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A study of n-type conduction in amorphous chalcogenide sputtered films

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Abstract. A detailed study of the x-ray photo-emission spectroscopy (XPS) and the transport properties of amorphous sputtered films with compositions approximate by a formula $\text{Ge}_{25}\text{Se}_{75-x}\text{Bi}_x$ where $x = 0-17.4$ is reported. The XPS result indicates that, on a local atomic scale, the chemical states of the films are a mixture of different bonding environments of GeSe_2 and Bi_2Se_3 for all compositions and that the Bi is introduced as a positive charged centre. The addition of 15.6 at. % Bi leads to an increase of ten orders of magnitude in the electrical conductivity as well as a decrease in the optical and electrical gaps. A negative sign of the thermo-electric power was observed for $x > 10$, indicating that the conduction type changed from p type (low x) to n type, which is in agreement with the glass. The results are interpreted as the effect of the shift of the Fermi level closer to the conduction band due to the incorporation of positive- U defects that unpin the Fermi energy.

1. Introduction

Until Spear and LeComber (1976) demonstrated that amorphous tetrahedral semiconductors could be doped, it was generally believed that in amorphous semiconductors an additive impurity atom would always satisfy its own valence requirements. This was known as the $8 - N$ rule (Mott 1967). Nevertheless, Mott (1976) did point out that the addition of certain metal impurities to chalcogenide glasses could form charged centres which according to the law of mass action would upset the equilibrium of the native charged defects, resulting in the unpinning of the Fermi level E_F , a doping effect.

Tohge *et al* (1979) first reported that the incorporation of more than 8 at. % Bi into $\text{Ge}_{20}\text{Se}_{80}$ glasses changes the conductivity from p to n type. Thereafter, a series of papers by Tohge *et al* (1980a, b), Nagels *et al* (1981, 1983) and Tičhy *et al* (1985) were published dealing with the electrical and optical properties of Ge–Se or Ge–Se–Te and Ge–S chalcogenide glasses containing Bi, Sb, As, Cu and In impurities. It is interesting to note that only Bi unpins the Fermi level and changes the carrier type.

Models to explain the observed shift of the Fermi level are based on two considerations—either the introduction of Bi as charged centres, or percolation between microcrystalline Bi_2Se_3 inclusions (see, e.g., a review by Elliott (1987)). The structural studies up to date include x-ray photo-electron spectroscopy (XPS) by Takahashi *et al* (1984) on amorphous Bi_2Se_3 films, Raman studies by Bhatia (1983) on the $(\text{GeSe}_{3.5})_{100-x}\text{Bi}_x$ system and extended x-ray absorption fine structure (EXAFS) by

Elliott and Steel (1986) and Elliott (1987) on the similar system $\text{Ge}_{20}\text{S}_{80-x}\text{Bi}_x$. The latter measurements determined the coordination of the Bi additives. According to their experimental data, at about 3 at. % Bi the formation of at least one partially ionic Bi^+-S^- bond at each site is suggested. They conclude then that the threefold-coordinated positive-charged Bi centre is responsible for upsetting the equilibrium for the native valence alternation pairs (VAPs) and the shift of the Fermi level.

2. Experimental details

Thin films of amorphous chalcogenide alloys with compositions $\text{Ge}_{25}\text{Se}_{75-x}\text{Bi}_x$, where $x = 0-17.4$ were prepared by sputtering in an Ar atmosphere at a partial pressure of 5×10^{-3} Torr. The base pressure was about 2×10^{-6} Torr. Prior to deposition the Pyrex chamber was baked out with IR illumination for about 4–5 h. Three different targets were used: $\text{Ge}_{25}\text{Se}_{75}$, $\text{Ge}_{20}\text{Se}_{70}\text{Bi}_{10}$ and $\text{Ge}_{20}\text{Se}_{67}\text{Bi}_{13}$. The desired amounts of Bi were placed on the surface of the first target in order to obtain the concentrations $x = 0-10$ (Mytilineou, and Davis 1980). The films were deposited on water-cooled Corning 7059 glass substrates. Typical thicknesses were about $1 \mu\text{m}$.

Electrical conductivity measurements were performed in both coplanar and sandwich electrode geometries using evaporated Au or NiCr contacts. In order to eliminate the formation of oxides, contacts were deposited immediately after the film deposition. Ohmic contacts were confirmed by linear I–V results.

Details of the thermo-electric power set up have been published elsewhere (Kounavis et al 1988).

Optical absorption as a function of photon energy was calculated from transmission spectra. A 75 W halogen lamp and a Jobin–Yvon 0.25 m monochromator were used to send monochromatic light onto a sample. The transmitted intensity from a clean substrate and the film were measured at any photon energy with a Si detector. The experiment is computer driven.

X-ray energy-dispersive spectrometry (EDS) was utilised to determine the film compositions. Auger electron spectroscopy (AES) analysis was used to examine the depth uniformity of the films. XPS was carried out with a cylindrical mirror energy analyser operated in a retarding mode. The pass energy was set at 25 eV, giving uncertainty in the binding energy (BE) of ± 0.2 eV. The BE was calibrated by assigning the Au $4f_{7/2}$ peak at 84.0 eV.

3. Results and discussion

The composition of sputtered films made at RF powers of 50 W, from the three targets $\text{Ge}_{25}\text{Se}_{75}$, $\text{Ge}_{20}\text{Se}_{70}\text{Bi}_{10}$ and $\text{Ge}_{20}\text{Se}_{67}\text{Bi}_{13}$ were determined by the EDS analysis to be $\text{Ge}_{28.8}\text{Se}_{71.2}$, $\text{Ge}_{20.8}\text{Se}_{66.0}\text{Bi}_{13.2}$ and $\text{Ge}_{17.8}\text{Se}_{66.0}\text{Bi}_{15.6}$, respectively, with a precision of about ± 2.2 for Ge and Se and ± 0.8 for Bi. Increase in the RF power results in an increase in the Bi concentration into the films. All Bi concentrations referred to in this work are determined by the EDS measurements. Auger depth profiles of the films have indicated that the composition is almost independent of depth.

Angle-resolved x-ray photo-electron spectroscopy (ARXPS) data shows that Ge segregated to the front surface of as-deposited samples, forming a monolayer of Ge oxide to protect the bulk from further oxidation. When 15–20 Å was removed by Ar sputtering,

Table 1. BE on the sputtered surface (-20 \AA) of three samples with 0, 1.1, 6.5, 10.3 and 15.6 at. % Bi.

State	BE (eV) for the following Ge : Se : Bi ratios				
	28.8 : 71.2 : 0	28.0 : 70.9 : 1.1	25.2 : 68.3 : 6.5	23.9 : 65.8 : 10.3	20.1 : 64.3 : 15.6
Ge $2p_{3/2}$	1219.0	1219.0	1219.0	1219.0	1219.0
Ge 3d	31.1	31.0	31.1	31.0	30.9
Se 3d	54.7	54.7	54.6	54.5	54.4
Se $3p_{3/2}$	161.1	160.7	160.5	160.2	160.2
Bi $4f_{7/2}$	—	158.3	158.4	158.2	158.2
Bi $5d_{5/2}$	—	25.0	25.3	25.1	25.1
$\Delta E(\text{Se } 3d\text{-Bi } 5d)$	—	29.7	29.3	29.3	29.3
$\Delta E(\text{Se } 3d\text{-Ge } 3d)$	23.6	23.7	23.5	23.5	23.5

Table 2. BES of Ge, Se and Bi core states in their elemental state.

State	BE (eV)	Reference
Ge $2p_{3/2}$	1216.6	This study
	1217.2	Wagner <i>et al</i> (1979)
Ge 3d	28.6	This study
	28.95	Shalvoy <i>et al</i> (1977), Wagner <i>et al</i> (1979)
Se 3d	55.2	Shalvoy <i>et al</i> (1977)
	55.3	Wagner <i>et al</i> (1979)
	55.5	Takahashi <i>et al</i> (1984)
Se $3p_{3/2}$	161.3	Shalvoy <i>et al</i> (1977)
Bi $4f_{7/2}$	156.8	Wagner <i>et al</i> (1979)
	156.9	Shalvoy <i>et al</i> (1977)
Bi $5d_{5/2}$	24.1	Shalvoy <i>et al</i> (1977)
	24.2	Takahashi <i>et al</i> (1984)

no indication of Ge oxide was found. Table 1 summarises the BE recorded on sputtered surfaces of samples with $x = 0, 1.1, 6.5, 10.3$ and 15.6 at. % Bi.

On the basis of Pauling's electronegativity values (Ge, 2.01; Bi, 2.02; Se, 2.55), Ge and Bi would become more positively charged in alloying with Se, simply because they would 'donate' electrons to the Se atoms. The upward-shifted BE of Ge and Bi core states and the downward-shifted BE of Se core states from their corresponding elemental values (table 2) would be expected in forming ternary alloys. Throughout the study there is no evidence of any electrical state present in the films; on a local atomic scale, Ge forms GeSe_2 tetrahedral bonding and Bi is incorporated with a Bi_2Se_3 structure. The absence of peaks between the chemical state GeSe_2 and the electrical Ge state, as well as between Bi_2Se_3 and Bi states, suggests that there are no Ge-Ge and Bi-Bi bonds present in our samples.

In a sample with 0 at. % Bi, the BES of the Ge $2p_{3/2}$ and the Ge 3d states are at 1219.0 eV and 31.1 eV (table 1), having 2.4 eV and 2.5 eV increases from their corresponding values of elemental state, respectively. Feltz *et al* (1975) have reported BES of 31.6 eV and 55.2 eV for the Ge 3d and the Se 3d states, respectively, in GeSe_2

alloy. Their BE values were corrected for surface charging by fixing the BE of the C 1s line at 285.0 eV which is 0.4 eV higher than the value of 284.6 eV used in this study. After compensation for the BE difference of the C 1s line, our data are in good agreement with their values. Furthermore, the energy separation of 23.6 eV between the Ge 3d and the Se 3d states (table 1) also agrees with the reported value (Feltz *et al* 1975). We conclude that the Ge is in a GeSe₂ bonding environment.

The BES and FWHMS of the above two Ge states (2p_{3/2} and 3d) are essentially unchanged in the ternary alloys, by adding various amounts of Bi up to 15.6 at. % (the highest content in this study) into the Ge–Se matrix (table 1). This result indicates that there is no change in the Ge chemical bonding environments; in other words, Ge maintains the same tetrahedral bonding structure throughout the ternary alloys.

The BE of the Bi 4f_{7/2} core line in the alloys is at 158.3 ± 0.1 eV, about 1.5 eV above its elemental state (table 2) which is higher than the value of 157.7 eV for the Bi₂Se₃ compound reported by Debies and Rabalais (1977) and is much closer to the value of 158.5–159.1 eV for Bi₂O₃ (Debies and Rabalais 1977, Morgan *et al* 1973). On as-deposited surfaces, it does not seem possible to have Bi oxide formation because Ge already has an oxide component. To make sure of this, we carried out ARXPS. If the Bi were in an oxide state, it would segregate out to the front surface of as-received samples and the peak intensity of the oxide component would become a function of the take-off angle. The data show that the Ge is the only element containing two components, i.e. the selenide and oxide. The peak intensity ratio of Bi to Se is independent of the take-off angle. From all the above information and the fact that on sputtered surfaces, where there is no evidence of O present, the Bi 4f_{7/2} state still shows the same BE, we rule out the possibility of Bi₂O₃ and assign the Bi to the Bi₂Se₃ state. Furthermore, the BE of the Bi 5d_{5/2} core line is at 25.0–25.3 eV, an increase of about 1.0 eV from the elemental state, which agrees well with the value of 25.0–25.1 eV recorded for the Bi₂Se₃ compound by Takahashi *et al* (1984). Similar to the Ge states (2p_{3/2} and 3d), the BE and peak shape of both Bi 4f_{7/2} and Bi 5d_{5/2} states are also not changed but keep the same Bi bonding environments in the alloys.

The BE of the Se 3d state recorded for a 0 at. % Bi sample is at 54.7 eV which is about the same as the values of Takahashi *et al* (59.4 eV) and Feltz *et al* (54.8 eV) (after compensation for the BE difference of the C 1s line) for GeSe₂ bulk material. This value represents a decrease of about 0.7 eV in BE, as expected, from the corresponding elemental state. In table 1, it shows that the BES of Se 3d and 3p_{3/2} have a small but systematic shift correlated with the amount of Bi in the films. The incorporation of Bi causes the BES of the Se states to move gradually from the GeSe₂ value towards the Bi₂Se₃ value. Nonetheless, the Se states (3p_{3/2} and 3d) also keep the same peak shape and FWHM. The XPS results clearly demonstrate that the chemical states of all the Ge–Se–Bi ternary alloys studied are mixtures of two different bonding environments on a local atomic scale. Macroscopically, they are homogeneous ternary films, as the Se states exhibit only one component and not two as in the characteristic case of a diphasic material.

The energy separation ΔE between Bi 5d_{5/2} and Se 3d states changes from 29.7 eV in a 1.1 at. % Bi sample to 29.3 eV in 6.5–15.6 at. % Bi samples, indicating that the ionicity of the Bi–Se bond becomes stronger with increase in Bi (1.1 < x < 6.5) and then remains constant (x > 6.5). This result supports Elliott's suggestion of partially ionic Bi⁺–S[–] bonds in the bulk Ge₂₀S_{80–x}Bi_x for x > 3 and is also valid for sputtered Ge₂₅Se_{75–x}Bi_x films. On the contrary, the energy separation ΔE between Ge 3d and Se 3d lines is more or less unchanged, suggesting that the characteristics of Ge–Se bonds are not influenced by the addition of Bi in the alloys.

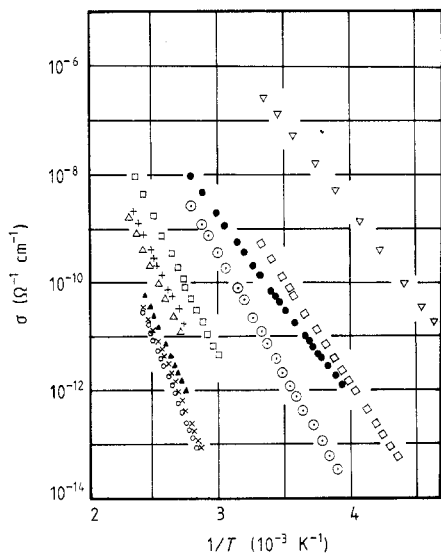


Figure 1. Electrical conductivity as a function of reciprocal temperature for different $\text{Ge}_{25}\text{Se}_{75-x}\text{Bi}_x$ alloys: \circ , $x = 0$; \times , $x = 1.1$; \blacktriangle , $x = 3.8$; \triangle , $x = 4.8$; $+$, $x = 6$; \square , $x = 6.6$; \odot , $x = 8.8$; \bullet , $x = 10.3$; \diamond , $x = 13.2$; ∇ , $x = 15.6$.

In figure 1 the DC conductivity σ of $\text{Ge}_{25}\text{Se}_{75-x}\text{Bi}_x$, with $x = 0-15.6$ is plotted as a function of inverse temperature for the different Bi concentrations. Measurements with both coplanar and sandwich electrode geometries were performed on the same sample. Data with $\sigma < 10^{-11} \Omega^{-1} \text{cm}^{-1}$ refer to the sandwich geometry. The variation in the conductivity with temperature could be described by

$$\sigma = \sigma_0 \exp(-E_\sigma/kT) \tag{1}$$

for the entire temperature range covered for almost all compositions with the exception of 10.3 at. % Bi which shows a kink at 300 K.

Annealing effects are relatively small, resulting in a decrease in the absolute value of σ and a slight increase of about 15–20% in the slope. All data in figure 1 refer to annealed samples. X-ray diffraction spectra obtained on samples before and after annealing show no indication of crystallinity.

Because of the conflicting problems posed by high resistivity and crystallisation of the films, annealing temperatures were chosen to cover a relatively satisfactory temperature range for conductivity measurements, but to avoid crystallisation. Compositions with $x < 6.5$ had been annealed only up to 140 °C, while those with $8.8 < x < 10.3$ had been annealed only up to 85 °C.

As we can see from figure 1 the conductivity at room temperature increases by 10 orders of magnitude with the addition of 15.6 at. % Bi while the activation energy E_σ is reduced from 1.35 eV to 0.53 eV, respectively.

The Seebeck coefficient S was measured for samples with $x = 10.3, 13.2$ and 17.4 (prepared at 75 W). All samples showed a negative coefficient. Owing to the high resistivity of the films and in an attempt to avoid crystallisation, the temperature range covered was limited. In figure 2 a plot of the Seebeck coefficient against reciprocal temperature is shown, indicating a linear variation with $E_s = 0.52$ eV. Owing to the high resistivity of the samples, thermopower measurements were not possible on films with $x < 10$.

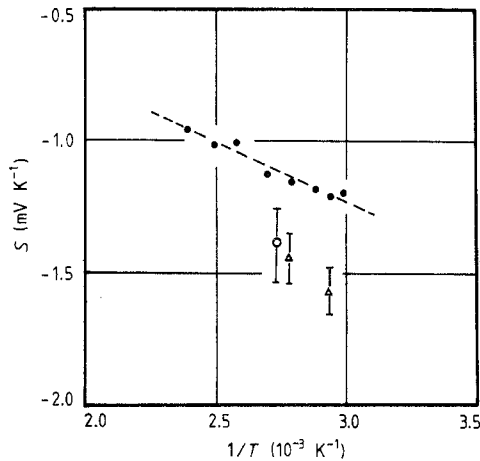


Figure 2. Thermo-electric power as a function of reciprocal temperature for different $\text{Ge}_{25}\text{Se}_{75-x}\text{Bi}_x$ alloys: ●, $x = 17.4$; △, $x = 13.2$; ○, $x = 10.3$.

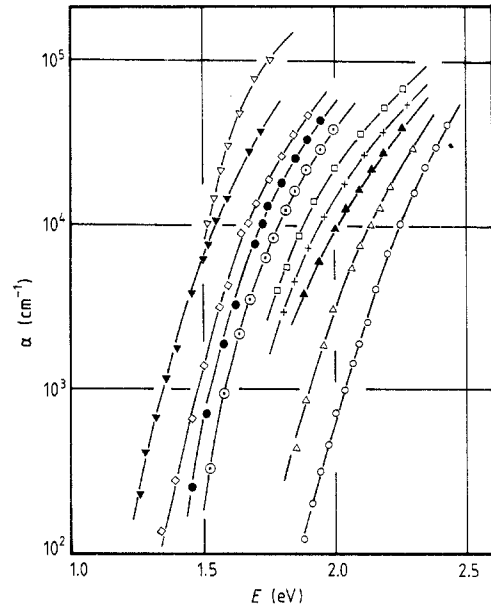


Figure 3. Optical absorption coefficient as a function of energy for different $\text{Ge}_{25}\text{Se}_{75-x}\text{Bi}_x$ alloys: ○, $x = 0$; △, $x = 1.1$; ▲, $x = 3.0$; +, $x = 3.8$; □, $x = 4.8$; ⊙, $x = 6.6$; ●, $x = 8.8$; ◇, $x = 10.3$; ▽, $x = 13.2$; ▿, $x = 15.6$.

Indirect evidence that films with 6.6 at.% Bi are p type is the fabrication of p-n devices with successive layers of 6.6 at.% Bi and 10.3 at.% Bi, respectively. Both layers were sputtered under identical deposition conditions without breaking the vacuum. The I - V characteristic of the devices indicates a typical p-n behaviour (Kounavis *et al* 1989).

The absolute value, about 1.5 mV K^{-1} , and the slope of the thermo-electric power suggest that conduction takes place in the extended states of the conduction band and not at some impurity states close to the Fermi energy. This conclusion is consistent with the large activation energies for the conductivity.

In figure 3 the optical absorption coefficient α as a function of photon energy is plotted. Owing to the effect of interference fringes the calculation of α was limited to values greater than $5 \times 10^3 \text{ cm}^{-1}$. The calculations were extended up to $\alpha \approx 10^2 \text{ cm}^{-1}$ using the method reported by Swanepoel (1982, 1984). According to this method, all optical constants, i.e. optical absorption, reflectivity, refractive index and thickness, can be calculated from the transmission spectrum only. To check the accuracy of our calculations the calculated refractive indexes and thicknesses were compared with the measured values for the same films. Inhomogeneities in the thickness were taken into account.

As is evident from figure 3, the optical absorption edge varies exponentially with photon energy for the whole range covered and shifts to lower energies as the concentration of Bi increases. Annealing has almost no effect on the optical absorption edge. The optical gap E_g is taken as the photon energy where the absorption coefficient is 10^4 cm^{-1} .

In figure 4 the pre-exponential factor σ_0 of the conductivity (equation (1)) is plotted. By increasing the Bi concentration up to 8.8 at.%, σ_0 decreases gradually and levels off

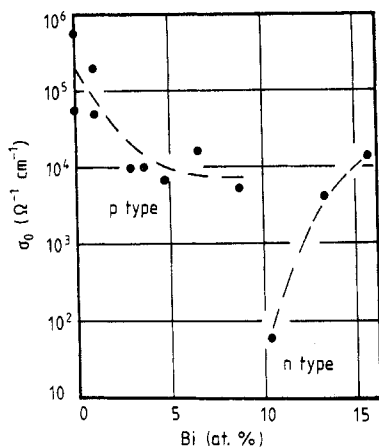


Figure 4. The conductivity pre-exponential factor σ_0 as a function of Bi concentration: —, a guide to the eye.

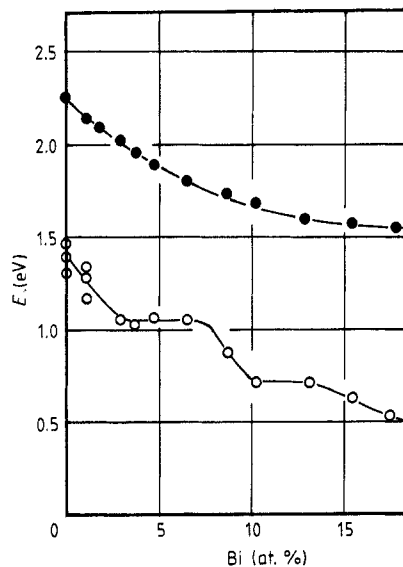


Figure 5. The activation energy E_σ for conduction (\circ) and the optical gap E_g (\bullet) are plotted as functions of the Bi concentration.

for $x > 4.8$. These values of about $10^4 \Omega^{-1} \text{cm}^{-1}$ indicate conduction in the extended states. The 10.3 at. % Bi alloy demonstrates a kink in the curve of $\ln \sigma$ against $1/T$ with σ_0 values of $50 \Omega^{-1} \text{cm}^{-1}$ and $1.5 \Omega^{-1} \text{cm}^{-1}$ for high and low temperatures, respectively, indicating that, at high temperatures, conduction may take place at localised states of the conduction band. By further increasing the Bi concentration, σ_0 increases up to $10^4 \Omega^{-1} \text{cm}^{-1}$ for the 15.6 at. % Bi specimen. A discontinuity is observed in σ_0 at about 9.5 at. % Bi, coinciding with the inversion of the conduction type. This is probably related to the shift of the Fermi energy closer to the conduction band, where transport through localised states at the band tails becomes predominant.

In figure 5 the activation energy E_σ for conduction and the optical gap E_g are plotted for different Bi concentrations. The optical gap decreases gradually with increasing x and levels off at $x > 12$. This variation is more smooth than that reported by Tohge *et al* (1980a, b) for bulk samples. Their lower values arise because they choose E_g at $a = 10^3 \text{cm}^{-1}$.

The variation in E_σ is more complicated. It shows a sharp decrease for $x < 3$, a levelling-off region for $3 < x < 8$, then another sharp decrease for $8 < x < 10$ and finally a levelling off for $x > 10$. Its similarity with the results on bulk glasses obtained by Tohge *et al* (1980a, b) and Nagels *et al* (1981) is remarkable.

A comparison of the variations in E_g and E_σ show the movement of the Fermi energy E_F relative to the band edges. In the region $x < 3$ the dramatic decrease in E_σ and the smooth variation in E_g indicate a relative shift of E_F closer to the valence band (as the material is p type). At $3 < x < 8$, E_F shifts towards the conduction band as E_g is continuously decreasing while E_σ is constant. The important result of this study is that E_F continuously shifts relative to the band edges with the addition of Bi.

The observed similarities between the transport properties of bulk glasses and sputtered films demonstrates that the deposition conditions held during sputtering are

appropriate for creating material of similar quality to that made by melt quenching. The observed weak annealing effects and the linearity of $\ln \sigma = f(1/T)$ and $\alpha = f(h\nu)$ suggest that the concentration of defects in the sputtered films is relatively low.

According to the experimental data from bulk as well as thin films, it can be assumed that similar types of charged defect dominate the properties of both materials, although, in the case of the bulk, defects are formed under thermal equilibrium in the melt while, in the sputtered films, they occur at the surface during deposition. As the atoms on the growing surface are in quasi-thermal equilibrium, the concentration of the charged defects, equilibrating at a deposition temperature T_s will be proportional to $\exp(-E/kT_s)$ where E is the creation energy for a VAP (Street *et al* 1985). The law of mass action and interconversion of the charged defects can be applied at the growing surface of the films during deposition; a condition that is not necessarily true for the states in the bulk of the film.

Street and Lucovsky (1979) have pointed out that ionicity effects in Ge chalcogenide compounds are responsible for the creation of some positive- U defects (in addition to the usual negative- U ones). In GeSe_2 , for example, C_3^+ can be bonded to two Ge atoms and one Se atom or to three Ge atoms. The first configuration can be inter-converted to a C_1^- when two electrons are added, and vice versa. This is the necessary requirement for a negative- U centre. In the second case where C_3^+ is bonded to three Ge atoms, the addition of two electrons results in a T_3^- defect and it does not seem possible to create the C_1^- by any simple reconstruction. The defect pairs C_3^+ and T_3^- have a positive U and do not pin the Fermi energy.

According to our XPS results the structure of a $\text{Ge}_{28.8}\text{Se}_{71.2}$ film is expected to be consistent with GeSe_2 tetrahedral units connected by Se bonds. It could be suggested that the addition of threefold-coordinated Bi introduces pyramidal units with Bi_2Se_3 structure that are incorporated in the tetrahedral GeSe_2 matrix.

There are several reasons why the number of $U < 0$ centres is expected to be reduced continuously with the addition of Bi. Incorporation of Bi could effect the defect concentration in two ways:

- (i) by creating new pairs of $U > 0$ defects related to Bi centres and
- (ii) by decreasing the possibility that C_3^+ bonded to Se atoms and more importantly, with small additions of Bi, centres such as C_3^+ bonded to three Se atoms may disappear.

In fact, from XPS data (table 1), no Se–Se bonds have been detected. When the concentration of $U > 0$ centres is predominant over $U < 0$ centres, the material is transformed to positive U and the Fermi level can become unpinned. Bi at small concentrations, i.e. $x < 2$, is expected to alloy with the Ge–Se matrix. At higher concentrations, a small percentage of charged bonds of Bi^+-Se^- type may be present as a result of the change in the BES of Se and Bi (table 1) (Takahashi *et al* 1984), in agreement with the prediction of EXAFS data by Elliott (1987). The existence of charged Bi centres may be responsible for the shift of the Fermi level towards the conduction band and the change in the conduction type.

4. Conclusions

In this work the inversion of the conduction type on sputtered films of Ge chalcogenide alloys with the incorporation of Bi is demonstrated for the first time. The shift of E_F above midgap happens at $7 < x < 10$ which is in good agreement with the bulk material.

On the basis of XPS results and the ionicity effects of Ge chalcogenide amorphous semiconductors, we argued that with the addition of Bi the positive- U defects become increasingly dominant over the negative- U defects, resulting in the unpinning of E_F , while the creation of charged Bi centres may be responsible for the upward shift of E_F and the n-type doping of the material.

Acknowledgments

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