STUDY OF THE RADIATION AND THERMAL-INDUCED CHANGES IN SOME GLASSES OF THE SYSTEM $As_4 Se_x Te_{6-x}$

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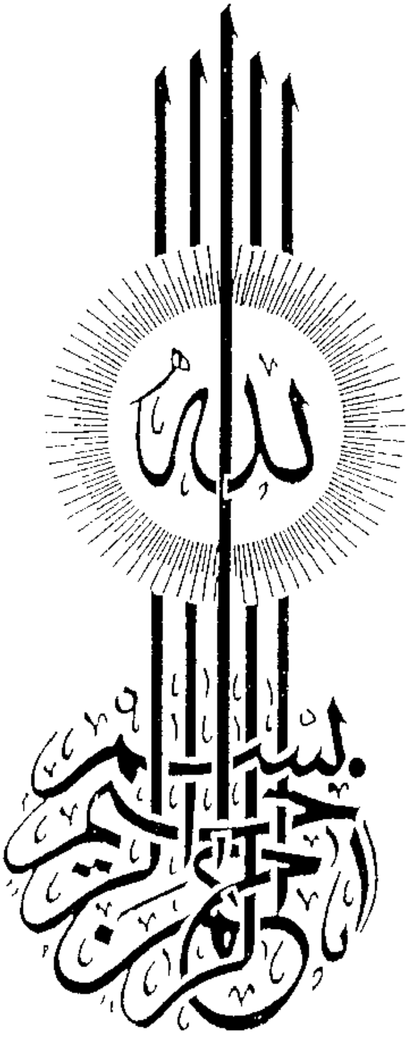
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ABSTRACT

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It is well known in crystalline semiconductors that conventional incorporation of atoms by substitutional doping increases the electrical conductivity by many orders of magnitude. Such doping is the bases of crystalline semiconducting industry and has recently been extended to amorphous silicon and germanium with hydrogen appearing to play an important compensatory role.

The present study describes how a new approach can be used to achieve desired change of the localized gap state and eventually controls the electrical properties of amorphous chalcogenide semiconductors. The change has been achieved by treating the amorphous semiconductors with composed thermal and gamma-irradiation.

Five glasses of the system $As_4Se_xTe_{6-x}$, with x = 1, 2, 3, 4, and 5 had been prepared from highly pure, arsenic, selenium and tellurium (99.999% purity), by melting together the constituents under vacuum (10^{-4} mm.Hg) in precleaned silica tubes at 800°C for about 3 hours and subsequently quenched in salt water. The product ingots were confirmed to be amorphous and homogeneous by X-ray diffractometry ($Cu\text{-}K_\alpha$ source) and DTA.

The effect of neutron and gamma-irradiation on the dc properties of the prepared glasses has been studied under different conditions of dose rates, annealing and/or radiation.

The main results can be summarized as follow :

I. TEMPERATURE-DEPENDENCE OF CONDUCTIVITY

1. The dc conductivity has been measured over a temperature range from ≃350°K down to liquid nitrogen temperature. Adopting the three mechanisms of conduction of Mott, different values for the pre-exponential factors (σ_o, σ_1 and σ_2) and activation energies (E_C-E_F, $E_A-E_F+W_1$, and W_2) have been obtained.

2. For a particular composition, it is found that $\sigma_2 < \sigma_1 < \sigma_o$ and $W_2 < (E_A-E_F+W_1) < (E_C-E_F)$. The increase of Te/Se ratio leads to the decrease of σ_2 and to the increase of both σ_1 and σ_o. Also both energy terms $(E_A-E_F+W_1)$ and W_2 increase with increasing the Te/Se ratio. Regarding conduction at low temperatures, by variable-range hopping near Fermi-energy, it has been found that $N(E_F)$ increases with the increase of the Te-content.

II. RADIATION AND THERMAL-INDUCED DEFECTS

1. No detectable effect on the temperature dependence of dc conductivity, for the samples treated at R.T. under pure neutron or under pure gamma-irradiation, has been found.

2. A detectable effect on the dc conductivity of the glasses under test has been observed when the samples irradiated during the heat annealing at temperatures near their glass transition temperatures, T_g's. This change in the electrical property is not of a purely

thermal nature since identical samples, which were annealed at strictly the same condition but without being exposed to radiation, show no change.

3. The effect of the composed thermal and gamma-irradiation begins to appear at a particular temperature T_{th} below which no appreciable change is observed. At T_{th}, the change is a function of the absorbed dose and annealing time (given at the same time) till a saturation state is approached. The saturation dose is different from one glass to the other. It seems that the saturation dose and the annealing time decrease with the increase of Te/Se ratio. Glass $As_4Se_1Te_5$ ($T_g = 397^oK$) went to saturation near 0.8 Mrad ($T_{th} = 383^oK$), glass $As_4Se_2Te_4$ ($T_g = 401^oK$) went to saturation near 1.5 Mrad ($T_{th} = 389^oK$), glass $As_4Se_3Te_3$ ($T_g = 410^oK$) went to saturation near 1.84 Mrad (at $T_{th} = 413^oK$), and glass $As_4Se_4Te_2$ ($T_g = 419^oK$) went to saturation near 3.5 Mrad ($T_{th} = 428^oK$). There is a relation between T_{th} and T_g, depending on sample composition. The difference $\Delta T = T_{th}-T_g$ is negative for compositions of Te/Se > 1, while for compositions of Te/Se $\leq$ 1 the effect appears only at temperatures slightly higher than T_g. In all cases, T_{th} is far below the crystallization temperature, T_c.

4. The change in the X-ray diffraction patterns and the DTA thermograms for glasses irradiated at $T = T_{th}$

indicate an even relaxed "amorphous" state is produced. This is attributed to the creation of defect centers increasing with the dose rate till an equilibrium state is approached. Radiation-induced structural transitions, however, have been observed upon annealing near or above T_c.

III. THERMAL-INDUCED TRANSITION

The phenomena accompanying the temperature-induced structural changes in the prepared glasses have been studied by DTA.

1. The value of T_g decreases with the increasing of the Te-concentration. The melting temperature T_m shows a minimum when the Te/Se ratio is near one. Unlike T_g and T_m, the features of T_c due to crystallization vary remarkably with the heating rate. It has been found that when the ratio Te/Se is less than one, the limiting factor for crystallization is the viscosity. For Te/Se ratio greater than one, the limiting factor is the nucleation.

2. The compositional dependence of the crystallization activation energy E, shows a minimum at equal proportions of selenium and tellurium, E = 1.08 eV for $As_4Se_3Te_3$. Here, it is interesting to note that the overall behaviour of the crystallization activation energy seems to be similar to that of the melting point for the glasses investigated.

INTRODUCTION

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Recent advances in the understanding of the electronic structure of amorphous semiconductors have followed from the postulate that well-defined defects are present in these materials(1), and, in fact, since some of these defects have a low creation energy, they can be present in concentrations sufficiently large to control the transport behavior(2). Of course, 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 behavior of crystalline semiconductors, and the entire semiconductors, and the entire semiconductor industry exists only because of the ability to fabricate inhomogeneous materials with well-defined defect profiles. Freed from the constraints of periodicity, amorphous solids can exhibit a much wider range of defects. Even in a one-component materials, we can envision strained bonds (with incorrect bond length or bond angle), atoms with a variety of non-optimal coordinations, and positively and negatively charged ions with varying average spatial separations. In multi-component alloys, weaker bonds can form instead of stronger. By their very nature, amorphous solids are ordinarily metastable, a transition to the lower-energy crystalline phase being retarded by a potential barrier which is essentially inaccessible below the glass-transition temperature of the material. Local relaxations can take place, but long-range crystallization does not occur. The disordered state is quenched in by rapid cooling or by direct depositions from a vapor or plasma phase onto a cold substrate. Consequently, the defect structure critically depends on the method of preparation. However, it is now clear that despite the enormous number of defect possibilities, identical preparation conditions do yield reproducible electronic properties, and the basic reason for this is the chemical nature of the atoms which constitute the material(3).

A striking and perhaps unique feature of the elemental amorphous semiconductors Si and Ge lies in the critical dependence of their electronic properties on the method of preparation and on the detailed experimental conditions during specimen deposition. This does not seem, however, to apply to other groups of amorphous solids such as the chalcogenides or the more complicated alloy glasses, where one finds generally good agreement in the electrical and optical data obtained in different techniques.

Spear and Le-Comber(4) had found that the position of the Fermi level in glow-discharge produced amorphous silicon (a-Si:H) could be controlled by doping. This discovering identified more clearly the position of amorphous semiconductor as a structure sensitive material similar to crystalline silicon and gallium arsenide in electronic devices.

The fact that sensitive doping can now be carried out in a systematic way opens up promising device possibilities. Spear and Le-Comber, S. Kinmond and M.H. Brodsky(5) have shown as a first step an amorphous thin film p-n junction (a-Si) prepared by the glow discharge technique. Another recent development has been the scaling up of the device area because the most obvious advantage of the amorphous device would lie in the large area that can be achieved easily and economically(6).

A large progress in the field of amorphous silicon solar cells and their technologies has been achieved(7). Amorphous Si:H can be doped n-type and p-type and its excellent photoconductivity and high absorption coefficient for visible light, as well as the possibility of mass producing thin films of this material on large areas, matches the present strong social need for low cost solar photovoltaic systems.

On the other hand, Ovshinsky's publication(8) on threshold and memory switching of amorphous chalcogenides in 1968 triggered a surge of interest in these materials, which contributed significantly in advancing our knowledge in amorphous solids. Numerous papers were published since then in an attempt to understand the threshold and memory switching as well as other properties of these materials. Moreover, the semiconducting chalcogenide glasses have been used as a membrane material for solid-state microelectronic electrodes. Chalcogenide glasses based on arsenic selenide or selenide/telluride and containing up to 25 mol.% of an appropriate metal, have been successfully used as ion-selective electrodes for Cu(II) and Pb(II) ions(9).

Considering chalcogenides such as As_2Se_3 and As_2Te_3, these have a comparatively narrow band gap, and are semiconductors. Unlike crystals and amorphous silicon they apparently cannot be doped , in that singly occupied donors and acceptors do not appear, though some impurities, namely those with less than 4 electrons outside a closed shell, shift the Fermi energy considerably as may occur when Cu, Ag, Ga, In or Tl are added to say As_2Se_3(10). Thermopower and field effect show that these materials are p-type, and that bulk of the evidence(11) favours the hypothesis that the Fermi energy is pinned by some kind of point defect quite near midgap but appreciably near to the valence band. Mott(11) has considered the defects, in chalcogenide glasses, to be selenium or tellurium dangling bonds, but probably As dangling bonds should be present too.

Chalcogenide glasses are well known to show appreciable photoconductivity when illuminated with light(12-20). Nevertheless, the conductivity change of these glasses irradiated with gamma-rays has not hitherto been investigated in detail. Edmond et al(21) measured the conductivity under the irradiation of gamma-rays and neutrons for