Brief Reports

Cubic-to-rhombohedral transformation in boron nitride induced by laser heating: In situ Raman-spectroscopy studies

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In situ Raman-spectroscopy studies were carried out on Ar-ion-laser-heated cubic boron nitride (cBN). Phase identification and temperature measurements were performed on micron-size particles and a pressure-compacted free-standing thin film of cBN. In both cases, cBN was shown to transform to the rhombohedral phase (rBN) above 1795 ± 80 K with characteristic Raman peaks at 790 and 1366 cm^{-1} at ambient conditions. The cBN-to-rBN transformation proceeds with a characteristic time of 1 s. The temperature variation of Raman modes of rBN were measured to 1800 K.

Cubic boron nitride (cBN) has a special place in superhard materials. It is the hardest known material next to diamond.[1] Commercial applications as a substitute for diamond come mainly in machine tools for ferrous alloys where use of diamond-coated tools results in a chemical reaction between iron-group metals and diamond. As compared to diamond, cBN has higher thermal stability under oxidizing conditions and a much lower chemical reactivity in the presence of iron-group metals. Boron nitride has five known structural phases,[2] namely, hexagonal boron nitride (hBN), cubic boron nitride (cBN), wurtzite phase (wBN), rhombohedral phase (rBN), and a disordered phase termed as "turbostratic" boron nitride (tBN). Here cBN and wBN are the denser superhard modifications produced by high-pressure–high-temperature processing in the presence of catalysts. At the present time, it is not possible to produce large high-quality cubic boron nitride crystals by conventional high-pressure–high-temperature processing. Alternative chemical-vapor-deposition (CVD) and laser processing techniques are being developed for large-area high-quality deposition. In this paper we address the issue of the thermal stability of cubic boron nitride by performing *in situ* Raman spectroscopic studies on laser-heated samples.

Exarhos and Schaaf[3] examined the thermal stability of hBN coating on graphite and found that hBN is stable to temperatures as high as 2325 K. Alvarenga, Grimsditch, and Polian[4] heated cBN to 1600 K and followed LO and TO Raman modes to the highest temperature. Herchen and Cappelli[5] heated cBN with tungsten filament and reported a phase transformation of cBN to hBN at 1840 ± 60 K. However in Ref. 5, a scanning spectrometer was used to take Raman spectra and this does not allow for real-time spectroscopic studies over a broad spectral range. On the other hand, in these studies the excitation laser spot size varied from 100 to 500 μm. In this paper, we investigate the details of the transformation process, such as the transformation rate and the dramatic temperature change during the transformation. In the present experiments, the same laser radiation (514.5 nm of an Ar-ion laser) is used both for heating as well as for performing Raman measurements. The real-time temperature measurements are provided by the intensity ratio of the Stokes and anti-Stokes Raman lines.[3,5]

The micro-Raman/photoluminiscence spectrometer as described in Ref. 6 was employed in this study. The Coherent Innova-70 CW argon-ion laser operated at 514.5 nm, which has an adjustable nominal output power ranging from 10 mW to 1.5 W, served both as a Raman excitation source and as a laser-heating source. The Ar-ion laser was operated in the light regulation mode whereby the output laser power is kept constant to within 0.5%. The laser is focused to a spot size of 1–2 μm; therefore, the power density on the sample can reach as high as 10^8 W/cm^2. The use of 600-g/mm grating resulted in the simultaneous coverage of the spectrum range from -2000 to $+2000$ cm^{-1} relative to the 514.5-nm

($19\,435.2$ cm^{-1}) laser line. The charge-coupled diode (CCD) array detector enables one to record the weak Raman signals (especially the anti-Stokes) within 1 s at high temperatures.

In the first set of experiments, the 2–4 μm-size cBN crystals from General Electric Superabrasives were placed on a glass slide and exposed first to a low power laser (60 mW), then to a high power laser (1 W). Figure 1 is the optical micrograph of the sample. Figure 2(a) is the spectrum of the cBN particle at low laser power (60 mW). Both Stokes and anti-Stokes Raman lines of cBN, the LO mode at 1302 cm^{-1} and the TO mode at 1052 cm^{-1}, are shown in the graph. Figure 2(b) shows the spectrum after the high-power laser was illuminated on the sample. The LO and TO modes of cBN completely disappeared after heating and new modes at 1358 and 789 cm^{-1} were observed at this temperature. This phase can be identified as hBN except for the extra peak at 789 cm^{-1}. However, it has been shown that rBN whiskers[7] at ambient temperature show two Raman peaks at approximately 1370 and 800 cm^{-1}. Therefore we identify the phase induced by laser heating to be rBN. The low-frequency peak at 789 cm^{-1} is also documented in the infrared reflectivity measurements on hBN.[8] This peak is designated as an out-of-plane mode for both hBN and rBN, as compared with the in-plane mode at 1367 cm^{-1}, but is Raman active only for rBN.[8] We investigated the possibility of BN reacting with air and producing a B_2O_3 phase. The Raman spectrum of B_2O_3 (99.98%, from AESAR) has characteristic Raman peaks at 209, 499, and 880 cm^{-1}. We did not see any experimental evidence of B_2O_3 formation.

The temperatures were calculated from the Stokes and anti-Stokes intensity ratio[9]

$$\frac{I_{St}}{I_{a\text{-}St}} = \left[\frac{\omega_l - \omega_s}{\omega_l + \omega_s} \right]^4 e^{\hbar\omega_s/kT}, \tag{1}$$
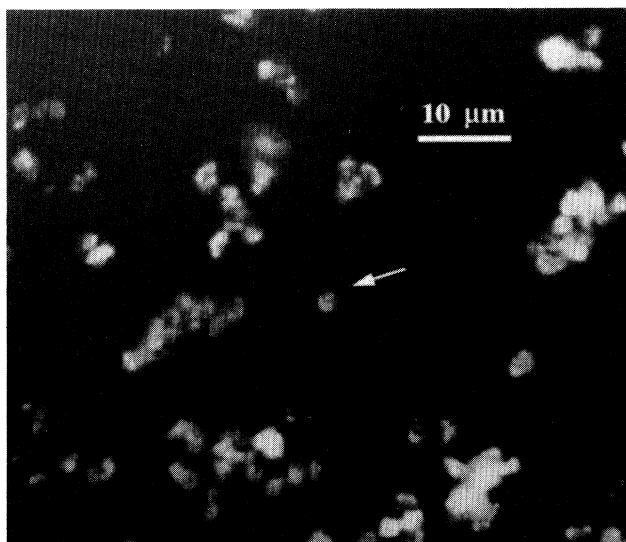

FIG. 1. Optical micrograph of 2–4 μm cBN powder. The cBN particle of 2–3 μm in diameter as indicated by an arrow was completely transformed by laser heating.
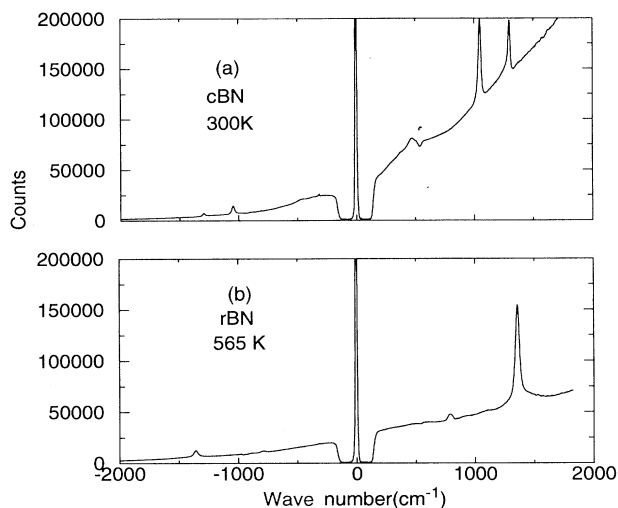

FIG. 2. Stokes and anti-Stokes Raman spectra from the (a) cBN particle of Fig. 1 before heating (upper panel) and (b) completely transformed rBN phase after laser heating (lower panel).

where I_{St} and $I_{a\text{-}St}$ are the intensities of the Stokes and anti-Stokes Raman lines, respectively, ω_s is the Raman frequency, ω_l is the absolute frequency of the laser line ($19\,435.2$ cm^{-1}), and T is the sample temperature in kelvin. $\hbar = 1.05 \times 10^{-34}$ J s.

The Stokes and anti-Stokes Raman peaks in Fig. 2 can be well represented by Lorentzian line shape and the measured intensities I_{St} and $I_{a\text{-}St}$ were taken to be integrated area under the peak. The measured transformation temperature from Eq. (1) and the temperature dependence of the Raman modes were compared to the literature values,[3,5] and the deviations were always within 5%. This comparison clearly demonstrates that a temperature measurement on micrometer-size laser-heated spots is possible using Raman spectroscopy.

It should be added that the subsequent attempt to heat the transformed rBN crystal was not successful because of low laser absorption. To obtain high-temperature data on the rBN sample, a special thin film (10-μm-thick) disk of cBN was produced by high-pressure compaction to 53 GPa in a diamond anvil cell.[10] The compacted sample was found to have plastically deformed into micrometer-size crystals due to the cold working which can be demonstrated by the linewidth of the Raman peaks.[11] Raman spectroscopy of the compacted cBN sample indicated that there was no pressure-induced phase transformation. The low-laser-power spectrum shows only the cBN LO and TO modes at 1302 and 1052 cm^{-1}, but with broadened line shapes. The full width at half maximum (FWHM) for the LO and TO modes are 26 and 31 cm^{-1}, respectively, as compared to 5 and 6 cm^{-1} for the cBN crystals of 0.5 mm size.

The compacted sample was exposed to a high-power laser of 1.1 W. Figure 3(a) shows the spectrum within 1 s after the laser was turned on. Transformation to a new phase was observed with a characteristic time of 1 s. Four Raman peaks appear in this spectrum, indicating
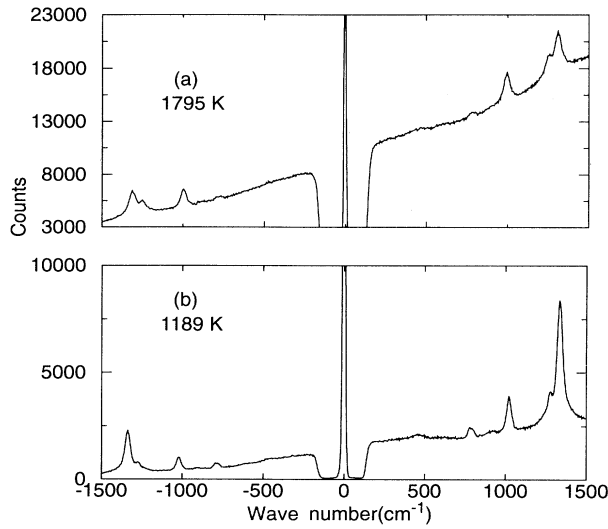
FIG. 3. Temperature drop during the transformation; (a) the mixed phase of cBN and rBN at the onset of the transformation at 1795 K, after 1 s of laser heating; (b) phase mixture at 1189 K, after 2 min of laser heating. Laser power is constant at 1.1 W for both spectra.
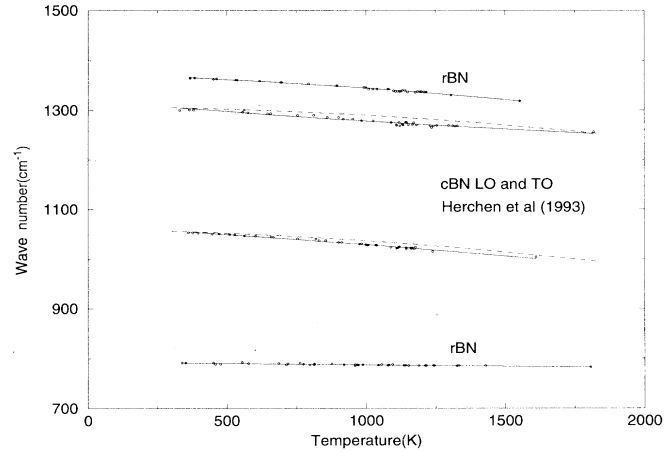

FIG. 4. Temperature dependence of the Raman modes for the cBN and rBN phases between 300 and 1850 K. The dashed lines are the literature values, and the solid lines are the quadratic fits to our experimental data. Temperatures for each Raman mode were calibrated individually with its own Stokes to anti-Stokes intensity ratio.

the phase mixture of cBN and rBN. The measured temperature is 1795±80 K, where the error is from the measurements by different Raman modes. The temperature was lowered as the transformation progressed under the same laser power. A stable temperature was achieved in 30 s. Figure 3(b) shows the phase mixture after 2 min of laser heating at 1189±20 K. Table I shows the Raman modes at 1795, 1189, and 300 K from the phase mixture. It should be added that we also see a weak Raman band around 500 cm^{-1} in the spectra shown in Figs. 2 and 3. The intensity of this band is not reproducible from one cBN grain to another; hence, we attribute this to an unknown impurity in the cBN powders.

Compared to micrometer-size particles, this compacted transformed sample was surrounded by the untransformed cBN that can absorb laser radiation. We were able to cycle the laser power and reheat this sample to about 1200 K. Figure 4 shows our measured ω-vs-T data for the four Raman modes. The temperatures for

each mode are calibrated individually with its own Stokes to anti-Stokes intensity ratios. The dashed lines are the literature values,[3,5] while the solid lines are the quadratic fits given below:

$$\omega_{rBN} = 1374.5 - 0.0183T - 1.13 \times 10^{-5}T^2 , \tag{2}$$

$$\omega_{cBN-LO} = 1320.2 - 0.0481T + 6.10 \times 10^{-6}T^2 , \tag{3}$$

$$\omega_{cBN-LO} = 1067.6 - 0.0345T - 4.44 \times 10^{-6}T^2 , \tag{4}$$

$$\omega_{rBN} = 794.1 - 0.00792T + 9.86 \times 10^{-7}T^2 , \tag{5}$$

where ω is in cm^{-1} and T is in K.

The rBN mode at 790 cm^{-1} has a very small temperature dependence as compared to the mode at 1367 cm^{-1}. The total change of its position is only 10 cm^{-1} from 300 to 1850 K (Table I). On the other hand, the mode at 1367 cm^{-1} shows a shift of 56 cm^{-1} in the same temperature range. There is a certain anisotropy of the lattice expansion upon laser heating. We calculated the intensity ratio of the 790-cm^{-1} peak to the 1367-cm^{-1} peak for all the data points obtained, and the striking result is that this ratio remains a constant value of 0.1±0.01 for every spectrum from 300 to 1800 K. The intensity correlation and the coexisting of these two peaks suggest that the rhombohedral phase rather than the hexagonal phase of boron nitride was achieved.

We offer the following conclusions.

(1) Isolated micrometer-size cBN crystals as well as pressure-compacted cBN film under a laser-heating environment show a transformation to rBN at a temperature of 1795±80 K.

(2) Our *in situ* Raman spectroscopic investigations reveal the characteristic time of transformation to be of the

TABLE I. List of the cBN and rBN Raman-mode frequencies at three different temperatures from Fig. 3. The frequencies decrease with increasing temperatures. The temperatures are measured by the intensity ratios of the Stokes and anti-Stokes Raman peaks.

Raman modes	1795 K (cm^{-1})	1189 K (cm^{-1})	300 K (cm^{-1})
cBN LO	1248	1272	1302
cBN TO	996	1022	1052
rBN	1311	1337	1367
rBN	780	787	790

order of 1 s. The change of Raman frequencies with increasing temperature shows a marked anisotropy with the in-plane mode showing a larger increase than the out-of-plane mode.

(3) This is exactly a reversal of the rBN-to-cBN transformation observed under shock loading.[12] This transformation path of cBN to rBN by laser heating is favored over other transformation mechanisms.

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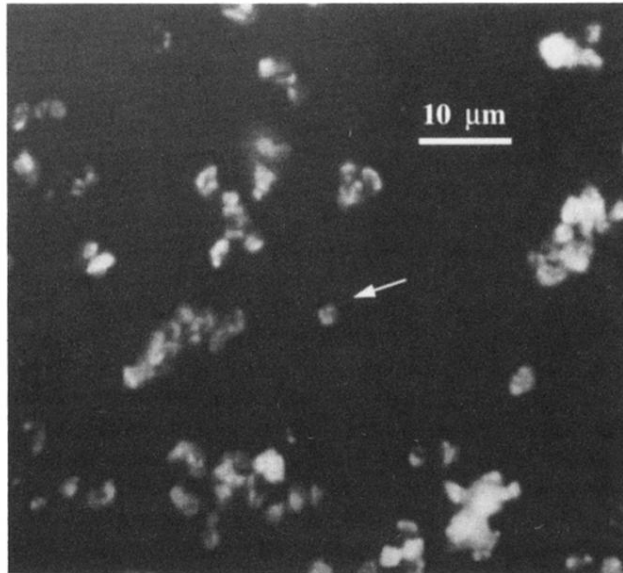[12] T. Sekine and T. Sato, J. Appl. Phys. **74**, 2440 (1993).

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