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Diamond anvil cell techniques are now well established and powerful methods for measuring materials properties to very high pressure. However, high pressure resistivity measurements are challenging because the electrical contacts attached to the sample have to survive to extreme stress conditions. Until recently, experiments in a diamond anvil cell were mostly limited to non-hydrostatic or quasi-hydrostatic pressure media other than inert gases. We present here a solution to the problem by using focused ion beam ultrathin lithography for a diamond anvil cell loaded with inert gas (Ne) and show typical resistivity data. These ultrathin leads are deposited on the culet of the diamond and are attaching the sample to the anvil mechanically, therefore allowing for measurements in hydrostatic or nearly hydrostatic conditions of pressure using noble gases like Ne or He as pressure transmitting media. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4809025]

I. INTRODUCTION

Recent advances in diamond-anvil cell methods have expanded the domain of static pressure experiments well into the megabar pressure range.[1] Among these measurements, resistivity presents particular importance for condensed matter physics research. It is a great tool for the investigation of superconductors or materials that become superconducting with the application of pressure. The measurement of electrical resistivity as a function of temperature is a direct probe that can distinguish insulating and metallic behavior.

The initial four-probe diamond anvil cell (DAC) resistivity approach developed by Mao and Bell[2] employed metallic wires held in electrical contact with the sample inside the sample chamber of the DAC using a solid pressure transmitting medium, such as NaCl. NaCl is known to be a relatively soft material but it is by no means a hydrostatic pressure transmitting medium. Another challenge with resistivity measurements is related to the shear stress that can develop at high pressures that often breaks the metal leads or produces a short circuit between leads because of their increased width under pressure due to plastic flow. Since high pressure samples tend to be small ($<100 \mu$m), another difficulty is the arrangement of the sample itself.[3] Grzyboski and Ruoff[4] used lithographic design of the electrical leads onto the diamond anvil directly where a solid pressure transmitting media "locked" the sample in place in electrical contact with the lithographic leads.

Further combinations of photolithographic and protective insulating layers were adopted to improve the method.[5] In order to make the lithographic depositions stable at even higher pressures (e.g., megabar), Weir *et al.*[6] developed techniques of diamond layers deposited on top of a photolithographic conductive deposition.

While obvious progress has been made in the direction of DAC resistivity measurements by reaching megabar pressures, still, one remaining issue was that for all adopted designs thus far, pressure transmitting media other than noble gases were used. In this paper we present a method that allows the use of an inert gas, such as neon, as a pressure transmitting medium, known to provide nearly hydrostatic pressure conditions. For instance, Ne provides a hydrostatic environment for pressures up to about 5 GPa (e.g., at or near 300 K); above this value, the pressure gradients remain very small: at 50 GPa the standard deviation of pressure is less than 1%.[7] In fact, only He is better as a chemically inert pressure medium, but it is known that He causes breakage of anvils (He embrittlement) through penetration into diamond anvils by a diffusion process enhanced by preexisting defects.[8] Using focused ion beam ultrathin lithography, we deposited Pt-based electrodes directly on the diamond. The electrodes are attached to the sample electrically and mechanically. The detailed design of our DAC resistivity experiment and the focused ion beam ultrathin lithography procedure are described below, and two sample data sets obtained with DACs are shown. Finally, we show designs of beveled diamonds with focussed ion beam (FIB) conductive depositions that survived pressures in excess of 200 GPa (down to 4 K in temperature).

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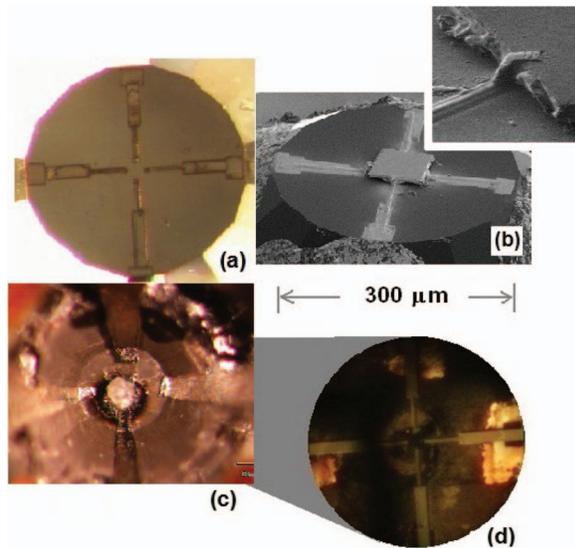
FIG. 1. Anvils with the electrical probes assembly. (a) The flat diamond culet with the FIB probes before the attachment of the sample. (b) The same diamond with the sample attached. The inset shows one probe running over the edge of the crystal sample. (c) The Pt metal leads inside the indented BN that will carry the signal from the sample to FIB electric probes further to the electronics. (d) Picture showing the culet, after the DAC was closed, with the attached sample and FIB probes in contact with the outer Pt-foil leads.

II. DESIGN

High pressure resistivity measurements using symmetric DAC[9] were carried out on small samples of approximately $40 \times 40 \times 10 \ \mu m^3$ cleaved and polished down from a few mm size well-characterized single crystals ($Pr_{1.85}Ce_{0.15}CuO_4$ and $Bi_{1.98}Sr_{2.06}Cu_2O_{8+\delta}$). The measurements were performed using a four-probe van der Pauw configuration.[10] The samples were attached to the flat tip of the diamond using FIB ultra-thin lithographic deposited Pt-based leads.[11] The inner end of these leads passed over the sample, thereby assuring electrical contact and rigid attachment of the sample to the diamond.

Figure 1(b) shows a $Pr_{1.85}Ce_{0.15}CuO_4$ crystal wired for the experiment on a 300 μm flat diamond culet. The inset presents the end FIB probe running over the edge of the sample. A picture of the same diamond with the FIB depositions before the sample was attached is shown in Fig. 1(a). The low resistivity Pt-based FIB probes were deposited from the precursor (trimethyl)methylcyclopentadienyl-platinum (STREM Chemicals 99%) in an FEI 620 DualBeam FIB/SEM with gas feed system.[12]

First, the diamonds were glued to the tungsten carbide seats using STYCAST 2850 FT epoxy and then the surface of the culet, to be deposited on, was cleaned and a conductive carbon coating was applied by sputtering. The conductive coating is applied to prevent charge build-up during milling. The coating is removed from the area underneath the contacts to be deposited to provide better adhesion to the diamond surface. Inside the FEI machine, the area from the flat diamond culet, to be deposited on, was then gallium ion milled to remove the carbon for a clean surface. The Pt-based lithographic leads are deposited at a typical thickness of approximately 0.5 μm as calculated from the ion current dose (typical value $\approx 2 \times 10^{17}$ A s/cm^2), area deposited, and the
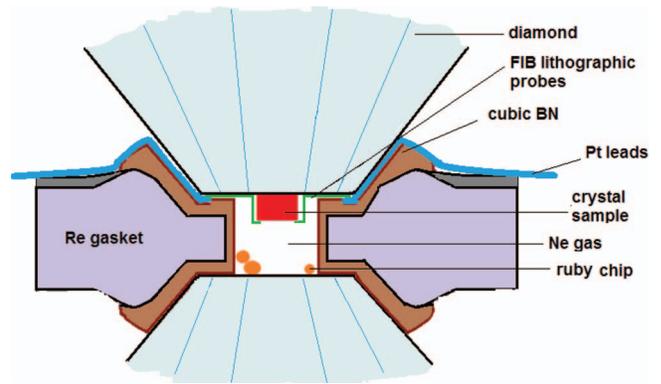
FIG. 2. Schematic drawing of the loaded resistivity DAC setup.

time of deposition. The deposited electrodes could be manufactured with 20 nm resolution, which allows the attachment of very small samples for measurements in a DAC, this approach has a potential for extending this technique to the highest possible pressures with DAC. After deposition, the electrical continuity of the depositions and insulation between depositions and the deposition-free culet of the diamond were checked using a micromanipulator and Keithley current sources and voltmeters. Typical measured value of resistance of our FIB probes was 130 Ω, so a resistivity of about 300 $\mu\Omega$ cm (assuming the probe is built primarily of two blocks: $80 \times 20 \times 0.5 \ \mu m^3$ and $80 \times 5 \times 0.5 \ \mu m^3$), which is close to the accepted value from the literature.[13] It should be noted that this value is an order of magnitude larger than the room temperature resistivity of pure platinum metal (10.42 $\mu\Omega$ cm). Nevertheless, the FIB probes were robust and reusable by cleaning the culet with the FIB probes using alcohol.

Previously, a Re or stainless steel gasket was indented first to 40 μm thickness and a $\sim 100 \ \mu m$ hole centered in the indentation was drilled. Cubic boron nitride (BN)/epoxy was indented inside the indented gasket, creating a continuous thin insulating layer. Four micro-electrodes made by cutting with a laser under microscope on 5 μm thin platinum foil were displayed in a radial position and indented in the BN/epoxy to match the FIB probes at the edge of the diamond culet (Fig. 1(d)), and so assured electrical connection from the sample to the electronics (Fig. 1(c)). The BN/epoxy was drilled in the center to match the gasket's hole, and the space created formed the sample chamber. Funamori and Sato present in more details the use of BN gasket for diamond-anvil experiments.[17] Ruby chips were placed inside the sample chamber and *in situ* pressure was determined by shining a laser on one of the ruby chips and measuring the calibrated fluorescence shift.[18] Finally, the DAC was closed in pre-compressed Ne gas at about 0.2 GPa using a home-built gas loading system. A schematic drawing of the loaded resistivity DAC setup is shown in Fig. 2. The DAC was placed in a cryostat and the electrical wires connected to standard electronics. During the experiment pressure was increased at room temperature and was measured *in situ* at low temperature using ruby fluorescence. Further details on high pressure experiments in DAC can be found in Ref. 19. The highest pressure attained in the $Pr_{1.85}Ce_{0.85}CuO_4$ high pressure DAC
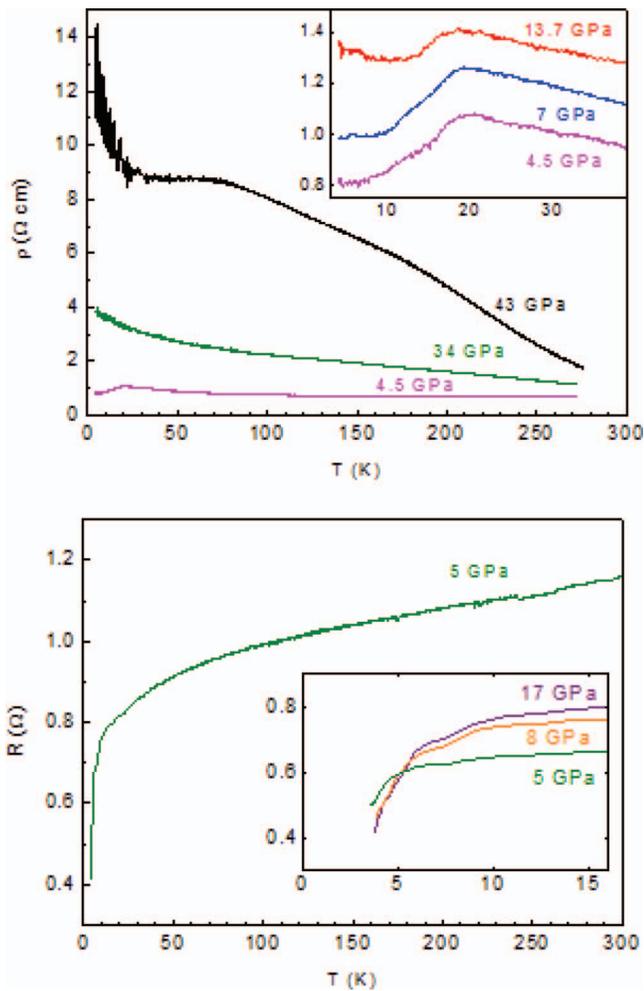
FIG. 3. Typical DAC high pressure resistivity data of $Pr_{1.85}Ce_{0.15}CuO_4$ in upper panel and $Bi_{1.98}Sr_{2.06}Cu_2O_{8+\delta}$ in lower panel. Adapted from Rotundu *et al.*[14] and Ćuk *et al.*,[16] respectively.

resistivity experiment was limited by the collapse of the gasket at 43 GPa.

III. EXPERIMENTAL TESTS

Figure 3 shows experimental data of two experiments using the designed anvils. Upper panel shows resistivity data versus temperature for a few selected pressures of the electron-doped $Pr_{1.85}Ce_{0.15}CuO_4$ (adapted from Rotundu *et al.*[14]). At 2.72 GPa X-ray data (not shown here) showed that 88%–98% of the phase T′[15] (which is superconducting) transforms into the insulating T.[14] The inset shows a very small pressure dependence of T_c of the T′ phase. From the high pressure resistivity data it was possible to show that the T phase here is insulating (impossible to determine from the X-ray data alone), and that with application of higher pressures this phase becomes even more insulating, as shown by the overall increase in resistivity. In the lower panel of Fig. 3 we show resistance versus temperature data of $Bi_{1.98}Sr_{2.06}Cu_2O_{8+\delta}$ (adapted from Ćuk *et al.*[16]) around the superconducting transition for selected pressures. Above the transition the expected metallic behavior is seen in the inset.
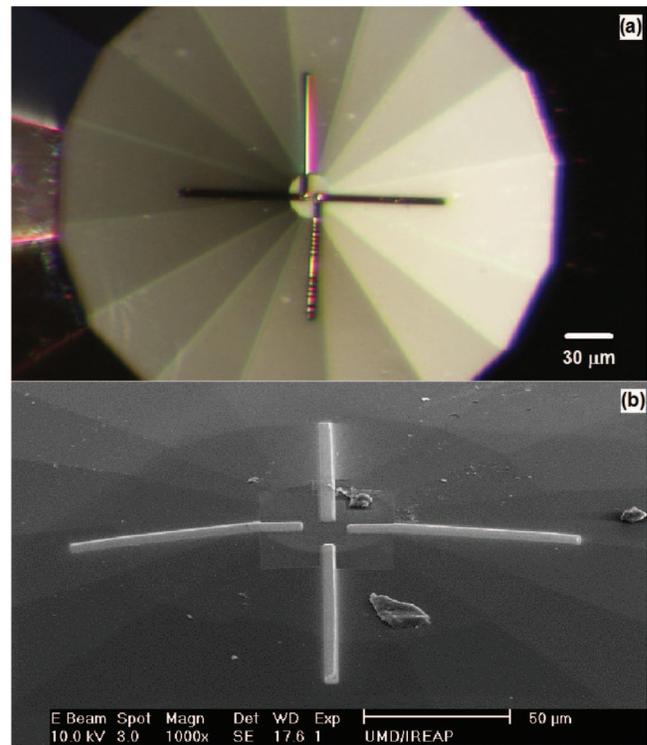
FIG. 4. Beveled diamonds with FIB lithographic electrical contacts for multimegabar DAC resistivity measurements.

Finally, similar design of FIB lithographic probes deposited on beveled diamonds that survived pressure tests in excess of 200 GPa (down to 4 K in temperature) are shown in Fig. 4. For instance in our recent experiments we succeeded in bringing NiO sample with four electrodes prepared by FIB to 240 GPa (BN/epoxy gasket, no pressure medium). In Fig. 4(a) there is a 30 μm culet diamond with quasi-four FIB probes of 4 μm width and 0.06 μm thickness. Figure 4(b) shows small-size culet diamonds with four probe FIB depositions.

IV. SUMMARY

In summary, we have developed a single crystal high pressure resistivity technique in quasi-hydrostatic pressure conditions by loading inert gas as a pressure transmitting medium and by attaching the sample to the diamond culet and wiring it using FIB ultrathin lithography. The setup proved to be stable to pressures as high as 240 GPa and temperature down to 4 K, therefore opening the possibility for DAC low temperature resistivity measurements at multimegabar pressures. We show two examples of DAC resistivity measurements in the 4–300 K temperature range and pressure up to 43 GPa using the above described setup with Ne pressure medium.

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