Quantum Confinement Effect in Diamond Nanocrystals Studied by X-Ray-Absorption Spectroscopy

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(Received 11 December 1998)

This study measures the x-ray-absorption spectra of a series of nanodiamond thin films with grain diameters ranging from 3.5 nm to 5 μm at the C K-edge using the sample drain current mode at room temperature. Resonance peaks resembling the C $1s$ core exciton are observed. The exciton state and conduction band edge are found to shift to higher energies with the decrease of the grain size indicative of the presence of the quantum confinement effect. [S0031-9007(99)09519-8]

PACS numbers: 78.70.Dm, 61.10.Ht, 71.24.+q, 71.35.−y

Quantum-size effects on the exciton and energy gap of semiconductor nanocrystals have received extensive interest in recent years [1–10]. Exciton energies and conduction/valence band edges (E_{CB}/E_{VB}) were observed generally to shift to higher/lower energies relative to those of the bulk compound with the decrease of the crystallite size. Recently, experimental studies have been greatly enhanced with the development of the nanodiamond thin film technique [11]. Substantial blueshifts of the conduction band edge in porous Si and Si nanocrystals with respect to that of the Si bulk solid were found by x-ray absorption spectroscopy at the Si $L_{2,3}$-edge [1,2] and electron energy loss spectroscopy (EELS) at the Si L_1-edge [3], respectively. The existence of quantum confinement effect was also found in Si nanocrystals by luminescence analyses [4] and in II-VI−based semiconductors by absorption spectra [5]. Theoretical studies also found the quantum confinement effect in nanocrystalline semiconductors when the size of the particle is smaller than some critical value [7–10]. The C K-edge x-ray absorption spectra of nanodiamonds have been reported previously [12]. However, the electronic structures of nanodiamonds are still unknown to our knowledge. Here, we report on the quantum-size effect on the exciton energy and conduction band edge based on our C K-edge x-ray absorption spectra for a series of nanodiamonds with various crystallite sizes.

The C K-edge x-ray absorption measurements were performed using the high-energy spherical grating monochromator (HSGM) beam line with an electron-beam energy of 1.5 GeV and a maximum stored current of 200 mA at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan. The x-ray absorption near edge structure (XANES) spectra of the C K-edge were measured using the sample drain current mode at room temperature. Photon energies for the C K-edge XANES were calibrated using the diamond thin film

[13]. The typical resolution of the spectra was better than 0.2 eV for the HSGM beam line. The nanodiamond films were grown by using microwave plasma enhanced chemical-vapor-deposition (CVD) technique. Transmission electron diffraction measurements showed a powder diffraction ring pattern that can be indexed to the diamond structure as shown in Fig. 1(a). The dark field transmission electron micrograph yielded a fine-grained structure as shown in Fig. 1(b). For each film, the grain-size distribution can be obtained by directly analyzing several tens of grains from the dark field images of the sample. According to these analyses, the average grain size (diameter) varied from nanometers to micrometers depending on the deposition condition of the film. The crystalline samples were also verified by x-ray diffraction. Details of the preparation procedure for these nanodiamond films can be found elsewhere [14]. The O K-edge XANES measurement showed negligible oxidation of the nanodiamond films.

Figure 2(a) shows the C K-edge XANES spectra of our nanodiamond-film samples grown on quartz substrate. After preedge background subtraction, the spectra were normalized using the incident beam intensity I_0 and keeping the area under the spectra in the energy range between 335 and 343 eV fixed. The spectral line shapes in the C K-edge XANES spectra of these nanodiamonds appear to be similar at first glance regardless of the crystallite sizes. However, a close look at the relative intensities of the near-edge features shows variations with respect to the size of these nanodiamonds as shown in Fig. 2(a). For x-ray energies in the XANES region, the excited photoelectron undergoes a transition from a core state to an unoccupied final state following the dipole-transition selection rule. It is well known that carbon atoms in a diamond form strong tetrahedral sp^3 hybrid bonds. Previous studies indicated that the XANES energy range for a diamond can generally be divided into two
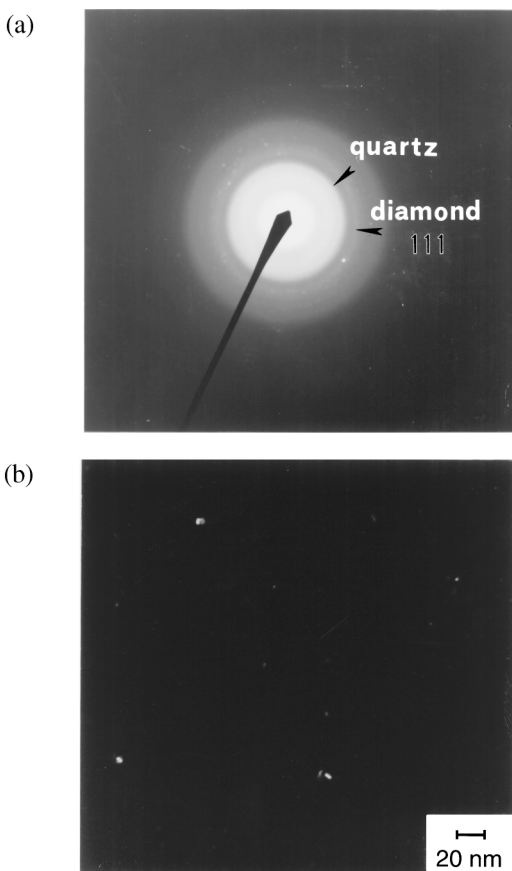
(a)

(b)

FIG. 1. (a) Electron diffraction pattern of the nanodiamond film with a grain size of 3.6 ± 0.8 nm deposited on a quartz substrate by microwave plasma enhanced CVD at 620 °C with methane concentration of 4%. The innermost diffraction ring is from quartz (101) and the second diffraction ring is from diamond (111). (b) TEM dark field image taken with the diamond (111) reflections, indicating that the film consists mainly of tiny crystallites with grain sizes <5 nm.

regions characterized by their specific features, namely (a) at ~289 eV is the C 1s core exciton resonance and (b) between ~290 and 302 eV is a relatively broad band of σ^* states [13,15,16]. The relatively small preedge peak at ~285 eV can be attributed to graphitelike sp^2 bonded carbon of π^* states [17,18]. The weak peak at ~287.5 eV (labeled by a vertical bar) has been previously attributed to the C-H bond on the diamond surface [12,19]. The large dip in the absorption spectrum at ~302 eV can be assigned to a second absolute gap in the diamond band structure [13].

According to Fig. 2(a), the spectra of these nanodiamonds contain a weak structure at the preedge region and display a strong and sharp excitonic peak immediately above the threshold. The excitonic peaks in the spectra of the diamond samples with crystallite sizes of 1, 2, and 5 μm clearly appear to be best resolved, which closely resemble that of a bulk diamond reported previously [13,20]. These features suggest that the diamond with a crystallite size in the range of μm already has an

electronic structure similar to that of the bulk diamond. In contrast, the excitonic peaks of nanodiamonds with crystallite sizes in the range of 3.6–63 nm are much broader and less resolved than those of the samples with crystallite size of μm. Among the nanodiamonds the one with a crystallite size of 27 nm has least resolved features. The unusually broader features in the spectrum of this
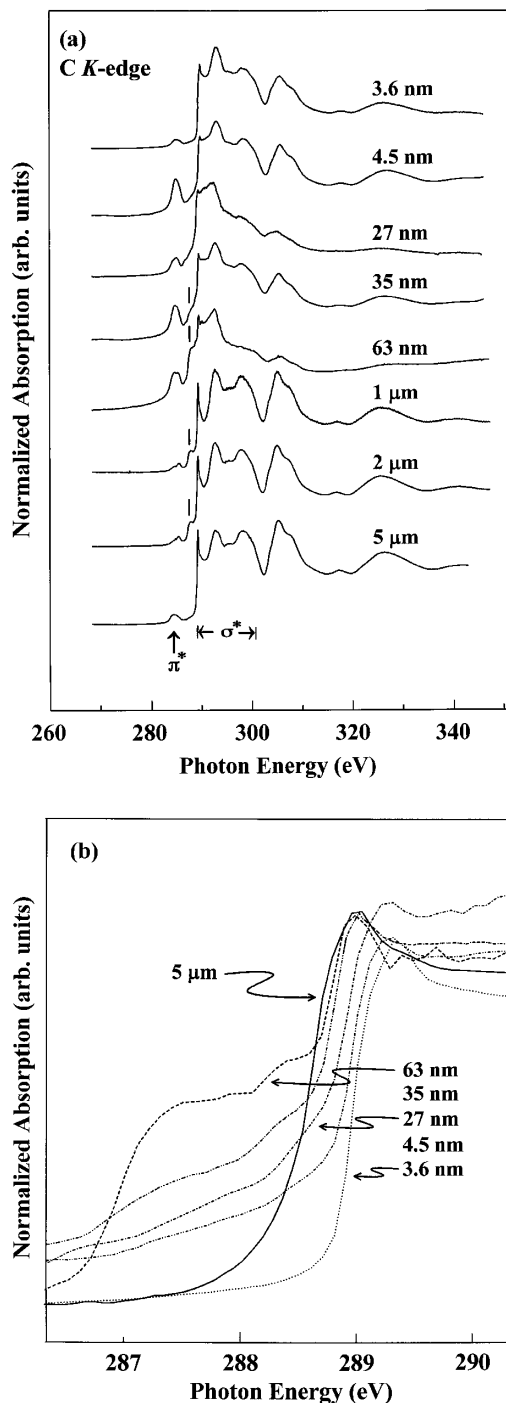

FIG. 2. (a) Normalized C K-edge absorption spectra of diamond nanocrystals. (b) This figure shows the region of the threshold edge in a magnified scale.

particular nanodiamond sample may be due to a larger concentration of defects. We can conclude from Figs. 2(a) and 2(b) that the features near the threshold edge of the C K-edge XANES spectra move slightly toward the higher energy side as the crystallite size decreases. This trend is similar to previous x-ray absorption spectroscopy and EELS studies of Si nanocrystals reported by van Buuren et al. [2] and Batson and Heath [3], respectively. They found that the conduction band edge shifts to the higher energy with the decrease of the particle radius. To our knowledge, this is the first observation of the blueshift of the excitonic resonance in nanodiamonds.

The exciton state can be formed by the creation of a bound electron-hole pair with the absorption of a photon. The exciton energy level, E_{ex}, is slightly lower than the bottom of the conduction band. The absorption spectra of semiconductors usually have a relatively sharp resonance superimposed with the threshold of the conduction band continuum [21]. The excitonic binding energy, ΔE_{ex}, is given by $\Delta E_{\text{ex}} = |E_{\text{ex}} - E_{\text{CB}}|$, i.e., the energy separation between the exciton state and the conduction band edge. To calculate C $1s$ ΔE_{ex}, we use the Lorentzain and arctangent functions to describe the exciton state and

the conduction band edge [15,22], respectively. Figure 3 shows an enlargement of the part of the absorption data and the fitted spectra for crystallite sizes of 3.6 nm and of 5 μm in Fig. 2 in the vicinity of the excitonic peak. According to Fig. 3(a), the excitonic peak of the nanodiamond with a crystallite size of 3.6 nm is located at ~1.0 eV below the C $1s$ ionization energy (290.4 eV) at the inflection point of the continuous step. In contrast, the excitonic peak of the diamond with a crystallite size of 5 μm as shown in Fig. 3(b) is located at ~0.19 eV below the C $1s$ ionization energy (289.2 eV) at the inflection point of the continuous step in agreement with previous studies [15,17]. The results of E_{ex} and E_{CB} as functions of the crystallite radius are plotted in Fig. 4. This figure clearly demonstrates that E_{ex} and E_{CB} in the C K-edge XANES of nanodiamonds shift toward higher energies as the crystallite radius decreases, especially when the crystallite radius is smaller than ~18 nm, an indicator of a widening of the energy gap caused by quantum-size effect. The inset of this figure reveals a similar trend to ΔE_{ex}, although the excitonic binding energy strongly depends on the local electronic band structures [7,8,13] and bonding environment around the absorbing atoms [23]. We find that, within the radius ranges of the nanodiamonds and microdiamonds studied, ΔE_{ex} as
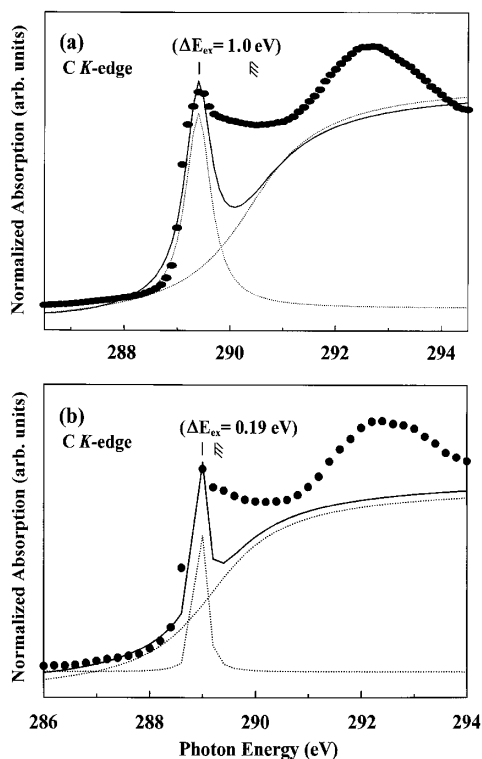

FIG. 3. These figures show the enlarged parts and the absorption data shown in Fig. 2 and the fitted spectra for crystallite sizes of (a) 3.6 nm and (b) 5 μm in the vicinity of the C $1s$ core exciton resonance about 4 eV above the Fermi level. Solid lines are calculated from the summation of the Lorentzian peak and the arctangent function shown by the dashed lines. The experimental data are shown by the filled circles.
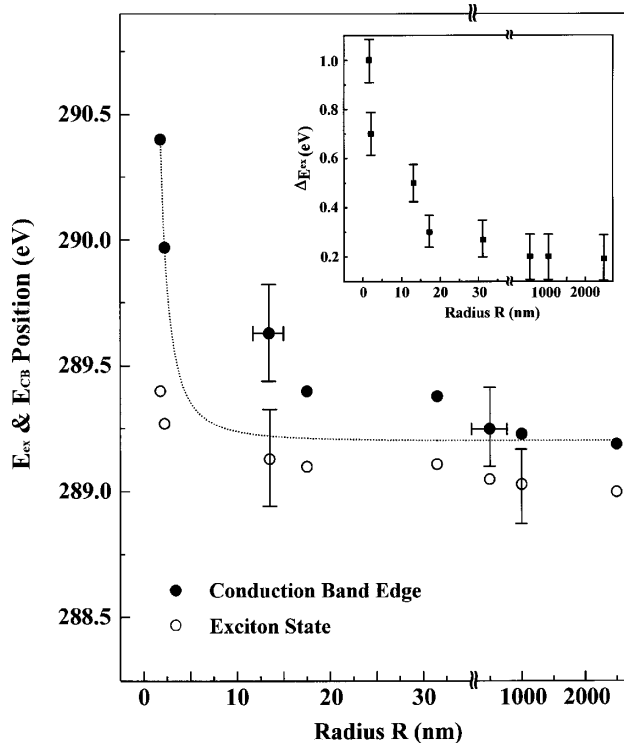

FIG. 4. The exciton state and conduction band edge of the nanodiamonds are plotted as a function of the crystallite radius. The dashed line is the least square fitting of all conduction band edge data to Eq. (1). The inset is the exciton binding energy shift of the nanodiamonds plotted as a function of the crystallite radius.

shown in the inset of Fig. 4 increases monotonically with the decrease of the crystallite radius when the radius is smaller than ~18 nm. It has been proposed that the electron and hole are forced to be closer to each other by the decreasing crystallite size, so that ΔE_{ex} increases with the decrease of the crystallite size [10,24]. In the CVD growth of diamond, H atoms are known to cover the diamond surface. They may also be present in the grain boundaries. A recent preliminary first-principles molecular-dynamics study of hydrogen mediated diamond film growth suggested that H atoms are on the surface not buried in the interior of the film during the growth process [25]. Thus, the C-H bonding affects only the local electronic properties near the surface and grain boundaries. Since the x ray penetrates an extended region of the diamond film, the measured adsorption spectra will be contributed dominantly by C atoms in the interior of the crystallites. Please note that for our smallest crystallite with $R = 1.8$ nm there are about 4300 C atoms in the crystallite and roughly 600 C atoms on the surface and/or grain boundary if the crystallite is more or less spherical. The influence on E_{CB} and ΔE_{ex} by the C-H bonding induced chemical shift is not important for the nanodiamonds studied in this work.

Batson and Heath [3] based on the effective mass approximation (EMA) theory [26] predicted that the shift of E_{CB} follows the equation

$$E = E_{re} + \frac{\hbar^2}{2m^*}\left(\frac{\pi}{R}\right)^2, \tag{1}$$

where E_{re} is the bulk reference energy and m^* and R are the electron effective mass and the radius of the nanocrystal, respectively. Using the E for the largest R, 2500 μm, as E_{re}, we have done least square fitting of the data of all our samples to Eq. (1) as shown in Fig. 4 and obtain an effective mass of 0.10 ± 0.02 m, which is reasonably close to that of the bulk diamond, 0.2–0.25 m [27]. This result suggests that for $R > 1.8$ nm, with which the crystallite contains more than 4300 C atoms, the conduction bands of the nanodiamonds more or less remain bulklike. This result also indicates that our data are adequate to elucidate the quantum confinement effect.

In summary, our results of the C K-edge XANES spectra of nanodiamonds show that the exciton state and conduction band edge shift to higher energies with the decrease of the crystallite size. This finding suggests a widening of the energy gap caused by the quantum confinement effect. These results also show that the crystallite size strongly influences the exciton binding energies.

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