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Bulk Amorphous Ga–Sb Semiconductors Prepared by Thermobaric Treatment: Formation and Properties

By

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The multistage process of solid state amorphization and subsequent crystallization of the quenched 'white tin' high pressure phase of Ga–Sb alloys containing 20 to 80 at% Sb was studied at ambient pressure by differential scanning calorimetry. The heats of both amorphization and crystallization were exothermic and equal to (3.5 ± 0.5) and (8.3 ± 1.0) kJ/mol, respectively. Formation of the bulk amorphous alloys free of any crystalline inclusions was observed for compositions with 47.5 to 52.5 at% Sb. The structure of the amorphous GaSb produced by solid state amorphization was studied by neutron diffraction. It is found to be nearly identical to that of a sample prepared earlier by sputtering.

1. Introduction

The process of solid state amorphization of metastable high pressure phases (HPP), heated at atmospheric pressure, has been studied for several binary systems, namely, Cd–Sb [1], Zn–Sb [1], Al–Ge [2] and Ga–Sb [3]. Recent X-ray and superconductivity measurements [4] have shown the HPP in the Ga–Sb system to have a homogeneity composition range in the vicinity of 50 at% Sb. So, one could expect formation, upon heating, of the bulk amorphous alloys with compositions different from the equiatomic one. These alloys are going to be promising candidates for studying the electronic structure of the amorphous state in this $A^{III}B^{V}$ system.

This paper reports the effect of alloy composition on the heat release accompanying amorphization and the subsequent crystallization of the HPP in the course of heating at ambient pressure. We also present results of a neutron diffraction study of the bulk a-GaSb and compare them with those obtained for GaSb films prepared by sputtering [5].

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2. Experiment

Ga-Sb samples containing 20, 30, 40, 45, 47.5, 50, 52.5, 55, 60, 65, 70, and 80 at% Sb were prepared by alloying appropriate amounts of Ga and Sb (both 99.999 wt% pure). Along with the polycrystalline GaSb alloy with 50 at% Sb obtained in this way, a GaSb single crystal was also used. No difference between their behavior was revealed in the subsequent differential scanning calorimetry (DSC) experiments. The Ga–Sb samples in the form of discs 5 mm in diameter and 1 to 3 mm in height were treated at 7 GPa and 520 K for 24 h in a 'Toroid' quasi-hydrostatic high pressure chamber and cooled to liquid nitrogen temperature before the pressure was released. An X-ray analysis of the samples was performed using a DRON-2.0 diffractometer (CuK_{α} radiation) at 100 K and ambient pressure. The thermal analysis was carried out with a PE DSC 7 differential scanning calorimeter, with a heating rate of 20 K/min. The neutron diffraction experiments were performed on the diffractometer LAD at the ISIS pulsed neutron source (Rutherford Appleton Lab. (RAL), U.K.) [6]. The pile of the a-GaSb pellets was packed into a cylindrical vanadium cassette of 9.5 mm diameter (a GaSb single crystal was used as reference material). The measurements were carried out in a standard top-loading cryostat at 100 K.

3. Results and Discussion

For all the alloys subjected to the above mentioned thermobaric treatment formation of the HPP of the 'white tin' type was observed. It was shown [4] that the lattice parameters of the HPP varied noticeably over the composition range from about 40 to 45 to about 55 to 60 at% Sb and remained nearly constant outside this interval. Furthermore, only the samples containing 47.5 to 52.5 at% Sb exhibited no reflections due to excess Ga or Sb in their X-ray patterns. Thus, the homogeneity region of the Ga–Sb HPP can only range at the most from 40 to 60 at% Sb and at the least from 47.5 to 52.5 at% Sb.

With the heating rate used, the HPP was considered to transform completely into the amorphous state below 350 K, since its lines were not observed in the X-ray patterns of the samples heated to this temperature. For the samples containing 47.5, 50, and 52.5 at% Sb, no crystalline lines were present at all as expected for the formation of fully amorphous alloys.

Representative DSC traces are shown in Fig. 1. Within experimental uncertainty, the heat of the amorphization process did not change over the homogeneity region for the 'white tin' phase (47.5 to 52.5 at% Sb); the heat was exothermic and equal to (3.5 ± 0.5) kJ/mol. The crystallization of the amorphous Ga–Sb phase occurred, according to the X-ray data, within the temperature interval 360 to 550 K, and was accompanied by a heat release of (8.3 ± 1.0) kJ/mol, see Fig. 2.

The temperature intervals for Ga–Sb HPP amorphization and crystallization are broad and the shape of the calorimetric curves changes gradually with alloy composition. One of the possible explanations for the complex character of the Ga–Sb HPP amorphization is that the short range order in the amorphous phase varies with temperature. If so, different stages of the amorphization process should depend on the composition of the HPP in a different manner, resulting in corresponding changes of the DSC curve.

Fig. 3 shows the structure factor S(Q) for amorphous GaSb obtained from the experimental diffraction pattern using the GENIE package available at RAL [7]. The positions



Fig. 1. Heat flow vs. temperature on heating quenched Ga–Sb high pressure phases at 20 K/min. The Sb content (in at%) of the different alloys is indicated for each curve. The endothermic peaks positioned at approximately 310 K for the samples with 30 and 40 at% Sb are due to the melting of the excess gallium. Note the difference in the vertical scales in a) and b)



Fig. 2. Heat flow vs. temperature on heating amorphous Ga-Sb samples at 20 K/min

and full widths at half maximum (FWHM) for the first two peaks (first sharp diffraction peak and the principal peak, respectively) of the structure factor are: $Q_1 = 1.78 \text{ Å}^{-1}$, $\Delta Q_1 = 0.33 \text{ Å}^{-1}$ and $Q_2 = 3.16 \text{ Å}^{-1}$, $\Delta Q_2 = 0.60 \text{ Å}^{-1}$. From the FWHM of the first sharp diffraction peak and the principal peak in S(Q) one can calculate the correlation



Fig. 3. The structure factor S(Q) for amorphous GaSb at 100 K



Fig. 4. The total radial distribution function, RDF(r), in amorphous GaSb obtained by Fourier transformation of S(Q)

lengths $\xi_{cc} = 2\pi/\Delta Q_1 = 19$ Å and $\xi_{NN} = 2\pi/\Delta Q_2 = 10$ Å which are related to chemical and density fluctuations.

The Q_1 and Q_2 values are different from $Q_1 = 1.87$ Å⁻¹ and $Q_2 = 3.19$ Å⁻¹ determined from the X-ray data for the amorphous GaSb prepared by sputtering [5]. The peaks in the S(Q) spectrum are noticeably asymmetric and exhibit some fine structure which was not seen before [5]. However, the main features of the spectrum for the amorphous GaSb samples prepared in the present work and by sputtering [5] are very similar.

The total radial distribution function, RDF(r), shown in Fig. 4, was obtained by Fourier transformation of the S(Q) spectrum (with $Q_{\text{max}} = 25 \text{ Å}^{-1}$) using the standard transformation technique [8]. The values of the position r and the FWHM Δr for the first peak in RDF are $r_1 = 2.66 \text{ Å}$ and $\Delta r_1 = 0.30 \text{ Å}$. At r > 3 Å there is a peak with a maximum at $r_2 = 4.32 \text{ Å}$ ($\Delta r_2 = 0.54 \text{ Å}$), a shoulder at the left side (3.1 to 3.6 Å) and three small peaks with maxima at 4.99, 5.18, and 5.60 Å.

The coordination numbers for the first $(r_1 = 2.66 \text{ Å})$ and second $(r_2 = 4.32 \text{ Å})$ neighbor shells determined from the areas under the corresponding peaks of the RDF(r) curve are $n_1 = 3.88$ $(2.15 \text{ Å} \le r \le 3.08 \text{ Å})$ and $n_2 = 11.73$ $(3.08 \text{ Å} \le r \le 4.76 \text{ Å})$. These parameters are rather close to those for the amorphous GaSb prepared by sputtering techniques [5]: $r_1 = 2.67 \text{ Å}$, $n_1 = 3.50(3.78)$ and $r_2 = 4.30 \text{ Å}$, $n_2 = 13.2$. The coordination number $n_1 = 3.88$, the ratio $n_2/n_1 = 3.02$, and the bond angle $\alpha = 2 \arcsin(r_2/2r_1) = 108.6^{\circ}$ from the present data are close to those for the structure with ideal tetrahedral bonding $(n_1 = 4, n_2/n_1 = 3, \alpha = 109.5^{\circ})$.

The nearest neighbor distance, $r_1 = 2.66$ Å, in bulk a-GaSb is equal to the sum of the covalent radii of Ga and Sb atoms, 1.26 and 1.40 Å, respectively. This is the r_1 value that one can expect if only unlike atoms are the nearest neighbors in a-GaSb. The covalent radii of Ga and Sb are noticeably different, so formation of bonds between like atoms should contribute to the spread in the nearest neighbor separations in a-GaSb.

This effect was observed in a previous study [5] where the spread for the a-GaSb sample was found to be about twice as large as for the samples of a-Ge (monoatomic substance) and a-GaAs (a compound with nearly equal covalent radii of the constituent atoms) prepared and studied under similar conditions. In our a-GaSb sample, the FWHM for the first peak of the RDF(r) corresponds to $\Delta r_1 = 0.30$ Å and is close to $\Delta r_1 = 0.278$ Å in a-Ge studied by neutron diffraction [8] with similar $Q_{\text{max}} = 23.2$ Å⁻¹ compared to 25 Å⁻¹ in the present work. One can therefore suggest that a-GaSb prepared in the present work is more chemically ordered than sputtered a-GaSb [5].

In conclusion, the quenched Ga–Sb high pressure phase, containing from 47.5 to 52.5 at% Sb, transforms completely into the amorphous state upon heating to 350 K at ambient pressure. Both the amorphization and the subsequent crystallization of the phase are multi-step processes. The structures of a-GaSb produced by solid state amorphization in the present work and by sputtering [5] were shown to be nearly identical. It is suggested that chemical order of the bulk sample is higher than that of the sputtered film.

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