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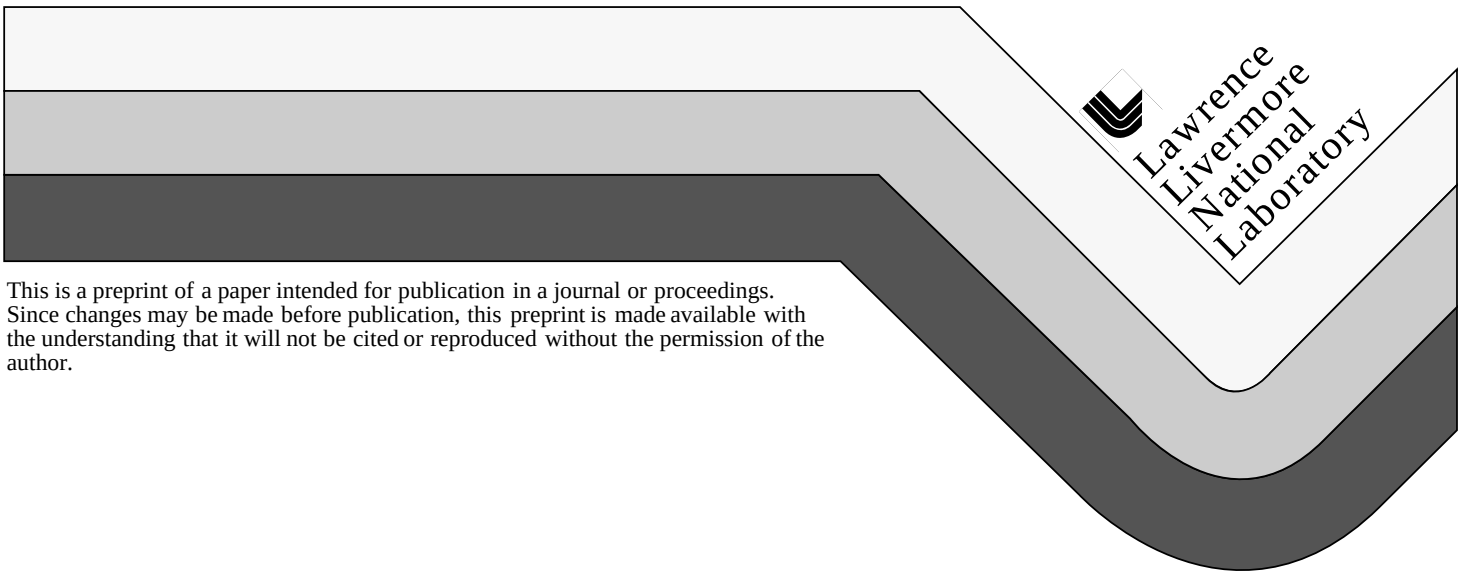

X-Ray Diffraction Studies Using Diamond Coated Rhenium Gasket to Megabar Pressures

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X-ray diffraction studies at megabar pressures are limited by the sample thickness between the diamond anvils. High strength gaskets are desirable to improve the quality of x-ray diffraction data. We present a technique which employs a microwave plasma chemical vapor deposited diamond layer on one side of a rhenium gasket. As a test case, we show energy dispersive x-ray diffraction data on rare earth metal neodymium to 153 GPa using a synchrotron source. The increased sample thickness results in an unambiguous crystal structure determination of a monoclinic phase in neodymium above 75 GPa.
[chemical vapor deposition, diamond, rhenium gasket, x-ray diffraction, neodymium]

1. Introduction

Single crystal diamonds and metal gaskets are the two most important components in a modern diamond anvil cell (DAC) designed for research in the multi-megabar (100-1000 GPa) pressure range. Single crystal diamond anvils are carefully selected with low internal strains, low impurity level concentrations, and high crystal perfection [1]. During pressurization of diamond anvil cells, the gasket plastically flows around the tips of the opposing anvils and acts to maintain a uniform stress distribution within the sample, as well as to hold the sample in place. With increasing pressure, however, the sample thickness is reduced due to the large deformation of the gasket itself. For the case of a gasket compressed in a DAC in an axially symmetric manner between flat rigid anvils with a no- slip boundary condition between the gasket and anvils, the following relation holds between the gasket flow stress σ, the sample thickness h, and the pressure distribution dP/dr.

$$\sigma = h\,(dP/dr). \qquad (1)$$

If the sample thickness, h, within the gasket hole becomes too small, the reduced sample volume degrades the x-ray diffraction signals as well as optical signals generated using laser excitation.

Equation (1) has been employed to measure the flow stress of rhenium at high-pressure [2] and more recently to measure the flow stress of uranium and tantalum at ultra-high pressure [3]. Recent finite-element modeling of diamond deformation at multi- megabar pressure [4] has under-scored the need for high yield strength gasket materials for optimizing sample thickness at high pressures.

To address this problem, microwave plasma-enhanced chemical vapor deposition (CVD) was used to deposit a layer of polycrystalline diamond onto a rhenium gasket. The high yield strength of the diamond layer prevents excessive thickness reduction of the sample in the gasket hole. Rhenium is chosen for the gasket material because of its suitability for high pressure/high temperature measurements and earlier high pressure studies have shown that the ambient pressure hcp phase is stable to 216 GPa [5]. While CVD diamond deposition is routinely carried out on materials such as silicon (for electronic-based applications) as well as on several metals such as tungsten carbide and titanium alloys (for wear-resistant applications), diamond coating of rhenium has largely been unexplored. Despite the thermally-induced stress expected in this coating, we have deposited a thick, well-adhered diamond layer on the rhenium gasket and used it in high pressure experiments to 153 GPa on rare earth metal neodymium. The success in coating rhenium with diamond and in obtaining high pressures in the DAC may be related to the unusually high melting temperature (3459 K) of rhenium. The diamond deposition temperature (1000 - 1500 K) is well below half of its melting temperature, at which point dislocations would normally begin to anneal out of the material and reduce the work-hardening effects induced during the gasket indentation process. Therefore, the CVD diamond coating process on rhenium would not degrade the work hardening of rhenium achieved during the pre-indentation process in a diamond anvil cell.

2. Experimental

A diamond anvil cell using bevel diamonds of 70 micron central flat, 7- degree bevel, and 300 micron culet size was employed in the present experiments. Before depositing the diamond film onto the gasket, the gasket was indented in the DAC and a 25-micron diameter sample hole was drilled according to standard procedures. The diamond deposition was performed using a 6 kW microwave plasma CVD system. Figure 1 shows optical micrographs (a) before and (b) after deposition of the approximately 10 micron-thick diamond layer on rhenium gasket. This coating was grown on one side of the gasket only at a processing pressure of 90 torr, a methane fraction of 2% (in hydrogen), a microwave power of 1 kW, and a substrate temperature of 1173 K. The rhenium substrate was placed on a 4 inch diameter pyrolytic graphite stage and the deposition time was 6 hours. The side of the rhenium gasket exposed to plasma was covered with a homogenous and well-adhered diamond layer. The film morphology shows well-faceted, micron-size grains, which are of high diamond phase purity as determined by Raman spectroscopy. Figure 2 shows the glancing-angle x-ray diffraction spectrum of the diamond-coated rhenium gasket. The spectrum was indexed to a mixture of cubic diamond phase and a hexagonal close packed phase of rhenium metal. The measured lattice parameter of the cubic diamond structure is 0.3564 nm, which is within 0.1% of the literature value. All high-pressure experiments were carried out using gasket coated with diamond layer on one side only. We expect some diamond coating of the inside walls of the gasket hole. However no cross-sectional studies on the gasket were performed to examine the details of diamond coating on the inside walls of the sample chamber.

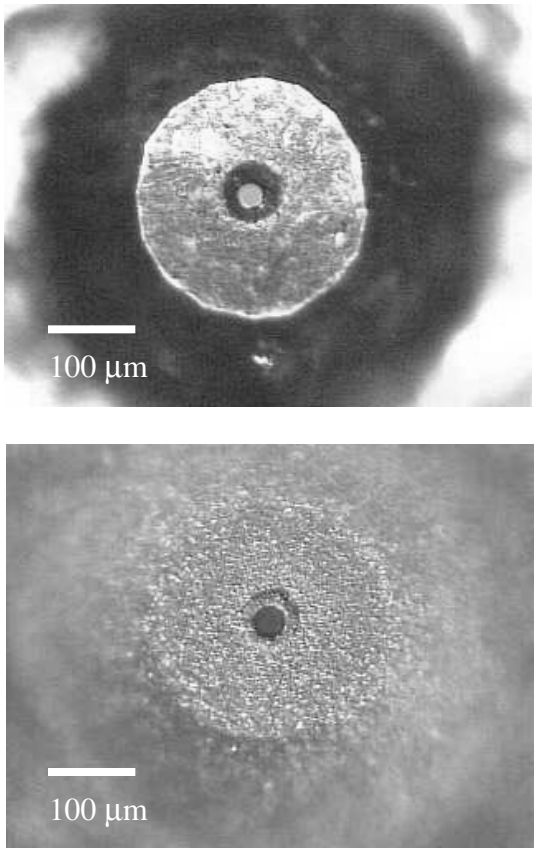

Fig. 1. Rhenium gasket shown (a) before and (b) after deposition of CVD diamond film. The sample hole is approximately 25 µm in diameter.

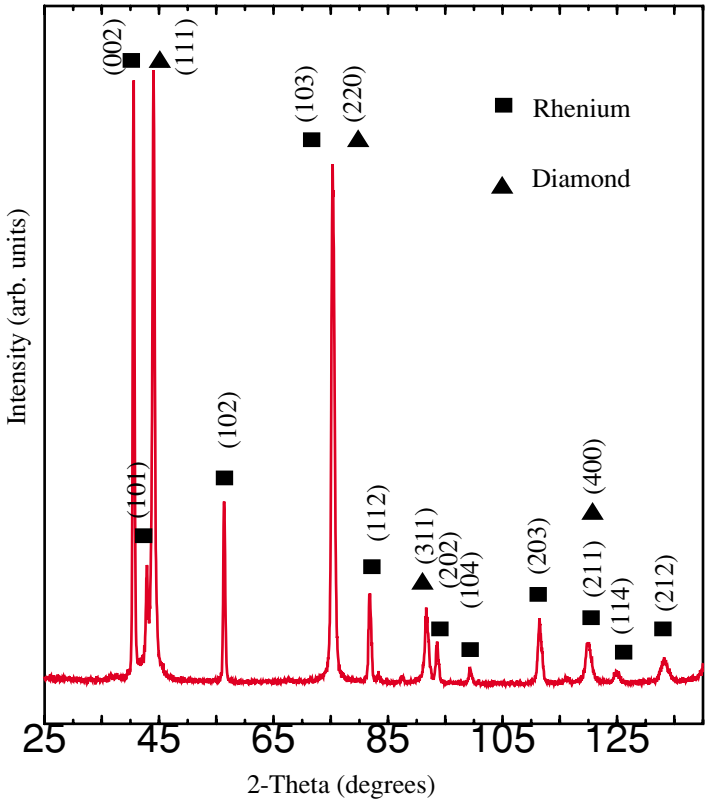

Fig. 2. X-ray Diffraction spectrum of diamond-coated rhenium gasket.

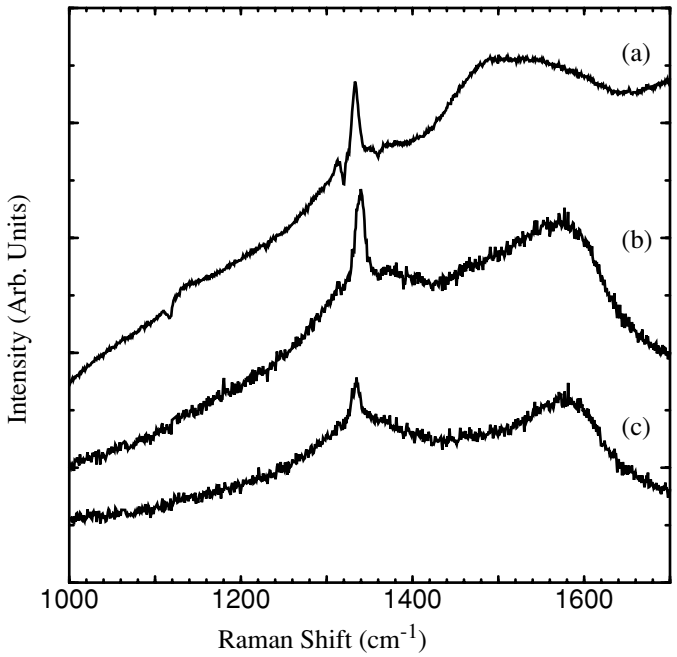

Fig. 3. Raman spectra of diamond films grown on rhenium gaskets at gasket temperatures of (a) 1282 K, (b) 1570 K, and (c) 1636 K.

In order to determine the effect of substrate temperature on diamond film quality, three films were grown on rhenium gaskets at temperatures of 1282 K, 1570 K, and 1623 K. Figure 3 shows the Raman spectra of these films. With increasing substrate temperature the diamond film quality deteriorates as more nanocrystalline graphite forms. This is indicated by more intense 1350 cm^{-1} and 1550 cm^{-1} bands. However, the film grown at the lowest temperature (1273 K) showed a higher diamond content as well as a broad band centered at 1490 cm^{-1} which is attributed to disordered networks of sp^3- and sp^2-bonded carbon. Therefore, there is an optimum temperature window around 1550 K where high quality diamond can be grown on the rhenium gasket.

3. Results

We have chosen the rare-earth metal neodymium as a test case sample for the applicability of the diamond-coated rhenium gasket. Copper was employed as an internal pressure standard in our x-ray diffraction study. Phase transformations induced by ultra-high pressures in rare-earth metals is an active field of study at the present time [6,7]. Complex crystal structures are observed in rare-earth metals at high pressures and identification of these phases is limited by the quality of the x-ray diffraction patterns due to thin samples (few microns) at megabar pressures. Neodymium crystallizes in the double hexagonal close-packed (dhcp) phase at ambient pressures. The following sequence of transformations is known for neodymium [9,10] to 60 GPa:

$$\text{dhcp} \xrightarrow{3.8\ \text{GPa}} \text{fcc} \xrightarrow{18\ \text{GPa}} \text{distorted fcc} \xrightarrow{40\ \text{GPa}} \text{hP3}$$

The ultra-high pressure behavior of neodymium above 60 GPa

is of interest to investigate the f-shell delocalization phenomenon and related phase transformations. We have investigated high-pressure transformations in neodymium to 153 GPa in a DAC using a diamond-coated rhenium gasket.

After the gasket was coated with diamond, a neodymium sample along with a copper pressure marker was placed in the gasket hole. Energy dispersive x-ray diffraction measurements were carried out at beam-line X-17C, NSLS, Brookhaven National Laboratory. A micro-collimated x-ray beam of 11 μm x 6 μm was employed in our x-ray diffraction measurements. In our experiments, the sequence of transformations observed below 60 GPa is similar to earlier results [8,9] as documented above. We observed a new phase transformation in neodymium at a pressure of 75 ±5 GPa from a hexagonal phase with 3 atoms/cell, hp3 phase [8] to a monoclinic C2/m phase [10]. Figure 4 shows the energy dispersive x-ray diffraction spectrum from the neodymium sample and copper pressure marker contained in the diamond-coated rhenium gasket at 89 GPa. The pressures are calculated from the equation of state of copper based on the procedures described in reference 5 and 6. The sample is indexed to the space group C2/m (monoclinic phase with 4 atoms/cell) as described in reference 9 with $a = 0.4858 \pm 0.0004$ nm, $b = 0.2712 \pm 0.0002$ nm, $c = 0.5051 \pm 0.0004$ nm, and $\beta = 118.6° \pm 0.2°$.

The four atoms occupy the 4(i) positions of C2/m with

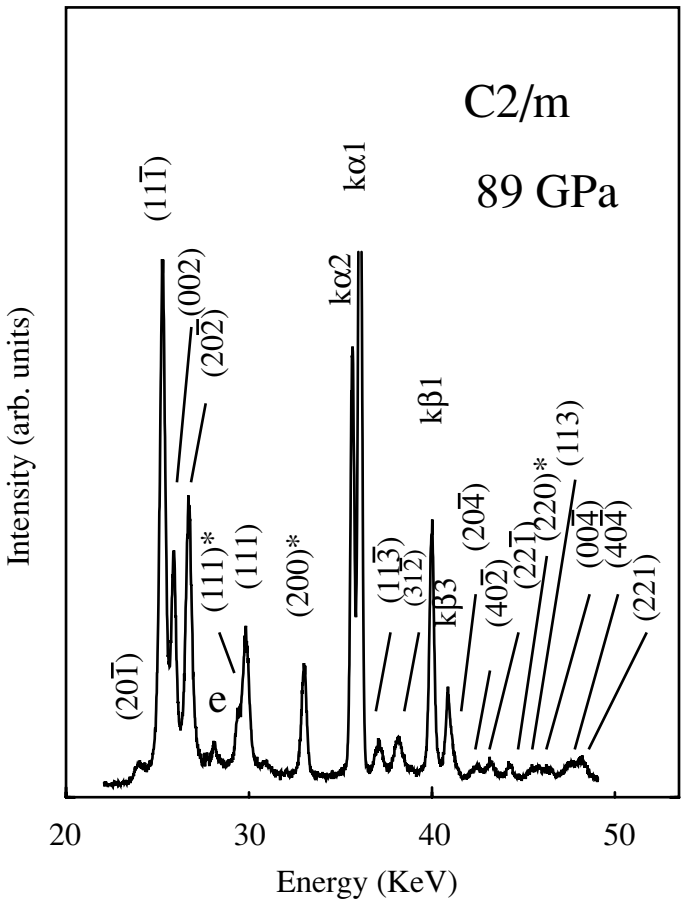

Fig. 4. Energy dispersive x-ray diffraction spectrum from Neodymium sample and a Copper pressure marker contained in a diamond-coated rhenium gasket at 89 GPa.

Table 1. Observed and calculated interplaner spacings dhkl and the observed and calculated intensities for the energy dispersive x-ray diffraction data for neodymium at 89 GPa.

hkl	d_{obs} (A)	d_{calc} (A)	I_{obs}	I_{calc}
11$\bar{1}$	2.287	2.287	100	100
002	2.218	2.218	32	47
20$\bar{2}$	2.128	2.128	51	41
111	1.850	1.851	31	55
11$\bar{3}$	1.418	1.417	8	20
31$\bar{2}$	1.371	1.369	10	3
20$\bar{4}$	1.262	1.262	12	5
22$\bar{1}$	1.185	1.186	4	1
113	1.116	1.114	4	5
00$\bar{4}$	1.107	1.105	1	2
31$\bar{4}$	1.093	1.092	6	1
40$\bar{4}$	1.062	1.059	4	2
221	1.046	1.046	6	1
312	0.937	0.936	2	1
11$\bar{5}$	0.909	0.908	2	1
421	0.886	0.886	7	1
131	0.852	0.853	2	1

coordinates (x, 0, z), ($\bar{x}$, 0, $\bar{z}$), (x + 0.5, 0.5, z), and ($\bar{x}$ + 0.5, 0.5, $\bar{z}$). These positional parameters for Nd are similar to values obtained for the C2/m phase in cerium at high pressures. Table I shows a comparison of the observed and calculated interplaner spacing dhkl and the observed and calculated intensities for the x-ray diffraction data for neodymium at 89 GPa. It can be seen from Table 1 that the C2/m phase gives an excellent fit to the observed seventeen diffraction peaks. The large numbers of observable diffraction peaks are due to a thicker sample afforded by the use of the diamond-coated rhenium gasket. The measured compression of neodymium at 89 GPa is V/Vo = 0.428. The C2/m phase is stable to the highest pressures of 153 GPa (volume compression V/Vo = 0.37). The diamond layer on top of the rhenium metal did not crack to the highest pressure in these experiments.

4. Conclusions

We offer the following conclusions:

(1) Diamond films as thick as 10 μm can be successfully deposited on rhenium metal using the standard CH_4/H_2

chemistry by a microwave plasma CVD process.

(2) High-pressure x-ray diffraction studies on a neodymium sample were successfully carried out to 153 GPa in a diamond anvil cell with excellent diffraction pattern quality. We attribute the excellent diffraction pattern quality to a thicker sample afforded by the use of diamond coated rhenium gasket.

(3) The high quality x-ray diffraction patterns resulted in a positive identification of a C2/m phase in compressed neodymium above 75 ±5 GPa. This C2/m phase is similar to the one observed in compressed cerium. This C2/m phase of Neodymium was found to be stable to pressures as high as 153 GPa.

(4) X-ray measurements in the radial direction are needed to measure stress anisotropy in the sample and the diamond-coated rhenium gasket. This would establish the maximum deviatoric stress supported by the diamond-coated gasket and the sample at megabar pressures.

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References

1. Liu J. and Vohra Y. K., *Appl. Phys. Lett*., **68,** 2049 (1996)
2. Jeanloz R., Godwal B. K., and Meade C., **Nature** (London) **349,** 687 (1991)
3. Weir S. T., Akella J., Ruddle C., Goodwin T, and Hsuing L., *Phys. Rev. B*, **58,** 11258 (1998)
4. Merkel S., Hemley R. J., and Mao H. K., *Appl. Phys. Lett.* **74**, 656 (1999)
5. Vohra Y. K., Duclos S. J., and Ruoff A. L., *Phys. Rev. B,* **36**, 9790 (1987)
6. Chesnut G.N. and Vohra Y. K., *Phys. Rev. B*, **57**, 10221 (1998)
7. Chesnut G. N. and Vohra Y. K., *Phys. Rev. Lett*., **82**, 1712 (1999)
8. Zhao Y.C., Porsch F., and Holzapfel, W. B., *Phys. Rev. B*, **50**, 6603 (1994)
9. Akella J, Xu J., and Smith G. S., *Physica*, **139** and **140 B**, 285 (1986)
10. McMahon M.I. and Nelmes R.J., *Phys. Rev. Lett.,* **78**, 3884 (1997)