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LETTER TO THE EDITOR

Homoepitaxial diamond films on diamond anvils with metallic probes: the diamond/metal interface up to 74 GPa

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Abstract. A (100)-oriented natural type-Ia brilliant-cut diamond anvil with thin zirconium electrical probes sputtered onto the culet was coated with an insulating film of diamond using microwave-plasma-enhanced chemical vapour deposition (MPCVD). The critical issue in this high-pressure study is the quality of the homoepitaxial diamond film and its correlation with the mechanical strength of the diamond film/metallic probe interface. We report the *first* high-pressure study on a homoepitaxial diamond film and underlying zirconium probes to a pressure of 74 GPa. The metallic probes were observed through a transparent lithium fluoride sample with ruby serving as a pressure sensor. After decompression, Raman spectroscopy revealed that the homoepitaxial film was free from deformation and delamination despite the presence of some sp^2-bonded carbon at the Zr/diamond interface and within the bulk of the film itself. The present study demonstrates that the presence of residual defects and graphitic impurities has no significant effect on high-pressure applications of homoepitaxial diamond films. This opens up new areas of research with diamond anvil cell devices including those of ohmic heating and electrical transport measurements at ultra-high pressures.

One application for single-crystal diamond is as anvils [1] in high-pressure research in diamond anvil cell devices. Two single-crystal diamonds are used in the opposed anvil configuration and, due to the high shear strength of diamond, enormous pressures can be generated and sustained. In one recent experiment using synthetic diamond anvils, a pressure of 370 GPa (3.7 million atmospheres) was generated at the tips of the anvils [2]. In these high-pressure applications, it is often desirable to modify the shape of the diamond and/or to provide an insulating layer on top of electrical conducting probes which may be used on the tips of the anvils. As a first step in this process, we have carried out high-pressure experiments with homoepitaxially grown diamond films on top of natural type-Ia brilliant-cut anvils which have thin zirconium probes sputtered to the culet. The motivation for this research is to evaluate the mechanical behaviour of the metal–diamond interface in high-pressure applications of these devices and to describe the quality of the diamond growth on the modified diamond anvils.

The study of material properties at high pressure is of intense scientific and technological interest. In particular, measurement of electrical conductivity in materials at high pressure can provide information about insulator-to-metal transitions. One such example involves compressing hydrogen to the point where its electrons are stripped away from the nucleus, thereby allowing the hydrogen to become metallic and possibly superconductive [3, 4]. Pressures in the Mbar regime will be needed for such transitions to occur and will require the use of bevelled diamond anvils. In the present study, we used flat diamond anvils

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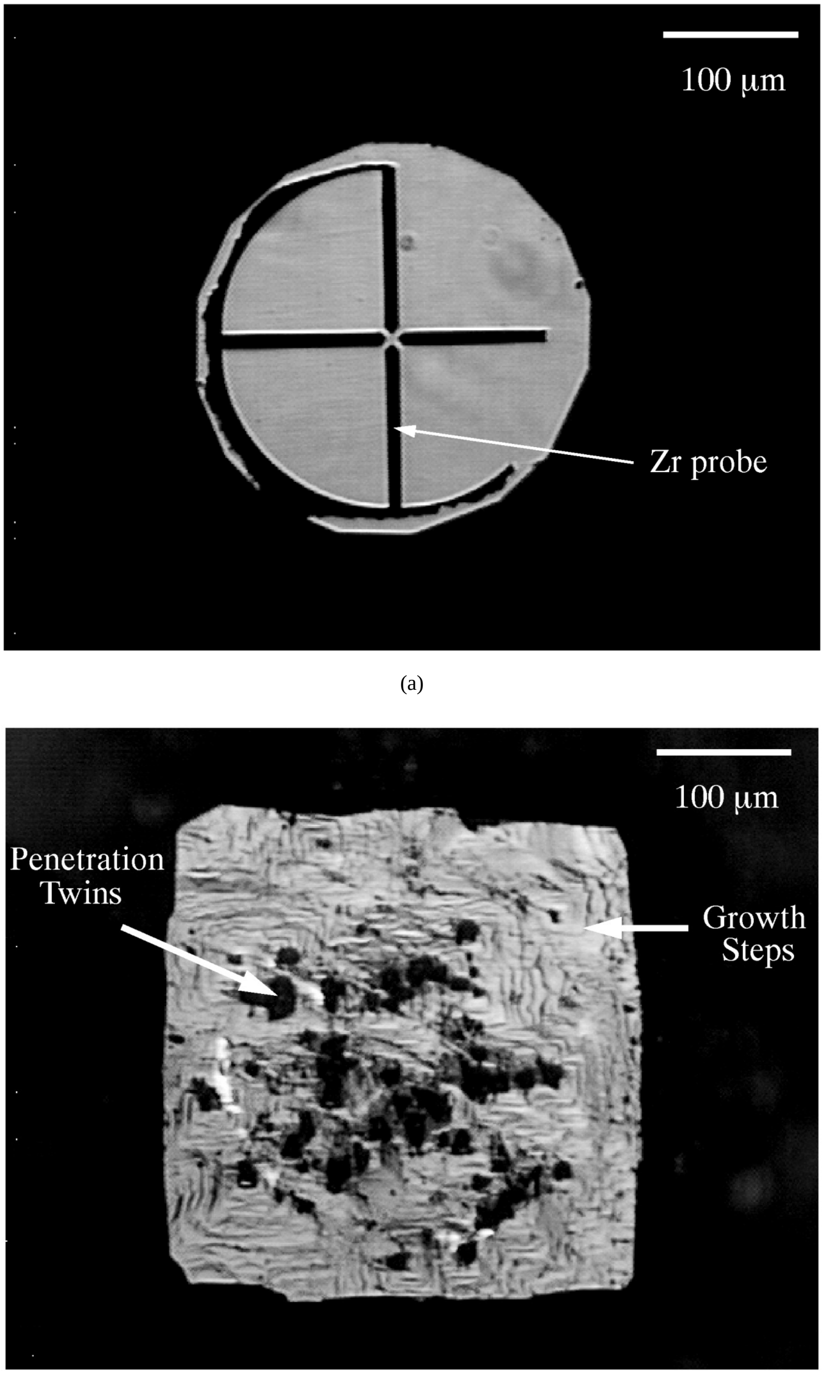
of 0.3 mm diameter and were able to successfully compress the homoepitaxially grown diamond layer to the upper limit of pressure expected for this anvil geometry.

Electrical transport measurements in DACs usually require fabrication of the electrical probes on the diamond itself. Electrical insulation is needed between the probes and the metallic gaskets which are used in high-pressure experiments. However, the upper pressure range in these experiments is generally limited to 70 GPa due to the pinching of probes at the edge of the diamond and to failure of the alumina insulating film. In this communication, we have developed an alternative method whereby insulation is provided by the homoepitaxial diamond film. In addition, zirconium metallic probes can be employed for direct ohmic heating of metallic samples under ultra-high pressures (70–400 GPa).

The homoepitaxial diamond film was grown in a MPCVD chamber using a 2% methane in hydrogen gas mixture. The 1/3 carat (67 mg) type-Ia diamond anvil was placed on top of a molybdenum substrate holder. The molybdenum holder was heat sinked into a copper block which was actively cooled (10 °C) with water during the experiment. The spatial extent of the plasma includes not only the top surface of the molybdenum holder, but the entire diamond anvil as well. Our previous experiments have shown that a high growth rate homoepitaxial diamond films can be obtained at substrate temperatures of 1100 °C [5]. In the present experiment the diamond anvil substrate temperature during deposition was 1100 ± 30 °C. The MPCVD chamber pressure during deposition was held constant at 90 Torr. The average microwave power was 850 W.

An optical transmission micrograph of the anvil culet before deposition showing the four zirconium probes is given in figure 1(a). The original culet is 300 μm in diameter. The probes were lithographically prepared, and approximately 0.3 μm thick and 10 μm wide. The as-grown diamond film is shown in figure 1(b) and has a thickness of 20 ± 3 μm. The film grew in the shape of a square [6], characteristic of (100)-oriented homoepitaxial growth, and the culet size after growth is 370 μm × 370 μm. The film surface contains several square growth steps similar to those described in the literature for homoepitaxial diamond growth [7, 8]. Also evident in figure 1(b) is the presence of dark surface defects which are attributed to localized crystal twinning. Twinning in vapour-grown diamond films has been explained in terms of a parameter, $\alpha = (V_{100}/V_{111})\sqrt{3}$, which describes the ratio of relative growth rates on {100} and {111} planes and can be used to characterize the film texture and crystal shape [8]. The twins exist only on the surface of the film and can be polished away to reveal a smooth surface for use in a diamond anvil cell.

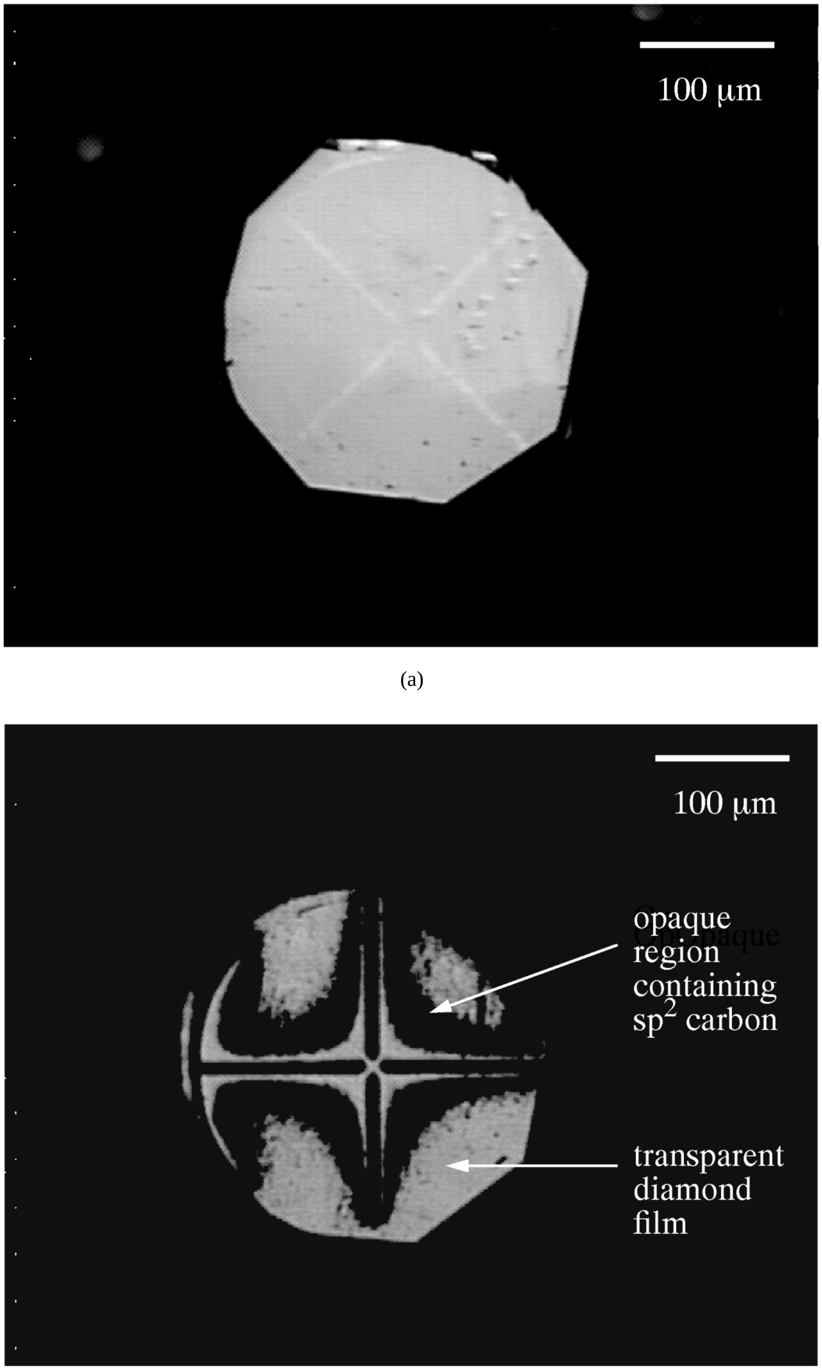
The as-grown film of figure 1(b) cannot be tested adequately in a diamond anvil cell because its surface roughness prevents uniform contact with the opposing anvil. To solve this problem we have developed a simple polishing apparatus consisting of a half-inch-diameter industrial-grade polycrystalline diamond disc attached to a high-rpm rotating wheel. The apparatus also allows facets to be cut into the diamond film at a given angle with respect to the culet to effectively reduce its diameter and therefore obtain a size match with the opposing anvil in the diamond anvil cell (DAC). An attempt to cut eight facets each at 30° with respect to the culet surface resulted in the optical micrograph of figure 2 shown in (a) reflection and in (b) transmission. Although the technique requires refinement, a roughly octahedral-shaped film was produced with a diameter nearly the same size as that of the original culet. The underlying zirconium probes were visible in reflected light even after the early stages of polishing due to the low thickness of the film and the optical transparency of diamond. The thickness of the film after polishing the culet face was determined by an optical depth-of-focus method to be 15 ± 3 μm. The average peak-to-valley surface roughness of the polished film was determined by surface profilometry to be 320 nm. The transmission micrograph of figure 2(b) reveals broad dark regions which surround each



(a)

(b)

Figure 1. Optical micrographs showing the tip of a (100) natural type-Ia diamond anvil taken (a) in transmission before deposition of a homoepitaxial diamond insulating layer using MPCVD, and (b) in reflection after deposition. The anvil tip and ‘four-finger’ zirconium probes shown in (a) are over-coated with an approximately 20 μm thick diamond layer. Growth steps are visible in (b) as well as dark spots on the film surface which are attributed to surface twins.



(a)

(b)

Figure 2. Optical micrographs in (a) reflection and (b) transmission showing the final stage of polishing the as-grown diamond layer for use in a diamond anvil cell device. The underlying probes can be seen even in reflected light. The opaque regions surrounding the probes in (b) contain sp^2-bonded carbon as confirmed by Raman spectroscopy.

zirconium probe and are presumably located at the metal/diamond film interface. The origin of these dark regions is not well understood. It may be that the metallic probes result in localized electromagnetic field enhancement during the initial stages of the microwave-plasma processing. This may promote the growth of some non-diamond-phase carbon, and hence lead to the lack of transparency in these areas.

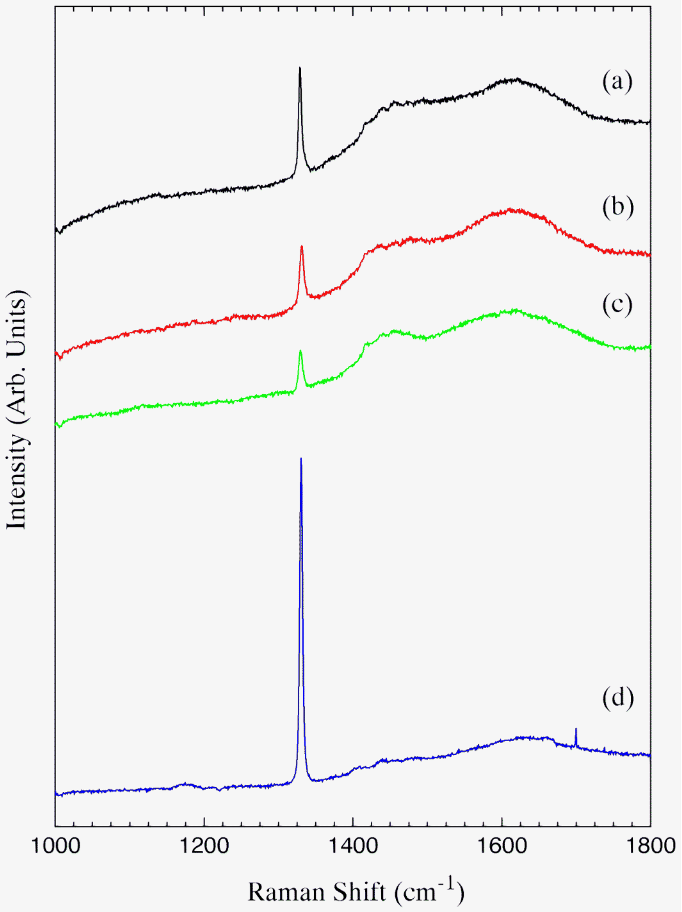


Figure 3. Micro-Raman spectra taken from the as-polished diamond film at (a) the centre of the film between the four probes, at (b) the non-transparent (dark) area surrounding each probe, at (c) the probe, and at (d) the transparent (lighter) area. The laser spot size in the lateral direction was 1 μm in diameter and the depth of focus (penetration) was 10 μm. The spectra show the film to contain some sp^2 carbon content in addition to the characteristic diamond peak at 1332 cm^{-1}.

Raman spectroscopy was performed to determine the quality of the as-grown and as-polished film at several locations. The as-grown and as-polished films show similar spectra with the exception that the as-polished film is of slightly higher quality. In all of the spectra observed there was a characteristic diamond peak at 1332 cm^{-1} as well as some degree of non-diamond-phase carbon present, the amount depending on the location on the film. Figure 3 shows Raman spectra taken at four characteristic areas of the film: (a) at the centre of the film between the four probes as seen in transmission, (b) over the broad dark regions as seen in transmission, (c) over the probes as seen in transmission, and (d) over the lighter

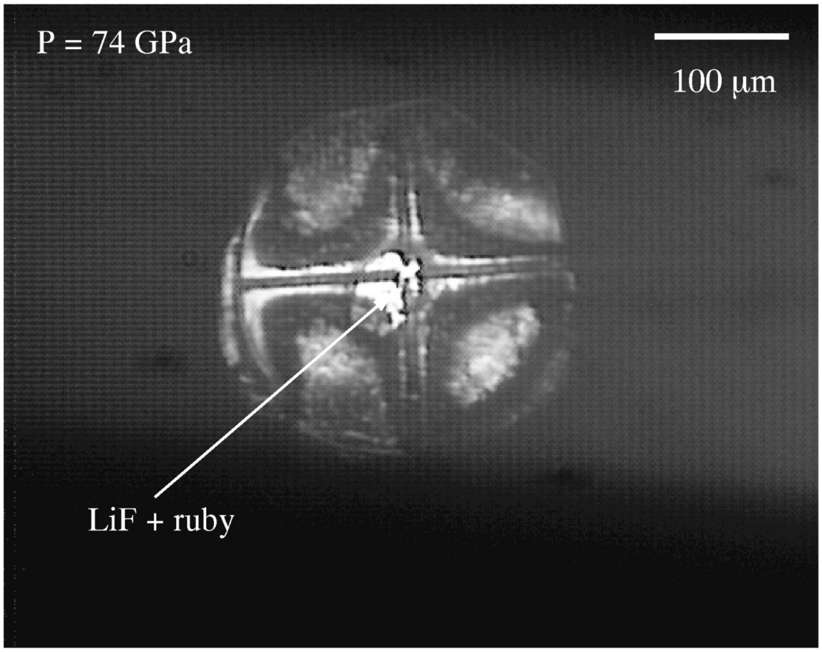


Figure 4. An optical micrograph of the homoepitaxial diamond film as seen through the diamond anvil cell view-port at 74 GPa. The transparent region in the centre is the LiF + ruby sample. The diamond film and electrical probes do not show any deformation up to the highest pressure.

transparent regions. The spectra for regions (a), (b), and (c) are very similar and show broad peaks centred at 1460 cm^{-1} and 1615 cm^{-1}. These peaks are attributed to a small amount of sp^2-bonded carbon (which has a Raman cross-section about 50 times that of diamond). The film quality on the transparent regions as seen in figure 3(d) is clearly better than that over the probes or over the broad dark regions. Similar experiments in growing homoepitaxial diamond films on anvils not containing metal probes result in higher-quality, more transparent films [5]. Therefore, the presence of the metallic probes appears to lower the quality of the diamond film.

In order to evaluate the mechanical integrity of the homoepitaxial diamond film it was employed as one of the anvils in a DAC. A natural (100)-oriented diamond anvil was used in an opposed anvil configuration against the synthetically grown homoepitaxial layer. The surface contact between the two diamond anvils should be near perfect, hence the need for a smooth polished finish of the grown diamond film. A steel gasket with a small (75 μm) hole in its centre is used to contain the sample to be studied at high pressure. Lithium fluoride (LiF) was placed in the gasket hole because it is has a wide band gap and is optically transparent over a very wide range of pressure. The LiF serves as an optical window for visually observing the zirconium probes and homoepitaxial film under high pressure. Small (10 μm) ruby crystals were also placed in the gasket hole so that the pressure could be determined by measuring the red-shift in wavelength of the R_1 fluorescence line of these crystals [9]:

$$P \text{ (GPa)} = 380.8[(\lambda/\lambda_0)^5 - 1]$$

where λ_0 (693.75 nm) is the wavelength of the R_1 line at atmospheric pressure and λ (nm) is the wavelength at pressure P. A maximum λ of 719.14 nm was reached in our experiment, corresponding to a pressure of 74 GPa.

The DAC was used to compress the LiF + ruby sample in increments of approximately 4 GPa. After each loading increment, the appearance of the film could be observed by optical microscopy via optical ports in the cell without relieving the pressure. Figure 4 shows an optical micrograph of the diamond film at 74 GPa. The edges of the gasket hole became deformed with increasing pressure, but the film and probes show no sign of deformation or spalling. The apparent decrease in transparency of the film at high pressure is due to bowing of the gasket and the corresponding scattering of light. After decompression of the DAC to ambient pressure the film was checked again and did not show any sign of deformation or spalling.

The integrity of the homoepitaxial diamond film up to a pressure of 74 GPa is impressive and even unexpected considering the significant presence of non-diamond-phase carbon. Our study suggests that the metal–diamond interface in the homoepitaxial film grown over the metal probes can withstand the stresses encountered in diamond anvil cell devices.

We offer the following conclusions.

(1) Homoepitaxial diamond films can be successfully grown on diamond anvils containing metallic conducting probes at their tips. The as-grown films, which are too rough for use in diamond anvil cells, can be polished using an industrial-grade polycrystalline diamond wheel and successfully employed in diamond anvil cell devices.

(2) Raman spectroscopy reveals the presence of sp^2-bonded carbon within the film. Despite these impurities, no deformation or spalling occurred up to a pressure of 74 GPa. Homoepitaxial diamond growth over the metallic probes can sustain the ultra-high stresses encountered in diamond anvil cell devices.

(3) With further developments, this idea can be employed for electrical transport measurements and direct ohmic heating of samples under ultra-high pressures.

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