

Preparation of Boron Doped Fullerene Film by a Thermal Evaporation Technique using Argon Plasma Treatment and Its Electrochemical Application

Arenst Andreas Arie^{1,2}, Bup Ju Jeon² and Joong Kee Lee^{1,2,*}

¹Battery Research Center, Korea Institute of Science and Technology, Seoul 130-650, Korea

²Dept. of Energy Resources, Hanbuk University, Dongducheon, Gyeonggi-do, 483-777, Korea

³Energy Conversion Technology Division, University of Science and Technology, Daejeon 305-333 Korea

*e-mail: leejk@kist.re.kr

(Received May 14, 2010; Accepted June 16, 2010)

Abstract

Boron doped fullerene C₆₀ (B:C₆₀) films were prepared by the thermal evaporation of C₆₀ powder using argon plasma treatment. The morphology and structural characteristics of the thin films were investigated by scanning electron microscope (SEM), Fourier transform infra-red spectroscopy (FTIR) and x-ray photo electron spectroscopy (XPS). The electrochemical application of the boron doped fullerene film as a coating layer for silicon anodes in lithium ion batteries was also investigated. Cyclic voltammetry (CV) measurements were applied to the B:C₆₀ coated silicon electrodes at a scan rate of 0.05 mVs⁻¹. The CV results show that the B:C₆₀ coating layer act as a passivation layer with respect to the insertion and extraction of lithium ions into the silicon film electrode.

Keywords : Boron, Doping, Fullerenes, Plasma, Lithium ion battery

1. Introduction

Since the invention of Fullerene C₆₀ by Kroto in 1985 [1], C₆₀ and its derivatives have been used in various applications, including solar cells [2], light emitting diodes [3] and hydrogen storage [4], due to their unique structure and properties. Pure C₆₀ films are semiconductor materials possessing a band-gap of 1.5 eV and an electrical resistivity of 10³-10⁸ Ω·cm at room temperature. In order to improve the conductivity of C₆₀ films, boron atoms can be introduced into the C₆₀ lattices. The preparation of boron doped C₆₀ films was firstly reported by Zou et al. [5,6], however no applications were proposed in their works.

In this study, the boron doped C₆₀ films were prepared by the thermal evaporation of C₆₀ powder using argon plasma treatment. The electrochemical application of the film is then introduced. Specifically, the boron doped C₆₀ film was used as a coating layer for silicon anodes in lithium secondary batteries. Furthermore, the effect of argon plasma treatment on the structural and electrochemical characteristics of the coated silicon electrodes was also investigated.

2. Experimental

For the deposition of the thin film, C₆₀ powder was loaded

into a tungsten boat, as depicted in Fig. 1. The substrate was located on a steel holder and placed about 10 cm from the boat. The substrates were a silicon wafer for the structural

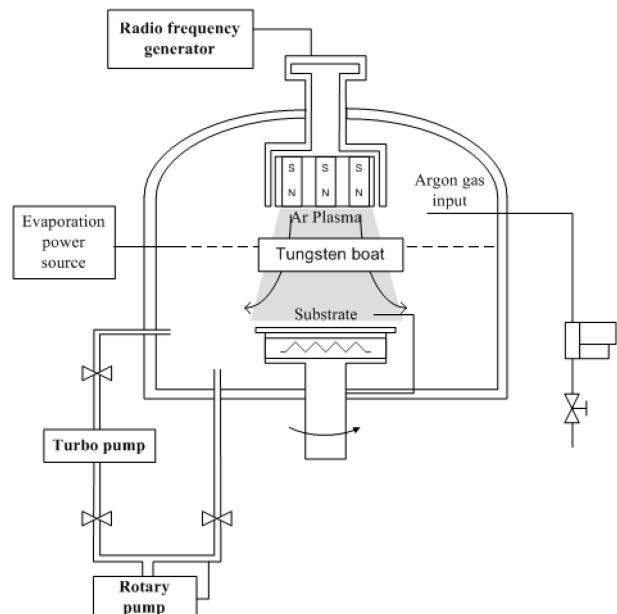


Fig. 1. Schematic diagram of thermal evaporation system to prepare the B:C₆₀ films.

studies and a silicon film on Cu foil for the electrochemical tests. Firstly, the pressure inside the chamber was reduced to a base pressure of 10^{-5} Torr using a rotary pump. After that, a mixture of argon and diborane (B_2H_6) was entered into the chamber with a flow rate of 30 sccm (standard cubic centimeters) to reach a working pressure of $2.5 \cdot 10^{-2}$ Torr. The flow rate was adjusted by a mass flow controller (MFC). Then, the radio-frequency generator was activated to generate the argon plasma. At the same time, the C_{60} powder was evaporated by thermal heat input. The resulting C_{60} vapor in the argon plasma environment was deposited in the form of a thin film on the substrate and the boron atoms were inserted into the fullerene film lattices. The substrate temperature was set at $150^\circ C$ and a plasma power of 100 W was used during the deposition process. For the comparison study, a pristine C_{60} film was also deposited by the thermal evaporation of C_{60} powder. The evaporation was done under the same conditions as that used for the B: C_{60} film without the argon plasma treatment.

The surface morphology and structure of the thin films were examined by scanning electron microscope (SEM), Fourier transform infra red spectroscopy (FTIR, Nicolet Almega XR, Thermo Electron Corporation) and x-ray photo electron spectroscopy (XPS, VG Scientific ESCALAB 200R). The electrochemical characteristics were studied by cyclic voltammetry (CV) measurements at a scan rate of 0.005 mV s^{-1} within a cut-off voltage range of $0\text{--}3\text{ V}$. For the CV tests, half cells were then fabricated in a dry room. The half-cells were fabricated by sandwiching a polyethylene (PE) separator between the B: C_{60} coated Si film electrode (as the working electrode) and Li metal (as the counter electrode). The half-cell ($2\text{ cm} \times 2\text{ cm}$) was then sealed in an aluminized polyethylene bag. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) ($1:1:1$ by volume).

3. Results and Discussion

Fig. 2 a shows the SEM photographs of the pristine C_{60} film synthesized by the thermal evaporation technique without argon plasma treatment. From the surface view, it can be seen that the film consists of many grains with different sizes, due to the evaporation of the C_{60} powder. In contrast, the B: C_{60} film shows a smaller grain size with a more uniform shape, as depicted in Fig. 2 b. It seems that the insertion of the boron atoms assisted by the argon plasma treatment during the deposition of the film contributes to the smaller grain size of the B: C_{60} film. From the cross-sectional SEM image in Fig. 2 c, the thickness of the B: C_{60} film is estimated to be 100 nm.

Fig. 3 shows the Raman spectra of the pristine C_{60} film deposited by the evaporation technique without argon

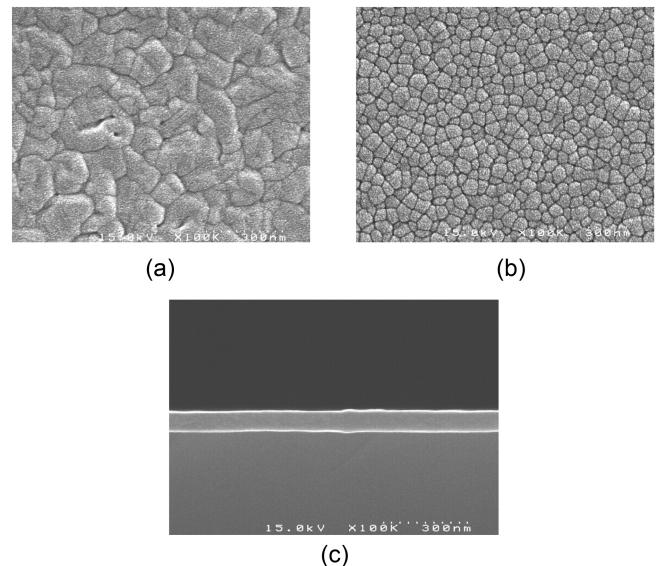


Fig. 2. Surface view SEM image of the (a) pristine C_{60} , (b) B: C_{60} thin film and (c) its cross-sectional view.

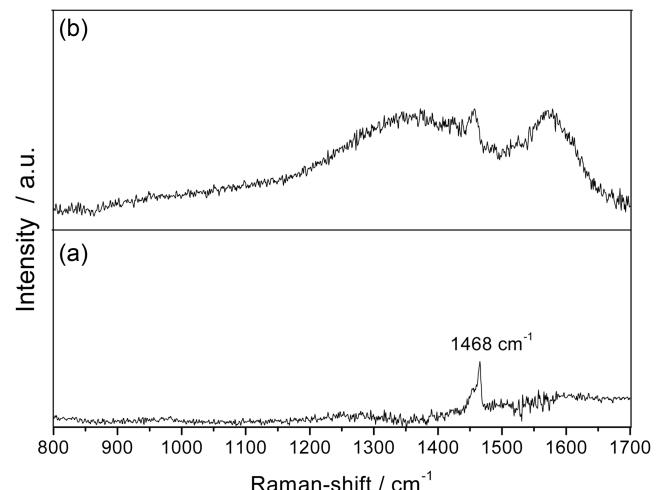


Fig. 3. Raman spectra of the as deposited (a) pristine C_{60} and (b) B: C_{60} thin film.

plasma treatment and the B: C_{60} film synthesized with argon plasma treatment. It can be seen that a strong peak at Raman shift of 1468 cm^{-1} , known as the pentagonal pinch mode, is observed in the case of pristine C_{60} film [7,8]. However, this pentagonal pinch mode are gradually separated and broadened but its existence is still recognized in the case of B: C_{60} films. This broadened peak in the vicinity of pentagonal pinch is the main indication of the typical fullerene C_{60} structure, which can not be found in other structure of carbon such as graphite, diamond or carbon nano-tubes [9-12].

Fig. 4 shows the FTIR spectra of the pristine C_{60} film deposited by the evaporation technique without argon

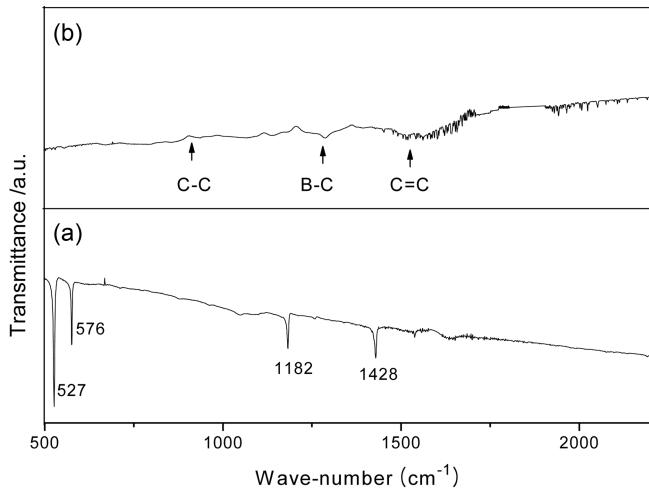


Fig. 4. FTIR spectra of the as deposited (a) pristine C_{60} and (b) $B:C_{60}$ thin film.

plasma treatment and the $B:C_{60}$ film synthesized with argon plasma treatment. In the case of the pristine C_{60} film, there are four dominant peaks detected at wave-numbers of 511, 527, 1182 and 1428 cm^{-1} . However, these four peaks are not found in the spectrum of the $B:C_{60}$ film, in which many new peaks related to the vibration of the bonding states of C-C, C=C and B-C are observed. Therefore, the bonding between boron and carbon in the $B:C_{60}$ film can be detected, due to the presence of the weak vibration of the B-C bond located at a wave-number of 1260 cm^{-1} .

Fig. 5a shows the C 1s XPS spectra of the pristine C_{60} and $B:C_{60}$ films. The C 1s binding energies of the pristine C_{60} and $B:C_{60}$ films are determined as to be 284.2 and 285.2 eV, respectively. The binding energy in the $B:C_{60}$ film is shifted to a higher value, due to the presence of stronger bonding between the carbon molecules. The full width at half maximum (FWHM) of the C 1s peak for the $B:C_{60}$ films is determined to be 1.58 eV. This value is obviously larger than that of the pristine form (0.96 eV). This higher FWHM value and broader spectrum of the $B:C_{60}$ films indicates that the linking among the fullerene molecules takes place during the deposition process. The presence of boron atoms in the fullerene lattices is evidenced by the B 1s XPS spectra of the $B:C_{60}$ film, as shown in Fig. 5 b. The peak centered at 189.4 eV is an indication of the bonding between boron and carbon in the fullerene film, which is consistent with the spectra found in the literature [13,14].

The electrochemical characteristics of the pristine C_{60} and $B:C_{60}$ films used as coating layers for silicon films were determined by cyclic voltammetry (CV) measurements. The aim of the CV tests is to investigate the reversible reaction between the lithium ions and silicon film as active materials. The CV curves of the pristine and $B:C_{60}$ coated silicon films at the first cycle at a scan rate of 0.05 mVs^{-1} are shown in

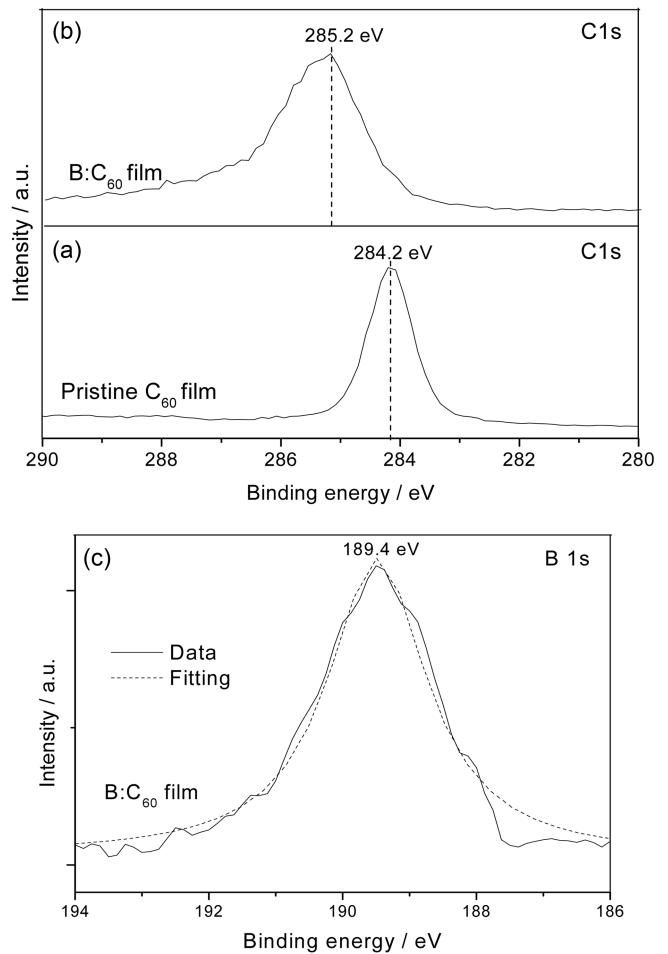


Fig. 5. XPS spectra of the (a) C 1s and (b) B 1s for pristine and $B:C_{60}$ films.

Fig. 6. For the pristine C_{60} coated silicon film, no anodic peaks are detected in the CV profiles. This indicates that the pristine C_{60} film blocks the insertion of lithium ions into the silicon film used as the active material during the charge-discharge tests. In contrast, the $B:C_{60}$ coated silicon film exhibits two pairs of cathodic and anodic peaks. It seems that the $B:C_{60}$ coating layer is effective in preserving the insertion and extraction of lithium ions during the charge-discharge tests. In other words, we can say that the $B:C_{60}$ coating layer is only acting as an inactive material during the electrochemical tests, the active host material for lithium accommodation is silicon, since the CV profiles of $B:C_{60}$ coated Si film is similar to that of bare Si film, as reported in our previous paper [15]. Additionally, the current intensity observed in the CV curve of the $B:C_{60}$ coated Si is higher than that of the pristine C_{60} . Based on the CV results, it can be said that the effectiveness of the argon plasma treatment during the deposition of the $B:C_{60}$ film in preserving the reversible reaction between the lithium ions and silicon

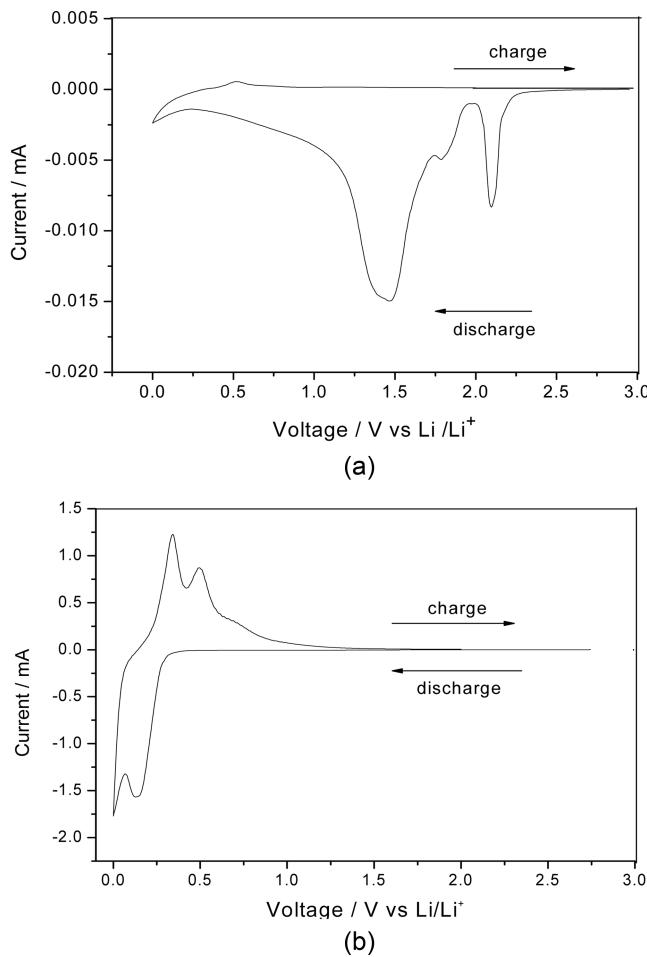


Fig. 6. Cyclic voltammetry curves of the (a) pristine coated Si and (b) B:C₆₀ coated Si electrodes at the first cycle under scan rate of 0.05 mVs⁻¹ between 0-3 V.

anode is very significant since it may establish a better path for the transfer of lithium ions at the electrode/electrolyte interface.

4. Conclusions

In summary, boron doped fullerene (B:C₆₀) thin films were successfully synthesized by a thermal evaporation technique assisted by argon plasma treatment. The presence of boron

atoms in the fullerene lattices was confirmed by SEM, XPS and FTIR analysis. The B:C₆₀ film was then utilized as a coating layer for silicon anodes in lithium secondary batteries. The CV results indicated that B:C₆₀ was quite effective in preserving the reversible reaction between the lithium ions and silicon. The argon plasma treatment during the deposition of the B:C₆₀ film contributed to the formation of a passivation layer.

References

- [1] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
- [2] Ariciftei, N. S.; Braun, D; Zhang, C; Srdranov, V.; Heeger, A. J.; Wudl, F. *Appl.Phys.Lett.* **1993**, *62*, 385.
- [3] Lee, J. Y.; Kwon, J. H. *Appl.Phys.Lett.* **2005**, *86*, 063514.
- [4] Sun, Q; Wang, Q; Jena, P. *Appl.Phys.Lett.* **2009**, *94*, 3058678.
- [5] Zou, Y. J.; Zhang, X. W.; Li, Y. L.; Wang, B.; Yan, H. J. *Mat.Sci.* **2002**, *37*, 1043.
- [6] Zou, Y. J.; Li, Y. L.; Zhang, X. W.; Wang, B; Yan, H. *Mat.Sci.Eng B* **2001**, *84*, 163.
- [7] Rao, A. M.; Zhou, P.; Wang, K; Hager, G. T.; Holden, J. M.; Wang, Y; Lee, W. T.; Bi, X. X.; Eklund, P. C.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. *Science* **1993**, *259*, 955.
- [8] Jin, Y.; Yao, C.; Wang, Z.; Xie, E.; Song, Y.; Sun, Y.; Zhang, C.; Liu, J.; Duan, J. *Nuclear Instr and Meth. in Physics Research B* **2005**, *230*, 565.
- [9] Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *J. Raman Spect.* **1996**, *27*, 351.
- [10] Wagberg, T.; Jacobsson, P.; Sundqvist, B. *Phys.Rev B* **1999**, *60*, 4536.
- [11] Rao, A. M; Eklund, P. C.; Hodeau, J. L.; Marques, L.; Nunez Regueiro, M. *Phys.Rev B* **1997**, *55*, 4766.
- [12] Zou, Y. G.; Liu, B. B.; Yao, M. G.; Hou, Y. Y.; Wang, L.; Yu, S. D.; Wang, P.; Cui, T.; Zou, G. T.; Sundqvist, B.; Wang, G. R.; Lin, Y. C. *Acta Phy. Sinica.* **2007**, *5172*.
- [13] Muhr, H. J.; Nesper, R.; Schnyder, B.; Kotz, R. *Chem. Phys.Lett.* **1996**, *249*, 399.
- [14] Kunzli, H.; Ganterbein, P.; Steiner, R.; Oelhaven, P. J. *Anal.Chem.* **1993**, *346*, 41.
- [15] Arie, A. A.; Chang, W.; Lee, J. K. *J. Solid State Electrochem.* **2010**, *14*, 51.