Amorphization from the Quenched High-Pressure Phase in III-V and II-VI Compounds

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The temperature dependences of phase transitions in GaSb, AlSb, GaAs, GaP, InAs, InP, ZnSe, and CdTe are studied by X-ray diffraction measurements under pressure up to 30 GPa at temperatures of 90-300 K. The phase transitions depend on paths in a pressure-temperature phase diagram. The structure of the recovered phase after decompression depends on the ionicity in bonding: amorphous for small ionicity, the stable zincblende structure for large ionicity, and microcrystalline for moderate ionicity. These results are discussed by using a configuration-coordinate model.

[amorphization, low temperature, synchrotron radiation, X-ray diffraction, phase transition]

1. Introduction

Recently many investigations of pressure-induced amorphizations have been made. There are two types of pressure-induced amorphization. One is an amorphization from the low-pressure phase during the pressurizing process and the other is an amorphization from the quenched high-pressure phase on decompression. The former has been reported for SiO₂, SnI₄, etc.[1, 2], and the latter has been reported for Si, Ge, GaAs, etc. [3-6].

The amorphization in Si and Ge has been reported by Imai et al.[4]. In Si and Ge, the phase transitions from the quenched high-pressure phase depend on paths in a pressure-temperature phase diagram. After decompression at low temperature, the high-pressure phase is quenched. On heating at low pressures, a phase transition from the quenched high-pressure phase to an amorphous phase occurs. Both the amorphous phase and the quenched high-pressure phase are thermodynamically metastable. On the phase transition between metastable phases, not only the difference in the free energy but also the potential barrier ΔU which has to be overcome by the thermal energy should be considered. A configuration-coordinate model was applied to interpret the path dependence of the phase transition[4]. In this model, the path dependence of the phase transition arises from the crossing of $\Delta U(P)$'s as shown in Fig.1, where ΔU_{am} and ΔU_{L} indicate the heights of potential barriers from the quenched high-pressure phase to the amorphous phase and that to the low-pressure phase, respectively.

Fig.1. Schematic pressure dependences of potential barrier ΔU (ΔU_{am} : ΔU to the amorphous phase; ΔU_{L} : ΔU to the low-pressure phase)[4].

If the high-pressure phase can be quenched down to the pressures where ΔU_{am} is smaller than ΔU_{L} , the amorphization occurs instead of the phase transition to the stable low-pressure phase. From the temperature of the phase transition, the height of ΔU can be estimated.

The heights of ΔU depend on the bonding strength and the ionicity. Therefore, it is interesting to study amorphizations in several compounds which have different bonding strength and the ionicity. We have studied the path dependences of the phase transitions in GaSb, AlSb, GaAs, GaP, InAs, InP, ZnSe and CdTe from the X-ray diffraction measurements under pressure at low temperatures.

2. Experimental

X-ray diffraction measurements were carried out by an energy-dispersive method using synchrotron radiation from a bending magnet (BL-6C₁) at the Photon Factory, KEK[4].

Crystalline samples were ground into fine powders suitable for diffraction measurements. The mixture of powdered sample and pressure marker (NaCl or KCl) was pressurized using pressure-transmitting medium (4:1 mixture of methanol and ethanol) in a diamond anvil cell. The diamond anvil cell was driven by He gas through bellows. This apparatus allowed us to control the pressure continuously even at low temperatures.

Intensity of X-ray diffraction is composed of the diffraction from the specimen and the scattering from the diamond anvils. The diffraction intensity from the sample was obtained by subtracting the background scattering intensity.

3. Results

In GaAs, with increasing pressure at 300 K, the zincblende (B3) phase transforms to the high-pressure phase at 13-17 GPa. When pressure is decreased from 25 GPa at 300 K, the high-pressure phase is quenched down to 10 GPa. At 10 GPa, the intensity of the peak from the high-pressure phase begins to decrease and new peaks appear. The width of new peak is three times larger than that for the crystalline phase. The peaks are located at the same positions as those for the B3 phase. It indicates that the phase transition occurs from the high-pressure phase to the microcrystalline phase with the B3 structure.

When pressure is decreased from 25 GPa at 90 K, the high-pressure phase is quenched down to 6 GPa. At 6 GPa the

Fig.2. X-ray diffraction patterns from GaAs on heating at 2 GPa (A: phase A which begins to appear at 6 GPa on decompression at 90K; mc: microcrystalline phase; and meta: metastable phase). At $2.5 \text{ \AA}^{-1}$ the peak from the pressure marker is observed.

intensity of the peak from the high-pressure phase begins to decrease and both narrow and broad peaks appear. The peak positions of the narrow peaks are different from those for the B3 phase and the high-pressure phase. This indicates that the phase transition to a metastable crystalline phase begins. The broad peak has a width 10 times larger than that for the crystalline phase, and is located near the peak position for the B3 phase. This phase may be an amorphous phase or a microcrystalline phase with the B3 structure with an extremely small diameter. Hereafter this phase is called phase A. With further decreasing pressure, the intensity of the peak from the high-pressure phase decreases and those for the phase A and the metastable phase increase. At 3 GPa, the other new peak appears. The new peak has a width about four times larger than that for the crystalline phase, and is located at the same position as that for the B3 phase. This peak is considered to arise from the microcrystalline phase with the B3 structure. At 2 GPa, the

Fig.3. Temperature dependences of $1/\text{FWHM}$ of the peak from the phase A and that from the microcrystalline phase with increasing temperature at 2 GPa. Dashed line indicates the results for the crystalline phase for reference.

high-pressure phase disappears completely.

Fig.2 shows the diffraction intensity from GaAs with increasing temperature at 2 GPa. At 90 K, three kinds of peaks from the specimen are seen: a broad peak from the phase A, a narrow peak from the metastable phase, and a narrow peak from the microcrystalline phase with the B3 structure. With increasing temperature, the width of the peak from the microcrystalline phase becomes narrower and the intensity increases, while the intensity of the peak from the metastable phase decreases. On the other hand, neither the width nor the intensity of the peak from the phase A changes. As the reciprocal of the full width at half maximum ($1/\text{FWHM}$) is proportional to the diameter of the microcrystal, the temperature dependences of $1/\text{FWHM}$ are summarized in Fig.3 for the microcrystalline phase and the phase A. The temperature dependences of the intensity are shown in Fig.4. With increasing temperature, the intensity of the peak from the metastable phase decreases while that from the microcrystalline phase increases. These indicate that the phase transition from the metastable phase occurs not to the phase A but to the microcrystalline phase.

Such experiments and analyses were also done for GaSb, AlSb, GaP, InAs, InP, ZnSe and CdTe.

4. Discussion

In GaAs, the broad peak whose width is 10 times larger than that for the crystalline phase appears on decompression at 90 K (phase A in Fig.2). Microcrystalline with an extremely small grain size can also give rise to broad diffraction peaks similar to the amorphous phase. The different temperature dependences of the width and the intensity between the phase A and the microcrystalline phase, however, indicate that the broad peaks are not due to the microcrystalline with an extremely small grain size. Furthermore, comparing the diffraction pattern from the phase A with that from amorphous GaSb (a-GaSb) prepared by a sputtering method[7], we found that the width and the position for the phase A were the same as those for a-GaSb. These indicate the broad peak from the phase A observed in GaAs is not the peak from the microcrystalline with an extremely small grain size but the peak from an amorphous phase.

Let's compare the diffraction patterns for various compounds to see the effect of the bonding character on the phase transition.

Fig.4. Temperature dependences of intensity from the phase A, the microcrystalline phase and the metastable phase with increasing temperature at 2 GPa.

Fig.5 shows the diffraction patterns obtained at 300 K and below 2 GPa after decompression at 90 K and heating below 2 GPa for III-V and II-VI compounds. In Fig.6, $1/\text{FWHM}$ of the main peak is shown as a function of the ionicity[8]. GaSb with a smaller ionicity in bonding shows the amorphous patterns, while ZnSe and CdTe with larger ionicities show the patterns of the stable B3 phase. On the other hand, in InAs and InP which have moderate ionicities, the phase transition to the microcrystalline phase with the B3 structure occurs. The values of ionicity of AlSb, GaAs and GaP are larger than that of GaSb and smaller than that of InAs or InP. In these compounds, the phase transitions to both the amorphous phase and the microcrystalline phase occur.

According to the configuration coordinate model, an amorphization occurs when the high-pressure phase can be

Fig.5. X-ray diffraction patterns obtained at 300 K and below 2 GPa after decompression at 90 K and heating below 2 GPa for GaSb, GaAs, InAs, and ZnSe. The amplitude of the scattering vector Q is scaled to the value of (111) diffraction peak of the crystal with the B3 structure (am: amorphous phase; mc: microcrystalline phase; B3: B3 phase; P: pressure marker; F: fluorescence X-ray).

quenched down to pressures where ΔU_{am} is smaller than ΔU_L . On the phase transition to the B3 phase from the high pressure phase, the change in the bond angle is large. For covalently-bonded materials the change in the bond angle causes a larger increase in the potential energy than that for ionic materials with the spherical Coulomb force. A large ionicity in bonding lowers the energy barrier ΔU . It narrows the pressure region where the high-pressure phase can be quenched. As a result, the phase transition to the stable B3 phase occurs. Strong covalency with a small ionicity in bonding keeps ΔU large. The high-pressure phase can be quenched towards lower pressure. Then ΔU_L and ΔU_{am} may cross. At lower pressures or lower temperatures than the value at crossing point, the amorphization from the quenched high-pressure phase occurs. In the case of the materials with the moderate ionicities, at low temperature the high-pressure phase can be quenched down to

Fig.6. The relation in the tetrahedrally-bonded materials between the ionicity[8] and $1/\text{FWHM}$ of diffraction peak obtained at 300 K and below 2 GPa after decompression at 90 K and heating below 2 GPa (●: amorphous phase; ▲: microcrystalline phase; and ■: B3 phase).

the pressure where ΔU_{am} is almost the same as ΔU_L . Because of a broad distribution of ΔU_{am} , the phase transitions to both the amorphous phase and the B3 phase occur. As shown in Fig.3, the grain size of the B3 phase in the mixture remains small even at 300 K. Below the crystallization temperature, the phase transition from the amorphous phase to the B3 phase does not occur. The amorphous phase around the grains of the B3 phase may prevent crystal growth of the B3 phase. In InAs and InP, the phase transitions to both the microcrystalline phase and the metastable phase occur. In these cases, the metastable phase may also prevent the crystal growth.

On the second compression at 300 K for GaAs, the diffraction intensity of the amorphous phase decreases without the width change, while the intensity of the microcrystalline phase increases with decreasing the width. This fact is also evidence that the amorphous phase is different from the microcrystalline phase.

It is concluded that the amorphization occurs when the high-pressure phase can be quenched down to lower pressures where ΔU_{am} is smaller than ΔU_L . A large ionicity in bonding lowers ΔU 's and obstructs quenching of the high pressure phase to the lower pressure even at low temperatures.

References

- [1] R.J. Hemly, A.P. Jephcoat, H.K. Mao, L.C. Ming and M.H. Manghnani, *Nature*, **334**, 52 (1988).
- [2] Y. Fujii, M. Kowaka and A. Onodera, *J. Phys.*, **C18**, 789 (1985).
- [3] E.G. Ponyatovsky and O.I. Barkalov, *Mater. Sci. Rep.*, **8**, 147 (1992); and references therein.
- [4] M. Imai, T. Mitamura, K. Yaoita and K. Tsuji, *High Pressure Res.*, **15**, 167 (1996).
- [5] J.M. Besson, J.P. Itie, A. Polian, G. Weill, J.L. Mansot and J. Gonzalez, *Phys. Rev.*, **B44**, 4214 (1991).
- [6] K. Tsuji, Y. Katayama, H. Kanda and H. Nosaka, *J. Non-Cryst. Solids*, **198**, 24 (1996); and references therein.
- [7] S. Minomura, O. Shimomura, K. Asaumi, H. Oyanagi and K. Takemura, *Proc. 7th Int. Conf. on Amorphous and Liquid Semiconductors*, Edinburgh, 53 (1977).
- [8] A. Garcia and M.L. Cohen, *Phys. Rev.*, **B47**, 4215 (1993).