

**MEASUREMENT OF SOME TRANSPORT
PROPERTIES OF $\text{Ag} - \text{As}_2\text{S}_3$
SEMICONDUCTOR GLASSES**

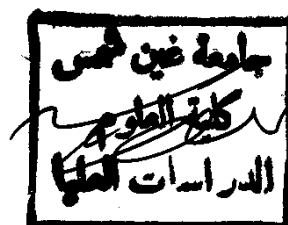
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Submitted in Partial Fulfillment of
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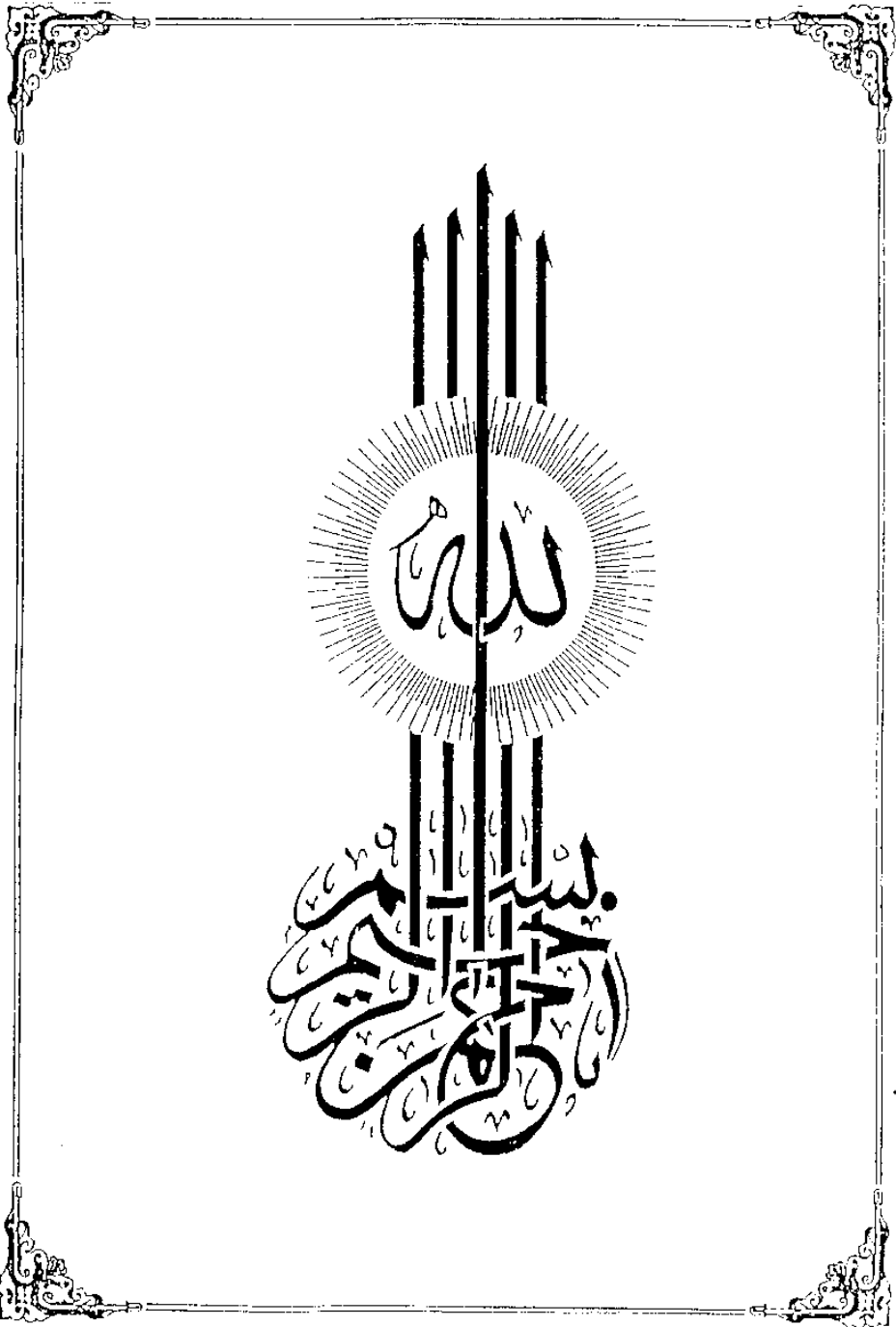
To
Physics Department
Faculty of Science
Ain Shams University

By
CAIRO SOLIMAN MOHAMED
(B. Sc., Physics)

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ABSTRACT

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The addition effect of the metallic element silver on the structural properties and crystallization kinetics of arsenic sulphided chalcogenide glass has been investigated using dc conductivity, X-ray diffraction, micro-structure and differential thermal analysis (DTA). For this task three compositions of the general formula $\text{Ag}_x(\text{As}_2\text{S}_3)_{100-x}$, with $x = 6, 15$ and 25 , have been prepared under vacuum from highly pure, arsenic, sulfur and silver (99.999% purity), by the ice-water quenching technique. The product ingots were designated as amorphous and homogeneous by X-ray diffraction (CuK_α source) and DTA measurements.

The main results and conclusions can be summarized as follows:

1. STRUCTURAL BASED INTERPRETATION FOR THE ELECTRICAL CONDUCTIVITY:

Below the glass transition temperature (T_g) the dc conductivity of the glasses increases with increasing absolute temperature (T) in accordance with the thermal activation formula: $\sigma = \sigma_0 \exp (-E_\sigma / 2 KT)$. The addition of silver (6-25 at.%) to As_2S_3 leads to a big decrease in E_σ (1.29 to 0.38 eV), relative small increase in

$\sigma_{20^\circ\text{C}}$ (1.4×10^{-12} to $5.6 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$), and very pronounced decrease in the pre-exponent σ_0 . The small variation in the value of σ_0 of As_2S_3 and $\text{Ag}_6(\text{As}_2\text{S}_3)_{94}$, (4 and $0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$), confirms the non-variation of the orpiment structure due to the addition of up to 6 at % Ag. The decrease in E_σ for the 6 at % Ag glass is discussed in terms of Mott's charged dangling bonds. The published X-ray radial distribution function tetrahedral base structure for higher Ag percentage glasses is confirmed by the value of E_σ and the very low value of σ_0 (less than $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$).

2. EFFECT OF ISOTHERMAL ANNEALING ON THE PREPARED GLASSES:

The step-wise technique has been used to follow the possible changes in the electrical conduction of the investigated glasses during the isothermal annealing at $T_g < 200^\circ\text{C} < T_m$. The isothermal time-dependence of the characteristic electrical quantities E_σ , $\sigma_{20^\circ\text{C}}$ and σ_0 has been drawn and correlated with the microstructural changes recorded for samples annealed at the same temperature, 200°C .

The effect of Ag on the interplanar spacings (d_{hkl}) on the relative intensities (I/I_0) of the

diffraction lines of As_2S_3 illustrates that the structure of the three- component system $\text{Ag-As}_2\text{S}_3$ can be represented as a solid solution of element (e.g.S), binary systems (e.g. As S , As_2S_3), and ternary systems (e.g. $\text{Ag As}_2\text{S}_2$, $\text{Ag}_6\text{As}_2\text{S}_6$) depending on the concentration of silver in the composition. When the effect of isothermal heating was studied, it was found that some phases crystallized first depending on Ag-content.

3. KINETICS OF THE NON-ISOTHERMAL INDUCED TRANSFORMATION:

The phenomena accompanying the thermal induced structural changes in the three glasses $\text{Ag-As}_2\text{S}_3$ have been studied by using DTA. Also, the mode of the amorphous-crystalline transformation (n) and the activation energy of crystallization (E) have been determined using a single scan technique through an improved simple DTA model. The values of n and E vary between 2.1-3.6 and 2.4-3.6 eV and are found to be compositional dependent.

INTRODUCTION

INTRODUCTION

The understanding of the electronic structure of amorphous semiconductors recently advanced from the postulate that well-defined defects are present in these materials⁽¹⁾, and the small creation energy of these defects let their concentrations sufficiently large to control the transport behaviour⁽²⁾.

In amorphous solids no ideal structures can be used as starting points for the listing of defects and impurities. Experimental techniques now exist for the determination of short-range order with varying degrees of ambiguity-little for elemental techniques exist for the observation of gross defects like large voids. Yet, when two amorphous samples of the same composition have different densities, it is only rarely that the source of that difference can be determined. It may be due to observable voids, unobservable voids, small variations in bond angles or distances which add up to appreciable density differences⁽³⁾.

The existence of defects in crystalline solids are well known and of great importance, but the constraints of large-range periodicity limit their nature. Nevertheless, defects such as vacancies, interstitials, and substitutional impurities often control the transport behaviour of crystalline semiconductor industry exists only because of the ability to fabricate inhomogeneous

materials with well-defined defect profiles. Halpern⁽⁴⁾ proposed that the most probable deviations from normal stoichiometric bonding were wrong bonds, namely the bonds As-As, S-S or Se-Se in As_2S_3 , and As_2Se_3 .

The chalcogenide alloy glasses appear to be of most particular value for switching devices, photoreceptors, infrared transmitting windows, memories, solid state micro-electronic electrodes, etc...

In chalcogenide glass memory devices, the memory effect, is the result of reversible structure change between high resistance amorphous state and low resistance crystalline state. Rapid reversal and reproducibility of the structure changes are found in alloy for which the tendency to crystalline and the ability to form a glass are properly balanced.

Chalcogenide glasses such as As_2S_3 and As_2Se_3 , have a comparatively narrow band gap. Unlike crystals, they apparently cannot be depend in singly occupied donors or acceptors, though some impurities, namely those with less than four electrons outside a closed shell, shift the Fermi energy considerably as may occur when Cu, Ag, Ga, In, or Tl are added to them⁽⁵⁾. Thermopower and field effect show that bulk of the evidence⁽⁶⁾ favours the hypothesis that the Fermi energy is pinned by some kind of point defect quite near midgap but appreciably near the valence band.

Arsenic sulphide, As_2S_3 , is one of the most extensively studied chalcogenide semiconductors, it forms the most 'stable' glass known and its applications in optical memory systems. This compound may be easily prepared in glassy state, with a definite structure containing only As-S bonds. Under a simplifying assumption⁽⁷⁾, i.e. only three types of structural unit (AsS , $\text{AsS}_{3/2}$ and $\text{AsS}_{5/2}$) occur in the system, the molar concentration of all these units were deduced. It was found that the maximum concentration of the building units $\text{AsS}_{3/2}$ at the stoichiometric composition did not reach 100%, and dropped with deviation from stoichiometry. Pronounced photostructural changes are accounted for by the fact that thin deposited layers of, for example, As_2S_3 contain at least three components, As_2S_3 , S and As_4S_4 , the proportions of which are changed by illumination.

The addition of some metals to As_2S_3 has been found to change physical properties, especially the transport properties of it. Iron, for example is found to quench the luminescence efficiency and also is found to be a pervasive inadvertent impurity in As_2S_3 chalcogenide glasses⁽⁸⁾. Nickel, is another example, when added to As_2S_3 forms glasses which have memory and threshold switching effects⁽⁹⁾. Threshold switches have a high resistance in the off-state ($>10^6 \Omega$) and a linear on-state.

When Cu is added to As_2S_3 ⁽¹⁰⁾, a space orientation of the layers is observed and the electrical conductivity increased with increase of Cu-content. Also, an inorganic evaporated photoresist has been developed on the basis of the light-induced changes in the solubility of As_2S_3 ⁽¹¹⁾. It is already finding application in the production of chromium masks, gratings for shaft and linear encoders, etc...

The inclusion of Ag atoms in As_2S_3 has been investigated structurally⁽¹²⁾. It is found that Ag atoms break up the As-S rings leading to early crystallization. The kinetics of photodissolution of Ag into As_2S_3 is of interest because of imaging applications, and is determined by the rate of change of the electrical resistance of a thin silver layer during illumination⁽¹³⁾. The dc electrical conductivity was found to increase by 10^2 in magnitude by the addition of silver (0.2 at.%) to As_2S_3 ⁽¹⁴⁾, it is also found that the resistivity of crystalline Ag_3AsS_4 ($2.4 \times 10^4 \Omega\text{-cm}$) is much lower than that of $\text{Ag}_2\text{As}_2\text{S}_4$ ($\sim 4 \times 10^7 \Omega\text{-cm}$)⁽¹⁵⁾. Photoelectric cells of AsS containing a large quantity of Ag exhibit a marked photovoltage. The photovoltage increases with increasing Ag-concentration being containing within $\text{As}_{15}\text{S}_{40}\text{Ag}_{45}$ glasses⁽¹⁶⁾. The polarity of photovoltage changes for different intensities of illumination. The polarity of photovoltage changes from positive to negative within several minutes for relatively high intensity of illumination and finally the photovoltage reaches to the

saturation level. The time, from the making a start of illumination to change the photovoltage polarity, decreases with increasing the intensity of illumination and further decreases with decreasing the temperature of cell.

Another application for AgAsS system is in optical memory systems. It has been reported, in general, that glasses in which exothermic transformation occurs by slow heating have the characteristic of memory type and some crystalline phases having low resistivity are formed after its reaction^(17,18). A memory effect of $\text{As}_2\text{S}_3\text{Ag}_x$ ⁽¹⁵⁾; ($x \geq 0.402$) relates closely to the formation of crystalline Ag_3AsS_3 . This memory effect is found at relatively high field. This memory state of low resistance can be changed back to high resistance state of the glasses by the application of large voltage pulse. Amorphous As_2Se_3 with photo-doped Ag also shows a non-volatile memory effect⁽¹⁹⁾, in which a memory time of some nanoseconds is observed. In this switching, the device has no so called "prememory time" in the process between switching and a memory state. Therefore, it is expected that improving the device structure will result in a more rapid memory performance.

The construction and properties of As_2S_3 -Ag film systems show their usefulness as hologram recording media⁽²⁰⁾.