TITLE: Acoustic Microscopy and Surface Brillouin Scattering of Amorphous Carbon Pressure-Synthesized from C60

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Acoustic Microscopy and Surface Brillouin Scattering of Amorphous Carbon Pressure-Synthesized from $C_{60}$

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ABSTRACT

Here, we report successful measurements by surface Brillouin scattering (SBS) and scanning acoustic microscopy (SAM) of the elastic properties of small specimens of amorphous carbon obtained from $C_{60}$ under high pressure and temperature. The superhard phases of amorphous carbon were synthesized from $C_{60}$ at pressure 13 - 13.5 GPa and temperature 800-900 °C. Two types of acoustic waves have been detected by SBS in superhard samples: surface Rayleigh wave and bulk longitudinal wave. The longitudinal velocity ($v_L$) in the hardest sample is slightly lower than longitudinal wave velocity in diamond in [110] direction. Simultaneous measurements of the Rayleigh and longitudinal wave velocities make it possible to determine shear and bulk elastic moduli of the specimens. Obtained elastic properties for amorphous carbon synthesized under pressure 13.5 GPa and temperature 900°C are close to those for diamond, indicating that bonds among amorphous carbon network are diamond bonding dominated.

INTRODUCTION

Recent interest in new superhard materials triggered by the discovery of the fullerene molecule $C_{60}$ has led to a series of extensive experimental studies of amorphous and nanocrystalline carbon phases and their properties in both bulk [1] and deposited as a thin film [2-4] states. Heating at relatively low pressures ($P<8$ GPa) has revealed one-dimensional (1-D)- and two-dimensional (2-D)-polymerization [5] of $C_{60}$ and subsequent collapse of the fullerene structure into graphite-like disordered carbon [6]. Heating the fullerite up to 1000-1300 K under the pressure 3 to 8 GPa leads to a formation of disordered phases with carbon atoms predominantly in $sp^2$ states. Heating $C_{60}$ at $P>8$ GPa results in formation of three-dimensional (3-D) polymerized amorphous phases of $C_{60}$, with large number of $sp^3$ atomic sites [7] and nanocrystalline composites (nanoceramics) of diamond and graphite [8], fueling the most recent debates on the existence of ultrahard fullerene-based phases with hardness higher than diamond [9]. The structure of all these phases contain large amount of 4-fold $sp^3$ atomic states. The existence of ultrahard fullerene phase with hardness higher than diamond was recently discussed [7, 9]. Such phases can be obtained only in extremely small size.

Here, we report successful measurements by surface Brillouin scattering and scanning acoustic microscopy of the elastic properties of two small bulk specimens of amorphous carbon synthesized from $C_{60}$ under high pressure and temperature. The results of these measurements are of importance in understanding the problem of phase transition of $C_{60}$ under high pressure and temperature and particularly the issue of existing ultra and superhard phases.
It has been shown that under high pressure and temperature $C_{60}$ crystals transform through a series of intermediate polymeric, amorphous and nanocrystalline carbon phases. Heating at relatively low pressures ($P < 8$ GPa) results in 1-D and 2-D polymerization of $C_{60}$ [5, 10] and subsequent collapse of the fullerene structure into graphite-like disordered carbon [6, 10]. The 3-D polymerized phases of $C_{60}$ [7], amorphous phases with a large amount of $sp^3$ atomic sites [11], and nanocrystalline diamond and graphite [7] are formed upon heating at these pressures. The formation of covalent bonds makes the new phases very stable. Hirai et al. [12] reported amorphous diamond prepared from $C_{60}$ by shock compression. Based on the indirect scratching observations [13] and measurements made by time-resolved acoustic microscopy [14], Blank et al. [9] postulated that superhard and ultrahard phases could be synthesized from $C_{60}$. However, their experimental results have not been independently confirmed. Further, there might exist some discrepancy in their measured values of elastic constants [7] as fullerite materials obtained under high pressure are not homogeneous and consist of several phases with different elastic properties. The dimensions of the different phases vary from tens to hundreds of microns. Thus, Brillouin spectroscopy and acoustic microscopy, which provide high lateral (1 - 30 μ) and axial (1 - 100 μ) resolution in elastic properties measurements, are valuable tools for characterizing such specimens.

The first experimental SBS study of the fullerene product resulting from laser irradiation of a $C_{60}$ single crystal [15] revealed that high laser intensities must be used to detect Brillouin scattering. Sound velocities measured in that experiment (280-700 m/s) are substantially lower than the value reported in literature for solid $C_{60}$. The shift of the Brillouin doublets observed by Manfredini et al. [15] was in the energy range typical for slow polymer or carbon gels. Polymerized phases obtained under high T-P are much stiffer. One would therefore expect normal laser intensity to produce SBS spectra from hard fullerene materials. To our knowledge Brillouin scattering studies of bulk hard phases synthesized from $C_{60}$ have not been conducted yet.

**EXPERIMENTAL DETAILS**

**Specimens**

Two bulk amorphous carbon (a-C) samples, employed in this study, were synthesized from $C_{60}$ fullerite powder at 13 to 13.5 GPa, 800±100°C (sample A) and 900±100°C (sample B) at the Institute for High Pressure Physics, Moscow. Fullerite powder was produced at the Russian Scientific Center “Kurchatov Institute”.

**Brillouin light scattering**

Brillouin light scattering is generally referred to as inelastic scattering of an incident optical wave field by thermally excited elastic waves in a sample [16]. The phonons moving in thermal equilibrium with very small amplitudes can be viewed as a moving diffraction grating by an incident light wave. Mechanism of the light scattering by moving diffraction gating can be explained by the two concepts of Bragg’s reflection and Doppler shift. Brillouin light scattering can be viewed as a Bragg’s reflection of the incident wave by the diffraction grating created by thermal phonons [17].
For the backscattering geometry, the surface acoustic modes which cause the diffraction of the incident light have wave vector \( q \) given by

\[
q = \frac{4\pi \sin \theta}{\lambda},
\]

\( \lambda \) is the wavelength of the incident laser light, and \( q \) is the projection on the surface of the scattering wave vector. The moving corrugating surface scatters the incident light with a Doppler shift, giving scattered photons with shifted frequencies. The frequency shift \( \delta f \) in the light scattering is related to the surface wave velocity \( v_{\text{SAW}} \) by equation

\[
v_{\text{SAW}} = \frac{\lambda}{2 \sin \theta} \delta f
\]

At room temperature and above, the Brillouin scattering efficiency or intensity for scattering from the surface of an opaque materials by dynamic rippling of the surface can be represented as [17]

\[
I(\omega) = A \frac{T}{\omega} \text{Im} \, g_{33}(q, \omega)
\]

where \( \omega \) is the angular frequency shift of the light; \( T \) is the absolute temperature; factor \( A \) depends on the medium (density and permittivity), scattering geometry, polarization and incident photon frequency; \( g_{33}(q, \omega) \), Fourier coefficient of the elastodynamic Green's function. A comprehensive description of how \( g_{33}(q, \omega) \) is calculated for a multilayered anisotropic medium is given in [17].

Elasto-optic interaction or scattering of light by bulk sound waves result from fluctuations in the dielectric constant caused by the phonons moving in thermal equilibrium. The interaction arises from changes in the refractive index produced by the strain generated by sound waves; the change in refractive index is related to the strain through the elastooptic constants \( p_{mn} \), which determine the degree of interaction between the light and the material [16]. In backscattering, sound velocity \( (V) \) can be expressed as a function of the frequency shift and refraction index \( n \) by the following formula

\[
V = \frac{\lambda \delta f}{2n}
\]

Brillouin light scattering technique is ideally suited for studying the elasticity of bulk materials and, especially, thin films [18, 19]. It has proven to be a very effective technique for investigating the near-surface elastic properties of opaque bulk materials.

**Acoustic Microscopy**

Acoustic microscopy is a relatively new technique that has been developed for non-destructive characterization of the mechanical microstructure of solid materials with a resolution
of 1 μm [20]. A schematic diagram of an acoustic microscope working in the reflection mode is presented in Fig. 1. In conventional acoustic microscopy, a monochromatic sound wave is focused onto a specimen by means of an acoustic lens. The same lens is used to record the signal reflected back from the sample. A liquid couplant, usually water, is placed between the lens and the sample. The spherical lens, i.e. the lens with a spherical cavity, focuses sound onto a spot of size comparable to the sound wavelength in the fluid. The fringes, appearing in the acoustic images around cracks and other discontinuities, are Rayleigh wave fringes; they are seen on defocused images as a result of the interference between waves reflected normal to the specimen surface and waves associated with surface Rayleigh waves [20].

**RESULTS AND DISCUSSION**

Surface scattering from the Rayleigh waves (incident angle = 60°) gives the velocity of 6.5 km/s for the top face of the sample A and 10.1 km/s for the top face of sample B. The top face is a surface where pressure has been applied. The velocity of surface wave along sample surface B is 8% lower than that for [100] diamond. Bulk scattering from the bulk longitudinal wave (LW) can be observed for sample B. Refractive index for the sample is not known. Assuming it to be

![Figure 1. Schematic geometry of the defocused acoustic lens. BE is the trajectory of specular wave, and ADFC is the trajectory of leaky Rayleigh surface acoustic wave (SAW). In the ray model the leaky Rayleigh wave is excited by ray AD, striking the surface at the angle \( \theta_R = \frac{V_w}{V_R} \). Here \( V_w \) is the velocity of the longitudinal wave in coupling liquid and \( V_R \) is the velocity of Rayleigh wave.](image)
close to that for $C_{60}$ (n=2.52) [15], the longitudinal velocity in sample B is then equal to 17.5 km/s. The longitudinal velocity ($v_L$) in the sample B (17.5 km/s) is higher than that in cBN (15.8 km/s) or in ta-C films (15.5 km/s) and is slightly lower than longitudinal wave velocity (18.6 km/s) in diamond in [110] direction.

An acoustic image of sample A made by acoustic microscope (Leitz ELSAM) is shown in Fig. 2. The image was taken from the side surface of sample A. The fringe width in the cross section of the fibers can be used to determine the Raleigh velocity. The fringe distance is simply half a wavelength of the Rayleigh wave. This gives the Rayleigh wave velocity of 8.0 ± 2.1 km/s. We note that, though the error in the measured Rayleigh wave velocity by SAM is higher than that determined by SBS, the SAM measurements have revealed strong anisotropy in the elastic properties of sample A.

![Acoustic image of sample A](image)

Figure 2. (a) Acoustic image of sample A at 400 MHz, and at a defocus $z = -20 \mu m$, field of view 700 $\mu m \times 700 \mu m$. (b) Optical image of the same sample field of view 700 $\mu m \times 700 \mu m$.

CONCLUSIONS

1. Elastic properties of the superhard phases of amorphous carbon synthesized from $C_{60}$ at pressure 13 - 13.5 GPa and temperature $900\pm100^\circ C$ have been obtained by surface Brillouin spectroscopy.

2. The longitudinal velocity in the sample B is higher than that in cBN or in ta-C films and is slightly lower than longitudinal wave velocity in diamond in [110] direction.

3. Measured elastic properties for amorphous carbon obtained under pressure 13 - 13.5 GPa and temperature $900\pm100^\circ C$ are close to those for diamond.
4. The SBS and SAM techniques have potential value in characterizing extremely small size specimens such as hard amorphous carbon phases.

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