituent materials inside the tube in the furnace was necessary for realizing the homogeneity of the composition. After synthesis, the tube was quenched into ice water. The glassy ingots could be obtained by drastic quenching. Then materials were removed from the tubes and kept in dry atmosphere. The proper ingot was confirmed to be completely amorphous using

x-ray diffraction and differential thermal analysis. Thin films of the selected compositions were prepared by thermal evaporation technique under vacuum 10⁻⁴ torr with constant thickness 100 nm. The effect of radiation, optical and some other effects on composition were studied.

The structural properties of $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ amorphous semiconductor in the powder and thermally evaporated thin films have been investigated. Differential Thermal Analysis, DTA, for $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ in the powder form showed that an endothermic peak in the DTA curve results from an increase in specific heat at the glass transition temperature T_g . The absence of any sharp exothermic peak in the DTA curve is good indicator for absence of the structural changes. The analysis of X-Rays Diffraction Patterns (XRD) of $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ in the powder form confirmed amorphous state. Scanning electron microscope SEM micrographs were made for Se-Bi-Sb films deposited at room temperature. The film consisted of individual grains, which are irregular in size and shape and separated by well-defined inter-grain boundaries. By adding In, further separation of the surrounding media gives rise to large grains in size at x=10 at%. Then large grains can be seen for partially crystalline at x=20 at% the grain sizes become smaller for x=30 at% and the number of grains become larger.

The density of the as prepared glasses of the system $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ films has been determined by the hydrostatic method with an accuracy of \pm 0.05 %. It has been noticed that the density increases by increasing In from 5.691 gm/cm³ for the composition $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ at x=0% to 5.786 gm/cm³ for composition $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ at x=30%.

The optical properties of $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ have been characterized by the measurements of the transmittance and reflectance in the wave length 200-1100 nm for the deposited films. The type of the electronic transition responsible for optical properties is indirect allowed transition with transport and onset energy gap in the range $1.89x10^{-3}-1.79\ x10^{-3}\ eV$. The values of the optical energy gap E_{opt} were found to decrease with increasing In content which could be due to the fact that In has a metallic behaviour.

The absorption spectra of $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ is recorded in the UV region. Some important parameters such as coordination number N_{co} , the number of constraints (N_S) , the parameter (r) determined the deviation of Stoichiometry. If there is a linear dependence between the bond strength and the average band gap, and if one allows their superposition to describe the compounds, then the addition of In will affect the average band gap. By increasing the In content, the average bond strength of the compound decreases, and hence E_g will decrease. In order to emphasize the relationship between E_g and the average bond strength more clearly, E_g is compared with H_S/N_{co} which is the average single-bond energy in the alloy.

The electrical properties of $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ alloys include the measurements of DC conductivity for $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ films and the measurements of switching. The DC conductivity of $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ thin films has been measured as function of temperature. The dependence of the electrical DC conductivity on the temperature showed the existence of two distinct linear regions with two activation energies ΔE_1 and ΔE_2 .

The switching measurements have been made for Sb₂₀Bi₂₀Se_(60-x)In_x thin films and the addition of In has led to an increase in both the threshold voltage (V_s) and threshold current (I_s) from 1.6 volt and 1.2 µA respectively at x=0 up to 5.8 volt and 2.5 μA respectively at x=30 for constant film thickness d=100 nm. As for the holding voltage (V_h), it was found to increase with the increase of In content from 0.3 volt at x=0 to 4.8 volt at x=30. On the contrary, the increase of In content has caused a decrease in the holding current (I_h) from 48 μ A at x=0 to 18 μ A at x=30 for a constant thickness 100 nm. It was proved that the threshold power increased by increasing In This means that the quality of switching is reduced by increasing the In content. The addition of In content decreases the cohesive energy and consequently affects the switching properties. Raising the film temperature improved the switching characteristics where the threshold voltage decreased and the threshold current increases. Also, the addition of In reduced the filament temperature, thus reducing the switching ability. Increasing the In content from x=0 to 10, 20 and 30 led to an increase in the switching rise time from $t_r = 25$ to 40, 100 and 200 nano second respectively and a decrease in the cohesive energy from C.E. = 3.884 to 3.607, 3.329 and 3.053 eV respectively. These results indicate that composition Sb₂₀Bi₂₀Se_(60-x)In_x shows good electrical threshold switching results and promises a useful threshold switching device in computer applications and memory.

Finally, the study of effect of gamma rays on the $Sb_{20}Bi_{20}Se_{(60-x)}In_x$ showed that the gamma radiation did not have a noticeable effect, for a dose of 15MRad showed a constant value in the transmittance upon the addition of In.

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