

Synthesis of "amorphous" diamond from graphite under static high pressure and high temperature

Hiroaki Ohfuji¹, Masato Katagiri¹, Shoko Odake^{2*}

¹GRC, Ehime Univ., ²Grad. School Sci. Univ. Tokyo

Amorphous diamond is a unique carbon material which is characterized by x-ray and electron diffractometry as amorphous in the long-range order and by electron energy loss spectroscopy as diamond in the short-range order. It was first synthesized from C₆₀-fullerene by shock compression and rapid-quenching techniques (Hirai et al., 1991) and also recently obtained from neutron radiated graphite by similar experimental techniques (Niwase et al., 2009). The key for the successful synthesis of amorphous diamond seems to be, 1) the presence of modified sp²-bonded carbon in the starting material to induce simultaneous and homogeneous nucleation of diamond and 2) extremely rapid quenching from high temperature to minimize the grain growth of individual nuclei.

Here, we conducted a series of laser-heated diamond anvil cell (LHDAC) experiments using three types of low-crystalline carbon materials to test whether amorphous diamond can be obtained by static high pressure experiments. The starting materials used are: (1) finely milled graphite (FMG), (2) glassy carbon (GC) and (3) amorphous carbon (AC) obtained by the zeolite-templating method. All the high pressure and high temperature experiments were conducted at 25-26 GPa and 2000 K (heating duration: 30 sec). After laser-heating, the heated area (ca. 15-20 μm in diameter) of each sample in a DAC became transparent, suggesting the phase transition to diamond. Raman spectra collected from the transparent regions of the recovered samples showed a diamond Raman peak at 1332 cm⁻¹, except for the sample from the experiment using FMG, which showed no diamond peak but showed an extremely broad peak in the range 1450-1500 cm⁻¹. Similar broad peaks were also observed in the spectra from the periphery of each heating spot (relatively low-temperature regions). TEM observations on the cross-sections of the laser-heated areas revealed that euhedral diamond grains with sizes of a few to several tens of nanometer have crystallized in the samples from GC and AC runs, while extremely fine, sub-nanometer particles of diamond have formed in the sample from FMG run. Selected area electron diffraction (SAED) patterns from the latter sample show significantly broad Debye-Scherrer rings of diamond (111), (220) and (311), and no diffraction spots are visible even in the SAED collected from <50 nm areas. Furthermore, high-resolution TEM images obtained from the corresponding areas exhibit neither distinctive grain boundaries nor diamond lattice fringes, indicating that this material lacks long-range order of diamond structure. The formation of similar "amorphous-like" diamond was also observed in the periphery of the laser-heating spots (i.e. low-temperature regions) of the samples from FMG and AC runs, where a broad Raman peak (1450-1500 cm⁻¹) was observed.

The result of the present study suggests that low-crystalline carbon materials which involve a considerable amount of modified sp² (sp³-like) bondings and relatively low heating temperature (ca. 1500 K) are essential for successful static high-pressure synthesis of amorphous diamond. The former provides preferential nucleation sites for diamond, resulting in explosive spontaneous nucleation and the latter plays a roll in suppressing the subsequent grain growth to freeze the unique amorphous characteristics.