Viscosity of Molten GaSb and InSb[1]

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Viscosities of molten GaSb and InSb as III–V compound semiconductors were measured using an oscillating viscometer to study the thermophysical properties of semiconductor melts. A specially designed quartz crucible was used to prevent the evaporation of Sb from the melts. The measurements were performed in the temperature ranges from the melting point to about 1490 K for GaSb and from supercooled temperatures to about 1340 K for InSb. The viscosities obtained for both GaSb and InSb showed good Arrhenius linearity despite their wide temperature ranges. The activation energies of GaSb and InSb were almost the same, although the absolute viscosity of GaSb was slightly higher than that of InSb. It was concluded that most semiconductors including Si and Ge show Arrhenius behavior and have a low viscosity. The reason for the low viscosity is considered to be related to their melt structure, which may be similar to that of molten metals with low melting points.

KEY WORDS: gallium antimonide; indium antimonide; high temperature; molten state; oscillating viscometer; semiconductors; viscosity.

1. INTRODUCTION

As semiconductors are important materials in highly industrialized societies, demands for large-scale and high-quality crystals are increasing. Therefore, computational simulations on the processes of crystal growth from the melt are being attempted to produce high-quality semiconductors. Although the simulations need reliable values of the thermophysical properties of the semiconductors for the molten and solid states, values reported for the

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molten state show large discrepancies; for example, for the viscosities of molten silicon, the difference among the investigators is almost 40% [1–3]. One investigator reported different values when using different materials of the crucible [3]. Furthermore, most of them showed non-Arrhenius-type behavior for the temperature dependence of the viscosity. The present authors reported that the abnormal behaviors were suspect [4]; namely, the temperature dependence of the viscosity of molten silicon showed normal Arrhenius-type behavior, and no difference was found when using different crucibles. However, molten silicon shows a viscosity considerably lower than that of molten metals with high melting points. A low viscosity was also found in molten germanium [5] and might be important to understand the general behavior of molten semiconductors. Therefore, the authors planned to study the viscosity not only of elemental semiconductors but also of compound semiconductors. The present paper reports the results of viscosity measurements on molten GaSb and InSb as compound semiconductors.

2. EXPERIMENTAL

As most semiconductors have a low viscosity and are used at high temperatures, an oscillating method is considered to be the most reliable for measuring viscosity at these conditions. Class III–V compound semiconductors have a high vapor pressure, which includes Group V elements in molten states. This results in a composition change of the melt from the stoichiometric composition and makes the experiment difficult. The oscillating viscometer has been improved for high temperatures, and the crucible was made of quartz in which the melt could be sealed completely.

Figure 1 shows a schematic of the viscometer. The crucible was connected with a tungsten rod to an inertia disk made of aluminum, and a mirror block was suspended by a thin platinum alloy suspension wire. The oscillation was initiated electromagnetically by a device installed above and under the inertia disk. The decrement in the oscillation was detected by using two photosensors. A spot of laser light passes on the sensors and four time intervals are measured in a period. They vary due to the decay of oscillation. The resolution of time measurement was 0.1 ms, and the period of the oscillation was typically 3 to 5 s, with a standard deviation of less than 0.3 ms. Detailed procedures for determining the period and the logarithmic decrement from the time intervals were described in previous papers [6, 7].

The viscosity of the melt was calculated using a successive approximation method based on Roscoe's equation [8]. As the logarithmic decrement and the moment of inertia for the empty crucible are required in the calculation of viscosity, they were determined for individual crucibles as a
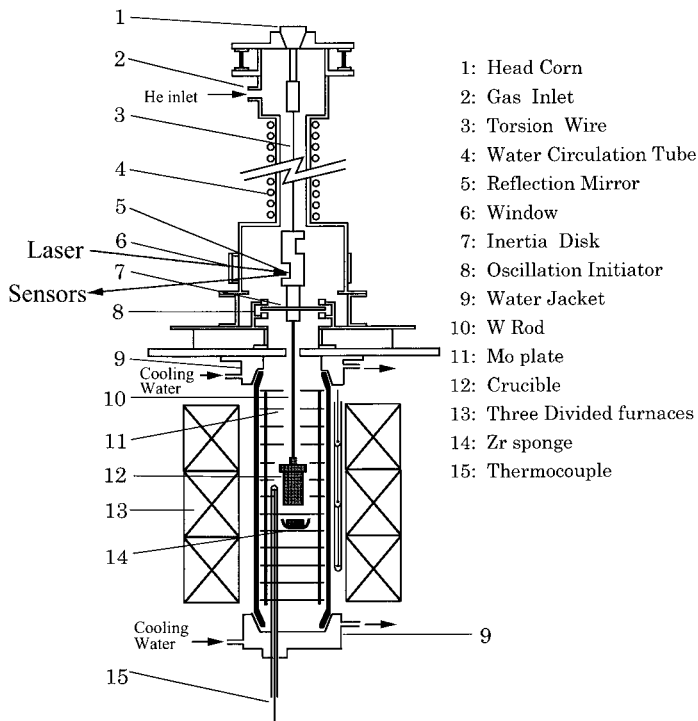
Fig. 1. Schematic of the oscillating viscometer.

1: Head Corn
2: Gas Inlet
3: Torsion Wire
4: Water Circulation Tube
5: Reflection Mirror
6: Window
7: Inertia Disk
8: Oscillation Initiator
9: Water Jacket
10: W Rod
11: Mo plate
12: Crucible
13: Three Divided furnaces
14: Zr sponge
15: Thermocouple

function of the temperature in the overall temperature range prior to the experiments. The temperature of the suspension wire was kept constant at 308.2 K by circulating warm water around the wire because the elastic modulus of the suspension wire was changed on changing the temperature, which affected the period of oscillation. The atmosphere in the viscometer was dry helium that was chemically inert and had the lowest viscosity. Furthermore, small zirconium pieces were placed under the crucible to remove the residual oxygen in the atmosphere.

Improvement of the temperature profile around the crucible is very important to secure the reliability of the temperature measurement and to prevent convection flow in the crucible. Therefore, the furnace used in this work consisted of three heating units, which were independently controlled. The units contained spiral $MoSi_2$ heater elements which were available up to about 1900 K in air. Furthermore, many molybdenum plates for thermal shielding were placed above and below the crucible. The temperature gradient around the crucible could be kept within 0.5 K, and the temperature

at the top of the crucible was carefully set slightly higher than that at the bottom to prevent convection flow in the crucible.

The crucible used for compound semiconductors and the procedure for sealing the sample are shown in Fig. 2. The container consisted of double crucibles. The outer crucible was a screw-capped cylinder made of nickel and was connected to the tungsten rod. The inner crucible was made of synthesized quartz, which has a higher resistance against elevated temperature than conventional quartz. The quartz crucible had a flat bottom and a precisely ground wall to just fit into the nickel crucible. A cylindrical top plate was welded to the inner wall of the quartz crucible containing the solidified sample under vacuum as shown in Fig. 2. The rest of the quartz crucible and the rod for the top were cut off after the sealing. The inner diameter of the quartz crucible was about 17 mm and was determined to a precision of 0.05 mm prior to the experiment. The depth of the melt was estimated to be about 65 mm by using the mass and density of the sample. At the highest temperatures in the experiments, about 0.2 mm of gap was probably formed between the quartz and the nickel crucibles due to the difference between the thermal expansion of nickel and that of quartz. However, this gap did not affect the experiments because no movement other than a slow rotational oscillation of the quartz crucible was expected, and the nickel crucible containing the quartz crucible was suspended statically by the wire. Indeed, no irregular oscillation was found in all the experiments.
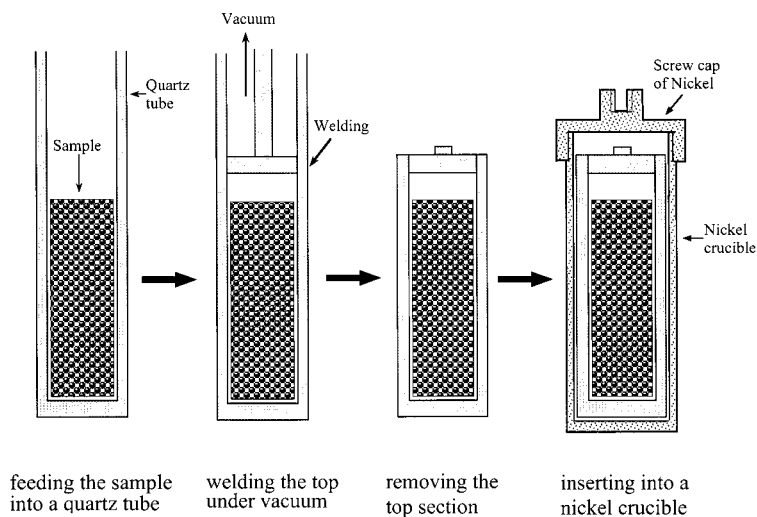

Fig. 2.   Procedure to seal the sample into the crudible.

The compound semiconductor samples of GaSb and InSb were synthesized by mixing and melting 5N-purity Ga and Sb, and In and Sb, in the quartz tube with a LiCl–KCl eutectic mixture as the flux.

The densities of molten GaSb and InSb used for calculating the viscosity were the values measured by the current authors [9] and are listed in Table I.

3. RESULTS AND DISCUSSION

The measurements were carried out in the temperature ranges from just above the melting point to 1490 K for GaSb and from supercooled temperatures to 1340 K for InSb. The experimental procedure was as follows. First, the measurement was started at a temperature about 50 K higher than the melting point, then the temperature was increased to a selected maximum temperature, and, finally, it was decreased to a temperature just above the melting point. Two cycles of this procedure were repeated to confirm the reproducibility of the measurements. For the final reduction in temperature, the measurement was terminated when the solidification of the melt was detected by observing the logarithmic decrement. In the case of InSb, the viscosity could be measured down to a temperature about 20 K lower than the melting point. However, no abnormal behavior was observed around the melting point.

The viscosities of molten GaSb and InSb obtained in this work are shown in Tables II and III. Figures 3 and 4 compare the viscosities of molten GaSb and InSb with literature values, respectively. Both results apparently show good Arrhenius linearity, and the activation energies are almost the same, although the viscosity of molten GaSb is somewhat higher than that of molten InSb. The behavior is different from literature results as shown in the figures. For the case of molten GaSb, the results reported by Glazov et al. [10] and Kakimoto and Hibiya [11] are completely different from each other and are also different from the present result. Glazov and co-workers' value exceeds the present result by more than a factor of two at lower temperatures, and it decreases steeply at higher

Table I. Density (ρ; 10^3 kg·m^{-3}) Equations of Molten GaSb and InSb as a Function of Temperature (T; K)

Substance	Equation
GaSb	$\rho = 6.733 - 6.668 \times 10^{-4}T$
InSb	$\rho = 7.030 - 6.370 \times 10^{-4}T$

Table II.   Viscosity of Molten GaSb

Temperature, T (K)	Viscosity, η (mPa·s)[a]
991.9	0.9559
1000.7	0.9464
1016.8	0.9304
1049.1	0.8917
1072.3	0.8680
1111.5	0.8306
1151.1	0.8012
1189.3	0.7711
1229.6	0.7452
1268.2	0.7257
1306.3	0.7115
1344.4	0.6950
1383.1	0.6782
1430.6	0.6666
1487.9	0.6463

[a] $\log \eta = -0.5404 + 514.0/T$.

Table III.   Viscosity of Molten InSb

Temperature, T (K)	Viscosity, η (mPa·s)[a]
779.6	1.2336
792.3	1.2106
809.7	1.1639
822.8	1.1087
858.7	1.0356
893.2	0.9820
926.4	0.9186
966.1	0.8882
1004.7	0.8243
1027.2	0.8220
1047.6	0.7883
1093.3	0.7388
1145.1	0.7154
1193.0	0.6899
1241.8	0.6681
1271.5	0.6539
1290.5	0.6348
1339.0	0.6194

[a] $\log \eta = -0.6314 + 558.9/T$.

temperatures in an unusual manner. On the other hand, Kakimoto and Hibiya's values for GaSb are similar to the present results at lower temperatures. However, the rate of decrease of the viscosity slows at higher temperatures. The activation energy at higher temperatures is considerably lower. Both of the literature viscosities apparently show non-Arrhenius behavior. For the case of molten InSb, the literature value is completely different from the present results. The viscosity value reported by Glazov is high, and a non-Arrhenius behavior similar to that of molten GaSb is also found. Glazov reported non-Arrhenius behavior not only for GaSb and InSb but also for other molten semiconductors, Si and Ge. However, in the case of Si and Ge, the activation energies of Glazov decrease with increasing temperature, in contrast to GaSb and InSb.

The present authors consider that molten semiconductors including Si and Ge show Arrhenius behavior similar to that of conventional molten metals based on the present and our previous studies [4, 5], which were carefully performed to study both the absolute viscosity and the temperature
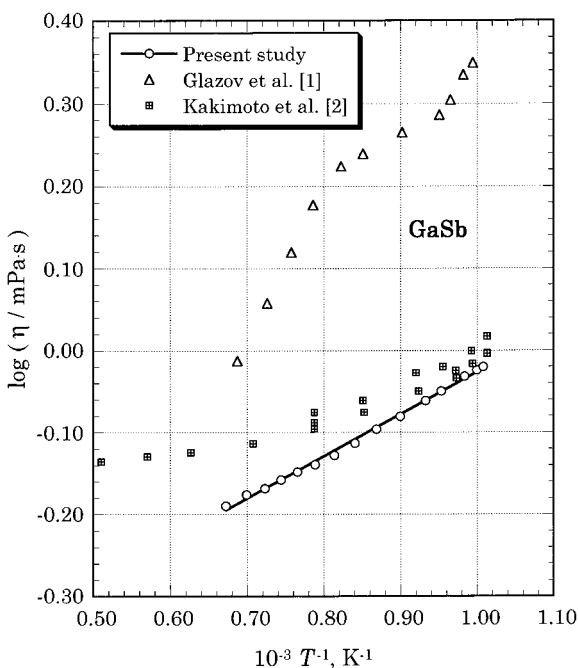

Fig. 3.   Viscosities of molten GaSb compared with literature values.
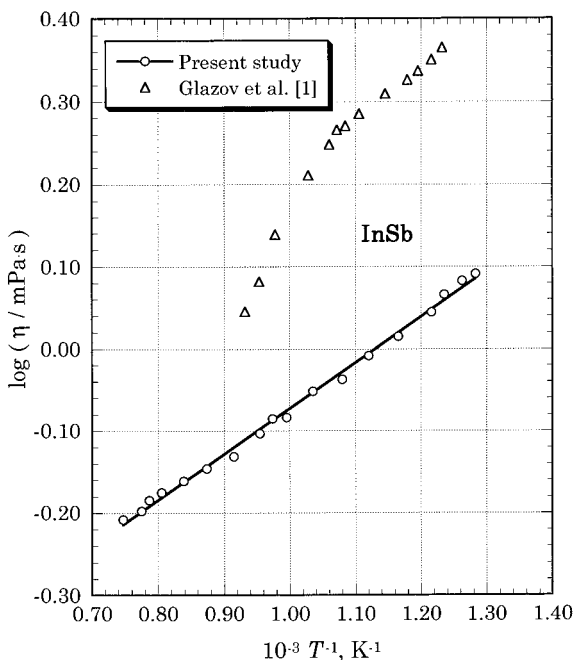
Fig. 4.   Viscosities of molten InSb compared with literature
values.

dependence of molten semiconductors. This is reinforced by considering the
literature values. That is, the tendencies of the temperature dependence
reported by Glazov et al. and Kakimoto and Hibiya are inconsistent with
each other, although both reported non-Arrhenius behavior. Therefore,
their results are considered to be unreliable. The present values of the acti-
vation energies and the absolute values of the viscosity for molten GaSb
and InSb, which are considerably low and similar to those of molten metals
with low melting points, are also similar to those of molten Ge. These
results probably suggest the structural similarity of molten semiconductors.
The solid structure of semiconductors is a diamond-type structure, which is
not close-packed. Therefore, the volume of semiconductors decreases on
melting by breaking of the structure. However, their molar volumes are
considered still to be larger than those of hypothetical metallic structures in
the molten states. The viscosity is well known, in general, to depend on the
volume in the liquid state. This results in a viscosity lower than that
expected for molten semiconductors. The similar activation energy is also
considered to come from the similar structure of the melt because the acti-
vation energy reflects the type of the bonds among the constituent species.

4. CONCLUSION

Viscosities of the molten semiconductors GaSb and InSb were measured precisely using an improved oscillating viscometer. The molten semiconductors were sealed in the quartz crucible completely to avoid the evaporation of Sb from the melts. Viscosities obtained showed a good Arrhenius linearity, similar to elemental semiconductors and other molten metals. The activation energies of GaSb and InSb were almost the same although the absolute viscosity of GaSb was somewhat higher than that of InSb. Their values were similar to the values of molten Ge obtained by the authors. It was concluded that most semiconductors show Arrhenius behavior similar to that of the conventional molten metals and have a low viscosity as a result. The reason for the low viscosity is considered to be that the melt structure is similar to that for molten metals with low melting points.

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