MELTING OF DIAMOND

Motohiro TOGAYA

Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Single crystals of diamond were melted at 6 to 18 GPa in a 6–8 anvil type high-pressure apparatus using flash heating by a bank of capacitors. Samples of boron-doped semiconducting diamond were heated directly by the discharge current. The melting behavior was determined by measurement of the resistance change with the inserted energy and the observation of the quenched phases and their textures by X-ray microdiffraction and scanning electron microscopy. The liquid carbon formed is metallic and the resistances show little dependence on pressure within the range of 6 to 18 GPa, while it was suggested, from the pressure dependence of the inserted energy required to melt it, that the melting line of diamond has a positive slope. At 18 GPa, the liquid carbon was segregated into metastable graphite, which formed an oblate spheroid region and contained a small amount of diamond, and the diamond, forming a crust surrounding the graphite. The diamond resolidified from the liquid is a polycrystalline aggregate with a radial texture similar to ballas-type natural diamond.

1. Introduction

Since the original work of Bundy\textsuperscript{1)}, the melting of carbon at high pressure is a topic that has been of much interest over the past three decades and has been studied as a function of temperature and pressure by many researchers. However, major uncertainties remain today about the melting of diamond and the properties of liquid carbon.

Bundy proposed the melting line of diamond with a negative slope\textsuperscript{1)}, combining the graphite–liquid–diamond triple point determined in his experiments with the results of shock wave experiments by Alder and Christian\textsuperscript{2)}, which were later shown to be incorrect\textsuperscript{3),4)}. A negative slope of the melting line of diamond has been questioned as to both experimental results\textsuperscript{5),6)} and theoretical arguments\textsuperscript{7)–9)}.

Recently, a positive slope of the diamond melting line has been suggested from the experiments on the laser pulse heating of diamond in a diamond anvil cell\textsuperscript{15)} and the measurements of sound velocity and electrical conductivity in shock-compressed graphite\textsuperscript{6)}. These experimental results are consistent with the theoretical phase diagram of carbon by Young and Grover\textsuperscript{10)} and van Thiel and Ree\textsuperscript{11)}, and also the theoretical work of Yin and Cohen\textsuperscript{9)}, who predicted that the diamond phase dominates the phase diagram of carbon.

The purpose of this study is to investigate the melting behavior of diamond and the resolidification of liquid carbon.

2. Experimental

The experiments were carried out at pressures of 6 to 18 GPa in a 6–8 anvil type high-pressure apparatus, using flash heating by discharging a bank of electrolytic capacitors. In order to heat directly by the discharge current through the diamond, boron-doped semiconducting diamond was used as the starting material and was also preheated to make the initial resistance further decrease. Table 1 shows the boron concentration, resistivity and dimension for two kinds of single

<table>
<thead>
<tr>
<th>Sample</th>
<th>Boron concentration (ppm)</th>
<th>Resistivity ((\Omega)-cm)</th>
<th>Dimension (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBC 10</td>
<td>~200</td>
<td>(\leq 1)</td>
<td>(~0.5\times0.3\times0.7) fragment</td>
</tr>
<tr>
<td>TC 100</td>
<td>20–30</td>
<td>2–3</td>
<td>0.5\times0.5\times1.4 rectangular</td>
</tr>
</tbody>
</table>

Table 1. The boron concentration, resistivity and dimension of diamond used

crystal diamond used. Figure 1 shows sample assemblages in the octahedral high-pressure cell for a TC 100 sample. As the initial resistance of TC 100 is very high, the diamond was preheated by a one-turn circular graphite heater using another flash-heating circuit.

The sample was put between both graphite electrodes and surrounded by an h-BN wall with a graphite heater to preheat because of its high resistance. The discharge current was passed from upper copper and graphite electrodes into lower, grounded ones; this ground is common to that of the preheating heater. In the SBC 10 sample, the resistance is of the order of 10 Ω and preheating was not required. As the wall material, h-BN and diamond (non-doped powder 0–1 μ) were used at pressures of below and above 13 GPa, respectively.

Figure 2 shows the flash heating circuit used in this experiment. The main heating circuit is comprised of a 96 mF electrolytic capacitor bank $C_1$, a main thyristor switch $SCR_1$, a main resistor $R_1$ (10 mΩ) and the sample $R_s$. The preheating circuit consists of a 24 mF capacitor bank $C_2$, a switch $SCR_3$ and the graphite heater $R_3$.

In the case of TC 100, when the resistance of the sample was reduced to 10 Ω by preheating, the main thyristor $SCR_1$ was fired. The quench experiments were done using the thyristor $SCR_2$, which stopped the heating of the sample by passing a current through it. The voltage drop across the sample and the current through it were simultaneously measured by a two-channel digital waveform memory (Autonics S210). The heating power, inserted energy (integration of the power) and resistance versus time curves were derived from the voltage and current data, and finally the resistance was obtained as a function of the inserted energy.

As an experimental procedure, in the respective samples at each pressure the resistance vs inserted energy (or time) curves were first collected in the free discharge at the voltage of 100 V. Secondly, the irregularities in the resistance were associated with the transformation to liquid carbon from observations of the texture of the sample quenched at each point. At the same time, the pressure dependence of melting behavior was investigated in connection with the inserted energy instead of the temperature. Finally, all samples recovered at each pressure were examined specifically in terms of the structure and texture of phases of the resolidification of liquid carbon by X-ray microdiffraction (XMD) and scanning electron microscopy (SEM).

3. Results and discussions

3.1 Behavior of boron-doped diamond

Figure 3 shows the resistance vs inserted energy curves for the TC 100 samples at 6, 10 and 15 GPa, respectively. Each curve indicates a typical resis-
tance change of an impurity semiconductor with increasing temperature; i.e., the resistance decreases in the impurity region and increases through a minimum due to the decrease of carrier mobility in the saturation region. If no phase change occurred with a further increase in temperature, each decrease of resistance after showing maximum could be interpreted as the behavior in the intrinsic region. After the large drop, the resistance in each case tends to approach almost the same value, less than 0.1 Ω. This result shows that the diamond in each case has been transformed to the same state, such as liquid. Figure 4 shows an SEM photograph of the sample quenched at the inserted energy of 18 joules (2.5 ms after beginning to heat) at 10 GPa. A radial texture was found in the central portion of the sample recovered in the original shape. It is consequently concluded that the carbon is in a liquid state under conditions of resistance less than 0.1 Ω. The reaction process of diamond to liquid at the pressures of 6 and 10 GPa must be considered in terms of three possibilities: its direct melting, reaction through graphitization, and the competition between these two processes. If it is possible for diamond to undergo metastable melting due to rapid heating in the graphite stable region, in the same manner as graphite underwent metastable melting in the diamond stable region in our experiments\(^{12}\), the shift of the resistance change, corresponding to the transformation to liquid carbon, toward higher inserted energy suggests that the melting line of diamond has a positive slope.

As a comparable experiment, the resistance vs inserted energy curves of SBC 10 at 6, 10, 15 and 18 GPa are shown in Fig. 5. Each curve monotonically decreases with increase of the inserted energy. The resistance changes show no minimum value and differ from those of TC 100. This is considered to show the characteristics of an impurity semiconductor with a very heavily doped impurity concentration. After showing a little irregularity, the respective resistances tend to approach the same resistance value. This situation is the same as that of TC 100, and the transformation to a liquid state was confirmed from the quench experiments. At the shoulder point in each curve the diamond remained unchanged and at the point of about 0.05 Ω resistance the sample recovered from each pressure showed a remarkable radial texture resulting from freezing from the liquid state. Although it is impossible to quantitatively discuss the pressure dependence of melting, because of the slightly different dimension among the SBC 10 samples, as a general trend the melting temperature shows an increase with increasing...
pressure in the comparison between the inserted energy for 6 and 10 GPa and that for 15 and 18 GPa.

3.2 Electrical properties of liquid carbon

In both TC 100 and SBC 10 samples, the pressure dependence of the resistance of the liquid carbon is very slight, as shown in Figs. 3 and 5. The observed resistance of liquid carbon in TC 100 is 30 ～ 50 mΩ, including the resistance of the graphite electrode in both sides. Though it is very difficult to evaluate the resistivity with accuracy, the liquid is considered to be metallic or semimetallic with a resistivity lower than 400 μΩ·cm at least, while the liquid phase formed by the melting or metastable melting of graphite indicated metallic or semimetallic behavior.[12] The properties of liquid carbon derived from melting experiments of both diamond and graphite are consistent with each other. Therefore, the liquid prepared from pure diamond with no boron content is also said to indicate the same property.

Recently the pressure dependence of the electrical conductivity of liquid carbon has been discussed[13],[13] and it has been suggested that the liquid transforms gradually from a conducting to a less conductive and perhaps insulating liquid, well above the triple point of graphite–liquid–diamond. However, as mentioned above, in our experiments the liquid still retains the conductive state at 18 GPa, above the triple point pressure.

3.3 Resolidification of liquid carbon

At pressures of 6 and 10 GPa, in experiments with both TC 100 and SBC 10 samples, the liquid carbon resolidified completely to graphite with a radial texture, as seen in Fig. 4. In the samples freely subjected to discharge at the capacitor voltage of 100 V, the graphite electrode and the wall were also partially melted, as well as the diamond sample. In these cases at 6 and 10 GPa the liquid, mixed between carbon and BN as the result of contamination, solidified to two phases of graphite and h-BN. At 15 GPa, however, in the case of TC 100 with an h-BN wall, the liquid contaminated with BN resolidified to a mixture of diamond and c-BN with traces of graphite and h-BN.

When there was no contamination with other materials except carbon, such as in the experiment on SBC 10 with the diamond wall at 18 GPa, the liquid carbon was segregated, with metastable graphite as a dominant phase forming an oblate spheroid region with a radial texture, and the diamond as a recessive phase as a crust surrounding the graphite, as shown in Fig. 6. This solidification condition is the same as that of the liquid presented by the metastable melting of graphite at the same pressure.[12] The examination of the graphite portion by XRD revealed that the graphite solid contains about 15% diamond and the d-value of the (002) line of graphite is about 3.37 Å. Observation of the diamond portion by SEM showed that its diamond is a polycrystalline aggregate with a radial texture and outcrops of small euhedral faces, as shown in Fig. 7. The visual observation of the diamond fragment also showed that the diamond is partially transparent and colorless.

Bundy reported, in his melting experiment on diamond formed in situ from boron-doped graphite at 14 GPa[1], that the liquid carbon froze separately into a central spheroid region, consisting of a half and half mixture of diamond and graphite, and a diamond crust gray-white in color. His experi-
ments presented the question, why did the liquid not all freeze to diamond? The same question is also noted in our experiments at pressures higher than those used by Bundy. Considering that the carbon and BN mixed liquid presented diamond and c-BN after freezing in the experiment at 15 GPa, in order to resolve the question about the emergence of metastable graphite from the liquid carbon at 15 and 18 GPa, it is necessary to consider the kinetics of solidification; e.g., the effect of cooling rate, as well as the relaxation of the whole cell and the change of local pressure accompanying the phase transformation during freezing, on the basis of a liquid less dense than diamond (positive slope of melting line of diamond) and denser than graphite in the metastable state.

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REFERENCES