JOURNAL OF MATERIALS SCIENCE **37** (2002) 1043–1047

Bonding character of the boron-doped C_{60} films prepared by radio frequency plasma assisted vapor deposition

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Boron-doped C_{60} thin films were synthesized firstly by a radio frequency plasma assisted vapor deposition technique using C_{60} as a precursor. The surface morphology of the samples was observed by atomic force microscopy, and their chemical bonding characters were investigated by x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. The results show that the boron atoms are incorporated into the fullerene molecules in the samples, and the boron heterofullerene $C_{60-n}B_n$ was synthesized. Plasma polymerized C_{60} molecules were also found in the samples besides the boron heterofullerene. The effects of radio frequency power and the substrate position on the growth of the B-doped C_{60} films were studied. The results indicate that the higher energies and densities of the reactive radicals in the plasma are favorable for the formation of the boron heterofullerene $C_{60-n}B_n$ or polymerized C_{60} molecules.

1. Introduction

The doping of fullerenes has a strong influence on the molecular, as well as bulk, properties of this new modification of carbon. Many fullerene derivatives with special physical and chemical properties have attracted a great deal of interest [1–3]. Exo- or endo-hedral doping has been reported widely [4] whereas less is known about doping through substitution with neighboring elements of carbon-like boron or nitrogen. Substitutional doping is intriguing because of the profound change in the carbon network that may lead to a novel class of fullerenes with interesting chemical and physical properties. Since the atomic radius and electronegativity of boron are close to those of carbon, substitutional doping by boron atom is easily realized in carbon-based materials. Theoretical studies imply that C can be replaced by B in the fullerene cage to form a stable structure [5, 6]. The substitutional doping of the C_{60} with B can change significantly energy levels near the Fermi level and the band gap between the highest occupied molecular orbital and the lowest unoccupied orbital, although structure and binding energies are almost unchanged. This opens up a potential application field of fullerenes as semiconductor components since their band gap and electronic polarizations can vary widely with substitutional doping.

Since the discovery of the arc discharge of graphite in helium as an efficient method of fullerene production, several attempts [7–11] have been made at the synthesis of fullerene molecules doped with boron or nitrogen atoms. Guo *et al.* [9] have synthesized boron-doped fullerene by laser vaporization of a graphite pellet containing boron nitride powder. Further studies, however, were not conducted because of difficulties in disassociation and refinement of the B-doped fullerene. Muhr *et al.* [10] also reported that boron heterofullerenes could be generated by arc evaporation of doped graphite rods in a modified fullerene reactor. More recently, it was reported that macroscopic quantities of B-doped fullerenes, such as $C_{60-n}B_n$ and $C_{70-n}B_n$, were synthesized by a DC arc burning method by Cao and co-workers [11]. However, in all cases, the synthses of B-doped fullerene molecules were conducted using the arc discharge of graphite. The B-doped fullerenes must be extracted and isolated from the soot product which includes many other fullerenes. In the case of B-doped fullerenes these have been no reports so far on attempts to preparate boron heterofullerenes using C_{60} as a precursor. The subject of this paper, is a simple procedure that has produced boron heterofullerene thin films using C_{60} as a precursor. The bonding characters of the boron heterofullerenes thin films were investigated by

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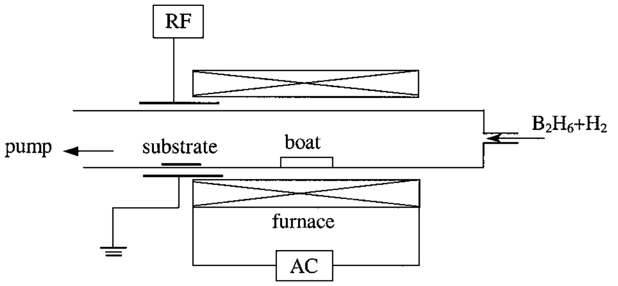

Figure 1 A schematic diagram of the RF plasma assisted vapor deposition apparatus.

x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy.

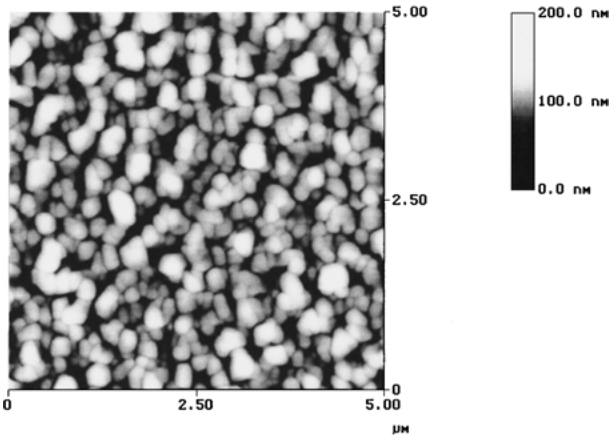

Figure 2 A typical AFM image of the B-doped C_{60} thin films.

2. Experimental

The B-doped C_{60} thin films were deposited on infrared (IR)-transparent Si (100) substrates by a radio frequency (RF) plasma assisted vapor deposition (PAVD) technique using C_{60} as a precursor. A schematic diagram of the experimental apparatus is shown in Fig. 1. The growth chamber is a quartz tube, 45 mm in diameter. Two parallel molybdenum plates were used as electrodes to form a capacitance coupling plasma reactor system. The C_{60} powder (>99.9% purity) was placed in a quartz boat located at the center of the quartz tube. The growth chamber was evacuated to the base pressure of 1×10^{-5} Torr and then back filled with the reactive gas (B_2H_6 and H_2) to a pressure of 2×10^{-2} Torr. The flows of the reactive gas were regulated exactly by mass flow controls. After heating the quartz boat to a temperature of 773 K, the C_{60} powder was evaporated. The evaporated C_{60} and the introduced reactive gas then made a gas mixture. The mixed gas was excited into the plasma state by RF induction at 13.56 MHz, with the RF power varied from 20–100 W. The source temperature was controlled at 773–823 K, and the substrate temperature was about 423 K. The films were deposited for 2 hours; the thickness of the films as measured by a TENCOR alpha-step profilometer was usually between 200 and 400 nm. The surface morphology of the samples was observed by atomic force microscope (AFM) using an OMICRON Compact Lab SPM system. The XPS analysis was carried out with an ESCALAB 220I-XL spectrometer using Mg K_α X-ray radiation. FTIR transmission measurements were performed at normal incidence in a WQF-400 spectrophotometer in the wavenumber range between 400 and 4000 cm^{-1}.

3. Results and discussion

A typical AFM image of a 0.28 μm thick film is shown in Fig. 2, in which the average size of the grains is about 200 nm. The smooth morphology and regular shaped grains indicate good crystallining. Additionally, the x-ray diffraction results indicate that the film has a face centered cubic (FCC) structure. The film surfaces consist mainly of rectangular FCC (001) faces and a few truncated triangular FCC (111) faces. According to the **PBC** theory [12], the faces having the slowest growth rate in the direction normal to the faces determine the crystal morphology. So the (111) faces should be expected as the main facets in the films since the growth rate of (111) faces is the slowest and they are the most stable faces in the FCC structure. Some researcher [13, 14] have found that the growth rate of the (001) faces is the lowest at low deposition rates, and both (111) and (001) faces have been observed on C_{60} film surfaces. In the present experiment, the growth rate (about 0.5 nm/min) is very low due to the presence of the reactive gas (B_2H_6 and H_2), thus more (001) faces instead of (111) faces appear in the films.

Fig. 3 shows the XPS spectra of C 1s and B 1s for a typical B-doped C_{60} film. A XPS spectrum (not show) of an undoped C_{60} film was also recorded for reference. The full width at half maximum (FWHM) of C 1s for the B-doped film is 2.1 eV, while the C 1s spectrum for the undoped C_{60} film is centered at 285.2 eV with a FWHM of 0.83 eV. The much broader peak in Fig. 3 suggests that there is more than one type of bonding scheme for C atoms in the B-doped C_{60} film. The XPS spectra were therefore resolved to investigate possible chemical bonding existing in the sample. As shown in Fig. 3, the deconvolution of the C 1s spectrum gives three peaks centered at 284.2, 285.3 and 287.0 eV, respectively. The peak at 285.3 eV can be assigned to the C-C bonding in the C_{60} molecules since the peak position is nearly same as that of the undoped C_{60} film, which is also in agreement with that of pristine C_{60} reported by others researchers [15]. It was reported that the binding energies of C 1s are 284.4 and 284.3 eV for BC_2N and $BC_{3.4}$, respectively [16, 17]. Therefore, the resolved peak at 284.2 eV can be attributed to B-C bonding in the boron heterofullerene $C_{60-n}B_n$. Additionally, the peak at higher energy (287.0 eV) can be assigned to C-O bonding. The presence of oxygen could be due to air exposure during the sample being transferred from the deposition apparatus to the XPS chamber.

The results of the deconvolution of the B 1s spectrum show the presence of two types of boron chemical states, centered at 189.3 and 191.3 eV. It is well known that the bonding energy of B 1s is 189.4 eV for $BC_{3.4}$ and 188.4 eV for B_4C [17]. Furthermore, Muhr *et al.* [10] reported that the B 1s core level energy in $C_{59}B$

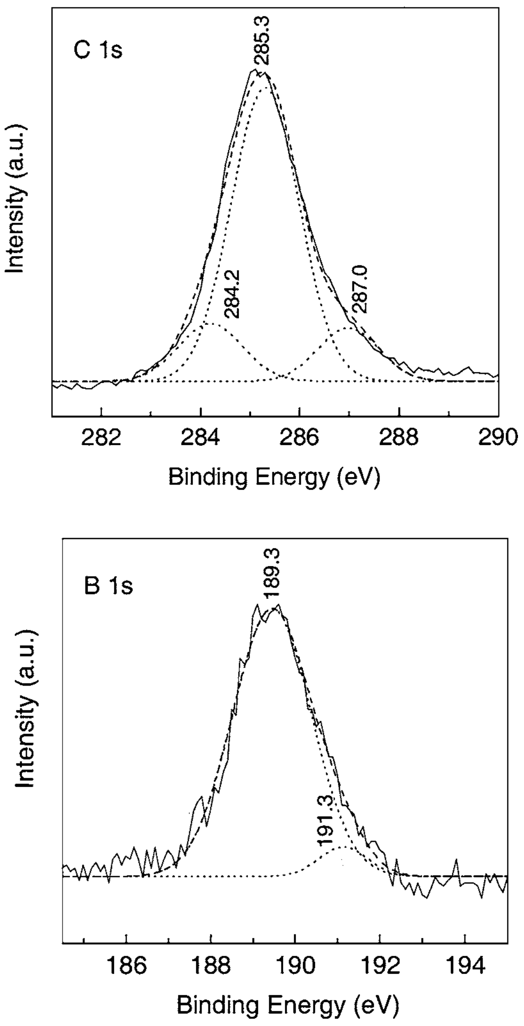

Figure 3 C 1s and B 1s XPS spectra of the B-doped C_{60} thin films. The solid and dotted lines are measurement and deconvolution spectra, respectively.

heterofullerene is 188.8 eV. So the peak at 189.3 eV is assigned to boron in the boron heterofullerene $C_{60-n}B_n$. For boron oxides and boric acid the B 1s level is expected at a binding energy of 192.4 eV [18], and thus the peak at 191.3 eV possibly relates to oxidized products. The absolute intensity of the B 1s peak is much lower than that of the C 1s peak, which is consistent with a low boron concentration in the material. For a $C_{59}B$ molecule, for example, the boron to carbon ratio is 1 : 59 so that the height of the B 1s peak is expected to ~2% of that of the C 1s peak.

Fig. 4a and b show the FTIR spectra of an un-doped C_{60} film and a typical B-doped C_{60} film, respectively. In Fig. 4a, there are four sharp characteristic peaks of C_{60} molecules centered at 527, 576, 1183 and 1428 cm^{-1}, respectively. However, except for the four C_{60} characteristic peaks, the FTIR spectrum of the B-doped C_{60} film (Fig. 4b) shows many new absorption peaks centered at 545, 640, 731, 885, 1007, 1197, 1616, 2518 and 3207 cm^{-1}, respectively. It is obvious that the absorption peaks at 2518 and 3207 cm^{-1} are due to the vibration of the B-H and C-H bonds, respectively. Annen *et al.* [19] reported that the IR absorption peaks corresponding to B-C bond were centered at the range of 1100–1200 cm^{-1} and 1500–1700 cm^{-1}. So the IR absorption peaks at 1197 and 1616 cm^{-1} possibly result from the vibration of the B-C bond in the boron heterofullerene $C_{60-n}B_n$. These results, as well as the XPS results, indicate that the boron atoms are incorporated into the fullerene molecules in the samples. It is well known that the conjugation of B atom and benzene can result in an IR absorption peak at 1400–1460 cm^{-1}. Similar absorption peak may exist in the present films. In addition, the absorption peaks of B-O bond and C-O bond are centered in the range of 1300–1500 cm^{-1}. Therefore, we propose that the superposition of these peaks and the C_{60} absorption peak at 1428 cm^{-1} leads to the broaden band centered at 1450 cm^{-1} as seen in Fig. 4b.

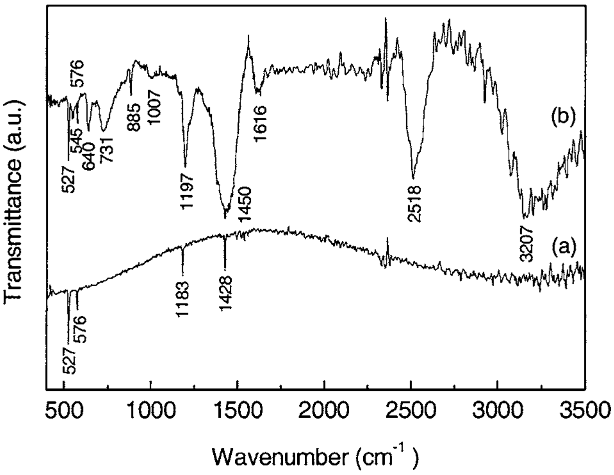

Figure 4 Typical FTIR transmittance spectra of (a) the undoped C_{60} thin film, (b) the B-doped C_{60} thin film.

It is well known that illumination, high pressure and high temperature can lead to a variety of polymerized fullerene structures [20–22]. Furthermore, plasma polymerization of C_{60} molecules has been reported widely also [23, 24]. It is reported that the infrared spectra of polymerized C_{60} have shown some new absorption peaks centered at 545, 890 and 1008 cm^{-1}. It may be possible to induce polymerization of C_{60} molecules under the present plasma conditions because of the intense illumination and high energy plasma. In Fig. 4b, the absorption peaks centered at 545, 885 and 1007 cm^{-1} are attributed to the polymerized C_{60} included in the B-doped C_{60} thin films. In addition, the silent modes of C_{60} can be activated when the symmetry of C_{60} molecule degenerates because of the boron doping. Therefore, the absorption peaks at 640 and 731 cm^{-1} possibly result from the silent modes of C_{60}, which are activated in the boron heterofullerene films because of the degeneration of molecule symmetry. In summary, many IR absorption peaks were observed in the FTIR spectra of the samples, and these peaks are mainly due to the pristine C_{60} molecules, the boron heterofullerenes, the plasma polymerized C_{60} and the oxidized fullerenes.

Fig. 5 shows the FTIR spectra of the B-doped C_{60} thin films prepared at various RF powers. It can be seen from Fig. 5 that the intensity of the four C_{60} characteristic peaks decreases with increasing RF power, i.e., the intensity ratio of the other peaks to the four C_{60}

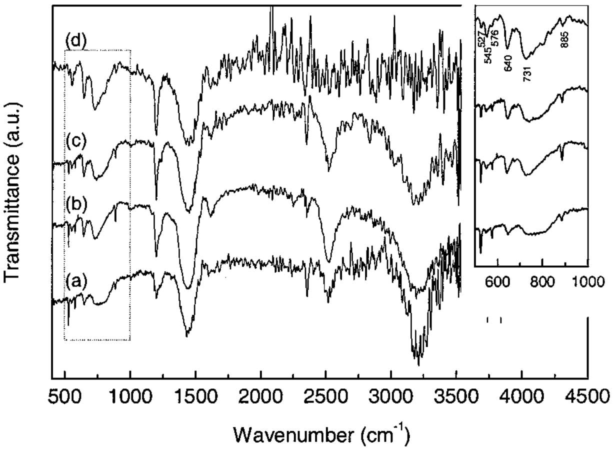

Figure 5 FTIR transmittance spectra of the B-doped C_{60} thin films synthesized with various RF powers of (a) 25 W, (b) 50 W, (c) 70 W, (d) 100 W.

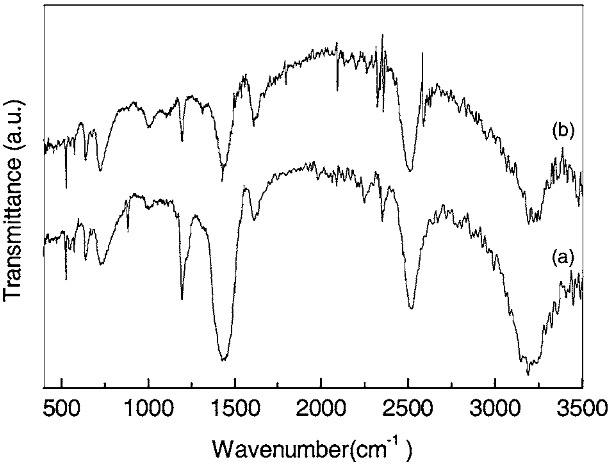

Figure 6 FTIR transmittance spectra of the B-doped C_{60} thin films prepared at (a) the center and (b) the edge of the plasma.

characteristic lines increases with increasing RF power. It is well known that the energies and densities of the reactive radicals in the plasma increase with incresing RF power. Therefore, in the case of the higher RF power, more C_{60} molecuels would be doped or polymerized, which results in relatively weaker intensity of the C_{60} characteristic peaks at higher RF power.

To investigate further the effects of the intensity of plasma on the formation of boron heterofullerene molecules, the substrates were placed at the center and the edge of the plasma, respectively. The two samples were deposited with RF power of 50 W. The FTIR spectra of the samples localized at the center and the edge of the plasma were shown in Fig. 6a and b, respectively. Although the FTIR spectrum in Fig. 6b is similar to that in Fig. 6a, the intensity of the absorption peaks due to C_{60} molecules is stronger in Fig. 6b. These results suggest that only a small amount of C_{60} molecules are doped or polymerized for the sample localized at the edge of plasma. It is proposed that the energies and densities of the reactive radicals are lower at the edge of plasma, so only a small proportion of C_{60} molecules is doped or polymerized. These results, indicate that higher energies and densities of the reactive radicals in the plasma are favorable for the formation of boron heterofullerene or polymerized C_{60} molecules.

4. Conclusion

The RF plasma assisted vapor deposition technique provides a simple way to produce the boron heterofullerene $C_{60-n}B_n$. The chemical bonding characters of the B-doped C_{60} thin films were investigated using XPS and FTIR experiments. These results confirm that the boron atoms are incorporated into the fullerene molecules in the samples, and the boron heterofullerene $C_{60-n}B_n$ was synthesized. Besides the boron heterofullerene, plasma polymerized and oxidized C_{60} molecules were also found in the samples according to the FTIR spectra of the samples. The effects of radio frequency power and the substrate position on the growth of the B-doped C_{60} thin films were studied. The results indicate that higher energies and densities of the reactive radicals in the plasma are favorable for the formation of the boron heterofullerene $C_{60-n}B_n$ or polymerized C_{60} molecules.

Acknowledgements

This work is partially supported by the Young Backbone Foundation of Beijing and the Foundation of Kuashiji Rencai Plan of Beijing.

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Received 1 June 2000
and accepted 30 March 2001