ELECTRICAL AND CRYSTALLIZATION STUDY OF SELENIUM - TELLURIUM AMORPHOUS SEMICONDUCTORS

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Mohamed Mohamed El-zidia

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Abstract

Selenium has semiconducting properties in both crystalline and amorphous states. The electrical properties of selenium in both states depend to a large extent on the conditions of preparing the samples as well as on the type and concentration of impurity atoms present in it. The presence of impurity atoms having different electronic configurations may lead to the appearance of acceptors and donners levels in selenium. Introducing atoms of the same configurations in selenium, may give different effects resulting from the change in size and electron affinity.

Tellurium lies with selenium in the 6th group of the periodic table. It has the same electronic configurations as selenium. The effect of adding tellurium atoms on the electrical properties and the crystallization rate of selenium has been studied by introducing 2.5 %, a 5 % and 10 % Te atom in semiconducting pure selenium.

These samples were subjected to heat treatment at three temperatures 65°C, 70°C and 80°C. These temperatures

were chosen between the softening point of selenium and its melting point. Annealing the samples at these temperatures was carried out by step-wise method, and after each step the three physical quantities, density (d), the electrical conductivity at 16°C and the activation energy (ΔE) of the conductivity process, were determined and taken as a measure of crystallization rate in the annealed samples.

The effect of tellurium on the electrical properties of selenium in the glassy and crystalline states, and on the crystallization rate of selenium were found to be as follows :

1- By increasing the tellunium content in pure selenium the electrical conductivity increases, while the activation energy decreases in glassy state i.e the process of liberation of electrons in the glassy state becomes easier by increasing the tellurium content.

2- In glassy state, the density of selenium decreases by increasing the tellurium content.

3- All the completely crystallized samples have semiconducting properties. Introducing tellurium in completly

crystallized selenium increases the electrical conductivity and the activation energy.

4- The increase of tellurium content increases the time necessary for complete crystallization of glassy state.

5- At the three considered temperatures 65°C, 70°C and 80°C it was found that:

(a) Crystallization increases the density, and the electrical condictivity, while the activation energy decreases for all samples of all compositions.

(b) Time necessary for complete crystallization decreases by increasing the temperature of crystallization for all samples of all compositions.

6- During the continuous crystallization process for $TeSe_{20}$ samples, four stages were observed:

(a) Normal heating.

(b) Nucleation period.

(c) Crystallization period.

(d) Asymptotic conductivity.

7- Applying Avrami's equation to kinetic of the process of crystallization was studied using the variations in the density "d", log $\tau_{16°C}$ and ΔE. The main results of this study are as follow:

. The process of crystallization is one dimensional process.

.. The rate of crystallization of all samples at three different temperature was calculated.

I N T R O D U C T I O N

CHAPTER I

1.1 Amorphous Semiconductors:

The study of glasses has been important historically because of their great technological value. Generally solid state physics has payed great attension to the studing of crystals. The amorphous materials on the other hand have disordered structure. The solving of the scientific and the technological problemes of the disordered solids is more complicated than that of the crystalline ones. Consequently, after attaining a remarkably level of scientific understanding of crystals, solid state physics can new hope for comparable achievement in connection with disordered materials. The intensive study of amorphous materials is connected with their unique properties which of considerable technological significance. For example:-

- The use of inorganic amorphous semiconductors in electrophotography and document copying.
- Application of selective crystallization of amorphous films induced by a laser beam to write digital information.
- The use of amorphous chalcogenides in memory switching device.

.... Finally the use of devices of the last kind in which the resistance of zero voltage is history sensitive state and can be used in random access computer memories[1].

There are many materials in condensed state which may be described as noncrystalline or amorphous. Most are composed of one or more elements from columns III-VI of the periodic table plus a few materials which include elements from columns II and VII. Other amorphous solids include conventional oxide glasses, oxide glasses containing transition elements[2] and films of metallic or semimetallic elements such as Ga, Sb, Bi[3], Mg-Bi and Mg-Sb[4] and $Te_{70}Cu_{25}Au_5$[5].

Then there are a large number of electronically conducting liquids which exhibit metallic or semiconductor like characteristic or combinations.

Furthermore, there are classes of materials which are usually found in both the amorphous and crystalline states. Other classes are always crystalline but highly disordered, these include ceramics, organic materials, transition metal

oxides, dielectrics, polar crystals, rare-earth chalcogenids, concentrated metallic alloys and heavily doped semiconductors.

1.2. Models and theories of the amorphous semiconductors:

Wilson[6] (1931) on the basis of band theory had explained the properties of perfect crystalline semiconductors. This theory is based on the fact that inside the perfect crystalline lattice there is perfect periodic potential connecting with the periodicity of the atoms in the solid lattice. In 1960 Ioffe and Regel[7] proposed a very severe limitation on the applicability of band theory to disordered materials, that the mean free path L cannot become shorter than the de Brigli wave length of the electron, λc. This leads to a lower limit on the carrier mobility of about 100 cm^2/volt.sec. at room temperature. As a less severe alternative, they suggested that L cannot be less than the nearest neighber distance a in the material. The minimum allowable room-temperature value in this case is about 5 cm^2/volt.sec.

However, these values assume a free-electron mass. For the narrow-band case Friedman[8] estimated that the band model applies if the mobility $u \geq 0.1\ w/KT$, where w is the band width. However, the experimental data on amorphous semiconductors do not suggest a limitation beyond which band structure concepts break down completely.

Single crystal has perfect periodicity. An immediate consequence of this perfect periodicity is the Bloch-Floquet[9] theorem that the one-electron wave functions must be of form

$$\psi = \psi_{kn}(r) = e^{ik.r}\ U_{kn}(r)$$

Where the wave vector K is in the first Brillouin zone, $U_{kn}(r)$ has the periodicity of the crystal structure, and n is the band index. Thus all wave functions in the crystal are extended, the magnitude of ψ possess perfect phase coherence, i.e. long range order in the phase. The corresponding one electron energies $E = E_n(K)$ fall into continuous bands of allowed levels separated by forbidden gaps. The energy $E_n(K)$ is a continuous function of K within each band and periodic except at certain

symmetric points and lines. There are well defined band edges which correspond to the absolute minimum or maximum of E as function of K for each band. The density of states n(E) has square root singularities at there edges as shown in Fig. (1a). Topological consideration show that other critical points, saddle points, must occur within the band, also giving rise to square root singualarities in n(E). All these features, and particularly the extended nature of the states, their perfect phase coherence, and sharp band edges, are consequences of the perfect translational order of the crystal.

M. H. Cohen[10] make a review on the band models of amorphous semiconductors. The simplest possible model is shown in fig. (1b). There are a valence band with a tail of localized state above E_v and a conduction band with a tail of localized states below E_c. Thus only a pseudogab exists between the valence and conduction bands. Such simplest model is probably not adequate for elemental and compound amorphous semiconductors. Though there materials are translationally disordered, the short-range order is in general so well defined that structural defects