Electrical transport measurements for superconducting sulfur hydrides using boron-doped diamond electrodes on beveled diamond anvil

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Abstract

A diamond anvil cell (DAC) has become an effective tool for investigating physical phenomena that occur at extremely high pressure, such as high-transition temperature superconductivity. Electrical transport measurements, which are used to characterize one of the most important properties of superconducting materials, are difficult to perform using conventional DACs. The available sample space in conventional DACs is very small and there is an added risk of electrode deformation under extreme operating conditions. To overcome these limitations, we herein report the fabrication of a boron-doped diamond microelectrode and undoped diamond insulation on a beveled culet surface of a diamond anvil. Using the newly developed DAC, we have performed in-situ electrical transport measurements on sulfur hydride H$_2$S, which is a well-known precursor of the pressure-induced, high-transition temperature superconducting sulfur hydride, H$_3$S. These measurements conducted under high pressures up to 192 GPa, indicated the presence of a multi-step superconducting transition, which we have attributed to elemental sulfur and possibly HS$_2$.

Keywords: high pressure, sulfur hydrides, boron-doped diamond

(Some figures may appear in color only in the online journal)

1. Introduction

High-pressure techniques have promoted the design of several functional materials, such as hydrogen-storage alloys [1], thermoelectric materials [2–4], superconductors [5–10], and so on [11]. This is particularly so in the case of pressure-induced room temperature superconducting materials, which are hydrogen-rich [12, 13]. Highly compressed sulfur hydride, H$_2$S at 150 GPa exhibits high-transition temperature ($T_c$) superconductivity, which $T_c$ is higher than 200 K [14, 15].
A record-high $T_c$ above 250 K closer to room temperature was reported in lanthanum hydride at pressure above 170 GPa \cite{16, 17}. Theoretical prediction indicates that a compressed Li$_2$MgH$_{16}$ might exhibit room temperature superconductivity \cite{13}.

It is technically challenging to perform the high-pressure synthesis of superconducting hydrides because of the complex compression-pathway in their temperature–pressure diagram, as highlighted in \cite{18}. Moreover, at extremely high pressures, conducting an \textit{in-situ} electrical transport measurement for the observation of zero resistance in the superconducting state is also quite difficult. A diamond anvil cell (DAC), which consists of a pair of opposing diamonds with polished culets, is a unique tool to generate static high pressure above 100 GPa \cite{19, 20}. By inserting electrodes and insulating layers within the sample space of a DAC, it is possible to perform the \textit{in-situ} electrical transport measurements under high pressure \cite{21}. However, such measurements are extremely difficult and technically challenging because, to measure the sample resistivity, four electrodes have to be accommodated within a sample space that is less than 100 $\mu$m. Additionally, there is always a risk that the electrodes and insulation can break under the applied pressure.

To overcome these aforementioned problems, an improved configuration of DAC for the electrical transport measurements under high pressure has been reported in the literatures \cite{22-24}. A combination of a culet-type diamond as the top anvil and a box-type nano-polycrystalline diamond \cite{25} as the bottom anvil has been used in the cell-assembly. Further, a bottom anvil equipped with microelectrodes of a boron-doped diamond (BDD) \cite{26, 27} fabricated by combining a microwave-assisted plasma chemical vapor deposition (MPCVD) method and the electron beam lithography (EBL) technique \cite{22, 23}. The fabrication of an undoped diamond (UDD) layer on the diamond anvil has also been reported \cite{24}. The electrical transport measurements can be performed by placing the sample and a gasket on the bottom anvil directly. Since the electrodes and insulating layers are grown on the diamond anvil epitaxially, these components can be repeatedly used until the diamond anvil breaks.

In this study, we have successfully fabricated the BDD microelectrodes and the UDD insulating layer on a beveled culet diamond anvil instead of the conventional box-type anvil to achieve higher-pressures and to measure with ease the electrical transport properties in the superconducting hydrides. Using the newly developed DAC, we have performed a low-temperature and high-pressure synthesis together with \textit{in-situ} electrical transport measurements on sulfur hydrides H$_2$S, which is a well-known precursor for high-$T_c$ H$_3$S \cite{14, 15}. The temperature dependence of the sample resistance was measured via a standard four-probe method using the physical property measurement system (PPMS/Quantum Design). The crystal structures obtained under high pressures were analyzed using synchrotron-based x-ray diffraction (XRD) measurements.

2. Fabrication for BDD electrodes and UDD insulating layer on the beveled anvil

BDD electrodes and UDD insulating layers were fabricated by following the procedures as shown in figure 1. The shape of the electrodes was drawn by a resist via the EBL technique in combination with scanning electron microscopy (SEM; JEOL, JSM-5310) equipped with a nanofabrication system (Tokyo Technology, Beam Draw) on the beveled anvil. A TiC intermediate layer formed between the diamond and Ti layer during annealing at 450 $^\circ$C for 1 h in a furnace with Ar gas-flow to enhance adhesion of the metal mask. The epitaxial BDD was selectively grown by a hydrogen-induced MPCVD using CH$_4$ as a source gas on the uncovered region of the anvil surface. The boron/carbon ratio was tuned to 2500 ppm using C$_3$H$_6$B gas. The total pressure, gas flow rate, and the microwave power during the growth process were maintained at 70 Torr, 300 sccm, and 500 W, respectively.
Figure 2. Schematic and photographic image of diamond anvil cell (DAC) with boron-doped diamond (BDD) electrodes and undoped diamond (UDD) insulating layer for the synthesis of superconducting sulfur hydride.

Figure 3. (a) Time dependence of the resistance of the compressed sample, where $t = 0$ implies just after the compression from ambient pressure to 120 GPa. (b) Temperature dependence of the resistance is measured under various pressures up to 154 GPa. (c) Magnified plot for the temperature dependence of the resistance.

The BDD electrodes were obtained after the wet etching treatment to remove the metal mask and impurity of graphite using a mixture of HNO$_3$ and H$_2$SO$_4$ at 400 ºC for 30 min. As shown in figure 1 (d), the UDD insulating layer was deposited on around the BDD electrodes using similar processes except for the growth condition of diamond. The total pressure, gas flow rate of H$_2$ and CH$_4$, and the microwave power during the growth of the UDD layer were maintained at 35 Torr, 400 sccm, and 350 W, respectively.

3. Sample preparation

The in-situ electrical transport measurements were performed for sulfur hydrides using the newly developed DAC. Figure 2 shows a schematic and optical microscope image of DAC with the BDD electrodes and the UDD insulating layer used for the synthesis of superconducting sulfur hydride. The diameter the first and the second culets of beveled anvil are 300 µm and 100 µm, respectively. The sample space surrounded by the UDD insulation is 15 µm × 20 µm. The gasket used in this study is a rhenium plate whose central portion is composed of cubic boron nitride (cBN). The hole of 30 µm diameter to be used as a sample chamber was fabricated by a focused ion beam (Hitachi High-Technologies, SMi9800SE) at the center of the cBN part of the gasket. Raman spectrum of the culet of top diamond anvil [28] recorded by an inVia Raman Microscope (RENISHAW) was used to estimate the pressure values.

The sample preparation for sulfur hydrides was performed via a low-temperature and high-pressure pathway following
a previously reported protocol [15, 29] for the synthesis for high-$T_c$ H$_2$S. Just before compression, the DAC was cooled by dipping it into liquid nitrogen and the temperature of the sample space was monitored by a thermocouple. H$_2$S gas was allowed to flow around the gasket hole, where it cooled down and subsequently solidified. When the temperature of the sample was approximately 200 K, which resulted in the liquefaction of solid H$_2$S, a screw used for increasing the stroke length of DAC was rapidly squeezed. Under this condition, the pressure within the sample space was rapidly increased up to 120 GPa.

4. Electrical transport measurements for sulfur hydrides

The electrical resistance measurements were performed after the sample had reached room temperature. Figure 3(a) shows the time dependence of the resistance of the compressed sulfur hydride, where $t = 0$ indicates the condition when the final pressure of 120 GPa was attained. The sample resistance drastically decreased from 77 kΩ to 330 Ω within approximately the pressure evaluation using Raman spectroscopy for approximately 1 h, which was an indication that a rapid chemical reaction known as room temperature annealing of sulfur hydride had occurred [14]. The resistance of the sample continued to decrease over night and finally reached a value of 80 Ω after approximately 8 h, which is a decrease of more than three orders in magnitude. An optical micrograph of the sample space (shown as the inset of figure 3(a)) exhibits an inhomogeneous morphology indicated by the presence of bright and dark regions.

After $t = 26$ h, when the resistance had further decreased to 38 Ω, we started our measurements to evaluate the temperature dependence of the resistance at a given pressure. The pressure was increased up to 154 GPa to examine the superconductivity of the sample (figure 3(b)). Initially, the compressed sample exhibited a semiconductor-like behavior between 300 and 30 K. From ~25 K at 120 GPa, we observed a sudden decrease in the resistance which hinted towards a superconductor-like behavior. With an increase in the applied pressure (till 154 GPa), the sample resistance continued to decrease. Figure 3(c) shows a magnified plot of the temperature dependence of the resistance between 30 and 10 K at various applied pressures. A common feature of these plots is that the resistance exhibits a first drop ($T_{c1}$) at approximately 25 K and then a second drop ($T_{c2}$) below 15 K before finally reaching zero. Although $T_{c1}$ hardly exhibits any dependence on the applied pressure, $T_{c2}$ decreases with an increase in the pressure. It is plausible that $T_{c1}$ and $T_{c2}$ represent different origins.

To confirm whether the aforementioned drops in resistance in the compressed sample represent a different origin
of superconductivity, we measured the temperature dependence of the resistance under a magnetic field, which was varied from 0 to 7 T at 154 GPa, as shown in figure 4(a). $T_{c1}$ gradually decreased with an increase in the applied magnetic field. On the other hand, $T_{c2}$ vanished for magnetic field above 2 T. To determine the value of the critical field required to suppress the $T_{c2}$ phase, we conducted a series of measurements at lower values of the magnetic field (<2 T), as shown in figure 4(b). Figure 4(c) shows the temperature dependence of upper critical field $B_{c2}$ estimated from the Werthamer–Helfand–Hohenberg approximation [30] for Type II superconductors in a dirty limit. The extrapolated values of $B_{c2}$ for $T = 0$ K, i.e. $B_{c2}(0)$ were 53.0 T and 28.2 T for $T_{c1}$ and $T_{c2}$, respectively, under 154 GPa. From the Ginzburg–Landau formula $B_{c2}(0) = \Phi_0/2\pi\xi(0)^2$, where the $\Phi_0$ is a fluxoid, the $\xi(0)$ is the coherence length at zero temperature, the obtained values for $\xi(0)$ were 2.5 nm and 3.4 nm for $T_{c1}$ and $T_{c2}$, respectively.

Here, we note a possible higher onset $T_c$ in the observed superconductivity. Figure 5 shows a zoomed-in plot of the temperature dependence of resistance around $T_{c1}$ under different magnetic fields. By the visual inspection of the separation between the resistances above 30 K, the onset of transition was determined to be ~35 K. The onset gradually shifts to lower temperatures with increasing strength of the magnetic field. To demarcate the onset of the transition, we have plotted the differential curves of resistance vs. temperature, $dR/dT$ at two different magnetic field strengths, 0 T and 7 T as shown in the inset of figure 5. We can see a clear separation in the differential curves from around 35 K for both 0 T and 7 T. This result is suggestive of the existence of a higher-$T_c$ region above 35 K in the sample chamber and is similar to that observed in high-quality boron-doped superconducting diamond [31].

Interestingly, a slow but continuous decrease in sample resistance was observed even at 154 GPa. To promote the chemical reactions, we placed the DAC itself into an oven and annealed at the various temperatures as shown in figure 6(a), where $t = 0$ means just after the $R$-$T$ measurement at 154 GPa. The inset is the XRD pattern for the sample at 154 GPa before and after the laser heating. (b) Temperature dependence of the resistance under various pressures up to 154 GPa. (c) Magnified plot for the temperature dependence of the resistance.

Figure 6. (a) Time dependence of the resistance at various temperatures up to 100 °C, where $t = 0$ means just after the $R$-$T$ measurement at 154 GPa. The inset is the XRD pattern for the sample at 154 GPa before and after the laser heating. (b) Temperature dependence of the resistance under various pressures up to 154 GPa. (c) Magnified plot for the temperature dependence of the resistance.

Figure 7. Comparison of the reported $T_c$ values in sulfur hydrides including both experimental and theoretical studies. The $T_c$ from the experimental reports are shown with solid symbols and the theoretical values are shown with open symbols.
the temperature dependence of the resistance (after laser heating) from 154 GPa to 192 GPa in 0–300 K and 10–30 K, respectively. The sample resistance after heating also exhibited a continuous decrease with increasing pressure. Unlike \( T_{c1}, \) which did not show any dependence on the applied pressure, \( T_{c2} \) increased with the increase in pressure. Both the diamond anvils broke when the pressure was beyond 192 GPa.

Figure 7 displays a comparison of the reported \( T_c \) values in sulfur hydrides including experimental as well as theoretical studies. \( T_c \) obtained from the experimental reports \([14, 15, 33]\) are shown with solid symbols while the theoretical values \([34–38]\) are shown with open symbols. The criterion of \( T_c \) values for our experimental data is shown in figure S1 (available online at https://stacks.iop.org/SUST/33/124005/mmedia). The pressure dependence of \( T_{c2} \) in our experiments corresponds quite well with elemental sulfur. The relatively rapid suppression of \( T_{c2} \) with an increasing magnetic field together with the pressure-phase diagram suggests that the \( T_{c2} \) in our experiments originates from the superconducting high-pressure phase of elemental sulfur \([14, 39]\). On the other hand, the behavior of \( T_{c1} \) is not in agreement with any of the previously reported \( T_c \) from sulfur hydrides, including the higher and lower- \( T_c \) phases. Among the reported sulfur hydrides, the theoretically calculated pressure-phase diagram for C2/c HS2 is in good agreement with our data \([36]\), although in the present case \( T_{c1} \) was measured only up to 192 GPa. Here our sample preparation procedures were slightly different from the previous study \([15, 32]\). Einaga et al. filled \( H_2S \) in the sample chamber at low temperature and increased the pressure up to a few GPa to avoid the decomposition to H and S above 25 GPa at room temperature \([18]\). The DAC was cooled down and kept at 200 K by cryostat and then the pressure was increased to 150 GPa. In our experiment, the pressure was rapidly increased just after filling \( H_2S \) in the sample space. One plausible reason for the appearance of hydrogen-poor phase HS2 could be the decomposition of \( H_2S \) and the elimination of hydrogen from the sample chamber. Although the pressure-phase diagram suggests the possible candidate of the product in our experiment, further studies are required to understand the origin of the 30 K class high- \( T_c \) superconductivity.

5. Conclusion

The BDD microelectrodes and the UDD insulating layer were successfully fabricated on a beveled culet anvil to perform the in-situ electrical transport measurements under extremely high pressure above 100 GPa. The mother material \( H_2S \) for high- \( T_c \) superconducting \( H_2S \) was compressed using the newly developed DAC. A two-step superconducting transition with zero resistance was observed. From the electrical transport measurements conducted under different magnetic field strengths and the pressure-phase diagram, we show that the phase with lower- \( T_c \) (15 K) and the phase with higher- \( T_c \) (30 K) possibly originate from elemental sulfur and C2/c HS2, respectively. The newly developed DAC would provide an impetus to all the future investigations in high-pressure physics.

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