Nature of Semiconductor-to-Metal Transition and Volume Properties of Bulk Tetrahedral Amorphous GaSb and GaSb-Ge Semiconductors under High Pressure

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Electrical properties and compressibility of bulk amorphous semiconductors a-$(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ (x = 0 and 0.27) were investigated at high pressure. Discontinuous crystallization of a-$(\mathrm{GaSb})_{0.73}(\mathrm{Ge}_2)_{0.27}$ occurs at 4.7 GPa. In a-(GaSb) the continuous volume anomaly occurs at 3–7 GPa, whereas the semiconductor-to-metal transition occurs at 3–4 GPa. Metallization of a-(GaSb) occurs by the percolation mechanism involving interaction of nanoregions with higher coordination. Bulk moduli of amorphous compounds at normal pressure are less (35 and 40 GPa for $x = 0$ and 0.27, respectively) than that of crystalline (GaSb) (55 GPa) and exhibit strong softening long before the transitions.

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The application of pressure to amorphous semiconductors often results in a drastic change of their electrical properties. For example gradual decrease of semiconducting gap and finally metallization occur in chalcogenide glasses $\mathrm{As}_2X_3(X = \mathrm{S, Se, Te})$ in the pressure range 10–20 GPa [1]. This process does not involve any significant structure reconstruction and is thought to be due to Anderson type electron delocalization [1]. On the other hand, discontinuous metallization takes place in a-Se [2], a-$\mathrm{Ge}_x\mathrm{Te}_{1-x}$ [3], a-Ge [4], and some other amorphous semiconductors. This phenomenon is connected with crystallization of amorphous phase. Otherwise the information on the properties of amorphous tetrahedrally bonded semiconductors ($\mathrm{Si, Ge}, A^{\mathrm{III}}B^{\mathrm{V}}$, and $A^{\mathrm{II}}B^{\mathrm{VI}}$ compounds) under pressure is rather scanty and sometimes contradictory [4–7]. Metallization of amorphous tetrahedral semiconductors is usually considered to be connected either with structural reconstruction (amorphous semiconductor to crystalline state or to metallic glass) or with Anderson-like electron transition. Up to date, most of all investigations of these materials were made using thin films. Recently [8–10] the new method of preparation of bulk amorphous samples of some tetrahedral semiconductors (GaSb, Ge, Si, GaSb-Ge) using solid state amorphization [11] of high-pressure phase was developed. This offers the study of different bulk properties which are very important for understanding the nature of semiconductor-to-metal transition in bulk amorphous materials under high pressure.

The purpose of the present work was to investigate semiconductor-to-metal transition in bulk amorphous GaSb and GaSb-Ge samples under high hydrostatic pressure and to obtain quantitative information about the volume change during this transition. It should be mentioned that bulk amorphous GaSb does not crystallize at room temperatures at least up to 6 GPa [12].

The bulk samples of amorphous GaSb and GaSb-Ge were prepared by the method described earlier [8] but with lower temperature of annealing under pressure ($T <$ 700 K). The amorphous nature of the samples was confirmed by x-ray diffraction, high resolution electron microscopy, and calorimetric investigations. A "toroid" device [13] was used to prepare samples and to study them under pressure. The preparation procedure includes NaCl as a quasihydrostatic pressure transmitting medium. In this case toroid device was calibrated by the resistivity jumps in Bi (2.55; 2.7; 7.7 GPa) and Sn (9.6 GPa). Measurements of electrical resistivity were performed both in quasihydrostatic (NaCl) and hydrostatic (4:1 methanol-ethanol) pressure transmitting media by a four-probe method. The compressibility at hydrostatic pressure up to 9 GPa was investigated by means of the strain gauge technique developed earlier [14]. In this technique the resistive strain gauge is bonded to the sample with an epoxy or another glue and allows us to measure linear strain under pressure. The strain gauges were calibrated up to 9 GPa using Decker equation of state for NaCl.

It's worth mentioning now that until recently only few papers dealt with the volume measurements on amorphous substances in the pressure range ~10 GPa. Volume measurements in a piston-and-cylinder type piezometer are usually restricted by the limit ≈3 GPa, and researchers developed optical methods for studying linear strain of the samples placed in a transparent diamond anvil cell. Amorphous selenium [2] and silica glasses [15] were studied by this method. The strain gauge technique is very promising in this field owing to its precision and relative simplicity.

Hydrostatic pressure was created inside the teflon container placed in the compressible gasket of the toroid device and measured by the calibrated manganin gauge. All measurements were made near room temperature. The rate of the pressure change was in the range 0.05–0.5 GPa/min. The structure of the samples after high pressure treatment was tested by x-ray diffraction.

The typical pressure dependences of resistivity for a-GaSb samples both at hydrostatic and quasihydrostatic environments are presented in Fig. 1 (curve 1 and 2). In

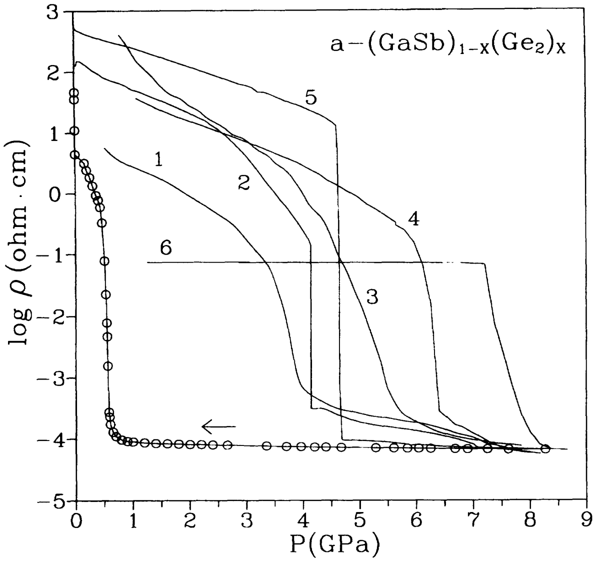

FIG. 1. Resistivity of amorphous a-$(GaSb)_{1-x}(Ge_2)_x$ alloys vs quasihydrostatic (1, 3, 4) and hydrostatic (2, 5) pressure. 1 and 2 correspond to a-GaSb ($x = 0$); 3 and 5—$x = 0.27$; 4—$x = 0.75$. 6—resistivity of single crystalline sample. For curve 5 the data corresponding to the pressure release (○) are also presented.

the case of a-GaSb measurements were made at quasihydrostatic pressure with the use of pressed contacts as at hydrostatic pressure—using high conductive glue. The transition of a-GaSb to metallic state occurs at $P \approx 3-4$ GPa in both cases, that is lower than the pressure of GaSb I → GaSb II transition in single crystal (7.4 GPa). The value of the pressure of semiconductor-to-metal transition in a-GaSb is in good accordance with previous data for thin films [7]. The resistivity in metallic state of a-GaSb at $P = 4.5$ GPa is an order of magnitude higher than that of GaSb II high-pressure metallic phase (see Fig. 1, curve 1 and 2). Subsequent increase of pressure up to 8 GPa leads to the decrease of the resistance to values very close to those of GaSb II. There is some difference between hydrostatic and quasihydrostatic data. At quasihydrostatic pressure metallization occurs smoothly, and in hydrostatic conditions the resistivity decrease consists of two parts: smooth change and sharp drop.

Resistivity of germanium substituted gallium antimonide a-$(GaSb)_{1-x}(Ge_2)_x$ at low Ge concentrations ($x \leq 0.54$) exhibits smooth behavior under quasihydrostatic pressure (Fig. 1, curve 3). At high Ge concentrations a-$(GaSb)_{1-x}(Ge_2)_x$ samples transform to metallic state more sharply (Fig. 1, curve 4). At hydrostatic environment a-$(GaSb)_{1-x}(Ge_2)_x$ samples show discontinuous metallization (Fig. 1, curve 5). The resistivity drops 5 orders of magnitude in a very narrow pressure interval $\Delta P = 5$ MPa. This process looks like discontinuous crystallization observed earlier in a-Se and a-Ge [2,4]. The difference between hydrostatic and quasihydrostatic data may be interpreted if we take into account that pressure gradients encourage the continuous relaxation of internal stresses which can be a possible starting mechanism of discontinuous transition at hydrostatic pressure. The difference between the resistivity levels for the amorphous samples with the same compositions at normal pressure is defined by the fluctuations of preparation conditions. The short-range structure and the stability of these samples are quite similar, as the transport properties may significantly differ [8].

It should be mentioned that the reverse transition in a-GaSb starts at pressure depending on the maximum pressure achieved. The hysteresis is $\Delta P \approx 0.5$ GPa at $P_{\max} = 4.5$ GPa and $\Delta P \approx 2.5$ GPa at $P_{\max} = 8$ GPa. The samples after releasing pressure conserve the amorphous tetrahedrally bonded structure. The reverse transition in a-$(GaSb)_{1-x}(Ge_2)_x$ ($x = 0.27$) starts at $P = 0.6$ GPa and slowly goes at fixed pressure. The resistivity of the sample continues to rise at normal pressure. This rise may be an indicator of gradual amorphization of the sample which starts at $P = 0.6$ GPa and occurs for a long time.

Volume measurements are very important to make a more reliable conclusion for the mechanism of semiconductor-to-metal transition in a-GaSb in comparison with that in GaSb-Ge. Figure 2 shows the relative volume vs pressure dependences for crystalline and amorphous GaSb and GaSb-Ge samples. One can note that crystalline and amorphous samples of the same

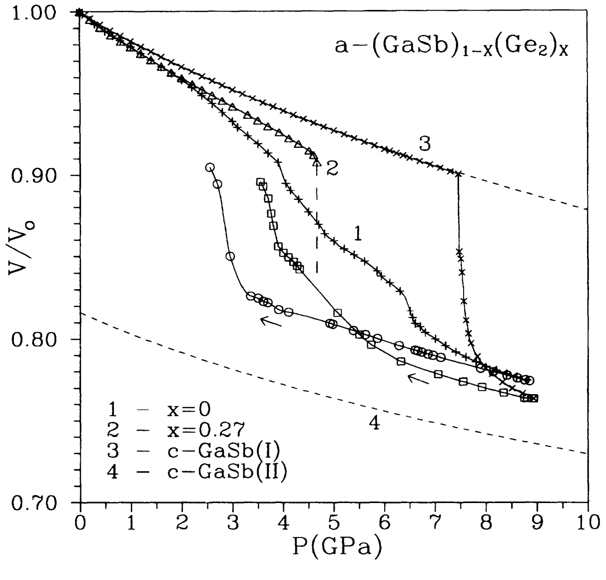

FIG. 2. Relative volume change of amorphous a-$(GaSb)_{1-x}(Ge_2)_x$ alloys and crystalline GaSb vs hydrostatic pressure. Dashed lines—x-ray data [16], using Birch equations for GaSb I (continuation of 3) and GaSb II (4) phases. (+, ×, △)—increase and (○, □)—decrease of pressure. The error value is less than the symbol size.

compositions have the similar density (the difference is less than 3%).

Our data for crystalline GaSb I (initial sample is a single crystal) are in excellent agreement with the Birch equation of state fit of x-ray data [16]. The transition GaSb I → GaSb II starts at $P = 7.4$ GPa as moderately fast (for a few seconds) 5% drop of volume. In the pressure range 7.4–9 GPa the relative volume has strong pressure and time dependence owing to the kinetics of I → II transition. At the maximum pressure attained in our experiment (9 GPa) the transition is not completed and $\approx 15\%$ of GaSb I coexists with GaSb II as can be seen from comparison of our strain gauge data and x-ray data [16]. The reverse transition GaSb II → GaSb I seems to start at 5.7 GPa and goes rather rapidly at $P \leq 4$ GPa (Fig. 2). The typical uncertainty of the volume measurements by the strain gauge technique is about 3% of the maximum volume change [14].

Relative volume of a-$(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ ($x = 0.27$) changes smoothly up to 4.7 GPa (Fig. 2, curve 2). At this pressure a sudden drop of volume takes place, indicating pressure induced phase transition. The process is so fast ($\tau \leq 0.1$ sec), that the bonding layer of glue between the sample and the strain gauge is disturbed and no quantitative data can be obtained at $P > 4.7$ GPa. This volume drop was observed for all samples of this composition. Since the final volume after transition is unknown the curve 2 on Fig. 2 is interrupted. Pressure inside the teflon cell drops during time τ by the value $\Delta P \approx 0.1$ GPa. Taking into account the sample and cell dimensions and ΔP value one can evaluate the volume change at the transition $\Delta V/V \approx 20\%$. Obviously the spontaneous crystallization of a-$(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ ($x = 0.27$) to GaSb II-like structure takes place at $P = 4.7$ GPa, what confirms the resistivity data.

It was very interesting to compare volume behavior under hydrostatic pressure for a-GaSb and the germanium substituted one. Relative volume vs pressure curve for a-GaSb is shown in Fig. 2 and exhibits a region of anomalous compression in the pressure range ≈ 3–7 GPa. Nevertheless, the volume change in a-GaSb is continuous and no fast crystallization takes place. The total volume change for bulk amorphous GaSb at $P = 9$ GPa is very close to that for crystalline GaSb. This fact gives strong support to interpretation of semiconductor-to-metal transition in a-GaSb as a continuous process of change of the average nearest-neighbors coordination from $Z = 4$ (as in GaSb I) to $Z = 6$ (as in GaSb II). In the pressure range 3–7 GPa the compression is to some extent irregular and kinetically dependent. For example, compressibility near 4 and 6.5 GPa (Fig. 2, curve 1) is higher than the average value in the region of transition. One can note that a possibility of continuous coordination change in amorphous materials during compression has been documented earlier for silica glass [17–19].

Using these data one can conclude that metallization of a-GaSb cannot be explained as Anderson delocalization. On the other hand, a sharp transformation amorphous semiconductor → dense metallic phase does not take place either. The main change of electrical resistivity of a-GaSb (which can be considered as a dielectric phase) takes place at pressure range 3.0–4.1 GPa. At $P = 4.1$ GPa the volume change owing to the transition to the metallic phase is about 20% of the total value of volume anomaly observed in a-GaSb in the pressure range ≈ 3–7 GPa (Fig. 2). From percolation considerations the metallic level of macroscopic conductivity appears in random mixture of dielectric and metallic phases at $\approx 17\%$ of the metallic phase. Thus the volume data are in accordance with percolation mechanism of metallization in a-GaSb at high pressure.

In amorphous substances atomic level microstresses connected with fluctuations of interatomic distance and interbond angles lead to inhomogeneous compression reaction of atomic configurations of different types. Under high pressure the topology of more high stressed atomic configurations can gradually transform to a more close packed state. We believe the pressure application to a-GaSb leads to the formation of nanoregions (few coordination spheres) with $Z \sim 6$. At subsequent pressure increase these regions grow and interact with an amorphous matrix and each other. The metallization of a sample obviously corresponds to the percolation through these clusters with higher coordination. Further growth and mutual interaction of the metallic nanoregions leads probably to an appearance of microcrystallites of high pressure GaSb II phase. The x-ray experiments [12] made on bulk a-GaSb samples showed the presence of crystalline GaSb II phase at $P \approx 7$ GPa.

The pressure dependences of bulk moduli for a-$(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ and crystalline GaSb I are shown in Fig. 3. At normal pressure the bulk moduli of amorphous

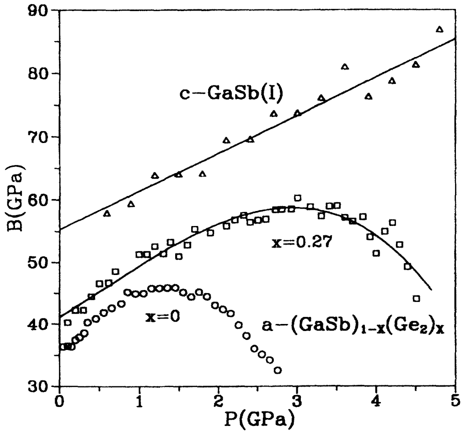

FIG. 3. Bulk modulus of amorphous a-$(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ alloys and crystalline GaSb vs hydrostatic pressure.

compounds are less (35 and 40 GPa for $x = 0$ and 0.27, respectively) than that of crystalline GaSb (55 GPa). No data are available in literature on the bulk modulus of a-GaSb. Before the present work the bulk moduli of amorphous tetrahedrally bonded semiconductors were evaluated only for a-Ge films from extended x-ray absorption fine structure (EXAFS) data [20] and using a low frequency sound velocity technique [21]. Whereas the sound velocity measurements gave the 40% decrease of modulus for amorphous state, the EXAFS shows 30% increase. Note that the EXAFS data allow us to calculate the pressure dependence of average interatomic distance between nearest neighbors and consequently the bond bulk modulus. As has been mentioned above, in amorphous solids the gradual increase of the average coordination number is possible during compression. The average bond-length in this case may weakly decrease or even increase. This could easily produce a large positive or even negative bulk modulus for the nearest-neighbor bond distance, yet the actual macroscopic bulk modulus would still be positive and in accord with the velocity data.

Pressure dependences of bulk moduli for a-$(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ (Fig. 3) display rather complicated behavior. At low pressure the bulk modulus of an amorphous compound rises, which is the normal reaction of a compressible solid to an external pressure. But the strong softening of modulus begins at 1.5 GPa for a-GaSb and 3 GPa for a-$(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ ($x = 0.27$) long before semiconductor-to-metal transition. This softening indicates the processes of gradual changes of average coordination.

The values of the pressure derivative of bulk modulus $B' = dB/dP$ at low pressure are higher for a-$(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ ($B' \approx 10$) than that of crystalline GaSb (≈ 6). More fast hardening of moduli for amorphous materials at low pressure may be interpreted as closure of microvoids.

As a conclusion the metallization observed under high pressure in bulk amorphous tetrahedrally bonded GaSb and GaSb-Ge semiconductors has a percolation nature. The conductive conglomerate of microregions with higher coordination ($Z \sim 6$) seems to be formed in a lower coordinated ($Z = 4$) amorphous matrix at an increase of pressure. This process, depending on germanium content, nonhydrostatic stresses, and temperature, can proceed as very fast crystallization at certain pressure or continuously in a wide pressure range. At the final stage of the continuous process the microregions with higher coordination obviously grow and become crystalline. The question still remains unsolved on the size and nature of nanoregions with higher coordination at the intermediate stages of continuous transition (3–7 GPa for a-GaSb), but it should be the subject of further structural investigations.

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