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Raman spectroscopy of single nanodiamond: Phonon-confinement effects

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In this paper, we devise techniques for immobilizing and allocating a single nanodiamond on the electron beam (e-beam) patterned smart substrate. The properly designed coordination markers on the semiconductor substrate and the high throughput of the confocal microscope provide us with a convenient tool to single out a nanodiamond with a size less than 100 nm and to study Raman spectroscopy. We observe a redshift in energy and broadening in the linewidth of the sp bonding Raman peak when the size of the diamond is decreased from 90 to 35 nm. The observed shifts and linewidth broadening arise from the phonon-confinement effects and are in good agreement with calculations reported by [Ager et al. Phys. Rev. B 43, 6491 (1991)] and [Yoshikawa et al. Appl. Phys. Lett. 62, 3114 (1993)]. © 2008 American Institute of Physics. [DOI: 10.1063/1.2912029]

In recent years, considerable attention has been focused on the development of techniques for solving applied problems in biology, protein chemistry, molecular biology, etc. In particular, the designs of various biomarker systems based on the Raman and fluorescent properties of nanoparticles hold much promise, as opposed to conventional organic fluorophores which suffer from poor photostability, narrow absorption spectra, and broad emission features. Recent advances in the synthesis of the semiconductor nanocrystals have resulted in biomarkers which are brighter, more sensitive, photostable, and biocompatible. They have found applications in a variety of biological experiments such as cellular imaging, long-term in vitro and in vivo labeling, tissue structure mapping, and single-particle investigation of dynamical cellular processes.

More recently, sub-100 nm nanodiamonds with nitrogen point defects have been used as single-particle biomarkers in experiments of fixed and live Hela cells. It has also been recently demonstrated that diamonds with a nominal size of 100 nm or less are capable of producing stable fluorescence from color centers after surface treatment with strong oxidative acids. The fluorescent nanodiamonds could possibly be used as fluorescent biomarkers for in vitro as well as in vivo studies at the single-particle level. Although there are some reports on the optical properties of diamond particles, most of the studies focus on diamond particles in clusters or powder form. In this work, we demonstrate phonon properties on a single diamond nanostructure basis by dispersing, immobilizing, and allocating a single nanodiamond on silicon substrates patterned with coordination markers by using (electron beam) lithography techniques. We also report the size effects on the Raman spectra of a single nanodiamond with a confocal microscope.

The methods for dispersing the diamond nanoparticles and the preparation of the patterned smart substrates are given in Ref. 17. A drop of the well diluted nanodiamond solution is placed on the patterned template. After the sample dries out, the surface is scanned by scanning electron microscopy (SEM) to allocate a single nanodiamond. Figure 1(a) shows the SEM scanning results of two separated single nanodiamonds with sizes of 90 and 35 nm (indicated by the yellow circles in the figure), respectively. Most importantly, from the SEM image, we can ensure that there is no other nanodiamond within the laser focus spot but the selected target before the Raman spectrum measurements. After the target is allocated, their corresponding coordinates are as-

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FIG. 1. (Color online) (a) SEM images of the 90 and 35 nm nanodiamonds near the coordination markers. (b) Optical image of the template with the e-beam defined pattern.
signed. Figure 1(b) shows the optical image of the patterned substrate. The dimension of the coordination markers is properly designed so that they can still be clearly seen under the optical microscope. The entire template is moved via an X-Y stepping motor to the given coordinate to position the targets under the laser spot, while the optical image of the substrate is simultaneously monitored on a television screen. The Raman signals are collected through the microscope objective and are analyzed by a 0.32 m spectrometer equipped with a liquid nitrogen cooled charge coupled device-detector at the excitation wavelength of 532 nm. The excitation power density from the diode-pumped solid state laser was controlled under 10 KW/cm² in order not to damage the Si substrates. The optical signal can be further optimized by adjusting the focal plane position along the z axis via the piezodriven objective lens. The acquired spectra are averaged several times until a good signal-to-noise ratio is achieved.

For the single 90 nm nanodiamond, a Raman peak due to the sp³ bonding structure in the diamond was detected at the energy of 1329 ± 1.5 cm⁻¹ (with a 2400 groove grating) with a linewidth of ~3 cm⁻¹, as shown in Fig. 2. This peak is redshifted by ~3 cm⁻¹ as compared to the bulk diamond. When more than two single nanodiamonds are included within the laser spot, we begin to observe the sp² bonding Raman signal at the energy of ~1600 cm⁻¹ in the spectra shown in Fig. 3. This Raman signal (the D and G bands as reported in Ref. 18) originates from a thin graphite layer on the surface of the nanodiamond and is too weak to be detected in the case of a single nanodiamond.

The Raman spectrum from the single 35 nm nanodiamond, as shown in Fig. 4, shows a Raman peak at ~1325 ± 1.5 cm⁻¹. Note that its line shape looks asymmetric and is broadened to 80 cm⁻¹. A Raman peak at 520 cm⁻¹ from the silicon substrate was simultaneously monitored in the measurements. However, we did not observe any shift in energy or change of line shape on this Si Raman peak. The Raman peak intensity also linearly increased with laser power up to 25 mW. Therefore, we concluded that the laser heating or laser-induced thermal effects were insignificant. The Raman spectra were also calibrated by using this Si Raman peak. A strong Raman signature from the D and G bands also appears at the energy of ~1600 cm⁻¹. Its intensity is comparable to the sp³ Raman peak, which indicates that this single 35 nm diamond may contain a higher percentage of graphite structure than the 90 nm one.

A theoretical model (known as the phonon-confinement model) was first proposed by Richter et al. to explain the observed shift to lower frequency and the broadening of the Raman line in microcrystalline Si. More recently, results of
In summary, by combining a confocal microscope and an e-beam patterned smart substrate, we have been able to study nanodiamond phonon properties on a single nanostructure basis. In contrast to earlier reports on nanodiamond powder or clusters, the factors arising from size distribution can be ruled out and the results can be compared to calculations in parallel. The observed energy redshift and asymmetrical linewidth broadening of the Raman peak in the experiments as the nanoparticle size decreases are attributed to the phonon-confinement effect.

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See EPAPS Document No. E-APPLAB-92-041816, for the methods of dispersing the diamond nanoparticles and the preparation of the patterned smart substrates. For more information of EPAPS, see http://www.aip.org/epaps/numbering.html.


