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ELECTRONIC PROPERTIES OF BI-MODIFIED AMORPHOUS THIN FILMS OF Ge20Te80-xBIx

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Abstract
An investigation of the effect of addition of Bi impurities on the electrical, optical and thermoelectric properties of vacuum evaporated amorphous thin films of Ge20Te80-xBix, (x = 0, 0.19, 2.93 and 7.35) has been carried out. The synthesized thin films were characterized by x-ray diffraction and electron probe microanalysis Analysis of the results revealed that Bi modification of the amorphous semiconducting thin films does not induce a clear-cut carrier sign reversal. This is in contrast to the observation of a pin transition in bulk glassy compositions Ge20Te80-xBix, at x 3.5. This dissimilarity may be explained by the fact that the bonding in the bulk glass and the corresponding thin film may be different. This fact is possibly responsible for creation of some additional Bi-induced p-type defects with increase in Bi concentration. The optical energy gap has been found to be approximately equal to twice the thermal activation energy in all the four compositions studied in this work.
Keywords
Amorphous, Evaporated, Impurities, Nitrogen, Semi-conductors, Vacuum

1. INTRODUCTION

Amorphous chalcogenide semiconductors have been intensively investigated because of their technologically important electronic and optical properties. Amorphous germanium chalcogenide semiconductors GexM1-x (M=S, Se and Te) form an important class of amorphous materials because of their unique electronic properties [1,2]. They are generally p-type semiconductors and are insensitive to the addition of impurities in small amounts because they possess a pinned Fermi level. However, they have been found to exhibit a pin transition in their electronic conduction when chemically modified with large concentrations of Bi (11, 7 and 3.5 at.% in Ge-S. Ge-Se and Ge-Te glasses respectively) in bulk form [3-5]. This unique property of Bi impurities is not yet fully understood and is, therefore, a topic of current interest. For their possible applications in electronic and optoelectronic systems it is desirable to study these Bi impurity-modified materials in thin film form. We have, therefore, started a systematic study of the electronic and photoelectric properties of the well characterized amorphous thin films of Ge20Te80-xBix for the first time. In this paper we report the effect of Bi impurities on the DC electrical conductivity, the optical absorption in the fundamental optical absorption edge region and the thermoelectric power of these thin films.

2. EXPERIMENT

Bulk compositions in the system Ge20Te80-xBix were prepared by melting together the appropriate amounts of high-purity (99.999%) elements in evacuated and sealed quartz ampoules at around 800-1000 °C for about 12 h and with continuous agitation in a rotary furnace. After giving proper heat treatment the ampoule was quenched in ice-cold water. The resulting bulk alloy samples thus obtained were used to prepare thin films by flash evaporation in a vacuum of 1x 10^(-6) Torr obtained with a liquid nitrogen trap. Properly cleaned Corning glass slides were used as substrates. The substrate was cooled with liquid nitrogen down to 77 K. The evaporation rate during deposition of the film was kept around 10-20 As Films with thickness ranging from 1750 to 3000 A were prepared.

3. RESULTS

3.1. CHARACTERIZATION

The prepared films were characterized by x-ray diffraction (XRD) and electron probe microanalysis (EPMA). The appearance of broad structure and the absence of any sharp peak in the XRD plots confirms the non-crystalline nature of the films. The composition of the films was determined with EPMA, keeping the accelerating voltage at 25 kV. It was found that the composition of the flash evaporated film is quite near to that of the corresponding starting bulk alloy.

3.2. ELECTRONIC TRANSPORT

The temperature dependence of DC electrical conductivity of various compositions (x = 0 , 0.19, 2.93 and 7.35) in the temperature range 200-500 K (up to crystallization temperatures) has been studied. The conductivity was found to exhibit a single activation energy in the temperature range of measurement and the set of data was fitted with the expression sigma = sigma{0} cxp (- delta * E / k * T) The values of thermal activation energy deltaE pre-exponential factors sigma{0} are summarized. The values of pre-exponential factor sigma are in the range 10 ^ 2 - 10 ^ 3 * Ohm ^ - 1 * c * m ^ - 1 which indicates band conduction. The thermal activation energy, deltaE, decreases with the addition of Bi impurities. A typical plot of log{sigma} - 1 / T up to the crystallization stage of the film with x = 2.93 is presented. The two points indicate that on lowering the temperature of the film after crystallization the conductivity did not follow the original path. The estimated temperature of onset of crystallization is also included. The values of the conductivity at 300 K, shows increase in the conductivity by a factor of about five by the addition of 7.35 at.%

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Bi. The temperature dependence of thermoelectric power (TEP) for the four compositions (x = 0, 0.19, 2.93 and 7.35) was determined. The present results for temperature dependence of TEP in the film with x = 0 (ic. Ge20Te80 were found to be similar to those of Vanderplas and Bube [6]. The composition and temperature dependence of thermo-electric power at different temperatures is exhibited. The slope of the temperature dependence of TEP at higher temperatures has also been determined for various compositions. There seems to be a significant effect of addition of a small quantity (X = 0.19) of Bi on the thermoelectric power. On further increase in Bi impurities the temperature dependence is comparatively much less affected. Though the TEP considerably decreases from its positive value x = 0 and approaches zero at low temperature it does not seem to become negative Perhaps a composition between x = 0.19 and 2.93 might show carrier sign reversal. In fact at lower temperature the signal is very weak as thermoelectric power approaches zero, and it becomes difficult to ascertain its sign. For bulk liquid-quenched Ge20Te80-xBix glasses, carrier sign reversal has been observed at x = 3.5 [5].

Thermoelectric power measurement is useful for determining the transport mechanism in amorphous semiconductors. The temperature dependence of TEP (Seeback coefficient, S) corresponds to the energy difference between the Fermi level and the energy level where charge transport occurs. In an amorphous semi-conductor TEP due to holes excited into the extended states below Ev (position of valence band mobility edge) is given by [7]

S = k/e * ((Ef - Ev)/(kT) + C) = k/e * (Es/(kT) - beta/k + C) ……. (1)

where C is a constant and is taken to be 1 for amorphous semiconductors. Ef is the Fermi level energy and ß is the temperature coefficient of the energy gap of the semiconductor

Ef - Ev = Es - beta*T ……(2)

Fitting the expression for S from equation (1) to the high-temperature experimental TEP data (S - 1 / T) values of Es, the activation energy of thermoelectric power, have been obtained. It is found that Es < Delta*E (the thermal activation energy) in all the compositions. The difference E0 = Delta*E - Es for the Bi-modified compositions turns out to be 0.17 eV to 0.2 eV. For the amorphous GexTe1-x thin films the corresponding difference E0 has been reported to be 0.03 eV to 0.15 eV at high temperature (400 K) [8]. The value of ß is 10 ^ - 4 eV K ^ - 1 which is an expected value for a semiconductor. The observed inequality Es < Delta*E is generally associated with the fact that the carriers in the localized band tail states also make a contribution to TEP and the mobility of the carriers may have a temperature dependence of the thermally activated type [7].

4. DISCUSSION

As proposed by Phillips [15], the germanium chalcogenide glasses can be described as small chemically ordered clusters embedded in a continuous random network. In GexTe100-x systems, depending upon the relative concentration of Ge and Te, the presence of stoichiometric GeTe2, GeTe and chains of Te is known [16]. According to the Phillips constraint theory [16], the composition with $x = 20$ is an ideal glass in which the number of operative constraints equals the number of degrees of freedom. Glasses with $x < 20$ are under-cross-linked and the glasses with $x > 20$ are over-constrained. The constraint theory has recently been applied to explain the presence of the p-n transition in Ge20M80-xBix (M=S, Se and Te) glasses [5, 15]. The glasses in the system Ge20Te80-xBix, may be taken as phase-separated glasses with glassy Bi2Te3, clusters embedded in the background matrix of GeTe2, and Te chains or layers The binary alloy is just at the stiffness threshold. As the Bi concentration is increased in the binary alloy Ge20Te80 the Bi2Te3, clusters, having a tetradymite structure, find themselves in a matrix of increasing mechanical rigidity. These alloys in the bulk form exhibit a p-n transition at $x = 3.5$ [5]. At $x < 3.5$ the mechanical misfit between Bi2Te3 and GeTe2, clusters is relieved by distortion of Te chains or layers. For $x > 3.5$ the rigidity of the combined elastic medium of Te and GeTe2, increases steadily. These features are reflected in the pressure-induced effects observed in this class of glasses [5] The n-type defects responsible for the carrier sign reversal at x=3.5 have been associated with the tetradymite structure of amorphous Bi, Te, clusters [5] $x < 3.5$ the n-type dangling bond defects situated on the surface of Bi2Te3, clusters mostly undergo reconstruction.

In the present investigation of amorphous thin films of Ge20Te80-xBix, a clear-cut has not appeared in the compositions x = 0, 0.19, 2.93 and 7.35.The presence of wrong bonds in vapour-deposited chalcogenide semiconductors has been confirmed in several studies [17, 18] Films of nominally the same composition, but prepared by vacuum deposition onto the substrate held at temperatures below the glass transition temperature, display a very different bond-type distribution [19] It seems that the films prepared from the bulk composition Ge20Te80-xBix do not have similar bonding to that in the corresponding bulk alloy. As a result of this possible difference, the types of characteristic charged defect centres in the bulk and in the thermally evaporated thin film of the alloy may be dissimilar. A more complex electronic structure is induced in the thin film. We assume that amorphous clusters of tetradymite structure are also present in the thin film. The peculiar behaviour of the Ge-Te-Bi system may have some connection with the bonding arrangements in the tetradymite structure of Bi2Te3. The tellurium atoms in Bi2Te3, form two types of bonds, and the two sites are labelled Te(2) and Te(1). The atomic arrangement can be visualized in terms of the layer structure [20] . This consists of stacking of quintuple-layer' leaves, where in cach leaf the layers occur in order T * e ^ (1) - Bi - T * e ^ (2) - Bi - T * e ^ (1) The Te(2) atoms are surrounded almost octahedrally by six bismuth atoms, the bond length of the Te(2) Bi

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bond being 3.22 A. The bismuth atoms are bonded to three Te(2) atoms on one side and to three Te(1) atoms with a bond length 3.12 A on the other side. The Te(1) atoms have three nearest-neighbour bismuth atoms in the same leaf. The presence of two types of Te(1) and Te(2) atoms forming bonds of different bond lengths with Bi is important. The shorter Bi-Te(1) distance suggests that this bond is stronger than the other type and there is an ionic component along the Bi-Te(1) bond. Unlike the bulk glass, in the thin films of Ge-Te-Bi the environment and bonding arrangement seem to lavour reconstruction of the n-type dangling bond defects situated on the surface of tetradymite a-Bi_2Te_3, clusters with octahedral structure This would possibly retard carrier-sign reversal.

The compositional dependence of thermoelectric power shown in figure 3 exhibits first a rapid decrease in the hole contribution to the Seeback coefficient at small Bi concentration. However, as the Bi concentration is increased the presence of p-type Bi-induced defects begins to dominate the electronic transport. This rapid rise in the number of proposed p-type Bi-induced defects is responsible for the sudden change in the trend of compositional dependence of thermoelectric power. This produces a neck-like curve presented in figure 3. In the Bi-modified compositions, TEP increases with temperature. This behaviour can be understood by proposing that Bi-impurity-induced defect states are present in the bandgap of the semiconductor. The increase in TEP with temperature may arise due to the excitation of electrons from extended states in the valence band to the localized states in the gap, thus creating vacancies (holes) in the valence band. This would increase the TEP with increase in temperature in accordance with thermal excitation. A similar type of behaviour of the TEP has been observed for a-Ge [21], a-Si: H [22] and a-As_2,$SeTe_2$, [23,24] It has also been observed that $E_s < \Delta E$ in all these systems [22,24] It has been proposed that the non-zero value of E, may be due to presence of a long-range static potential that modulates the energy of the mobility edge in space [23]. The origin of this potential could be the electrostatic potential of the characteristic charged defect centres present in the chalcogenide glasses [25] The electrostatic potential thus created can account for
$E = \Delta E - E_s$, values in the range of 0.1 to 0.2 eV. The present investigation cannot provide any more informa tion on the origin of Bi-induced effects. In the recent publication by Sedeek and Fadel [26] it has been reported that the amorphous thin film composition $Ge_{20}Te_{75}Bi_5$, does not exhibit n-type conduction.

5. CONCLUSION,

we have investigated the effect of incorporation of Bi impurities on the electrical properties of the well characterized amorphous thin films of $Ge_{20}Te_{80-x}Bi_x$. It has been found that Bi modification of the amorphous semi-conductor does not induce a clear-cut carrier sign reversal like the one observed earlier in the bulk glass [5]. It is proposed that such a behavior is due to the possible difference in the bonding arrangement/environment around the Bi impurities in the thin films and

the bulk glass compositions. The optical energy gap Epie found to be approximately equal to twice the thermal activation energy (2*deltaE) in all the compositions.

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