Temperature dependence studies of the liquid structure of GaSb by neutron diffraction

Jun'ichiro Mizuki†, Koichi Kakimoto†, Masakatsu Misawa‡, Toshiharu Fukunaga§ and Noboru Watanabe‡

† Fundamental Research Laboratories, NEC Corporation, 34-Miyukigaoka, Tsukuba, Ibaraki 305, Japan
‡ National Laboratory for High Energy Physics, 1-1 Oho, Tsukuba, Ibaraki 305, Japan
§ Department of Crystalline Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Abstract. The liquid structure of GaSb has been investigated by neutron diffraction for temperatures ranging from 800 to 1050 °C. In contrast with expectations from viscosity measurements, no drastic change in structure was observed over this temperature range. However, the structure factor $S(Q)$ presented a shoulder on the high-Q side of its first peak at all temperatures, suggesting the existence of short-range ordering in the molten state. The radial distribution function shows 5.4 ± 0.5 atoms up to the second-nearest neighbours. The data can be explained by a structural model based on β-Sn-like short-range order. The anomalous temperature dependence of the viscosity is also discussed with this structural model of the molten state.

1. Introduction

It is well known that semiconductor compounds are important materials for electronic devices. The quality of their single crystals, however, is rather poor in comparison with that of Si, partly because the crystal consists of two elements. In order to overcome this problem, we believe that the physical properties in the molten state, such as viscosity, thermal diffusivity, thermal expansion coefficient and structure, should be investigated. In particular, structural studies of molten semiconductor compounds offer the possibility of investigating questions related to the crystal growth from the melt as well as chemical ordering and its influence on the electronic properties.

Although most experimental and theoretical efforts so far have focused on the liquid phase of the elemental semiconductors and, in particular, Si and Ge [1–5], recently the liquid structure of GaAs was studied using both experimental [6] and theoretical methods [7], and it was found that the structure has many similarities to those of liquid Si and Ge. Furthermore, viscosity measurements on semiconductor compounds, such as liquid GaAs and GaSb, were performed by Kakimoto and Hibiya [8, 9] to obtain information on the structure of the melt. They observed that the temperature dependence of the viscosity did not follow the Arrhenius relation, indicating a change in the activation energy with temperature. This observation may suggest a change in structure with temperature. To date, as far as we know, direct observation of the temperature dependence of the structure of molten semiconductor compounds has not been made. Therefore, it is desired to employ a diffraction technique for obtaining direct information on the structure.

In this paper we present the results of neutron diffraction measurements on the molten state of GaSb over the temperature range from 800 to 1050 °C and discuss a structural model and the relation between the structure and the viscosity.

2. Experimental procedure

The neutron diffraction experiment was carried out using the $S(Q)$ instrument (HIT) installed at the pulsed-neutron source of the National Laboratory for High Energy Physics in Tsukuba. A so-called 'imaging furnace' was made for high-temperature neutron diffraction measurements. The furnace consists of a double ellipsoidal mirror with two halogen lamps as the heat source. Temperatures as high as 1100 °C can be readily attained by focusing radiation from the two halogen lamps onto the sample using a gold-plated internal ellipsoidal reflector. The temperature fluctuation of the sample in a quartz sample container 50 mm in length and 8 mm in inner diameter was measured to be within ±2 °C. Details of the furnace will be described elsewhere [10]. The sample preparation was as follows. Ga and Sb of 99.9999% purity were combined in a quartz tube of 8 mm inner diameter and heated to about 800 °C to make a GaSb compound (the melting temperature of GaSb is 712 °C). This compound was transferred to another quartz tube 8 mm in inner diameter and 0.8 mm in wall thickness to make a sample 40 mm in height which was then sealed in vacuum (this length was necessitated by the incident neutron beam size). The sample temperature was monitored with a thermocouple in thermal contact with the bottom of the cell. Since it was not possible to install the thermocouple in the sample through the quartz tube, it was necessary to calibrate the temperature at the bottom of the cell in order to determine the actual sample temperature. This was done by setting two thermocouples, one in the cell, in which Ga metal was kept, and one at the bottom of the cell. The temperature relation between the two was obtained over the desired temperature range prior to the neutron diffraction experiment [10].

The structure factors $S(Q)$ at 800, 900 and 1050 °C were obtained from the measured intensity after several corrections, including subtraction of the cell intensity, absorption, multiple scattering, and normalization with a vanadium standard [11]. The procedure for these corrections has been reported in [11] in detail. Since the cell intensity was dependent on temperature, it was necessary to measure it at the desired temperatures. To do so, a vanadium foil 25 μm thick was set inside the cell wall in order to increase the temperature of the empty quartz cell with the halogen lamps (if not, the temperature of the cell does not increase because the power of the halogen lamps is not absorbed by the cell).

3. Experimental results

Prior to the neutron diffraction experiment, the temperature dependence of the viscosity of molten GaSb was measured over the temperature range from 720 to 1400 °C, as seen in figure 1. The figure shows the relationship between the logarithmic value of the viscosity data and the reciprocal temperature. If the viscous flow of the melt is a single-activation-energy process, the viscosity should vary according to the Arrhenius equation, as previously observed for Li, Rb and Cs [12]; the molten state structure of these elements can be understood with a hard-sphere model. As seen in this figure, however, the temperature dependence of the viscosity for GaSb does not follow the Arrhenius relation. It is clear that the activation energy changes at about 950 °C from 0.93 to 1.1 eV with decreasing temperature. This suggests that the potential barrier for activating the viscous flow changes at 950 °C; in other words the structure may change at that temperature in some sense.

Therefore, our neutron diffraction experiment was performed at 800 and 900 °C, where the liquid is expected to be in the 'low-temperature phase', and at 1050 °C, where it is expected to be in the 'high-temperature phase'. Figure 2 shows the structure factors $S(Q)$ at these temperatures. Unexpectedly, significant differences between the $S(Q)$-factors at these temperatures were not observed, except for broadening of the patterns for increasing temperature. The common distinctive feature of the structure factors is that the first diffraction maximum has a small shoulder on its large-angle side. This shoulder is not observed for molten structures of Al and Pb [13], which can be understood using a hard-sphere model. Also, we simulated the total structure factor $S(Q)$ of liquid GaSb using the formalism of Ashcroft and Langreth [14], assuming that the structure is of a hard-sphere type. In this simulation the scattering amplitudes b_{Ga} for Ga and b_{Sb} for Sb were 0.72 and 0.5641, respectively, the diameters σ_{Ga} for Ga and σ_{Sb} for Sb were 2.82 and 3.18, respectively, and the packing parameter η used was 0.47, taken from the standard published data [15, 16]. Despite the variation in these five parameters over a reasonable range, the calculated $S(Q)$ showed no shoulder. Therefore, although the structure of a binary liquid such as GaSb is intrinsically not so simple as that of Al and Pb because it has three partial correlations, it can still be said that the liquid structure of GaSb is not explained by the hard-sphere model, and that some other model should be devised, possibly with an anisotropic short-range order. Figure 3 shows the experimental pair correlation function at 800 and 1050 °C. The asymmetric shape of the first peak seen at both temperatures is very noticeable when compared with that of normal liquid metals whose structures can be understood with the hard-sphere model mentioned above. This implies that the first peak centred at about 2.95 Å could be analysed as two peaks corresponding to two kinds of nearest-neighbour distance, although it is difficult to discern the exact position of the second peak. The radial distribution function at 800 °C is shown in figure 4. The number N of nearest-neighbour atoms is found from the area of the first maximum:

$$N = 2 \int_0^{R_{max}} f(R) \, dR$$

where $f(R)$ is the radial distribution function and R_{MAX} is the position of the first peak. The peak shape in the figure was assumed to be a symmetric Gaussian. We obtained $N = 5.4 \pm 0.5$ atoms, assuming that the nearest neighbour consists of the opposite species. The error comes from the ambiguity of R_{MAX}. This value is quite similar to that observed for liquid GaAs by Bergman *et al* [7]. These low coordination numbers in comparison with those of normal liquid metals, which are closely packed with a coordination number ranging from 12 to 14, result in the absence of oscillations above the first-nearest neighbours (figure 3) and indicate the persistence of covalent bonding even in the liquid [17].

4. Discussion

The most promising model for the molten structure of GaSb is a 'β-Sn'-type structure, which is similar to that reported for liquid Si [1], Ge [1] and GaAs [7]. The environment in this structure consists of four nearest neighbours in the corners of a flattened tetrahedron (quadrilateral), which make a plane, with two others slightly farther away located perpendicular to the plane, as shown schematically in figure 5. This model is supported by the fact that the first peak of the pair correlation function could be analysed as two peaks with coordination numbers of four and two (see figure 3) as mentioned in the previous section. Although there is no evidence that the two peaks refer to coordination numbers of four and two, the intensity at the shorter distance is higher than that at the longer. This indicates that
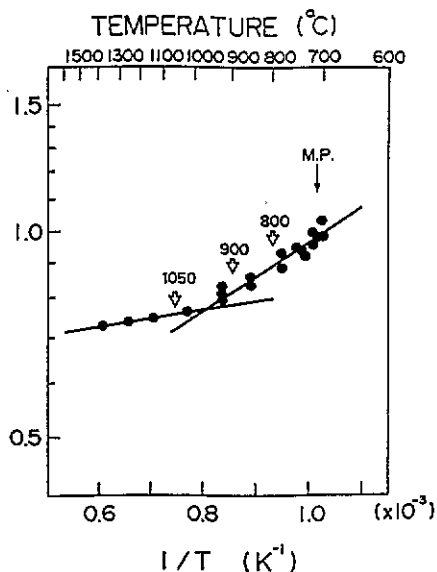
TEMPERATURE (°C)

Figure 1. Temperature dependences of viscosity for molten GaSb: M.P., melting point of GaSb. The lines were drawn to guide the eye; the line at high temperatures gives 0.93 eV for the activation energy, and the line at low temperatures gives 1.1 eV.
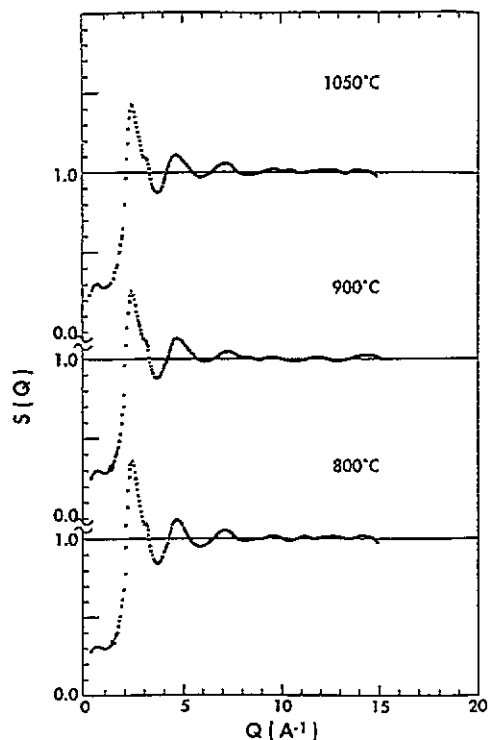

Figure 2. Structure factors of molten GaSb observed at 800, 900 and 1050 °C.
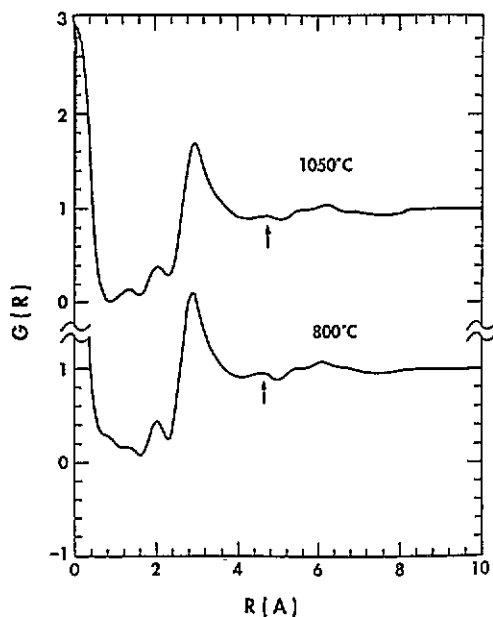

Figure 3. Pair correlation function of molten GaSb calculated from the observed $S(Q)$ at 800 and 1050 °C.

the number of atoms located at the first-peak position must be more than that at the longer. Thus, the number of nearest-neighbour atoms is close to six, experimentally. However, since the liquid state is rather dynamic, it may be better to say that the time-averaged structure is 'β-Sn'-like, and the number of observed nearest-neighbour atoms turns out to be a little less than six, within our experimental uncertainty. Recall that, in calculating the number N of nearest-neighbour atoms from the radial distribution function, the nearest neighbour was
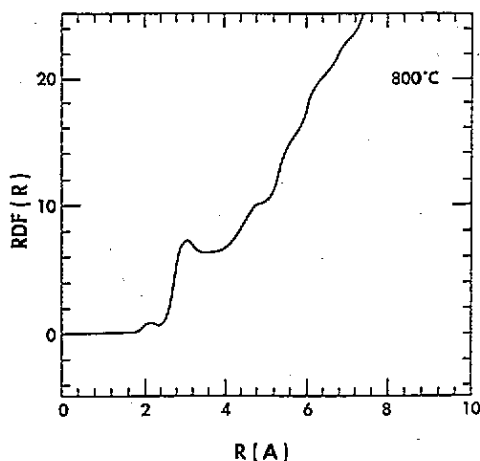
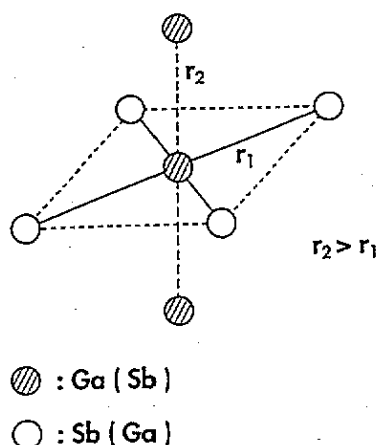**Figure 4.** Radial distribution function (RDF) of molten GaSb calculated from the observed $S(Q)$ at 800 °C.

: Ga (Sb)

: Sb (Ga)

Figure 5. β-Sn-type structural model for molten GaSb. r_2 is slightly longer than r_1. The atoms located in the plane at distance r_1 are the same kind of atom as at the centre; on the other hand the atoms perpendicular to the plane with distance r_2 are different kinds of atom from that at the centre.

assumed to be of the opposite species. However, if we assume the β-Sn structure which has two and four neighbours of the same and different species, respectively, the result for N changes by less than 1%. Also, a similar local atomic arrangement for liquid GaAs was predicted using *ab-initio* molecular dynamics methods [6], in which each Ga (As) has 2.6 (2.2) and 3.9 neighbours of the same and opposite species, respectively, within a sphere of radius equal to the first-nearest-neighbour distance. From this calculation the same species are located at a slightly greater distance than the opposite species. This is consistent with a 'β-Sn'-type structural model. Another point that we should emphasize is that the electrical conductivity of GaSb becomes metallic upon melting. This feature is also consistent with the fact that under pressure the zincblende structure of GaSb transforms to a β-Sn structure with an accompanying change in the electrical conductivity from semiconducting to metallic [18–20].

We now have to explain why there is an anomalous feature in the temperature dependence of the dynamical viscosity with no corresponding drastic change in the 'β-Sn'-type structure. One possible qualitative explanation is the following. As shown in figure 5, this structure is anisotropic. In the high-temperature region, however, the diffusing atoms could experience an averaged potential because the anisotropy is smeared out thermally. On the other hand, in the low-temperature region the diffusing atoms could experience the anisotropic potential. This results in the observed temperature dependence of the activation energy of viscous flow. This would also be consistent with the fact that the viscosities of the elements show simple Arrhenius behaviour and can be understood with the hard-sphere model which has spherical symmetry. A possible reason why our neutron scattering experiment always sees anisotropic structure is that neutrons interact with the system on a time scale of the order of 10^{-13} s, a value expected to be much faster than the time constant for atomic diffusion. Another plausible model to explain the temperature dependence of the viscosity is that the correlation at the middle-ranged distance may change with temperature. With decreasing temperature, this correlation may increase, resulting in a higher potential barrier for viscous flow. This correlation change can be seen in the second small peak in the total correlation function (arrow in figure 3) and/or the radial

distribution function (figure 4). Although not very pronounced, this peak seems to broaden slightly with increasing temperature. To summarize, in general, local anisotropic short-range ordering of atoms in the molten state may cause a rather unusual temperature dependence of the viscosity. This can explain why Si [21], Ge [21] and GaAs [8] as well as GaSb show similar temperature dependences of the viscosity, although a microscopic picture of how viscous flow is related to local structures is still an open question.

In summary, we have investigated by neutron diffraction the liquid structure of GaSb at different temperatures. No significant change in the structure was observed over a temperature range from 800 to 1050 °C. However, anisotropic short-range ordering was observed over the entire temperature range. This short-range ordering could be explained with a 'β-Sn'-type model structure. It could be that this anisotropic short-range ordering causes the unusual temperature dependence of the viscosity which shows the existence of at least two activation energies in the molten state.

In order to understand this structure in more detail it is necessary to obtain the partial pair correlation functions, although that is not possible using the present experimental data. To do this we need to perform similar neutron diffraction experiments on samples containing different concentrations of Ga and/or Sb isotopes, providing a variety of neutron scattering amplitudes. Another interesting question is how the anisotropic short-range ordering with nearly six nearest-neighbour atoms transforms to a zincblende structure with four nearest-neighbour atoms upon reducing the temperature through the melting point. We hope in the future to answer this question by both experimental and theoretical methods.

References

[1]   Waseda Y and Suzuki K 1979 *Z. Phys.* B **20** 339
[2]   Stich I, Car R and Parrinello M 1989 *Phys. Rev. Lett.* **63** 2240
[3]   Gabathuler J P and Steeb S 1979 *Z. Naturf.* a **34** 1314
[4]   Iserwood S P and Orton B R 1972 *J. Non-Cryst. Solids* **8–10** 691
[5]   Jank W and Hafner J 1990 *Phys. Rev.* B **41** 1497
[6]   Zhang Q-M, Chiarotti G, Selloni A, Car R and Parrinello M 1990 *J. Non-Cryst. Solids* **117–8** 930
[7]   Bergman C, Bichara C, Chieux P and Gaspard J P 1985 *J. Physique* **46** C8 97
[8]   Kakimoto K and Hibiya T 1986 *J. Electrochem. Soc.* **133** 2649
[9]   Kakimoto K and Hibiya T 1989 *J. Appl. Phys.* **66** 4181
[10] Kakimoto K, Mizuki J, Nishimura H, Misawa M and Fukunaga T 1993 at press
[11] Suzuki K, Misawa M, Kai K and Watanabe N 1977 *Nucl. Instrum. Methods* **147** 319
[12] Andrade E N Da C 1934 *Phil. Mag.* **17** 497
[13] Waseda Y, Takahashi F and Suzuki K 1972 *Sci. Rep. Res. Inst. Tohoku University* **23** 127
      Waseda Y and Suzuki K 1972 *Phys. Status Solidi* b **49** 339
[14] Ashcroft N W and Langreth D 1967 *Phys. Rev.* **156** 685
[15] Koester L, Rauch H and Seymann E 1991 *At. Data Nucl. Data Tables* **49** 65
[16] Shannon R D and Prewitt C T 1969 *Acta Crystallogr.* B **25** 925; 1970 *Acta Crystallogr.* B **26** 1046
[17] Stich I, Car R and Parrinello M 1989 *Phys. Rev. Lett.* **63** 2240
[18] Minomura S and Drickamer H G 1962 *J. Phys. Chem. Solids* **23** 451
[19] Jayaraman A, Klement W Jr and Kennedy G C 1963 *Phys. Rev.* **130** 540
[20] Jamieson J C 1963 *Science* **139** 762
[21] Glazov V M, Chizhevskaya S N and Glagoleva N N 1969 *Liquid Semiconductors* (New York: Plenum) p 70