Technique for x-ray markers at high pressure in the diamond anvil cell

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X-ray markers as powder or foil can interfere with optical studies on a sample. Use of the gasket itself as an x-ray marker requires careful collimation of the x-ray beam so that only the gasket material adjacent to the sample is studied. (The pressure drops rapidly as the radius increases in the gasket.) By depositing a thin half-micron thick marker on the wall of the sample hole, these problems are eliminated and a large beam can be used, but for pressure measurements only the submicron layer will be involved. © *2005 American Institute of Physics.*
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At pressures to 3 GPa range, the free piston gauge allows accurate measurements of pressure.[1] In 1973 Ruoff and Lincoln[2,3] developed a dynamic absolute pressure gauge (based on the simultaneous measurement of length and elastic constants) and demonstrated its very high accuracy by calibrating the freezing pressure of mercury at the triple point of water (0.7571 GPa) and comparing this with free piston gauge results. This was later extended greatly by Zha *et al.*[4] to 55 GPa. It is likely that it will be a long time before this technique is used in the multimegabar regime.

X-ray marker materials whose isothermal $P(V)$ relationships are deduced by shock experiments [by conversion of Hugoniot or $P_H(V)$ data to isotherms] provide the only primary pressure gauges in the multimegabar range.[5] The difference between P_H and P at a given pressure is least for very stiff materials with very high melting temperatures.[6] Suppose the experimentalist wishes to do optical studies on a sample, and hence, does not want to mix an x-ray marker powder with the sample or to place a foil in the sample region. One way to circumvent this problem is to use a highly collimated x-ray beam and to diffract from the gasket material (the marker now) at the edge of the sample hole. This is successful[7] but requires tedious collimation and very careful alignment as there is a large pressure gradient in the radial direction in the gasket.

The present technique eliminates these difficulties, by studying a marker whose spatial distribution in the radial direction is only half of a micron immediately adjacent to the sample.

In the present article we describe a method which allows precise measurement of the pressure at the edge of the sample without the need for a tiny collimator. This involves placing a thin (submicron) layer of Pt by ion beam deposition.

Figure 1 shows a 0.5-μm-thick Pt deposition on the wall of the sample hole which has a diameter of 17.5 μm. It must be noted that most of the sample is located near the perimeter of the hole. The gasket hole was formed by focused ion beam (FIB) milling.[8] The FIB system used in this work is a dual-column instrument (model DB235) made by FEI, Inc. (Hillsboro, OR). The gallium ion beam removes material from a specimen in locations definable with submicrometer precision. The field-emission electron column provides high resolution scanning electron microscopy, often a very useful adjunct to the milling process.

The measured milling rate of the tungsten gaskets is about 1.7 $\mu m^3/(pA\ s)$. The milling rate is linear provided that the aspect ratio of the hole is not too large. As an ion-milled hole deepens the sputtered material is removed less efficiently. The aspect ratio and the available ion current therefore set a practical limit on the diameter and depth of ion-milled holes. We used an ion beam current of 7 nA. Milling times varied from 20 min to 1 h depending on the desired hole diameter and the local thicknesses of the gaskets formed by the indenting procedure. A 7 nA beam current provides a reasonable milling rate with our FIB. The beam diameter, a function of the current, is still small enough to provide a sharply defined hole. The ion beam diameter at 7 nA is nominally about 150 nm. The beam is rastered in a circular pattern to form the holes. An auxiliary oscilloscope display shows the ion-excited secondary electron signal generated as the ion beam is swept over the area of the hole. The oscilloscope display has sufficient spatial resolution to show quite clearly when a hole completely penetrates a gasket.

Platinum deposition is achieved by introducing a gaseous organoplatinum compound into the analysis chamber through a retractable needle connected to a heated crucible. The needle is positioned about one diameter from the surface by the gasket hole. The sample is tilted and the ion beam is programmed to raster over a rectangular area on the sidewall of a gasket hole. The organoplatinum gas is decomposed and

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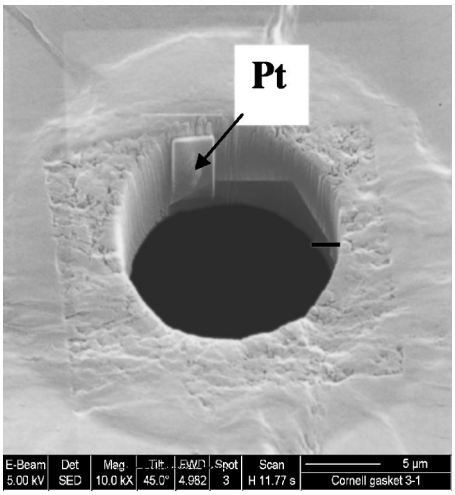

FIG. 1. Sample hole (17.5 μm diameter) in tungsten gasket preindented with a 35 μm diameter tip to a thickness of 8 μm. On the inside wall is the Pt deposit of dimensions (in μm) $2.8\times4\times0.5$ μm.

metal is deposited in the desired area. The ion beam is still removing some surface material, but at a beam current of 4–6 pA/μm^2 metal deposition is the dominant process.

Figure 2 shows two diffraction peaks of Pt which were used to obtain the pressure of 301 GPa. Dislocations and plastic deformation change certain peak positions in face-centered-cubic materials. The (111) and (222) peaks shift equally in opposite directions thus canceling a change in the measured lattice parameter and, hence, in the pressure.[9] Methane was used as the pressure medium. Its behavior is described elsewhere.[10] The x-ray marker was used to calibrate an optical pressure scale to 301 GPa based on the Raman signal from the surface of the center of the diamond tip to 301 GPa.[11] The x-ray marker technique should be helpful in carrying out research at pressures greater than those at the earth's core.[12,13]

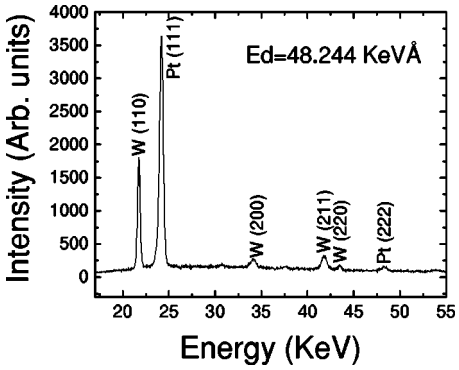

FIG. 2. The diffraction pattern at 301 GPa showing the two Pt peaks.

The technique could be used in other ways for ultrapressure research. Thus, three thicker wall supports could be deposited with the top of the support at the midpoint of the height and these could support a specimen to be heated by a laser without much heating of the diamond anvils.

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[1] D. H. Newhall, L. H. Abbot, and R. A. Dunn, in *High Pressure Measurements* edited by A. A. Giardini and E. C. Lloyd (Butterworths, Washington, DC, 1963), p. 339.
[2] A. L. Ruoff, R. C. Lincoln, and Y. C. Chen, J. Phys. D **6**, 1295 (1973).
[3] R. C. Lincoln and A. L. Ruoff, Rev. Sci. Instrum. **44**, 1239 (1973).
[4] C. S. Zha, H. K. Mao, and R. J. Hemley, Proc. Natl. Acad. Sci. U.S.A. **97**, 13494 (2000).
[5] W. J. Nellis, J. A. Moriarty, A. C. Mitchell, M. Rose, R. G. Dandrea, N. W. Ashcroft, N. C. Holmes and G. R. Gathers, Phys. Rev. Lett. **60**, 1414 (1988).
[6] Y. K. Vohra and A. L. Ruoff, Phys. Rev. B **42**, 8651 (1990).
[7] A. L. Ruoff, H. Xia, and Q. Xia, Rev. Sci. Instrum. **63**, 4342 (1992).
[8] J. Orloff, C. Narayana, and A. L. Ruoff, Rev. Sci. Instrum. **71**, 216 (2002).
[9] C. S. Barrett and T. B. Massalski, *Structure of Metals* (McGraw-Hill, New York, 1966), p. 459.
[10] L. Sun, A. L. Ruoff, C.-Z. Zha, and G. Stupian, Phys. Rev. Lett. (submitted).
[11] L. Sun, A. L. Ruoff and G. Stupian, Appl. Phys. Lett. **86**, 014103 (2005).
[12] A. L. Ruoff, H. Xia, H. Luo, and Y. K. Vohra, Rev. Sci. Instrum. **61**, 3830 (1990).
[13] A. L. Ruoff, H. Xia, and Q. Xia, Rev. Sci. Instrum. **63**, 4342 (1992).