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Temperature and time dependence of the density of molten indium antimonide measured by an improved Archimedean method

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Abstract. The temperature and time dependences of the density of molten indium antimonide are measured by using an improved Archimedean technique, in which a single-bob probe with two equivalent arms is applied. In the measurement, the influence of the surface tension of the melts and the buoyancy of the protecting gas can be eliminated. The accuracy of the measured density is about 0.05%. The temperature dependence of the density shows a negative linear tendency in the range from 780 K to 960 K, and the coefficient of temperature dependence of the density $-\mathrm{d}\rho/\mathrm{d}T$ is 6.542×10^{-1} kg m^{-3} K^{-1}. The density is 6.582×10^{3} kg m^{-3} at the melting point. The volumetric thermal expansion coefficient of the melt increases linearly upon heating. The time dependence of the density shows that the liquid InSb is quite stable at a temperature just a little above the melting point and at higher temperatures, and that the transition from the lower-coordination-number state to the higher-coordination-number state will be completed at exactly the moment when the transition from the solid state to liquid state is entirely complete.

1. Introduction

Indium antimonide is one of the most extensively studied III–V semiconductor compounds. Because InSb has the smallest band gap and largest carrier mobility, it is a very attractive material for both fundamental studies and device fabrication. InSb crystals are of interest for optoelectronic applications in the 3–5 μm wavelength range [1] and as substrates for epitaxial growth of InAsSb [2]. InSb single crystals have been grown by several techniques, such as the Czochralski [3, 4], Bridgman [5], and vertical-gradient freezing [6] techniques. In general, the system of Czochralski (CZ) growth is the most common industrial method for producing InSb crystal. The complex coexistence of many factors, however, makes the growth conditions difficult to analyse. It is known empirically that such crystal growth techniques are strongly affected by melt flow caused by density and/or surface tension variation. In order to grow large-diameter crystals and achieve better control of crystal quality, the behaviour of molten InSb must be understood. In particular, knowledge of the fundamental physical properties of molten InSb is essential, because of the semiconductor–metal transition and the anomalous expansion of the density upon melting. For InSb, the transition from the lower coordination number 4 in the solid state to the high coordination number 5–6 [7] in the liquid state will occur when solid InSb becomes molten, and the density of liquid InSb is 12% larger than that of solid InSb at the melting point 809 K. However, there have been few reports on the physical properties of liquid InSb.

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Density is the most important property of molten states as regards studying other properties of melts. Although there have been some reports [8, 9] on density measurement for liquid InSb, the results were not systematic and not very accurate. In this paper, the temperature and time dependence of the density are examined for molten InSb by an improved Archimedean method with higher accuracy.

2. Principle of the measurement

In the Archimedean technique, the density of a liquid is calculated from the buoyancy force exerted by the liquid sample on a sinker or bob immersed in the liquid, which is suspended by a wire attached to the arm of a balance. However, this technique is prone to large errors arising from the convection flow of the liquid at high temperature and the influence of the surface tension on the wire suspending the sinker. To avoid the effect of surface tension, the double-sphere method [10] has been used. Usually the double-sphere probe is so long that more samples are needed in the crucible in order to immerse the whole probe. So we proposed a one-bob probe [11] with two equivalent arms as the probe in the experiment; see 'Part 2' shown in figure 1. The dipping depth of the probe can be smaller than that of a conventional double-bob probe. The advantage of this method is that of reducing the quantity of sample required and the temperature difference between the melt surface and the bottom of the crucible. Therefore, the method is favourable for measuring the density at temperatures near the melting point.

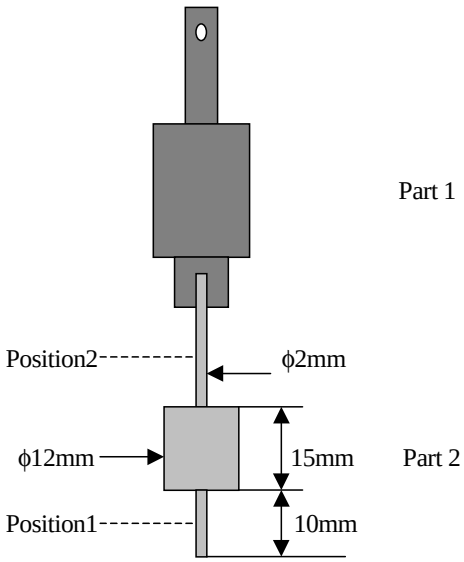

Figure 1. A schematic diagram of the single-bob probe used in the density measurement; 'Part 1' is the holder and 'Part 2' is the probe.

The influence of the surface tension can be cancelled by measuring the weight of the probe using one bob at various depths in the melt, and an accurate density for the melt ρ can be obtained from following formula:

$$\rho = \frac{(W_1 - W_2)}{V_2} \tag{1}$$

where W_1 is the weight of the probe when the melt surface is in position 1, W_2 is the weight when the surface of the melt is in position 2, and V_2 is the volume of the probe in the part between position 1 and 2, shown in figure 1. The volume of the probe V_2 can be measured in advance using the Archimedean volume measurement method at room temperature T_0 by using pure deionized water whose density has been accurately reported.

3. Experiment

To apply the method described above for the density measurement, the materials used as probes should meet certain requirements at high temperature. The bulk density of the probe should be as large as possible to avoid floating, and the material should be non-deformable and not reactive with the sample. A quartz crucible was used to contain the sample; this either does not react at all or reacts very slightly with molten semiconductor at high temperature [8]. The probe used in our experiment is made from high-purity SiC. It was found that SiC has good wettability and extremely low reactivity with molten indium antimonide. Unfortunately, the density of SiC is smaller than that of molten semiconductors. To deal with this problem, a heavy metal holder is added to the upper portion of the probe to push the probe against the buoyancy—as in 'Part 1' shown in figure 1. The volume of the probe used in the experiment is about 3×10^{-6} m^3 at high temperature. The volume V_2 of the probe at high temperature (T) is modified in considering the heat expansion by means of the equation

$$V_2 = V_2(T_0)[1 + 3\beta(T - T_0)] \tag{2}$$

where the thermal expansion coefficient of SiC, β, is 4.3×10^{-6} K^{-1} [12].

The starting material is polycrystalline indium antimonide, whose purity is guaranteed at over 99.9999%. The sample is molten in a pure quartz crucible with an inner diameter of 35 mm and a height of 70 mm, in which the depth of the melt is about 40 mm. The crucible is placed in a vertical furnace heated by a SiC tube heater, whose dimensions are 80 mm diameter and 500 mm height. In order to reduce the convection of the melt in the crucible during measurements, the crucible is placed at an appropriate position in the furnace such that the temperature of the upper region of the melt is slightly higher than that of the bottom part of the melt. Two thermocouples of Pt–10%Rh are used in the measurement: one near the SiC tube heater for controlling the temperature of the furnace, the other in the quartz tube on the side surface of the crucible for measuring the temperature of the melt. The fluctuation of the melt temperature is controlled within ± 0.5 K. The atmosphere in the vacuum system is maintained with a mixture gas composed of 92% Ar (purity 99.999%) and 8% H_2 (purity 99.999%), whose flow rate is 2 l min^{-1}, to protect the samples from oxidation. Before being filled with the gases, the chamber is evacuated to 1×10^{-3} Pa. The gas pressure in the system is kept at 1.1 atm.

The weight of the probe is measured by an AND FX-200 electronic balance with a sensitivity of 0.001 g. The relative error of the density measurement is about 0.05%.

4. Results and discussion

The temperature dependence of the density, which was measured several times during the heating and cooling procedure to confirm the reproducibility, in the temperature range from 780 K to 960 K, is shown in figure 2. Measurements for the first sample were made both during heating and during cooling; those for the second sample were made during heating. It is found that all of the data fall on the same curve, indicating that the effect of the surface tension could be satisfactorily cancelled with the single-bob method and that the results are more reliable.

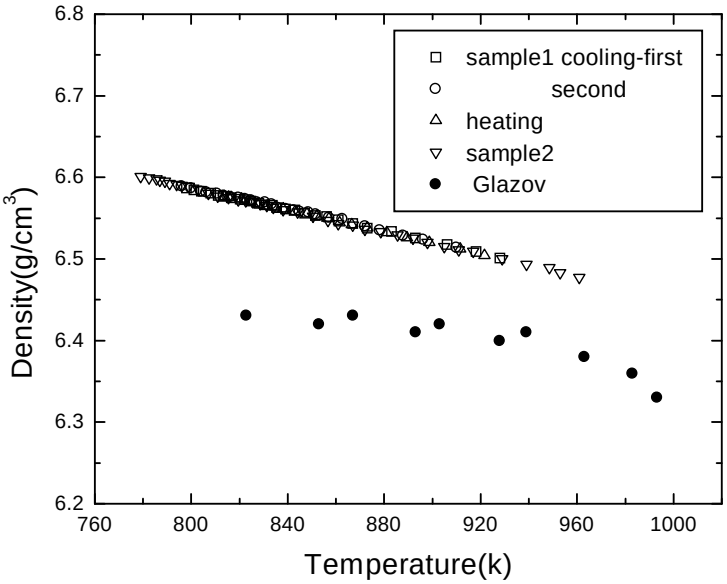

Figure 2. The temperature dependence of the density of molten InSb. Hollow symbols: results obtained by the present authors. Solid symbols: results obtained by Glazov *et al*.

The density of molten indium antimonide behaves as a negative linear function of the temperature. Consequently, the temperature dependence of the density of molten InSb can be represented as follows:

$$\rho(T) = -6.542 \times 10^{-1} T \text{ (K)} + C. \tag{3}$$

It can be seen that the coefficient of the temperature dependence of the density of molten InSb $-\mathrm{d}\rho/\mathrm{d}T$ is 6.542×10^{-1} kg m^{-3} K^{-1}, where C is a fitting parameter, which is 7.111×10^{3} kg m^{-3}. In the cooling process, no anomalous change can be observed at temperatures below the melting point ($T_{\mathrm{M}} = 809$ K), so the density of molten InSb at the melting point is obtained as 6.582×10^{3} kg m^{-3}, which is about 1.6% larger than the result obtained by Glazov *et al*, shown in figure 2. The details for the method used by Glazov *et al* to measure the density of liquid semiconductors were described in reference [8]. The purity of the InSb sample used in the experiment carried out by Glazov *et al* is 99.999%, which is lower than that of the sample in the present experiment. Due to one probe being used in the experiment, the surface tension of the liquid investigated will influence the value of the density. The total error in the determination of the density is of the order of 1.5%, which is larger than that of the present results, namely 0.05%.

Errors involved in measurement by the Archimedean technique may arise from the influence of the buoyancy of the gas, and the small amount of InSb material adhering to the probe. In our measurement the gas pressure was kept constant; the gas buoyancy is estimated to be 0.001 g, which can be considered negligible. By measuring the variation of the free weight of the probe W_0 throughout the whole process, it is observed that molten InSb neither adheres to nor reacts with the SiC probe. The measured variation of the buoyancy and the free weight of the probe as functions of temperature are shown in figure 3. The error in the measurement of the free weight is about ± 0.001 g. The results indicate that the single-bob method and the probe made of SiC enable us to carry out accurate density measurements for melts.

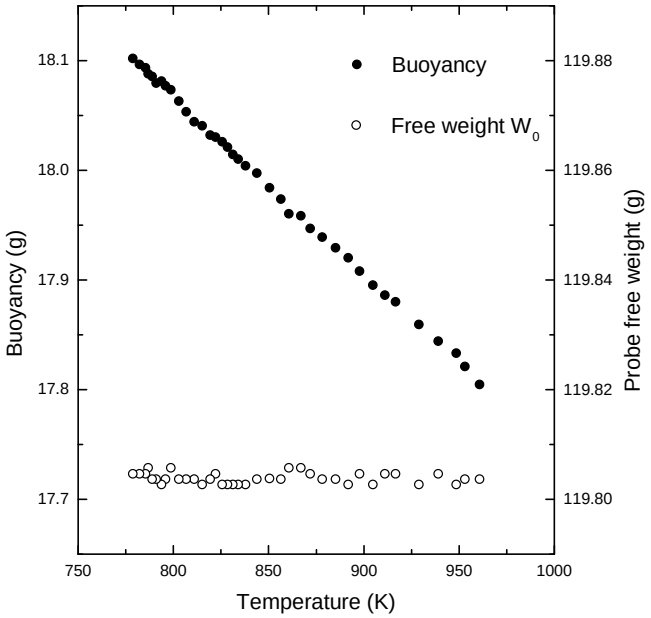

Figure 3. The variation of the buoyancy and the free weight of the probe during the density measurements.

The volumetric thermal expansion coefficient, β, is obtained from the temperature coefficient of the density ρ, as follows:

$$\beta = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T} = -\frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}T}. \tag{4}$$

The temperature dependence of the thermal expansion coefficient of molten InSb is shown in figure 4. It can be seen that the thermal heat expansion coefficient increases linearly upon heating.

The time dependence of the density of molten InSb near the melting point and at higher temperatures has been examined, and is shown in figure 5. The origin of the horizontal axis in figure 5 represents the moment of complete melting of solid InSb. The complete melting is confirmed by observing the disappearance of the floating solid InSb on the surface of the melt. The temperature of the surface is kept at 815 K, 818 K and 861 K. It is found that the density does not vary much with time at a temperature just a little above the melting point or at higher temperatures. This illustrates that the stability of liquid InSb is quite good and that no further structure changes happen just after melting or at higher temperatures, although the coordination number in the liquid state is larger than that in the solid state. This further demonstrates that the transition from the lower-coordination-number state to the higher-coordination-number state will be complete exactly at the moment when the transition from the solid state to the liquid state is entirely complete.

5. Conclusions

The temperature and time dependences of the density of molten InSb have been measured by using an improved Archimedean technique, in which a single-bob probe with two equivalent arms is applied. In the measurement, the influence of the surface tension of the melts and the

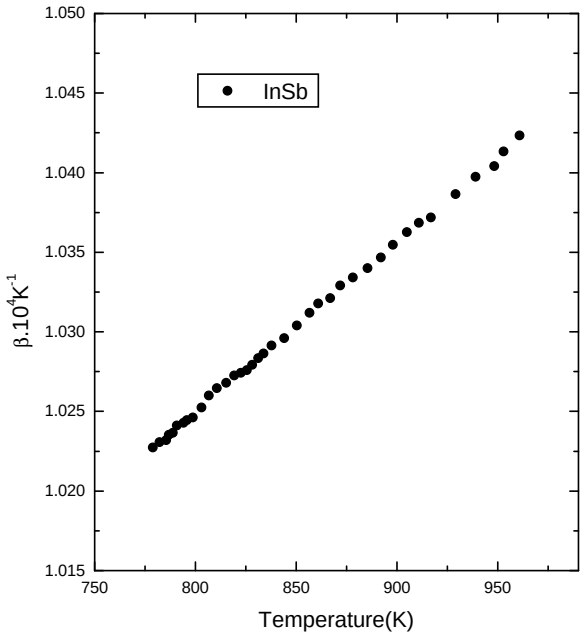

Figure 4. The temperature dependence of the heat expansion coefficient of molten InSb.

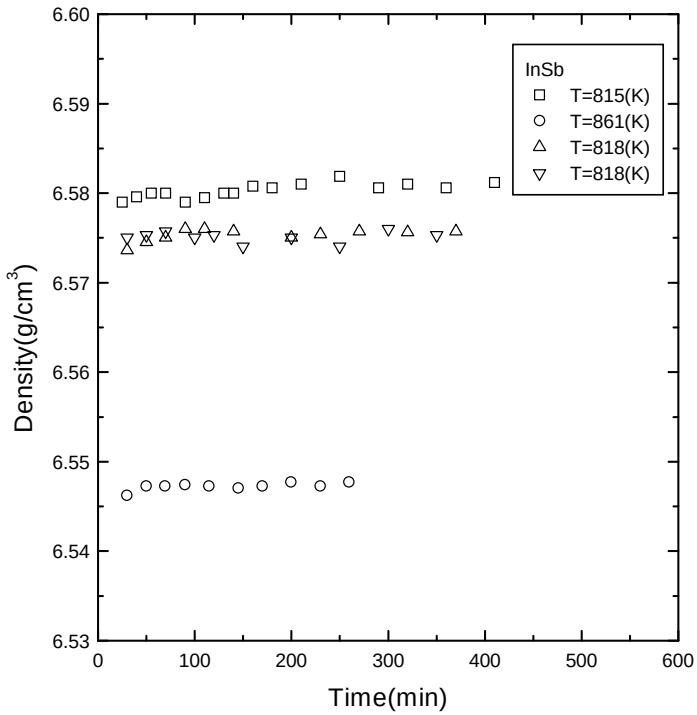

Figure 5. The time dependence of the density of molten InSb near the melting point and at higher temperatures.

buoyancy of the protecting gas can be eliminated. The accuracy of the measured density is about 0.05%. The temperature dependence of the density shows a negative linear tendency in the range from 780 K to 960 K, and the coefficient of temperature dependence of the density $-\mathrm{d}\rho/\mathrm{d}T$ is 6.542×10^{-1} kg m^{-3} K^{-1}. The density is 6.582×10^{3} kg m^{-3} at the melting point. The volumetric thermal expansion coefficient of the melt increases linearly upon heating. The time dependence of the density shows that the liquid InSb is quite stable at a temperature just a little above the melting point and at higher temperatures, and that the transition from the lower-coordination-number state to the higher-coordination-number state will be complete at exactly the moment at which the transition from the solid state to the liquid state is entirely complete.

Acknowledgments

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