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Trends in the microhardness of monocomponent and multicomponent chalcogenide glasses

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The results of Vickers microhardness (MH_v) measurements on several series of chalcogenide semiconductor glasses are presented. The glasses were prepared under vacuum by the melt quenching technique. Trends of the hardness are explained in terms of the natural and compositional changes of the glasses as well as their glass formation tendency. The compositional variation of MH_v at room temperature is characterized by being even for the binary system, Se–As; quasi-binary (ternary) systems, As_2Se_3–As_2Te_3 and AsSe–AsTe; and the ternary system, Ge–Se–Si; and by being uneven at certain specific concentrations for the binary isoelectronic system, Se–S ($<$ 5 at% S); quasi-binary system, As_2Se_5–As_2Te_5 (40 mol% As_2Te_5); ternary system As–Se–Tl (20 at% Tl); and quaternary system, As–S–Se–Te (Te : Se = 1). In addition, it is found possible to prepare samples of glassy selenium having certain predicted mechanical properties by controlling the temperature before quenching (T_s).

1. Introduction

There are several types of mechanical tests, described by Hayden *et al.* [1], used to study the hardness of a material. One of the most important methods is that of a Vickers microhardness tester. Such a tester measures the resistance of a material to an indentor. Yamane and Mackenzie [2] discussed the main factors being considered in the indentation process.

In addition to the geometrical long-range order (LRO) of the distribution of atoms in the lattice, the short-range order (SRO), or the mutual co-ordination of the atoms, plays a vital role in the semiconductor properties. It is worth noting that the increased mechanical strength is also related to SRO in both perfect single crystals, free of dislocations, and in geometrically randomized polymer crystalline solids. Indeed, vitreous solids do not possess long-range geometrical order (LRGO), but may possess a long-range structurochemical order (LRSCO). A study of vitreous solids should promote the detection of the quantitative principles relating the physicochemical properties of solids to the nature and magnitude of the short-range chemical bond forces among the particles. Regarding the absence of LRGO in glasses, such structurochemical interactions are not obscured by the influence of defects, so unavoidable in crystalline solids. Myuller [3] expressed the composition of a glass in terms of structural species or units (SU) that include, as much as possible, a fully determined number of bonds. In a covalently constructed structural unit of chalcogenide glass, the maximum number of neighbours of an atom is equal to that of valency bonds that the atom can form [4].

The tendency of chalcogenide systems to form glasses, as well as the physical and chemical properties of the glasses, is determined by the character of the chemical bond between the atoms that constitute the glass. The bond energy permits the isolation from the melt to characterize the tendency of the non-glass forming chalcogenides. The higher the bond energy, the narrower is the region of glass formation in a compound alloy [5]. However, an increased tendency to glass formation is possessed by chalcogenide compounds and alloys with predominantly covalent chemical bonds. That is, the bond existing between the components in chalcogenide glasses is practically covalent and the ionic component is negligible [4].

On the other hand, chalcogenide semiconductor glasses have almost flexible structure because of the presence of lone pair (non-bonding) electrons of chalcogen (S, Se or Te) atoms and the low average co-ordination number. It has been found in those glasses, and not necessarily in deposited films, that the co-ordination number is the same as in the crystal. This is in accordance with the 8-N rule [6], meaning that the number of neighbours of each atom is equal to that of covalent bonds (CB) which can be formed. Hence, it is reasonable to consider this as the state of lower free energy likely to be formed in a glass obtained by cooling from the melt. After all, glasses can be characterized as being composed of normal structural bonds (NSB) as well as deviant electronic configurations (DEC) and the activity of both cannot be separated from their surrounding environment [7].

In this paper, the experimental results of the change in the Vickers microhardness of several series of chalcogenide semiconductor glasses are reported and the trends are discussed in terms of the compositional changes of glasses and glass formation tendency. The work is carried out on monocomponent Se and

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multicomponent Se–S, Se–As, Ge–Se–Si, As–Se–Te, As–Se–Tl and As–S–Se–Te glasses. It should be mentioned that no significant data regarding the mechanical properties of these glasses have been reported.

2. Experimental procedure

Bulk individual glasses within the glass forming region of the investigated systems were prepared under vacuum (10^{-5} torr; 1 torr = 1.33×10^2 Pa) from highly pure components (99.999% purity) by the quenching technique from the melts. The scheme of sample preparation of the considered systems are given in [8] for Se–S, [9] for Se–As, [10] for Ge–Se–Si, [9] for As–Se–Te, [11] for As–Se–Tl and [12] for As–S–Se–Te. The ingots produced were confirmed as homogeneous glasses by taking measurements of hydrostatic density, X-ray diffraction and differential thermal analysis (DTA) and they were confirmed as semiconductors according to their conductivity–temperature relationships.

MH_v was measured at room temperature using a Vickers microhardness tester (Shimadzu type-M) attached to a data processor (Shimadzu Dataletty-150). A square pyramidal diamond indentor was used and the MH_v value (in kg mm^{-2}) was computed from the residual projected diagonal impression from the relation

$$MH_v = KP/d^n \quad (1)$$

where d is the length of the diagonal (mm), P is the contact load (kg) and K is a geometrical factor equal to 1.8544. In the case of load-independent microhardness, the Meyer number is equal to two, i.e. $n = 2$. However, when MH_v decreases or increases with P, n will be less or greater than two, respectively.

Polished specimens with parallel plane surfaces were selected for the study of microhardness. Loads ranging from 25–100 g were used for indentation, keeping the loading cycle at 10 s in all cases. The measurements were carried out at least six times for each case.

The glass transition temperature (T_g) was determined using a differential thermal analyser (Shimadzu model DT-30). A heating rate of 10 °C min^{-1} was employed.

3. Results and discussion

The data recorded on measurements of MH_v for individual glasses at different loads in the range 25–100 g over 10 s intervals showed no load-dependence, i.e. the Meyer number of Equation 1 is $n = 2$ and deviation, with respect to any case, did not exceed 2%. Accordingly, only the average values of MH_v (kg mm^{-2}) are given.

3.1. Selenium

Series of bulk selenium samples were prepared by the melt quenching technique. Temperatures ranging from 250–1000 °C were used for sample synthesis, keeping the synthesis time constant at 2 h, to ensure equilibrium, before subsequent quenching in an ice–water mixture. This procedure leads to the preparation of selenium in the glassy state. It has been stated by Popov [13] that there is a definite molecular structure for each temperature of liquid selenium (T_s) and this structure is preserved when the melt is rapidly cooled to room temperature. Here, the close values of the hydrostatic densities of selenium (4.28 ± 0.1% g cm^{-3}) obtained for samples of different T_s values suggest that no noticeable crystallization took place (crystallization of a glass is accompanied, as a rule, by an increase in density). The density of crystalline selenium is 4.75 g cm^{-3} [14].

Fig. 1 shows the change of MH_v with T_s. The value of MH_v decreases from 36 to 28 kg mm^{-2} (i.e. by about 22%) with an increase in T_s from 250 to 1000 °C. Such a change in MH_v is related to the degree of modification of the complex selenium mode of the glass produced. Glassy selenium (g-Se) prepared by quenching from the liquid state is known to consist of two types of atomic arrangement mixed together, polymeric chains, Se_n, and monomoric rings, Se_8 [13]. The first neighbours of any atom are arranged in the same chain or ring. The number of the second-nearest neighbours depends on the relative position of the molecules, which is also dependent on the shape and size of these molecules. The weight fraction of the ring component relies on the sample temperature before quenching (i.e. T_s), [13, 15, 16]. At the same time, the influence of the period during which the selenium was molten on the molecular structure is insignificant [13].

Misawa and Suzuki [17] studied the structure of liquid and amorphous selenium by pulsed neutron diffraction and concluded that it is best described by a model in which a single molecular species has both helical chain-like (*trans*) and ring-like (*cis*) arrangements. On the other hand, there is a large amount of experimental evidence indicating that many of the interesting properties of g-Se are controlled by defects (i.e. DEC) at which the bonding coordination differs from two. Such intrinsic bonding defects in g-Se are discussed in a paper by Lucovsky [18]. Accordingly,

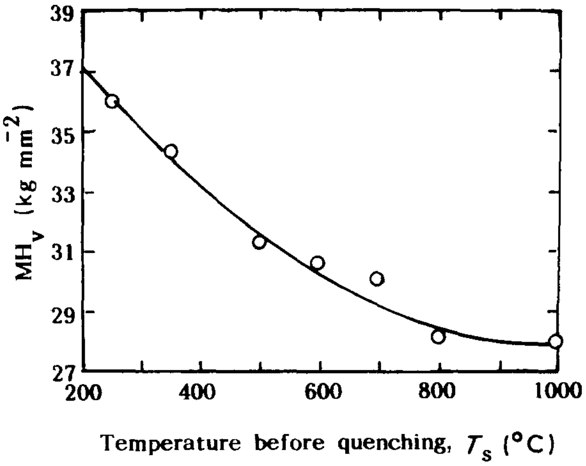

Figure 1 Dependence of room temperature MH_v of g-Se on the temperature before quenching (T_s).

the observed decrease of MH_v with T_s (Fig. 1) may be attributed to the effect of DEC and/or the decrease in the degree of polymerization of selenium molecules. i.r. studies [16] on g-Se indicated that an increase of T_s leads to a decrease in the weight fraction of the ring component and an increase in the relative concentration of polymeric chains.

3.2. Selenium–sulphur

Earlier study on a series of alloys ranging in chemical composition from pure selenium to pure sulphur indicated that binary compositions with a sulphur content from about 50 at % to just under 100 at % have a rubber-like nature [8]. In addition, it was possible to prepare homogeneous Se–S glassy alloys with sulphur contents of up to 60 at % (i.e. S_3Se_2).

Fig. 2 shows the compositional dependence of MH_v for freshly prepared Se–S glasses. The figure indicates nonmonotonic variation in MH_v for the compositions having up to about 5 at % S, after which the value of MH_v decreases monotonically with the addition of sulphur. A similar behaviour is observed for the compositional dependence of T_g (Fig. 3) as well as for some other structural properties [19, 20]. Here, if local valence requirements are to be satisfied in the Se–S alloys, then any structural groupings other than rings (probably Se_3S_5) or chains would appear to be excluded [21]. Although spectroscopic studies yield less information on chain components, theoretical analysis based on equilibrium in the liquid phase suggests that addition of sulphur reduces not only the concentration of atoms in chains but also the length of the chains [21]. So, the observed nonmonotonic variation of both MH_v and T_g with composition can be attributed to the microheterogeneity of the states of sulphur in both chains and rings of selenium. The minimum microheterogeneity in Se–S glasses is expected to lie in the compositions having less than 5 at % S [22]. On the other hand, the observed monotonic decrease of both MH_v and T_g with sulphur content reflects a decrease in the chain length.

3.3. Selenium–arsenic

Binary Se–As glasses can be easily obtained by fusing the components in the entire glass formation region from elemental selenium to alloys containing ~ 60 at % As. Fig. 4 clarifies the addition effect of As on MH_v of g-Se. The value of MH_v increases with As content on going from g-As_2Se_5 to As_2Se_3 and AsSe.

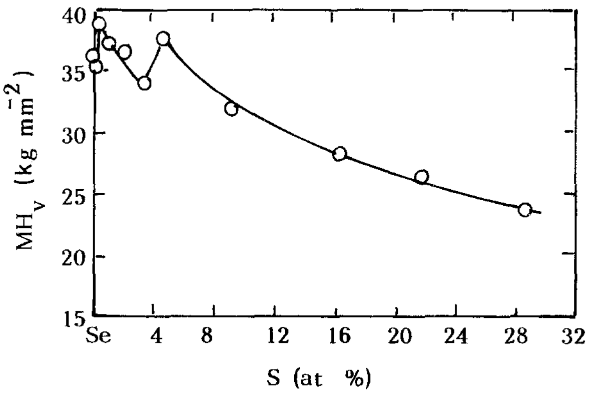

Figure 2 Dependence of MH_v on composition for the glasses in the system, Se–S.

As the hardness number, MH_v, by definition, is the load divided by the area of contact at the time when the penetration ceases, it reflects the stresses acting on the unit area at that moment. As a rule, the structural units (SUs) that constitute the glass network are determined by the nature and composition of the compounds present in the system. A schematic depiction of the SUs corresponding to the five groups of atoms considered, Se, As, $AsSe_{5/2}$, $AsSe_{3/2}$ and AsSe, is given in Fig. 5.

Stoichiometric As_2Se_3 is known from a great deal of experimental data to exhibit a strong tendency towards chemical ordering. That is, heteropolar As–Se bonds are energetically favoured over homopolar As–As and Se–Se bonds. This, however, does not exclude the presence of some homopolar bonds as deviant electronic configurations (DECs). So, g-As_2Se_3 is a prototype compound for a homogeneous chemically ordered continuous random network (CRN) model [23], incorporating mostly heteropolar bonds between two-fold coordinated Se atoms and three-fold coordinated As atoms. The density of g-As_2Se_3, $d = 4.49\ \mathrm{g\,cm^{-3}}$ and the arbitrary molar weight, $M = 193.36$. The fraction $d/M = 2.32 \times 10^{-2}\ \mathrm{mol\,SU\,cm^{-3}}$. Each SU contains

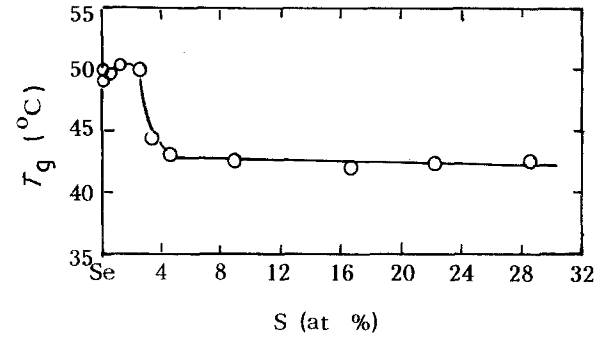

Figure 3 Dependence of glass transition temperature (T_g) on composition for the glasses of the system Se–S.

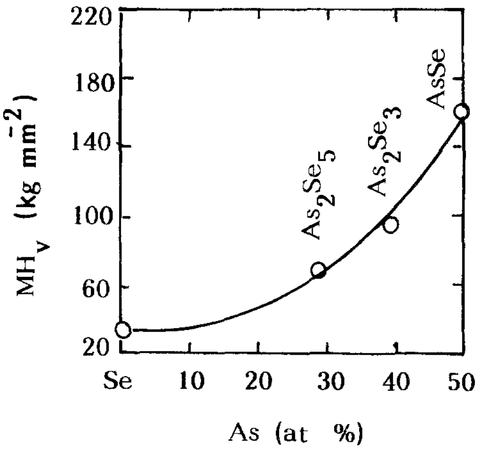

Figure 4 Dependence of MH_v on composition for the glasses of the system Se–As.

three As–Se bonds (Fig. 5d). Accordingly, the concentration of the covalent bonds is $[v] = 3 \times 2.32 \times 10^{-2} = 6.96 \times 10^{-2}$ mol cm^{-3}.

To obtain an estimate of the concentration of CBs in the binary glassy alloys of non-stoichiometric compositions, As_2Se_5 and AsSe, one can follow very closely the treatment of As_2Se_3 [4]. Thus, the concentration of CBs in g-As_2Se_5 (three As–Se bonds and one Se–Se bond, Fig. 5c) is $[v] = 3$ $(AsSe_{3/2}) + 1$ $(SeSe_{2/2})$, i.e. $4.8 \times 10^{-2} + 1.6 \times 10^{-2}$ mol cm^{-3}. Similarly, the concentration of CBs in g-AsSe (four As–Se bonds and one As–As bond, Fig. 5e) is $[v] = 4$ $(AsSe_{3/2}) + 1$ $(AsAs_{3/3})$, i.e. $11.26 \times 10^{-2} + 2.81 \times 10^{-2}$ mol cm^{-3}.

In conclusion, the observed monotonic increase of MH_v with As content (36–160 kg mm^{-2}, Fig. 4) on going from elemental selenium to g-AsSe (50 at % As) is the consequence of the increasing appearance of relatively strong Se–As bonds in the SUs. The respective cleavage energies of the single bonds, Se–Se, Se–As and As–As are 2.12, 2.25 and 2.0 eV [3].

3.4. Germanium–selenium–silicon

The introduction of germanium atoms with four valence electrons into the bundles of selenium chains cross-links them and results in the hardening of the network [24]. Study of the many different properties of glasses of the Se–Ge system indicates two discontinuities at the mechanical (20 at % Ge) and chemical (33 at % Ge) threshold compositions [25]. A study of the radial distribution function (RDF) of the atoms shows that the stoichiometric (chemical threshold) composition, $GeSe_2$, has the same SRO in both the crystalline and amorphous states [26]. In other words, the molecular structure of virgin, melt-quenched

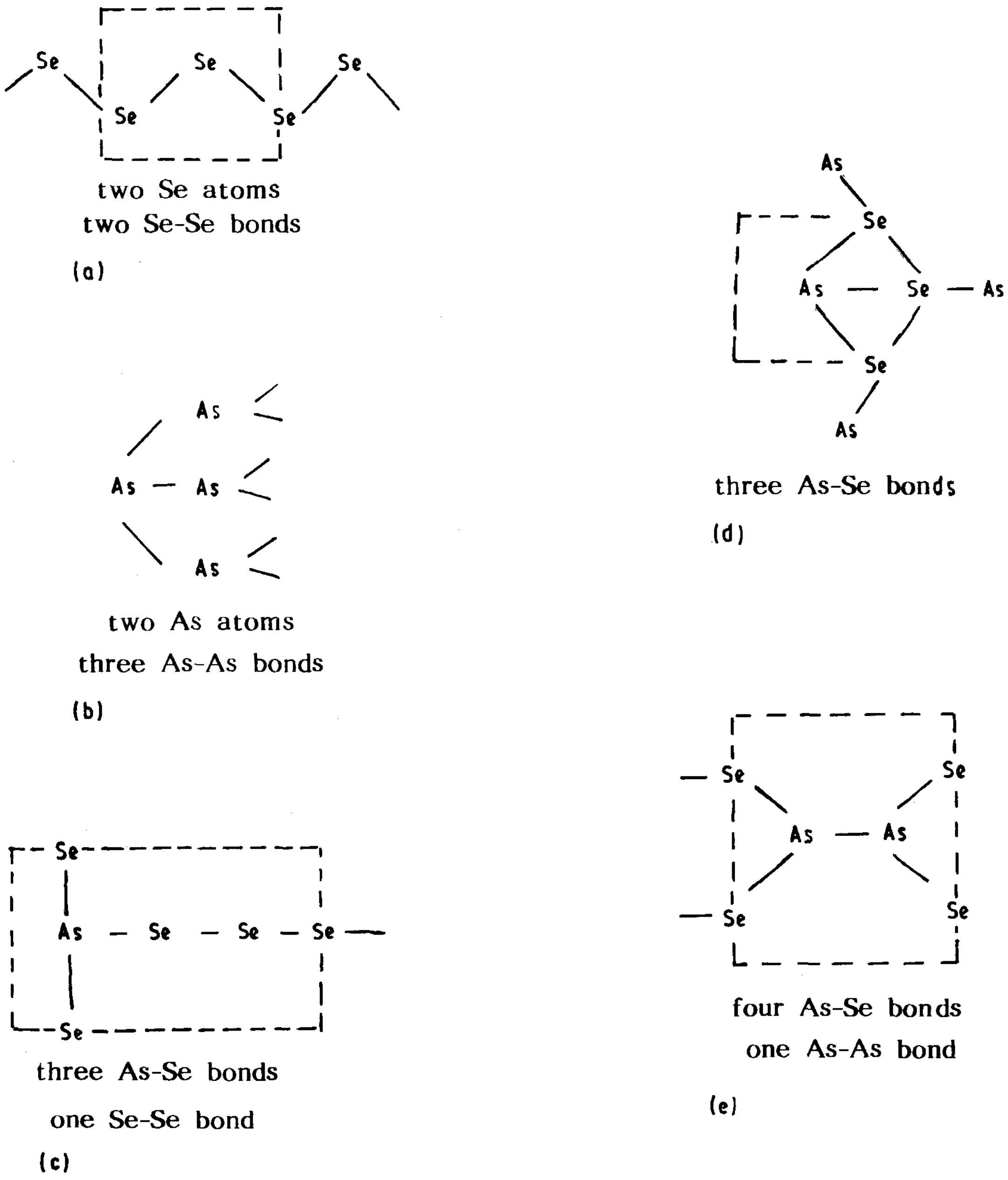

Figure 5 Schematic depiction of the structural units corresponding to five different groups of atoms, including a definite number of paired electron bonds. (a) Se, (b) As, (c) $AsSe_{5/2}$, (d) $AsSe_{3/2}$ and (e) AsSe (after Myuller [3]).

$GeSe_2$ glass is much more ordered than that expected from a CRN model [27]. Fig. 6 shows a schematic depiction of the SU of $GeSe_{4/2}$ [3]. Various results reflect the stability of $Ge(Se_{1/2})_4$ tetrahedral building blocks [27]. The concentration of heteropolar CBs in $GeSe_2$ is 7.39×10^{-2} mol cm^{-3} [24]. However, there is some uncertainty in the results published for $GeSe_2$. For instance, the respective values of MH_v and T_g lie in the ranges 235–260 kg mm^{-2} [24, 28] and 378–427 °C [10, 25, 27–31].

Glassy $GeSe_2$ was prepared under vacuum (10^{-5} torr) by quenching the melt in ice–water mixture [10]. The measured value of MH_v has found to be 254 kg mm^{-2} at room temperature. Starting from germanium diselenide $GeSe_2$, four different compositions having the chemical formula $(Ge_{1-x}Si_x)Se_2$ were prepared with x varying between 0.001 and 0.1 [10]. Here, the effect of substituting germanium with silicon resulted in a monotonic decrease of the hardness by 21%. The value of MH_v decreases from 254 kg mm^{-2} at $x = 0.0$ to 200 kg mm^{-2} at $x = 0.1$. It is worth noting that an investigation of the compositional dependence of the thermal, electrical and optical properties for such a new and interesting system is under consideration and the results will be published soon [10].

3.5. Arsenic–selenium–tellurium

The compositional dependence of MH_v for three different quasi-binary (ternary) glassy systems of As–Se–Te compounds is given in Fig. 7. The MH_v data for these compounds were taken from our earlier work [9, 32] and it can be observed from Fig. 7 that the trend in the composition versus the MH_v relation varies among the three systems as a result of substituting selenium by tellurium. Indeed, this trend is consistent with the difference in nature and concentration of the CBs in compounds of the stoichiometric system, As_2Se_3–As_2Te_3 (Fig. 7a) and those of the non-stoichiometric systems, AsSe–AsTe (Fig. 7b) and As_2Se_5–As_2Te_5 (Fig. 7c).

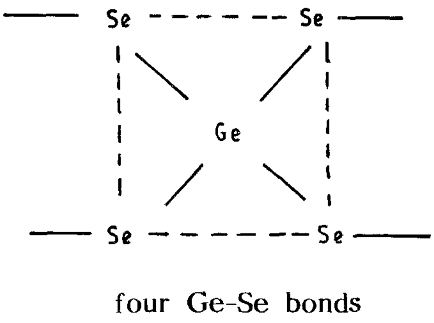

Figure 6 A schematic depiction of the structural units of $GeSe_{4/2}$ (after Myuller [3]).

In Fig. 7a, an abrupt change in the value of MH_v is observed due to a small introduction to tellurium in g-As_2Se_3: as the per cent of concentration of tellurium increases in the stoichiometric system, the mechanical property values slightly increases. Such an increase is attributed to increasing the concentration of As–Te bonds at the expense of the As–Se bonds in the compounds.

As mentioned in Section 3.3, there are two different types of CB, As–Se and As–As, having a ratio of 4:1, in the binary compound AsSe (Fig. 5e). The addition of AsTe to AsSe causes the formation of As–Te bonds at the expense of As–Se ones keeping the concentration of As–As bonds nearly constant (2.81×10^{-2}–2.63×10^{-2} mol cm^{-3}, [33]) in the compositional range investigated. This is accompanied by a monotonic increase in the value of MH_v (Fig. 7b) and this increase is more pronounced than those produced in the other two As–Se–Te systems investigated (Fig. 7a and c). The value of MH_v is 163 kg mm^{-2} for g-AsSe and increases to 350 kg mm^{-2} for g-AsSe·9AsTe.

An interesting trend in the composition versus MH_v relation can be seen in Fig. 7c for the other non-stoichiometric system, As_2Se_5–As_2Te_5. In the parent glass of this system, As_2Se_5, there are two types of CB, As–Se and Se–Se, with a ratio of 3:1 (Fig. 5c). Here, the substitution of tellurium for selenium leads to the consecutive formation of As–Te bonds at the expense of As–Se; and Se–Te and Te–Te bonds at the expense of Se–Se, with their relative concentration depending on the molecular per cent of As_2Te_5. This is likely to be the reason for the observed discontinuity in the value of MH_v at 88 kg mm^{-2} for g-$3As_2Se_5 \cdot 2As_2Te_5$.

Fig. 8 plots MH_v against T_g for the three ternary systems, As–Se–Te, investigated. The values of T_g

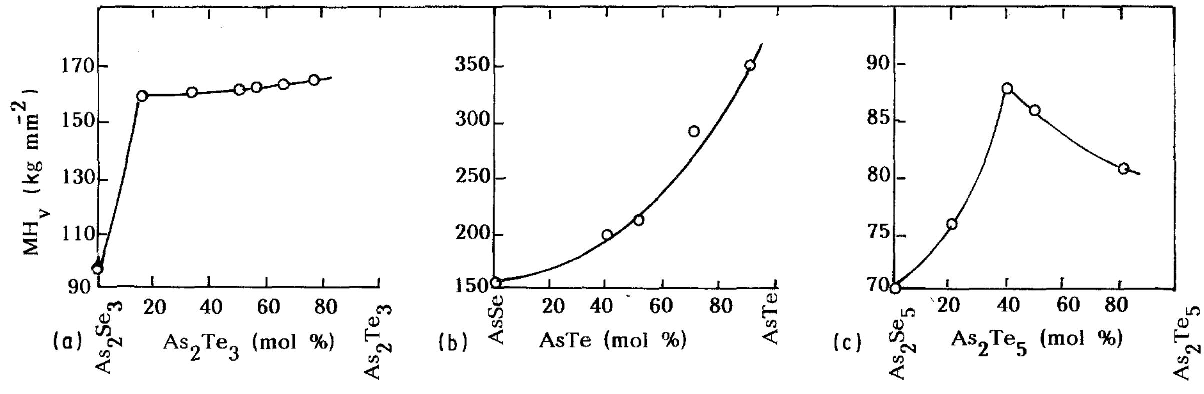

Figure 7 Dependence of MH_v on composition for glasses of the quasi-binary systems: (a) As_2Se_3–As_2Te_3, (b) AsSe–AsTe and (c) As_2Se_5–As_2Te_5.

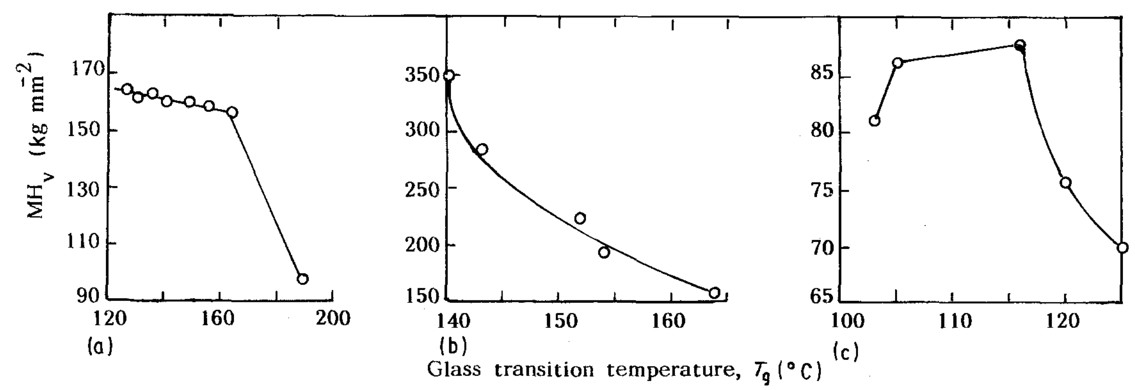

Figure 8 Dependence of MH$_v$ on T_g for the glasses investigated of the quasi-binary systems: (a) As_2Se_3–As_2Te_3, (b) AsSe–AsTe and (c) As_2Se_5–As_2Te_5.

are taken from [34] for As_2Se_3–As_2Te_3, [4] for AsSe–AsTe and [35] for As_2Se_5–As_2Te_5. Here, it is interesting to notice that the trends in the variation of MH$_v$ versus T_g (Fig. 8) are similar to those of MH$_v$ versus composition (Fig. 7), reflecting the direct effect of the nature (strength) and the concentration of the CBs on both MH$_v$ and T_g.

3.6. Arsenic–selenium–thallium

Fig. 9 shows an interesting trend in the compositional dependence of MH$_v$ for the ternary glassy system $Tl_x(As_2Se_3)_{1-x}$. There is a discontinuity in the curve at the composition of $x = 0.2$. Increasing or decreasing the value of x from 0.2 leads to a decrease in the hardness number of the glassy compound. Here, it is worth noting that thallium does not interact with arsenic [4]. Therefore, when arsenic chalcogenides are combined with thallium, SUs of the type shown in Fig. 10a are produced. The resultant dipoles can interact with one another to form quadrupoles and, accordingly, more complicated SUs of the types shown in Fig. 10b are produced [4].

The initial increase in mechanical property values and the subsequent decrease with increasing thallium per cent (Fig. 9) can be also seen in many electrical and thermal properties as well [11, 36]. A plot between the thermal activation energy of conduction, ΔE, against T_g showed a discontinuity in the curve at the composition of $Tl_{0.25}(As_2Se_3)_{0.75}$ [11]. At the same time, the value of both T_g and T_m decreases monotonically with the increase of thallium content in the glass [11]. However, the ratio T_g/T_m decreases until $x = 0.25$ and, conversely, the tendency for crystallization increases [36]. For a higher thallium content ($x > 0.25$), the ratio T_g/T_m increases and the tendency for crystallization decreases up to a certain value ($x \lesssim 0.8$) after which it is difficult to get glassy composition by quenching from the melts. Also, the T_c (exothermic crystallization) and T_m (melting temperature) peaks are clear and sharp for thallium content up to $x = 0.25$ and, for more thallium, the peaks are broad and not clear. Equally important, the compositional dependence of the activation energy of crystallization, E_{cryst}, is almost the reverse of that of the ratio T_g/T_m [36].

In conclusion, there is a discontinuity in plots of T_g/T_m, ΔE, E_{cryst} and MH$_v$ versus glass composition appearing at Tl = 20–25 at %. This argument is also confirmed through the plots of ΔE against T_g [11] and MH$_v$ against T_g (Fig. 11). Such behaviour has been correlated with the substantial difference between the thallium-bond configurations of thallium-rich ($x > 0.25$) and thallium-poor ($x \leqslant 0.25$) regions of the glasses $Tl_x(As_2Se_3)_{1-x}$.

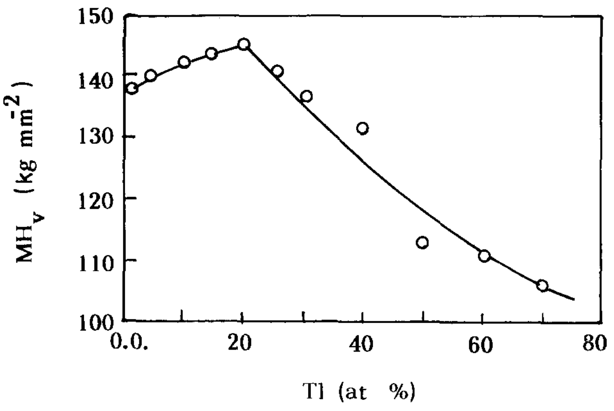

Figure 9 Dependence of MH$_v$ on composition for the glasses of the system $Tl_x(As_2Se_3)_{1-x}$.

3.7. Arsenic–sulphur–selenium–tellurium

Ten different compositions of the quasi-ternary (quaternary) chalcogenide system $(As_2S_3)_{1-x-y}(As_2Se_3)_x(As_2Te_3)_y$ were prepared in the glassy form from their stoichiometric binary components, As_2S_3, As_2Se_3 and As_2Te_3 [12]. Fig. 12 shows the variation of MH$_v$ with the atomic per cent expressed as the ratio S/(Se + Te). Such nonmonotonic variation in MH$_v$ corresponds to the change in nature and concentration of the CBs favoured for each composition. The value of MH$_v$ lies between 87 kg mm^{-2} ($4As_2S_3 \cdot 2As_2Se_3 \cdot 4As_2Te_3$) and 139 kg mm^{-2} ($7As_2S_3 \cdot 2As_2Se_3 \cdot As_2Te_3$). The value of MH$_v$ is 131 kg mm^{-2} for both $2As_2S_3 \cdot 4As_2Se_3 \cdot 4As_2Te_3$ and $3As_2S_3 \cdot 5As_2Se_3 \cdot 2As_2Te_3$.

For compositions having the same sulphur content, the value of MH$_v$ increases with increasing Te/Se ratio in the glass. The respective values of MH$_v$ are 127, 131 and 133 kg mm^{-2} for the glasses having $As_2S_3:As_2Se_3:As_2Te_3$ as 2:5:3, 2:4:4 and 2:3:5. Also, the value of MH$_v$ increases from 106 to

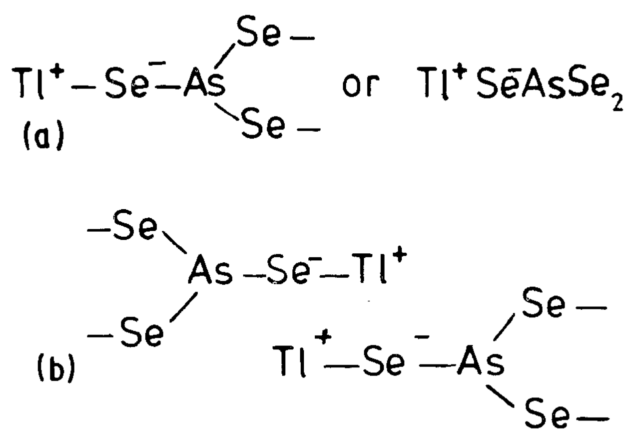

Figure 10 Schematic depiction of structural units corresponding to combination of arsenic chalcogenides with thallium for two types: (a) dipoles and (b) quadrupoles (After Borisova [4]).

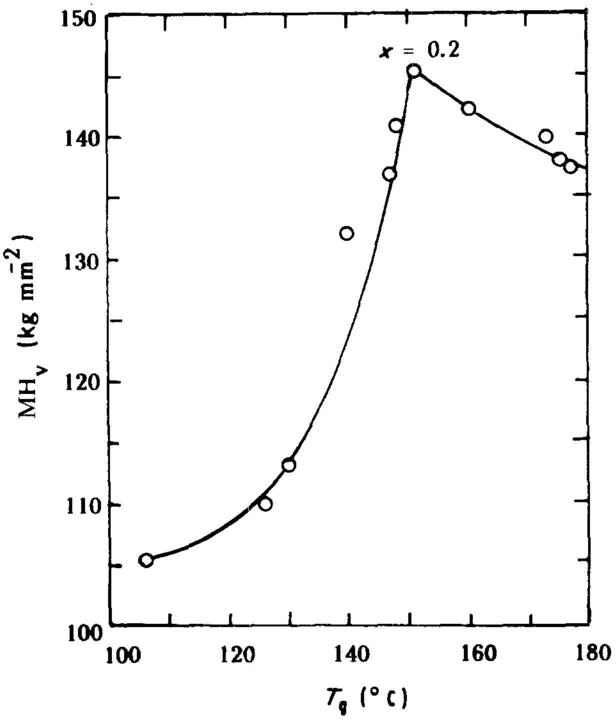

Figure 11 Dependence of MH_v on T_g for glasses of the system $Tl_x(As_2Se_3)_{1-x}$.

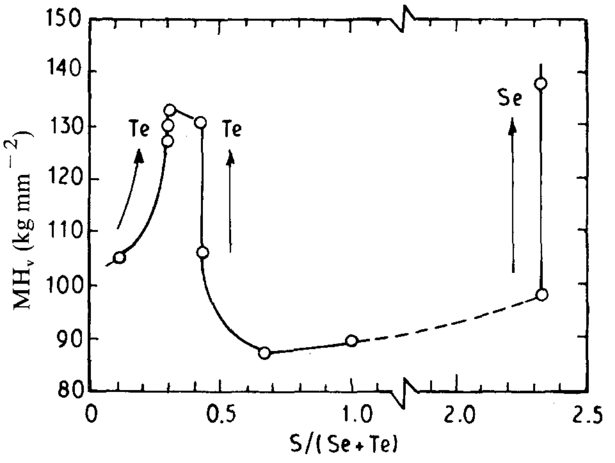

Figure 12 Dependence of MH_v on composition for the glasses of the quasi-ternary (quaternary) system $(As_2S_3)_{1-x-y}$ $(As_2Se_3)_x$ $(As_2Te_3)_y$. The direction of arrows points to the increase of selenium or tellurium when the percentage of sulphur content remains constant.

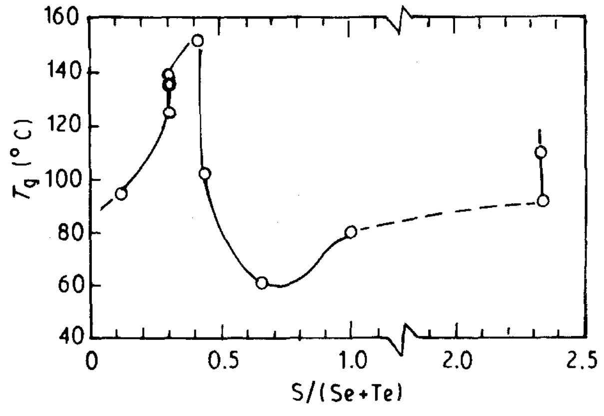

Figure 13 Dependence of glass transition temperature, T_g, on composition for the glasses of the quasi-ternary (quaternary) system $(As_2S_3)_{1-x-y}$ $(As_2Se_3)_x$ $(As_2Te_3)_y$.

131 kg mm^{-2} with increasing the ratio Te/Se from 0.167 to 0.4 for glasses having the same S/(Se + Te) = 0.43. The obtained results also indicate an increase in MH_v versus sulphur content for compositions having the same concentration of selenium. The values of MH_v are 87, 90 and 139 kg mm^{-2} for the glasses having components of As_2S_3 : As_2Te_3 as 4:4, 5:3 and 7:1, respectively, where all have the same concentration of As_2Se_3 (20 mol %). For the glasses having the highest concentration of As_2S_3 (70 mol %), the value of MH_v changes from 99 kg mm^{-2} for Se:Te = 1:2 to 139 kg mm^{-2} for Se:Te = 2:1. Here, it is interesting to note that the trend in the compositional dependence of MH_v (Fig. 12) is similar to that of T_g (Fig. 13).

On the other hand, a discontinuity trend in the relation between MH_v and T_g is shown in Fig. 14 as a result of the change in the relative molecular concentration of the three binary components of the system. Accordingly, the compositions having the same per cent of selenium or tellurium are characterized by the increase of their values of T_g (as well as MH_v) with sulphur. The values of T_g for the compositions having 20 mol % As_2Se_3 are 61, 68 and 110 °C when their

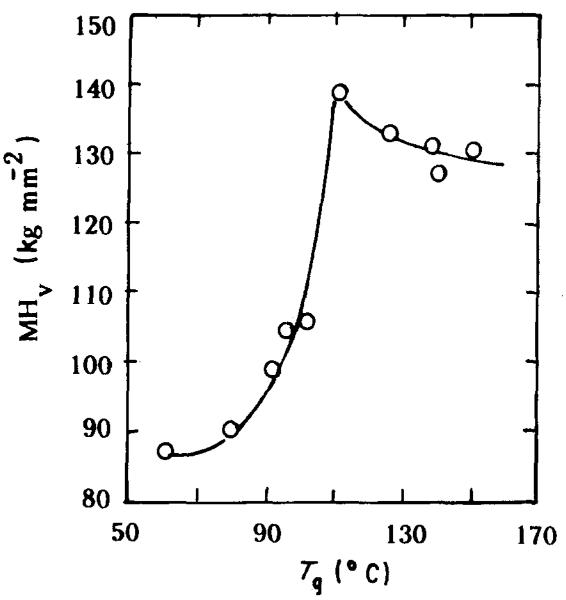

Figure 14 Dependence of MH_v on T_g for glasses of the system $(As_2S_3)_{1-x-y}$ $(As_2Se_3)_x$ $(As_2Te_3)_y$.

respective mole ratios of As_2S_3:As_2Te_3 are 4:4, 5:3 and 7:1. The values of T_g for the compositions having the same concentration of tellurium (10 mol %) are 95, 102 and 110 °C when their respective mole ratios of As_2S_3:As_2Se_3 are 1:8, 3:6 and 7:2. Also, glasses of 20 mol % As_2S_3 are characterized by the decrease of their values of T_g with tellurium content. The values of T_g are 125, 138 and 140 °C for the glasses having the ratios of As_2Te_3:As_2Se_3 as 5:3, 4:4 and 3:5, respectively. For the compositions having the highest sulphur content (70 mol % As_2S_3), the value of T_g changes from 91 to 110 °C with doubling the Se content at the expense of the tellurium content.

In addition, a discontinuity in the value of MH_v is observed in the composition which has equal proportions of As_2Se_3 and As_2Te_3. In other words, a plot of MH_v versus Te/Se for compositions having the same sulphur content (0.0, 20, 30, or 70 at %) declares a discontinuity at Te/Se = 1.0, i.e. at the composition $(As_2S_3)_2$ $(As_2Se_3)_4(As_2Te_3)_4$. Such a trend can also be seen in many other property–composition dependences, such as ΔE (thermal activation energy of conduction), σ_{RT} (d.c. conductivity at room temperature), σ_0 (pre-exponential factor in the conductivity formula $\sigma = \sigma_0 \exp(-\Delta E/kT)$) [12] as well as T_g. A discontinuity at the concentration of equal proportion of selenium and tellurium was reported [32] for the variation of thermal conductivity with composition in the quasi-binary system, As_2Se_3–As_2Te_3 and was explained by the change of the type and concentration of scattering centres in the glassy matrix.

4. Conclusions

A study of the compositional dependence of the mechanical properties for different chalcogenide glassy semiconductor systems allows us to draw the following conclusions.

1. It is possible to prepare samples of g-Se with certain predicted mechanical properties by controlling the temperature of synthesis (T_s).

2. The trend in the compositional dependence of MH_v reflects an even behaviour for the binary system Se–As, the quasi-binary systems As_2Se_3–As_2Te_3 and AsSe–AsTe, as well as the ternary system $(Ge_{1-x}Si_x)Se_2$.

3. An uneven trend for the compositional dependence of MH_v is observed for the isoelectronic system, Se–S, in the minimum microheterogeneity region (< 5 at % S). The observed monotonous decrease of both MH_v and T_g with $S \gtrsim 5$ at % reflects a decrease in the chain length.

4. A discontinuity is observed in the trends of both MH_v versus composition and MH_v versus T_g at 40 mol % As_2Te_5 for the non-stoichiometric quasi-binary system, As_2Se_5–As_2Te_5.

5. A discontinuity is observed in the trends of both MH_v versus composition and MH_v versus T_g at 20 at % Tl for the ternary system $Tl_x(As_2Se_3)_{1-x}$ in agreement with many electrical and thermal properties. That is, the introduction of thallium with smaller or larger concentration than 20 at % tends to weaken the glass structure of the compound.

6. An exact uneven behaviour is observed for the dependence of both MH_v and T_g on composition for glasses of the quasi-ternary system $(As_2S_3)_{1-x-y}$ $(As_2Se_3)_x$ $(As_2Te_3)_y$. A discontinuity in the relation of MH_v versus T_g is observed at the composition of the glass having the respective ratio 7:2:1 for their three binary components As_2S_3, As_2Se_3 and As_2Te_3. Also, at constant As_2S_3 content, the trend in the values of both MH_v and T_g exhibits a discontinuity at the composition having equal proportions (40 mol %) of As_2Se_3 and As_2Te_3. This is consistent with the criticality of other properties of these compounds.

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