JOURNAL OF MATERIALS SCIENCE 30 (1995) 443–446

Preparation of a new class of semiconductors: bulk amorphous tetrahedral solid solutions $Ge_{1-X}(GaSb)_X$

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A new method of preparation of bulk amorphous solids is successfully applied to the semiconductor solid solutions $Ge_{1-X}(GaSb)_X$. The method consists in the solid-state disordering of a high-pressure phase on decompression. Large mutual solubility can be achieved for high-pressure phases of Ge and GaSb. Amorphization of metallic solid solutions occurs on decompression even at room temperature. Some data concerning the structure and stability of the amorphous semiconducting solid solutions a-$Ge_{1-X}(GaSb)_X$ are presented.

1. Introduction

At present one can prepare amorphous tetrahedrally bonded semiconductors (Si, Ge, $A^{III}B^{V}$, $A^{II}B^{VI}$) only in the form of thin films ($d \leq 10^{-3}$ mm) by sputtering or evaporation methods [1]. The intensive investigation of such substances is connected both with pure fundamental scientific interest in topologically disordered covalent-bonded materials [1, 2] and with the extremely wide prospects for their technical applications [1]. Recently, new electronic materials in the form of amorphous semiconducting films of solid solutions, $Ge_{1-X}(GaSb)_X$, were obtained using evaporation with simultaneous ionization [3]. It should be noted that it is difficult to obtain enough chemically homogeneous amorphous solid solution by such a method [3]. On heating, homogeneous amorphous films crystallize to supersaturated crystalline solid solutions $Ge_{1-X}(GaSb)_X$ over the whole concentration range [3]. The decay of these solutions occurs on subsequent heating. One can mention that at normal pressure the system Ge–GaSb forms a diagram of eutectic type with small mutual solubility in the solid state (up to 2 mol% Ge in GaSb and up to 8 mol% GaSb in Ge) and a eutectic point at 40 mol% Ge at 630 °C [4].

In films of metastable supersaturated solid solutions the order–disorder transition from diamond-like structure to sphalerite-like structure at $X_{Ge} \simeq 40$ mol% occurs if we allow a change of concentration [5]. Numerical evaluation predicts that the electronic gap in these solutions has a minimum at 40 mol% Ge [6].

Usually amorphous films of tetrahedrally bonded semiconductors are obtained in rather non-equilibrium conditions (low temperatures, high degree of ionization etc.); it is thus not clear which of the properties of the films are connected with the method of preparation, influence of substrate etc., and which of them are defined by the internal characteristics of the amorphous network.

Recently a new method of making bulk amorphous samples of semiconductors (Si, Ge, GaSb etc.) using the decompression of high-pressure phases was developed [7, 8]. The share of the amorphous phase was 90–95% for GaSb and 40–70% for Si and Ge. To diminish the portion of the crystalline component in the amorphous samples obtained, one can

(i) decrease the temperature at which the decompression takes place
(ii) increase the decompression rate on
(iii) retard the diffusion processes in the high-pressure phase by introducing some portion of defects or dissolved atoms.

The inverse transition in solid solutions should also be retarded.

The high-pressure phases GeII and GaSbII have similar structures (β-Sn type) and a metallic type of bonding [9], so enhancement of the range of stability of solid solutions between these phases may occur. One can hope to obtain amorphous semiconducting alloys using the decompression of metallic solid solutions. In the present work the method of high-pressure solid-state amorphization was applied to prepare new materials, namely bulk amorphous semiconducting solid solutions $Ge_{1-X}(GaSb)_X$.

2. Experimental procedure

To obtain high pressure in the range 1–10 GPa we used a toroid-type high-pressure chamber [10] which was calibrated on the basic of the phase transitions in Bi (2.55, 2.7, 7.7 GPa) and Sn (9.6 GPa). Cylindrical samples of polycrystalline alloys $Ge_{1-X}(GaSb)_X$ ($0 < X < 1$) 1.5–3 mm height and 2–4 mm in diameter were inserted into containers made of NaCl or graphite. The heater was made of graphite or Ni. The samples were heated under pressure up to 400–1100 °C by passing an alternating current through the heater or through the sample itself to obtain homogeneous alloys with the maximum content of the solid solution. The heating rate was about 10 k s^{-1} and the cooling rate 500 K s^{-1}. The thermocouple was placed near the heater. The rate of decompression was $\sim$ 1 GPa min^{-1}.

The resistance of the sample was determined from the I–V characteristics of the current which was passed through it. The phase and structural analysis of the synthesized material was carried out by X-ray diffraction in an RKU-114 (CuK_α) chamber and with a DRON-3 diffractometer (MoK_α). A Derivatograph-C (MOM, Hungary) was used for the calorimetric measurements. The amount of tested material was in the range 1–20 mg and the heating and cooling rates were in the range 0.05–20 K min^{-1}. The calibration of the calorimetric measurements apparatus is described elsewhere [11].

3. Results

On increasing the pressure up to 8–8.5 GPa and subsequent heating, two jumps of resistivity were observed: the first decrease of resistivity is connected with the transition GaSbI → GaSbII, and the second one with the formation of metallic solid solutions. It should be mentioned that the metallization of pure GeI phase can occur at pressures higher than 9 GPa and upon heating of GeI, no resistivity jumps were observed at 8-8.5 GPa up to the melt. From the resistivity data obtained one can suppose that the homogeneous metallic phase is formed at pressure $P = 8$ GPa and $T > 400\,^\circ$C in a wide range of Ge concentration in Ge_{1-X} $(\mathrm{GaSb})_X$ alloys $(0.3 < X < 1)$. For $X < 0.3$ it is necessary to reach a pressure $p \simeq 8.5$–9 GPa to obtain the metallic phase. Thus a metallic solution is the stable phase at $P \simeq 8$ GPa for $0.3 < X < 1$, while for $X < 0.3$ the range of stability of solid solutions Ge_{1-X} $(\mathrm{GaSb})_X$ lies at higher pressures of $P \geq 8.5$–9 GPa. Such behaviour of the pressure for metallization of a solid solution is consistent with the concentration behaviour of the semiconducting gap [6].

At decompression of the metallic phase the amorphous state is obtained in the range $0.12 < X < 1$. The amorphous phase contains no crystalline component for $0.12 < X < 0.75$ (Fig. 1, curve A). For $0.06 < X < 0.12$ the mixture of solid solutions GeIV⟨GaSb⟩ and GeV⟨GaSb⟩ was produced, while for $0 < X < 0.06$ the solid solution GeIII < GaSb > was obtained (Fig. 2). GeIII (tetragonal, $a = 0.580$ nm, $c = 0.663$ nm, $Z = 12$) is a well-known metastable semiconducting phase of Ge. GeIV is the metastable phase which earlier was produced only on decompression of the GeII high-pressure phase at low temperatures of $T \simeq 150$–200 K [12]; it has a b.c.c. structure ($a = 0.697$ nm, $Z = 16$) similar to the SiIII phase. The GeV phase has a lonsdeylit-type structure ($a = 0.394$ nm, $c = 0.665$ nm, $Z = 8$) and it was obtained earlier during the indenting of thin Ge films [13]. Very recently the GeV phase was produced on heating (350–400 K) of the GeIV phase [7]. One can suppose that some share of GeIV-based solid solution transforms to GeV-based solid solution at room temperature over a few hours, so that X-ray diffraction reveals a mixture of these phases.

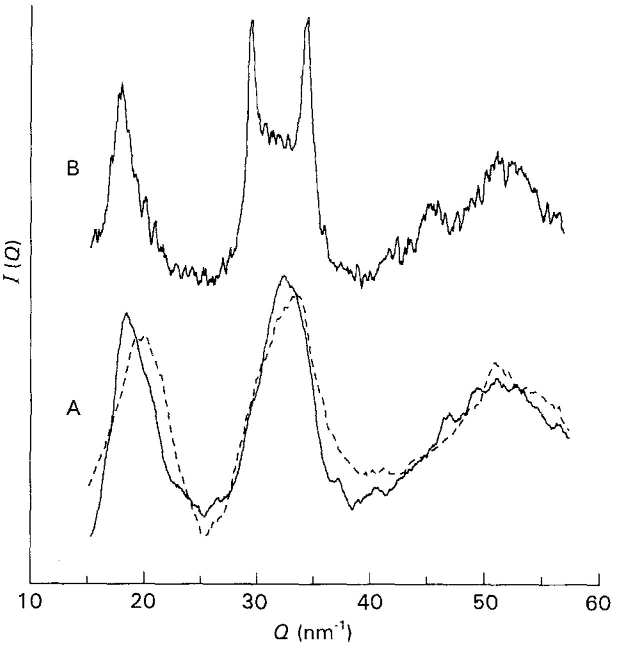

Figure 1 X-ray diffraction patterns for amorphous solid solutions Ge_{1-X} $(\mathrm{GaSb})_X$: (A) pure amorphous samples at (——) $X = 0.57$ and (– – –) $X = 0.14$; (B) amorphous phase with crystalline impurity for GaSb ($X = 1.0$).

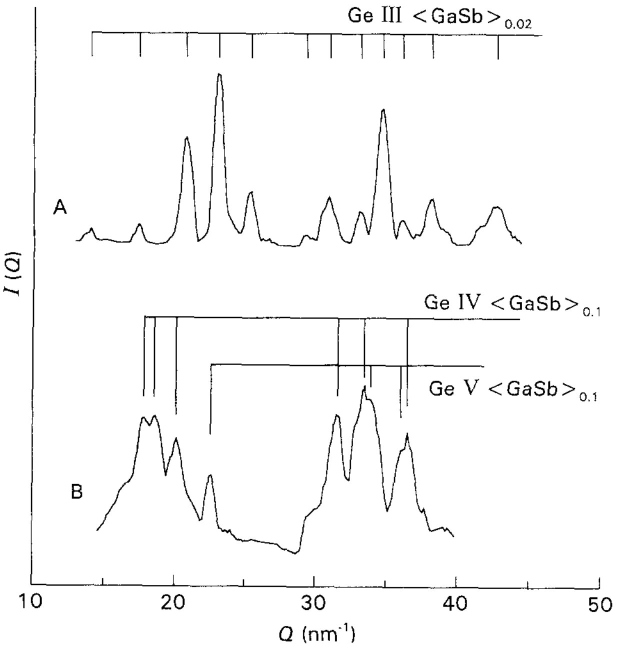

Figure 2 X-ray diffraction patterns for different crystalline metastable Ge⟨GaSb⟩ alloys: (A) GeIII$\langle\mathrm{GaSb}\rangle_{0.02}$ phase (crystallographic indices of visible selected peaks are 1 0 1, 1 1 1, 1 0 2, 2 0 1 + 1 1 2, 2 2 1, 1 0 3 + 2 2 0, 1 1 3, 3 0 1, 2 1 3 + 2 2 2, 2 2 3, 3 2 0 and 3 0 3 + 4 0 0 + 3 1 3); (B) a mixture of GeIV$\langle\mathrm{GaSb}\rangle_{0.1}$ (the peaks 1 2 1, 1 2 3 and 4 0 0 are indicated) and GeV$\langle\mathrm{GaSb}\rangle_{0.1}$ (the peaks 1 0 0, 0 0 2, 1 0 1, 1 1 0, 1 0 3 and 1 1 2 are indicated).

Experimental data concerning the types of phase produced and the pressure of the corresponding transition are presented in Table I. On heating, the metastable Ge_{1-X} $(\mathrm{GaSb})_X$ phases transform to more stable phases (Table II). The concentration dependencies of the crystallization temperatures of amorphous samples, both those obtained in the present work

TABLE I Concentration dependencies of the transition pressure and types of phase obtained on decompression of $\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ high-pressure alloys at $T = 300$ K.

X_{GaSb} (%)	P_{tr} (GPa)	Type of phase produced
0	8.0	GeIII ($a = 0.580$ nm, $c = 0.663$ nm)
0.02	–	GeIII⟨GaSb⟩ ($a = 0.582$ nm, $c = 0.665$ nm)
0.04	7.1	GeIII⟨GaSb⟩ ($a = 0.583$ nm, $c = 0.667$ nm)
0.06	–	GeIV⟨GaSb⟩ ($a = 0.702$ nm) + GeV⟨GaSb⟩ ($a = 0.397$ nm, $c = 0.660$ nm)
0.08	–	GeIV⟨GaSb⟩ ($a = 0.705$ nm, + GeV⟨GaSb⟩ ($a = 0.398$ nm, $c = 0.663$ nm)
0.1	5.8	GeIV⟨GaSb⟩ ($a = 0.707$ nm) + GeV⟨GaSb⟩ ($a = 0.400$ nm, $c = 0.665$ nm)
0.12–0.60	2.0–3.2	Amorphous Ge-based phase
0.60–1.0	1.8–2.0	Amorphous GaSb-based phase
± 0.01	± 0.3	

TABLE II Transformation of metastable Ge–GaSb phases on heating at normal pressure

Initial phase	Phase obtained	T_{cryst} (K)	Q (kJ mol^{-1})	E_{act} (kJ mol^{-1})
GeIII⟨GaSb⟩	GeI⟨GaSb⟩	550–600	8	160
GeIV⟨GaSb⟩	GeV⟨GaSb⟩	330–370	2–4	90
GeV⟨GaSb⟩	GeI⟨GaSb⟩	750–800	–	–
a-$\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ ($0.12 < X < 0.6$)	C-$\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$, solid solutions of GeI and GaSbI	650–750	10–12	300–400
a-$\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ ($0.6 < X < 1$)	c-$\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$, solid solutions of GeI and GaSbI	500–650	12–18	160–350
c-$\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$	GeI + GaSbI	800–900	2–6	–
		± 30	± 1.5	± 30

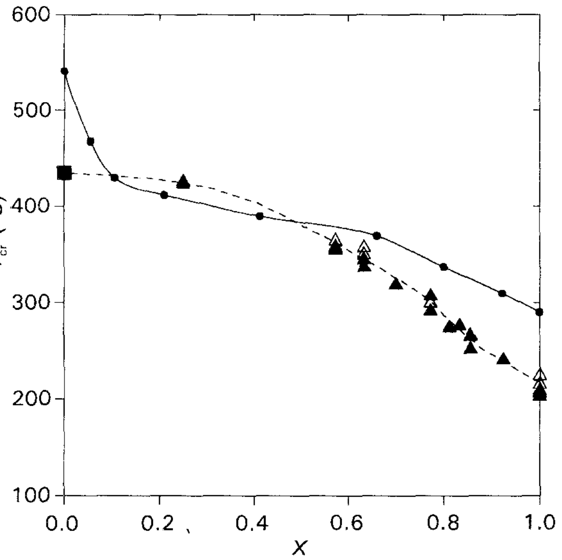

Figure 3 Concentration dependencies of crystallization temperature T_{cr} of a-$\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ samples (defined by the position of the maximum heat release peak on isochronal annealing) for ●-(——) thin films ([3], $\dot{T} = 5$ K min^{-1}) and (– – –) bulk samples (present data, $\dot{T} = 20$ K min^{-1}). The a-$\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ alloys were prepared at different temperatures T_{p} under high pressure: (△) $T_{\mathrm{p}} = 400$ °C, (▲) $T_{\mathrm{p}} = 1100$ °C. (■) Bulk amorphous Ge samples [7].

and corresponding data for films prepared by evaporation [3], are presented in Fig. 3. A good accordance between these data is seen at intermediate concentrations. For $X \to 0$ and $X \to 1$ the crystallization temperatures of the bulk samples are lower. This can obviously be connected with the influence of crystalline impurities in bulk samples on the crystallization kinetics.

A detailed analysis of the short-range order structure and calorimetric data for bulk amorphous solid solutions $\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ ($X > 0.55$) has been presented elsewhere [14]. Recently [5] it was found that the crystalline solid solutions $\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ have sphalerite-like correlations at $X > 0.6$ (GaSb-based structure) and diamond-like structure at $X \leq 0.6$. If we suppose that such a classification holds in amorphous solutions, one can conditionally subdivide the bulk amorphous samples obtained into two groups (see Table II). GaSb-rich amorphous samples at $X > 0.75$ have crystalline impurities of GaSb (~ 10 vol%, see Fig. 1 curve B). As mentioned above, Ge-rich solid solutions can be obtained in a pure amorphous state.

Bulk amorphous $\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ samples have a large electroresistance ($\sim 10\,\Omega$cm for $X = 1$ up to $10^5\,\Omega$cm for $X \simeq 0.2$–0.3 at $T \simeq 300$ K). These values are close to ordinary data for thin Ge-based amorphous films. A detailed description of the electrophysical properties of $\mathrm{Ge}_{1-X}(\mathrm{GaSb})_X$ for $X > 0.55$ was presented elsewhere [14].

4. Discussion

The method of solid-state amorphization of high-pressure phases is connected with the slow kinetics of phase transitions under high pressure at low temperatures [15]. At some decompression rates a metastable high-pressure phase can approach the P–T region of mechanical lattice instability [16]. A high-pressure phase becomes unstable in the course of transition to a stable one; however, the growth of crystalline phases is retarded and transformation to a disordered state occurs. At high temperatures the usual crystal–crystal transition takes place, while in the intermediate temperature region mixed crystal and amorphous material is formed after transformation. Such a "mixture regime" was obviously realized in the case of amorphization of pure Si, Ge and GaSb [7, 8]. If the "high pressure" phase has a composition which does not correspond to any "normal pressure" single phase, the transition should involve significant diffusion processes and amorphization is facilitated [15].

One can suppose that GaSb and Ge in "high pressure" forms have a better mutual solubility than in the semiconducting "low pressure" state. This may be explained by the difference in the types of bond in the metallic and semiconducting states. The covalent bonds are more "rigid" and distortion in the diamond or sphalerite structure in Ge–GaSb solid solution should result in higher stresses than those occurring in the metallic phase (β-Sn structure).

The transitions from the high-pressure phase GeII to crystalline phases GeI, GeIII and GeIV involve complicated atomic reconstruction and activation processes [17]. One can suppose that in Ge-rich solid solutions such transitions may be retarded. In addition, solid solutions based on GeIII and GeIV phases can become unstable at large enough concentrations of dissolved substance. This can facilitate the amorphization of the solid solution.

Thus, using the decompression of high-pressure phases one can obtain bulk amorphous semiconducting solid solutions. The dimensions of the samples produced are limited only by the capacity of the high-pressure chamber (such pressures can now be easily reached in a volume 2 cm × 2 cm × 2 cm). Preliminary data obtained in our group confirm that amorphization can be reached in the same way in $\mathrm{Ge}_{1-X}(\mathrm{InSb})_X$, $\mathrm{Ge}_{1-X}(\mathrm{InP})_X$ and $\mathrm{GaSb}_{1-X}(\mathrm{InSb})_X$ solid solutions. The detailed investigation of the amorphization of these substances will be presented in due course.

Subsequent investigation of the bulk amorphous samples and comparison of their properties with the properties of thin films is needed. Investigation of the mechanical properties and investigation of static and dynamic structure by means of neutron diffraction can only be made using bulk samples. That is why high-pressure solid state amorphization seems to be a very promising method of preparing amorphous solids.

Acknowledgements

This work was supported in part by a Soros Foundation Grant awarded by the American Physical Society. The authors are grateful to Dr S.V. Demishev for useful discussions.

References

1. M. H. BRODSKY (ed), "Amorphous Semiconductors" (Springer, Berlin, 1979) pp. 1–9.
2. N. F. MOTT and E. A. DAVIS, "Electron Processes in Non-crystalline Materials" (Clarendon Press, Oxford, 1979) pp. 1–7.
3. K. C. CADIEN, B. C. MUDDLE and J. E. GREENE, *J. Appl. Phys.* **55** (1984) 4177.
4. M. B. PANISH, *Proc. Electrochem. Soc.* **113** (1966) 626.
5. S. I. SHAH, B. KRAMER, S. A. BARNETT and J. E. GREENE, *J. Appl. Phys.* **59** (1986) 1482.
6. L. C. DAVIS and H. HOLLOWAY, *Solid State Commun.* **64** (1987) 121.
7. V. V. BRAZHKIN, A. G. LYAPIN, S. V. POPOVA and R. N. VOLOSHIN, *Pis'ma Zh. Ekp. Teor. Fiz.* (in Russian) **56** (1992) No. 3, 156 (JETP Lett. **56** (1992) 152).
8. S. V. DEMISHEV, YU. V. KOCICHKIN, A. G. LYAPIN, N. E. SLUCHANKO, M. M. ALEXANDROVA, V. I. LARCHEV, S. V. POPOVA and G. G. SCROTSKAYA, *J. Non-Cryst. Solids* **97/98** (1987) 1459.
9. E. YU. TONKOV, "High Pressure Phase Transformations" (Gordon and Breach, Philadelphia, 1992) pp. 414–426.
10. L. G. KHVOSTANCEV, L. F. VERESCHAGIN and A. P. NOVIKOV, *High Temp. High Press.* **9** (1977) 637.
11. V. V. BRAZHKIN, S. V. POPOVA and R. N. VOLOSHIN, *J. Non-Cryst. Solids* **136** (1991) 241.
12. C. H. BATES, F. DACHILLE and R. ROY, *Science* **147** (1965) 860.
13. V. G. EREMENKO, *Sov. Phys. Solid State* **17** (1975) 1647.
14. V. V. BRAZHKIN, S. V. DEMISHEV, YU. V. KOCICHKIN, D. G. LUNTS, A. G. LYAPIN, S. V. POPOVA, N. E. SLUCHANKO and S. V. FROLOV, *Zh. Ekp. Teor. Fiz.* (in Russian) **104** (1993) 3126 (*JETP* **77** (3) (1993) 465).
15. E. G. PONYATOVSKY and O. I. BARCALOV, *Mater. Sci. Rep.* **8** (1992) 1471.
16. N. BINGGELI and J. R. CHELIKOWSKY, *Phys. Rev. Lett.* **69** (1992) 2220.
17. V. D. BLANK, Z. V. MALUSHITSKAYA and B. A. KULNITSKII, Proceedings of the XXXth Annual Meeting of European High Pressure Research Group, Baku, 1992, *Fizika i technika visokih davlenii* (the Ukraine) **3** (1993) No. 2, 28 (in English).

Received 23 August 1993
and accepted 16 June 1994