

Supporting Information

Pauzauskie et al. 10.1073/pnas.1010600108

SI Text

Preparation of Amorphous Carbon Aerogel Precursor. The aerogel was prepared following ref. 1. Briefly, resorcinol (99%) and formaldehyde (37% in water) were purchased from Aldrich Chemical Co. Sodium carbonate (anhydrous) was purchased from J.T. Baker Chemical Co. All reagents were used without further purification. Resorcinol (1.235 g, 11.2 mmol), formaldehyde (1.791 g, 22.1 mmol), and sodium carbonate catalyst (5.95 mg, 0.056 mmol) were added to the reaction solution. The resorcinol-to-catalyst ratio (R/C) employed was 200. The sol-gel mixture was then transferred to glass molds, sealed, and cured in an oven at 85 °C for 72 h. The resulting gels were then removed from the molds and washed with acetone for 72 h to remove all the water from the pores of the gel network. The wet gels were subsequently dried with supercritical CO₂ and pyrolyzed at 1,050 °C under a N₂ atmosphere for 3 h. Bulk densities of the CAs (circa 0.040 g/cm³) were determined from the physical dimensions and mass of each sample.

Diamond-Anvil Cell Loading procedure. Specific diamond cell dimensions were not noted for every experiment, but generally the cell was equipped with diamonds with flat culets of 300 μm or 400 μm diameter or similar while initial cavity dimensions were probably in the range of 100–170 μm in diameter by approximately 35 μm thick. Gasket material was rhenium. Carbon aerogel sample material was loaded into the cavity using handheld needles in air. Neon (Airgas-Specialty Gases, UHP) was loaded into the cavity under high pressure (approximately 22,000 psi). Synthesis pressures were approximately 21.0 GPa, 22.5 GPa, and 25.5 GPa according to the ruby fluorescence scale. For the experiment at 21 GPa, this value of the pressure was measured before heating, for the other pressures after heating. Changes in pressure before, during, and after heating were assumed to be small. Ruby chips used for pressure measurement were not pre-annealed, but most pressures are probably accurate to within a fraction of gigapascal.

Raman Spectroscopy and Laser Heating. A schematic of the apparatus used to make Raman and nontime resolved photoluminescence measurements and to heat the sample contained in the DAC is shown in Fig. 1. Raman and photoluminescence measurements were made with the 488 nm line of an Ar-ion laser (Coherent Innova 90 C). Laser light was directed toward the sample using a laser band pass cube (Kaiser Optics) and for in situ measurements was focused onto it using a 20X near-IR corrected apochromatic objective lens (Mitutoyo). Scattered light was collected using the same objective and was focused onto a pinhole (to improve spatial resolution) before being collimated and directed into the spectrometer. A holographic filter (Kaiser Optics) was used to reject elastically scattered laser light. The spectrometer was a Jobin Yvon HR460 equipped with 300 lines/mm and 1,800 lines/mm gratings. The detector was an LN₂ cooled ccd (Roper Scientific). The system was calibrated using a neon lamp. Laser heating (2, 3) was accomplished using a Nd:YAG laser at 1,064 nm (Lee Laser). The heating laser is collinear with the 488-nm light and is focused onto the sample through the same objective. For in situ Raman measurements incident laser power was on the order of mW to 10 s of mW. Laser heating power was up to 10 W. Laser power was controlled using wave plates, the cubes and additional polarization dependent optics.

Temperature Measurement. The sample was laser heated until thermal emission was clearly visible. Additionally, motion of the sample within the DAC chamber during some experiments implies that the neon in the vicinity of the sample melts within typical heating time frames on the order of a few seconds, consistent with the reported melting temperature of solid neon. Rapid fluctuations in thermal emission intensity possibly exacerbated by large changes in the optical properties of the sample through the transition as well as motion of the sample in the melted neon make us doubtful of more precise estimates of the temperature of the transition via the preferred method of a Plank fit to the thermal emission.

In an additional experiment we used argon as a pressure medium (loaded as a cryogenic liquid). In the pressure range of approximately 26 GPa, the sample moved comparatively very little during heating (perhaps due to the elevated melting temperature of argon with respect to neon). Also, a newly installed fiber laser that was used for this experiment probably resulted in more stable heating. In any case, we were able to obtain more precise estimates of temperature from the measured thermal emission. We increased the incident laser power until just short of that required for the transition (indicated by a sudden change in optical transmission of the sample). In this way we obtained an estimate of the lower limit of the transition temperature of 1,580 K ± 40 K. Clear regions showed a new feature in the Raman spectrum due to the formation of diamond, but it appeared relatively weaker than in the case of neon. We struggled to locate and extract all the heated material after opening the diamond cell, but material we did recover and examine using SEM suggested substantial pore collapse. More experiments are necessary to confirm and account for these apparent differences.

Extraction of Recovered Sample TEM/STXM Preparation. After heating the diamond cell was opened in air. Sample material was removed from the DAC chamber with an etched tungsten scanning tunneling microscope needle (SPI Precision instruments, approximately 100-nm tip) attached to a motorized micropositioning stage (Märzhäuser Wetzlar) and attached to chemically etched silicon nanowires (4) or lacy-carbon coated transmission electron microscope grids (Ted Pella) as needed for optical or electron microscopy.

Confocal Time Correlated Single Photon Counting (TCSPC). Our experiment excites fluorescence using a 470 nm pulsed diode laser (LDH-P-C-470B, Picoquant). The laser light is reflected by a dichroic mirror (custom 470-nm and 635-nm double band dichroic, Omega Optical) and is focused by a high numerical aperture objective (Olympus, 0.95 NA). Fluorescence is collected by the same objective, passes through the dichroic mirror, and is separated by another dichroic mirror into two spectral channels. The spectral channels are defined by bandpass filters (650DF50, 695DF55 and 750DF50, Omega Optical), and fluorescence photons are detected with avalanche photodiodes (PDM series, Micro Photon Devices). Time delays between photon arrival and the laser pulse are measured using TCSPC via the PicoHarp 300 (Picoquant). See Fig. S7 for a detailed graphical schematic of the instrument.

Scanning Transmission X-ray Microscopy (STXM). Scanning transmission X-ray microscopy (STXM) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy (10) analyses were performed at the Lawrence Berkeley National Laboratory's

Advanced Light Source beamline 5.3.2 (5). Briefly, carbonized amorphous carbon aerogel and recovered diamond aerogel were transferred to lacy-carbon TEM grids as mentioned above and placed in the STXM's vacuum chamber under a helium environment. STXM employs a Fresnel zone plate lens (25 nm outer zones) to focus a monochromatic X-ray beam onto the sample. The sample scanning-stage was controlled interferometrically and transmission images were recorded with a scintillator-photomultiplier detector assembly. C 1s NEXAFS spectra from regions of interest were obtained from image sequences (i.e., stacks) collected at X-ray photon energies ranging between 280 and 320 eV (10). The theoretical spectral and spatial resolutions were ± 100 meV and 30 nm respectively. The photon energy was calibrated at the C 1s edge using the Rydberg transitions of gaseous CO₂ at 292.74 eV (C 1s \rightarrow 3s ($\nu = 0$)) and 294.96 eV (C 1s \rightarrow 3p ($\nu = 0$)). All STXM data processing was done using the IDL aXis2000 software (11) TEM analysis of the diamond aerogel following STXM measurements shows intense electron diffraction rings, suggesting that the nanodiamond grains were not destroyed by X-ray photoionization (Fig. S6).

Total Electron Yield (TEY) X-ray Absorption Spectroscopy of Bulk Diamond and 4-nm Detonation Nanodiamonds; Comparison with STXM Data for Diamond Aerogel. The total electron yield spectra of bulk and diamond nanoparticle materials were collected at Beamline 8.0 of the Advanced Light Source. Auxiliary spectra were also collected on diamond nanoparticles and Beamline 8.2 of the Stanford Synchrotron Radiation Laboratory. The resolution in these measurements was better than 0.1 eV. In general, the transmission measurements match the electron yield measurements. Perhaps the most readily observable difference is in the overall relative intensity of the spectra well above the absorption edge, i.e., >300 eV.

In this region, the intensity of the TEY nanoparticle spectrum is decreasing more with increasing incidence energy than the aerogel spectrum measured in transmission mode. This is not unexpected because these two methods do not probe the same volume of material at a given energy due to the different escape depth of electrons for each technique. In general, the TEY approach is more sensitive to surface material while STXM is more sensitive to bulk material. The nanoparticle 2nd gap depth is about 40–45% of the bulk; the diamond aerogel is about 25–35%. The sharp C 1s core-exciton peak, seen in the bulk diamond spectrum at about 288.3 eV, is broadened and not clearly resolved in either the nanoparticle or aerogel, but comparing these two, this region has a slightly more defined edge shape in the aerogel. This could indicate an exciton with a longer lifetime and thus

potentially some larger diamond crystallites. However, this effect cannot be unambiguously determined solely from this data because contaminants (e.g., C-O) would also contribute to the intensity in this region.

Finally, as stated in the text, the features below the diamond C 1s absorption edge have been correlated with sp², fullerene-like surface reconstructions at the diamond nanoparticle surface. The diamond-like nature of the aerogel is corroborated by the analogous EELS measurement (Fig. S5) exhibiting transitions associated with bulk diamond as well as some sp² carbon.

Discussion of the Formation Mechanism for Producing Diamond Nanocrystals from Amorphous Carbon Aerogel. The diamond-anvil cell allows for the production of temperatures and pressures where diamond is the thermodynamically stable phase of carbon. Laser heating provides sufficient energy to the pressurized aerogel to overcome kinetic barriers to this phase transition. Furthermore, hydrogen has been strongly implicated in the formation of nanodiamond crystallites from graphitic carbon (6). Additionally, hydrogen is known to be present in the amorphous precursor from infrared absorption measurements (1). At this time it is reasonable to speculate that the chemical transformation from amorphous carbon to cubic nanocrystalline diamond could proceed through a hydrogen-catalyzed mechanism. However, detailed simulations are required to determine the precise atomistic processes involved in this phase transition.

FT-IR Spectroscopy of Amorphous Carbon Aerogel. The micro Fourier transform infrared (μ -FT-IR) instrument used to measure amorphous carbon aerogel (Fig. S3) has been described in previous work (12). Briefly, μ -FT-IR spectra are collected using a long working distance (26 mm) reflective optics microscope. A glow-bar serves as the source of mid-IR radiation. A Bruker Optics Vector-33

interferometer is connected to an external detector that consists of a sandwiched array (single-channel) composed of InSb and HgCdTe. The spectral resolution of our FT-IR instrument was set to 2 cm⁻¹. A sample of starting aerogel material is compressed between two ZnSe optical windows and is approximately 5–10 microns thick when FT-IR data are collected. Recovered materials are suspended on the edge of diamond-anvil cell metal retaining gaskets in open air while μ -FT-IR spectra are collected. Recovered materials are nominally 10–20 microns in dimension. FT-IR sample spectra are normalized using atmospheric gas background spectra, and, when encapsulation windows are employed, by window material spectra. We plot our processed spectra in y-axis units of optical absorbance.

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