Physical Properties of Te-Se amorphous Semiconductors

THESIS

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ABSTRACT

The electrical conductivity σ, thermal conductivity α and density d have been determined as characteristic parameters of amorphous - crystalline transition process for eight glassy semiconducting samples of general formula $Se_x - Te_{1-x}$ ($1 \geq x \geq 0.714$). The samples were synthesised at 700°C ± 20°C for 6 hours in silica tube under vacuum 10^{-4} m.m.Hg. The samples were quenched at room temperature to obtain them in the glassy state. The measurements of σ and α were carriedout in specially designed construction. The main obtained results can be summarized in the following :-

1- In the amorphous, the electrical conductivity (log $\sigma_{20°C}$) increases from $-13.4\ \Omega^{-1}.cm^{-1}$ to $-9.2\ \Omega^{-1}.cm^{-1}$ by increasing Te concentration from 1.97% to 28.6%. The activation energy (E_g) decreases from 2.2 e.V to a certain minimum (1.2 e.V) at 10 % Te and increases again to reach 1.9 e.V when Te concentration becomes 28.6 %. The thermal conductivity (α) decreases from 2×10^{-2} to 7×10^{-3} cal/cm.sec.°C by increasing Te content to 10 %.

2- In the crystalline state the electrical conductivity (log $\sigma_{20°C}$) decreases from $-5.6\ \Omega^{-1}.cm^{-1}$ to minimum value ($-9\ \Omega^{-1}.cm^{-1}$) at 2.44% Te and increases again to reach $-4.5\ \Omega^{-1}.cm^{-1}$ when Te content becomes 28.6%. The activation energy (E_g) increases from 0.45 e.V to maximum value (1.1 e.V) at 2.44% Te and decreases again to reach 0.3 e.V when Te content reach upto 28.6 %. The thermal conductivity (α) decreases from 4×10^{-2} to 1.4×10^{-2} cal/cm.sec.°C by increasing Te to 10 %.

3- The crystallization process, was followed by following the change of the electrical conductivity, thermal conductivity and density. The kinetic study of the crystallization process was carriedout on the bases of Avrami equation $\theta = \exp(-k\, t^n)$ and the obtained results are.

The constant n has fractional values between 1 and 2 and decreases by increasing the temperature of crystallization. e.g. The value of n decreases from 1.35 to 1.1 by increasing the temperature from 80°C to 110°C for TeSe$_{12.5}$, the mean value of the rate of crystallization $\bar{k}$ increases by increasing the crystallization temperature e.g. $\bar{k}$ increases from 2.47×10^{-6} to 1.72×10^{-3} for TeSe$_{12.5}$ by increasing T from 80°C to 110°C. The values of $\bar{k}$ which obtained from σ, α and d are $\bar{k}_{\sigma}$, $\bar{k}_{\alpha}$ and $\bar{k}_d$ were slightly different for the given sample at the same temperature. e.g. at 80°C $\bar{k}_{\sigma}$, $\bar{k}_{\alpha}$ and $\bar{k}_d$ are 1.66×10^{-6}, 6.17×10^{-6} and 17.2×10^{-6} respectively for TeSe$_{12.5}$. The activation energy of crystallization process (E) was calculated using the results of σ, α and d, for the samples of Se-Te system. For every sample E_{σ}, E_{α} and E_d were slightly different. e.g. for TeSe$_{12.5}$ $E_{\sigma} = 53.7$, $E_{\alpha} = 59.7$ and E_d = 51.74 K.cal/mole.

INTRODUCTION

INTRODUCTION

The study of the physical properties of amorphous materials is of considerable technological importance. The application of such materials widly used in industry as examples : The amorphous materials is used as insulators, probably because the transport of charge through them occurs less readily than in crystalline materials.

The photoconducting thin film of amorphous semiconductors is widly used.e.g. the thin film of amorphous selenium or its alloys is used in the Xerography, which is of commercial importance application. Also, Sb_2S_3 is used as a photo-conducting thin film in television pickup tubes.

The glass is the amorphous material which with longest history of use. In the electronic industry it has largely been employed as a container material, this due to its good electrical isolation and high transparency.

Recently the glasses was used to produce the "delay line" required for colour television with low cost, (delay line is a device for storing the video signal for a line scan interval). The glasses used also, in the channel plate amplifier (the active element in this vacuum device is a disc made up of glass tubes).

In recent years the phenomena of switching and thershold properties(1) is noticed in amorphous semiconductors. The explanation of switching phenomena may be simply pictured by the fact that when amorphous semiconductor is saputtered film ($\sim$ 1 um thick) of a slabe chalcogenide alloy, with room temperature conductivity $10^{-5} > \sigma < 10^{-8}$ $\Omega^{-1}.cm^{-1}$, and then placed between two carbon or metal electrodes of about 5×10^{-6} cm^2 cross-sectional area. When the voltage drop exceeds a thershold voltage switching occurs very rapidly within switching time to the oN state(2,3,4).

The voltage drop of the oN state depends on the type of the electrodes (e.g. 1 Volt for Mo, and 1.5 for carbon electrodes) and independent on thickness. The oN state provided the current exceeds minimum, or holding current (I_h), the device remains conducting with a dynamic resist

However, if the current falls below (I_h), the threshold switch returns to its original high resistance (OFF state).

For the memory switch an amorphous semiconductor is used whose structure can be changed reversibly between two structural states, the amorphous state which has a high resistance, and microcrystalline state has low resistance.

(e.g. the memory materials are compositions like Te_{81} Ge_{51} X_4 where X represents Group I or II elements of the periodic table) i.e. the memory action in these devices is based on the reversible crystallization and revitrefication of the material in the current filement(5).

The glass or vitreous state, is belived to be that of a solid with molecular disorder of liquid frozen in structure, or those amorphous that have been formed by cooling a liquid. Such condensed materials can be classified according to the type of bonding responsible for their coherence, every class contains some members that can be put into the amorphous solid form(6).

The chemical bonding can be covalent, ionic, metallic, Van der Walls, hydrogen bonding or combination of these. most glasses fall into the predominately cavalent category.

Glass or amorphous solids can be, metallic, semiconductors or insulators. Some of semiconducting glasses are oxides containing basically Vandium and phosphorous oxide, but most of them called chalcogenide glasses in whose composition enter sulpher, selenium and tellurium. The bonding of chalcogenide is covalent with a smaller ionic contribution.

However, an important property established by the intense work on the chalcogenide glasses which differentiates them sharply from crystalline material or similar compositions, is that their conductivity depends little on purity or stoichiometry, for them the familiar shallow donors and acceptors of crystalline semiconductors does not seen to exist(7). This property has the result that the conductivity increases by many order of magnitude when they crystallize, which is certainly the reason why chalcogenide glass switches show a memory effect(8,9).

The structure of the glass adjusts itself so that each atom is surrounded by a number of nearst neighbours such that all its outer electrons are taken in bonds. The electrical conductivity (σ) of most of the chalcogenide glasses appears to be primarily intrinsic in its temperature dependence even for alloys of varying valence over wide ranges of compositions. In an intrinsic semiconductor, the current is carried by excited electrons. By intrinsic it is meant that, the position of the Fermi level E_F is controlled by densities of states in the conduction and valence bands. In such a situation, the Fermi level moves, linearly with temperature in such a way as to keep the total concentration of excited electrons equal that of holes. This means that the mobility of electrons with energies near the Fermi energy E_F is zero or negligibly small, or in which the number of states N(E) is zero there(10).

Therefore, in an intrinsic semiconductor having no impurity level in the forbidden energy gap, whose width is E_g, the electrical conductivity which is thermally activated will appear to obey an equation of the form

$$\sigma = \sigma_0 \ \exp. \ (- E_g/2 \ kT)$$

which holds over a wide range of temperature (T) for many chalcogenide glassy system(11). The activation energy (E_g) is mainly related to the binding energy between glass constituting atoms. The addition of heavier elements to the glassy compound often decrease the activation energy (E_g) and lighter elements increase E_g(12). Also, the rapid quenching tends to increase E_g at low temperature(13).

A technique which can be used together with a d.c. conductivity measurement to elicit information about the conduction mechanism is that of measuring the thermoelectric power. The investigation of the thermoelectric power (S) and its dependence on the temperature of the materials of monopolar conductivity gives useful information about the potential energy of the carriers taking part in the transfer, in other words, about the percolation level. In a thermoelectric power experiment, one measures the e.m.f. that is developed across a material when thermal gradient is maintained across the sample. Thus, the thermoelectronic power (s) associated with a charge "q" may simply represented by an equation of the form $S = -(\frac{k}{q})(E_s/kT)$ where E_s is the energy which characterized the thermal generation of the carriers, and K is Boltzmann constant. That is independently of the carriers scattering mechanism and the type of the conductivity (hopping or over-band), the slope of curve S = f (1/T) define the energy of the carriers participating in transfer. Therefore, the slope of the curve $\ln \sigma = f(1/T)$ which represent the activation energy E_g being the sum of the energy associated with the production of an equilibrium number of carriers (E_s) and the activation energy associated with the intrinsic hopping of phonons W_{hop}. The value E_s is essentially indpenant of temperature and, thus the thermoelectric power has found to vary linearly with reciprocal of temperature(14,15).

However, measurements of thermoelectric power for some chalcognide glasses have shown them to be positive indicating hole conduction, while Hall coefficient measurements on the same samples show negative values implying that the conduction is electrons(16,17,18). When such +ve sign for thermoelectric power and -ve sign for Hall effects of these glasses was interpreted interms of the formula appropriate for crystalline semiconductors, it yields an unreasonably high value for carrier concentration or alternatively a low value for the Hall mobility(19).

An important coefficient which considered for elicit the picture of trasport phenomena in amorphous and crystalline semiconducting materials is the coefficient of thermal conductivity (α), which is related to the phenon mean free path by the equation

$$\alpha = \frac{1}{3}\, C\, v\, l$$

where

$C = c\, n$ n is the concentration of molecules

c is the heat capacity

v is the phenon velocity which is nearly the sound velocity.

The determination of thermal conductivity coefficient and the analysis of the obtained results give additional information about the energy spectrum of electronic liquid with small values of σ, as well as the mechanism of heat transfere in the semiconductors.