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Electrochemical characteristics of amophous carbon coated silicon electrodes

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Abstract−The properties of carbon films deposited by the radio frequency plasma sputtering of a fullerene C_{60} target were investigated to elucidate the dependence on the plasma power. A radio frequency argon plasma power ranging from 50 to 300 W at a pressure of 1.3 Pa was applied for sputtering. This corresponds to a self-bias potential on the target ranging from −95 to −250 V and a maximum argon ion energy ranging from 240 to 575 eV. The analysis of the G and D peaks in the Raman spectra shows that the films are similar to tetragonal hydrogenated amorphous carbon annealed at 600-1,000 °C. The electron band structure of the carbon films deposited by the sputtering of C_{60} depends on the plasma power. The coating effect of these carbon films on the capacity performance of the silicon film electrode of lithium secondary batteries was significant in our experimental range. An electrochemical test revealed that such carbon thin film on the silicon electrode plays an important role in mitigating the capacity fading during the charge and discharge processes. The test revealed that the film formed at a plasma power of 300 W is the most effective.

Key words: Fullerene C_{60}, Carbon Film, r.f. Plasma Sputtering, UV-Vis Spectra, Raman Spectra, Anode of Lithium Secondary Batteries

INTRODUCTION

The pretreatment of an electrode by a carbonaceous film coating, which is only conductive for Li ions and not for electrons or solvent molecules, improves the electrode properties for the liquid electrode. This film layer provides electrode stability due to solvent co-intercalation and direct intercalation between the solvent and electrode or stored lithium [1]. Hydrogenated amorphous carbon (a-C : H) with various coating morphologies strongly affected the electrochemical performance, and the formation of a coating sector which was as small as possible led to a longer cycle performance as reported in our previous work [2]. It was reported that the lithium inserted in the hydrogen-containing carbon causes hysteresis in the electrochemical behavior [3]. Amorphous carbon (a-C) films that are hydrogen-free, therefore, should eliminate this hysteresis.

Usually, a-C films are produced by carbon ion beam, magnetron sputtering or laser ablation of graphite as well as with other ion sources [4,5]. C_{60} fullerene is also utilized as a precursor for manufacturing hydrogen-free a-C films by the ion sputtering of a C_{60} target [6], thermal C_{60} deposition with ion assistance [7], ion C_{60}^{+} plating [8] and other techniques [9,10]. It was revealed that the fullerene is the precursor that can be used for making carbon films with diverse structures, which varied from polymerized fullerene to a-C with different ratio and distributions of sp^2/sp^3 carbon. However, radio frequency (RF) magnetron sputtering, which is a powerful technique for producing films, has not been applied yet to investigate the possibility for obtaining hydrogen-free a-C films from fullerene.

In this work, hydrogen-free a-C films produced by the RF magnetron sputtering of C_{60} were produced. The structural properties of these films versus of the plasma power were investigated by Raman scattering and UV-Visible absorption spectroscopy for the first time. The distinguishing features between the films originating from both fullerene and graphite that were produced by sputtering under the same conditions were shown. The effect of the hydrogen-free a-C coated silicon electrode for lithium secondary batteries on the cycle performance was investigated.

EXPERIMENTAL

Hydrogen-free a-C films were prepared by the sputtering of a C_{60} target in a conventional magnetron with capacitive coupled RF plasma. The set-up, which is shown in Fig. 1, consists of a vacuum chamber (1), target (2), target holders with coaxially placed magnets (3), and substrate (4) on a revolving holder (5). The plasma was supplied by a 13.56 MHz generator (6) at 500 W, which was connected to the target through the matching system (7). The electric potential on the target against ground during sputtering was measured by an oscilloscope (Tektronix TDS 3012) (6). The base vacuum in the chamber was 5.3×10^{-4} Pa. Argon (99.9999%) was used as the plasma gas; its flow rate was maintained at 30 sccm and pressure at 1.3 Pa during sputtering. Each sample was sputtered for 30 min. Pieces of copper foil with amorphous silicon films deposited on them were placed on the substrate holders. Also, Si wafers and quartz plates were laid on the substrate holder for use as substrates to further measure the Raman scattering and the UV-Visible spectra. The temperature of the substrate holder was kept near 20 °C. The C_{60} film used as a target for sputtering was produced by the thermal

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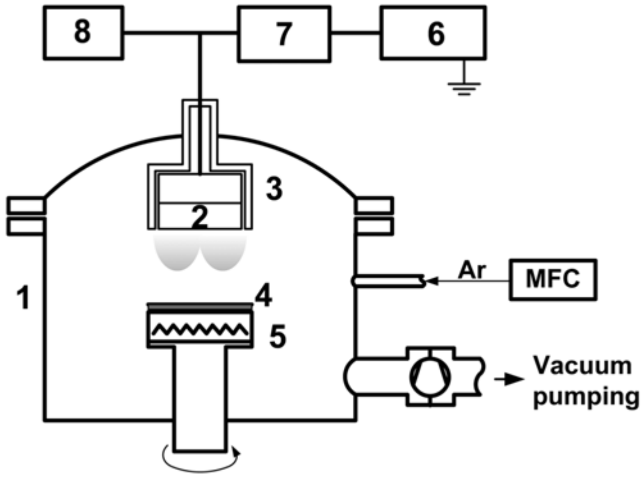

Fig. 1. Schematic of the magnetron system used for sputtering with a C_{60} target.

1. Vacuum chamber
2. C_{60} target
3. The set of magnets in the target holder
4. Substrate
5. The substrate stage
6. Radio-frequency generator (13,56 MHz, 600 W)
7. Matching block
8. Oscilloscope

deposition of C_{60} powder (99.5%, Astrin Inc, Russia) from a Knudsen cell onto a graphite disk with a diameter of 74 mm.

The UV-Visible adsorption spectra of the obtained carbon films were recorded in the range of 190-1,100 nm with a resolution of 1 nm by an HP Agilent 8453 UV-Vis spectrometer. Two spectrometers were used to record the Raman spectra at room temperature in a conventional backscattering geometry. The Raman spectra excited at the 514.5 nm line of an Ar-ion laser were recorded on a Jobin-Yvon LabRam HR with an LN2 cooled charge couple device (CCD) multichannel detector. The Raman spectra excited at 633 nm by an He-Ne laser were recorded on a Nicolet Almega XR Dispersive Raman Spectrometer (Thermo Electron Corporation, USA).

To prepare the electrode for electrochemical testing characteristics of the silicon thin film, the silicon thin films (a-Si : H) were deposited by the radio frequency plasma enhanced chemical vapor deposition system (RF PECVD) on copper foil with a thickness of 18 μm, which was used as both a current collector and substrate. During the deposition of the silicon thin films, the temperature was kept at 200 °C for 30 min. Argon and a mixture of hydrogen and silane were used as carrier and reactant gases. The RF power was maintained at 200 W at 50 sccm of argon, and then hydrogen-silane mixture was introduced at a flow rate of 15 sccm. A detailed description of the apparatus is available in a previous publication [11]. After the hydrogen-free a-C film was deposited on the a-Si : H thin film on copper foil by RF magnetron sputtering of C_{60}, it was used as the anode (3×3 cm) of a half cell without further treatment. The cells were fabricated in a dry room whose moisture content was maintained at less than 0.3%. The electrolyte employed in this study was 1 M $LiPF_6$ dissolved in a 1 : 1 : 1 (volume/volume) mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate. Polypropylene was used as a separator. A MACCOR (series-4000) testing system was used for the galvanostatic charge-discharge cycling test and cyclic voltammetry analysis. All cells were cycled at a constant current of 100 $\mu A/cm^2$ at room temperature. Charge-discharge cycling tests were performed with cut-off voltages of 2.0 and 0.0 V.

RESULTS AND DISCUSSION

The deposition of the hydrogen-free a-C film on the silicon electrode, which was prepared by the RF PECVD system, was carried out by the sputtering of a fullerene target at plasma powers ranging from 50 to 300 W. The energy of the sputtering ions, self-bias potential and peak-to-peak voltages on the target depend on the sputtering power. The self-bias potential and peak-to-peak voltages were measured experimentally and the ion energy was calculated, as shown in Table 1. The plasma power settings of 50, 130, and 300 W used for sputtering were chosen based on the supposed effect on the fullerene film. At a plasma power of 50 W, only a small portion of the ions exceeded the sputtering threshold of 200 eV for fullerene [12]. At a plasma power of 130 W, the maximum energy of the ions bombarding the target is slightly lower than the dissociation energy of C_{60} to individual carbon atoms. At 300 W, the calculated ion energy is close to 600 eV where the C_{60} structure is completely destroyed, and it results in the accumulation of a-C on the target surface. As shown in Table 1, the peak-to-peak, self-bias potentials on the target and the energy of the bombarding argon ions were easily determined from the plasma power; therefore, we will henceforth refer to the plasma power magnitude.

1. UV-Visible Adsorption Spectroscopy

UV-Visible adsorption spectroscopy was used to characterize the optical properties of the carbon films obtained by the RF magnetron sputtering of the C_{60} target. Fig. 2 shows the UV-Visible spectra of

Table 1. Peak-to-peak voltage, self-bias voltage, and maximum ion energy at various plasma powers used for sputtering of the C_{60} target

Plasma power, W	50	130	300
Peak-to Peak voltage, V	290	432	612
Average self-bias voltage, V	−95	−172	−248
Max. ion energy, eV	240	390	575

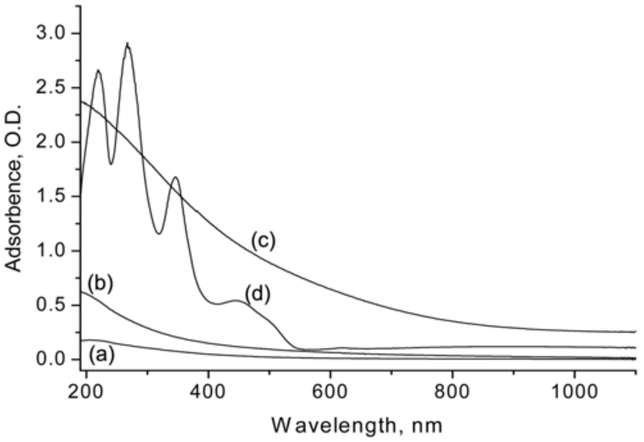

Fig. 2. UV-Vis spectra of the carbon films produced by the sputtering of a C_{60} target at plasma powers of (a) 50, (b) 130, (c) 300 W, and (d) fullerene film deposited by thermal evaporation.

the carbon films produced at plasma powers of 50, 130, and 300 W, as well as that of the pure fullerene film for the sake of comparison. All of the spectra were smooth without any features that could be characterized of fullerene molecules. The optical band gaps of the films were determined from the spectra using the Tauc relationship, $\alpha E=B(E-E_g)^2$, where α is the absorption coefficient, E is the photon energy, B is an empirical constant and E_g is the optical band gap [13]. Optical band gaps, E_g, of 1.6, 1.4, and 0.65 eV were estimated for the films produced at plasma powers of 50, 130, 300 W, respectively. The decrease in E_g between 130 and 300 W reflects the significant changes in the electronic band structure of the carbon films obtained at these conditions.

2. Raman Spectroscopy of the Carbon Deposits from C_{60} Sputtering

Raman scattering spectroscopy is a widely used method for investigating carbon and distinguishing one kind of carbon from another. The Raman scattering of a-C materials depends on many structural features, such as the clustering of the C sp^2 atoms, bond length and bond angle disorder, the presence of C sp^2 rings or chains, and the sp^2/sp^3 ratio.

Two intensive modes dominate in the Raman spectra of a-C. One of them called G-mode “graphite,” which is located in the vicinity of 1,580 cm^{-1}, corresponds to the in plane bond-stretching motion with E_{2g} symmetry of the paired C sp^2 atoms. It is present both in aromatic rings and olefinic chains. The second mode called D-disordered is like the breathing mode with A_{1g} symmetry of six-fold aromatic rings. The broadening of the D peak is correlated with the distribution of clusters of sp^2 carbon atoms with different orders and dimensions whilst the intensity of the D peak depends on the distorted aromatic rings [14].

The analysis of Raman scattering of the carbon films produced by RF sputtering of C_{60} allows us to elucidate the following:

- distinguishing between the deposits produced by sputtering of C_{60} or graphite;
- the dependence of the structure of the deposit produced by sputtering of C_{60} from the plasma power;
- the degree of similarity of the carbon deposit produced by sputtering of C_{60} with other amorphous carbons obtained by other techniques.

The question of interest is distinguishing between the films produced by the sputtering of C_{60} and graphite, because C_{60} is much more expensive than graphite and there is no reason to sputter C_{60} if the film produced by graphite is the same. To elucidate this point, the sputtering of the uncovered graphite target, which was used as the substrate for the fullerene film, was performed under the same conditions as those used for the sputtering of the fullerene film. Fig. 3 shows the Raman spectra (λ_{ex}=633 nm) of the films produced by the sputtering of fullerene and graphite at the plasma powers of 50, 130, and 300 W. The Raman spectra of all of the films originating both from graphite and fullerene depend on the plasma power. The common spectral feature of the films originating from fullerene is that they are missing the modes attributed to C_{60}. The strong G and D modes of a-C were observed in the spectra of the deposits produced from both fullerene and graphite at the plasma powers of 130 and 300 W, while the spectra from the films obtained at the plasma power of 50 W were too poor to be analyzed. The spectra of the films produced at the plasma power of 300 W are the most developed (see Fig. 3(c)). The G mode of the film originating from fullerene is downshifted as compared to the same mode of the film originating from the graphite precursor. It should be noted that the C=C chains in olefinic carbons are shorter than those in aromatic carbons and the chain vibration modes are higher. Therefore, increasing the ratio of the aromatic rings to olefinic chains will move the G peak to a higher energy. It means that in the film produced by sputtering C_{60} at the plasma power of 300 W the ratio of aromatic carbon atoms to the olefinic atoms is higher than in the films originating from sputtered graphite. The greater broadening of the

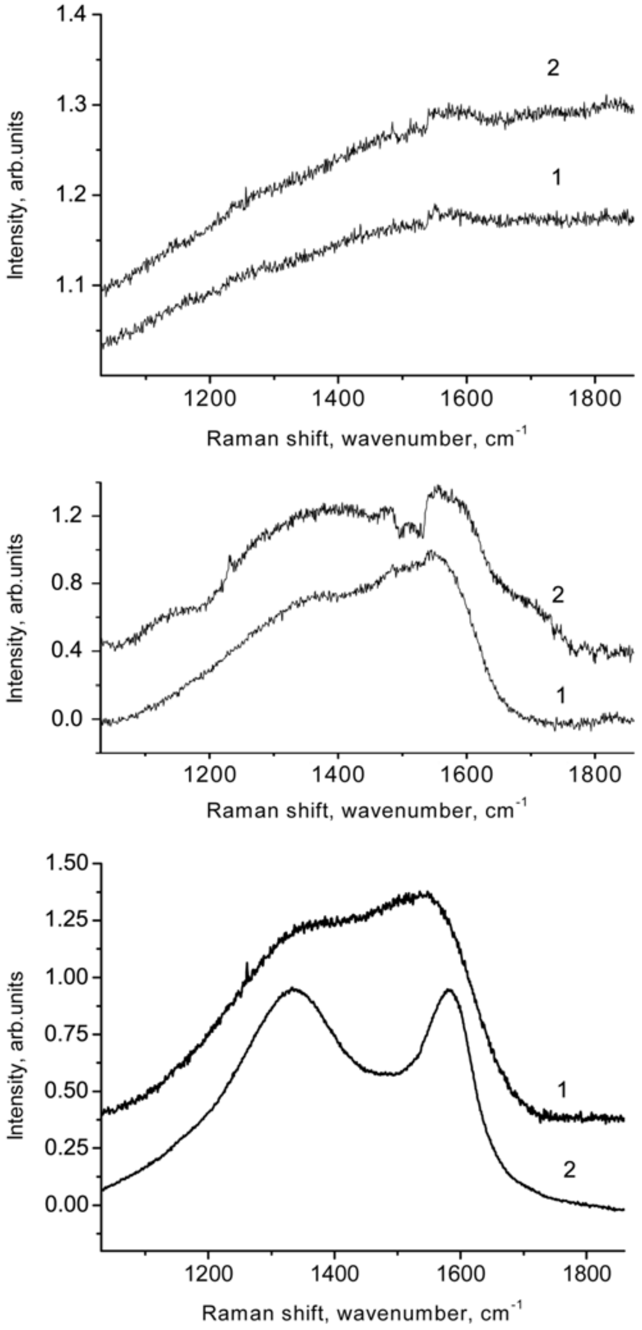

Fig. 3. Raman spectra excited at 633 nm (He-Ne laser) of films produced by sputtering at different plasma powers for C_{60} (line #1) and graphite (line #2) targets: (a) 50, (b) 130, (c) 300 W.

D mode observed in the film produced by fullerene sputtering could be attributed to the more disordering and wider size distribution of the clusters of aromatic carbon atoms in these films.

The distinction between Raman spectra of the films originating from fullerene and graphite that were sputtered at 130 W is less than that of those obtained at 300 W plasma power (see Fig. 3(b)) but also is appreciable. The position of the graphite G modes almost coincides in both kinds of films at this plasma power. The broadening of the D mode observed in the Raman spectrum of film produced by graphite sputtering is wider than for the film originating from C_{60} as contrasted to the sputtering at 300 W plasma power. Based on the analysis of Raman scattering, therefore, we can conclude that the carbon films originating from the sputtered fullerene and graphite have different structures, even under the same sputtering conditions. These distinctions become more significant with increasing plasma power that also means with increasing energy of the sputtering ions.

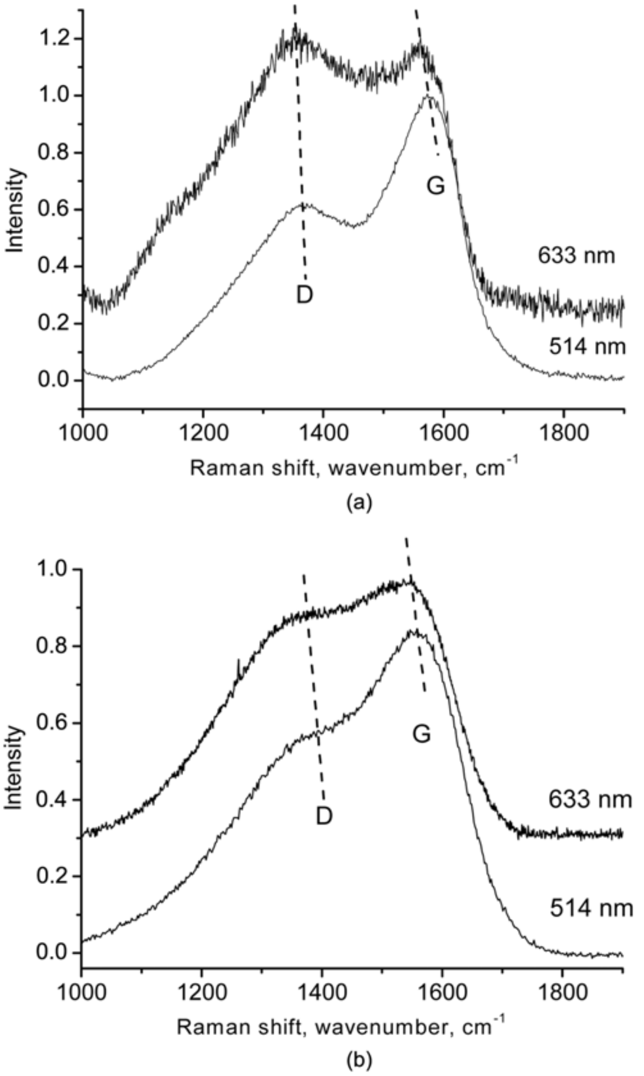

Fig. 4. The Raman spectra excited at 514 and 633 nm of the amorphous carbon films produced at plasma powers of (a) 130 and (b) 300 W for the sputtering of a C_{60} target.

The second point to be elucidated is the relationship between the structure of the a-C films resulting in C_{60} sputtering and plasma power. Fig. 4 shows the Raman scattering spectra with the laser excitation wavelength, 514 and 633 nm of the carbon films prepared by fullerene sputtering at 130 and 300 W plasma powers. The peaks near 1,580 cm^{-1} are assigned to the G band, while the peaks near 1,350 cm^{-1} are assigned to the D band. The peak positions, intensity, full width at half maximum (FWHM), and I(D)/I(G) resulting in Gaussian fitting of these Raman spectra are shown in Table 2.

It is known that carbon materials with different structures can give similar Raman spectra. Therefore, to compare one carbon material with another, a single parameter of the spectra is insufficient. Along with the position of the G peak, the dispersion *vs.* excitation energy was used for comparing the a-C film produced by fullerene sputtering. The G peak does not disperse in graphite itself, nanocrystaline graphite, or glassy graphite. The G peak disperses, *e.g.*, depending from excited energy, only in more disordered carbon, where the dispersion is proportional to the degree of disorder. The G peak dispersion is revealed for films produced by sputtering at plasma powers both 130 and 300 W. This is a proof that both carbon films originating from fullerene sputtered at different energy are amorphous.

The positions of the G and D peaks of the films that originated from the sputtered C_{60} depend not only on the excitation energy but also on the plasma power. In the sample produced at the plasma power of 130 W, the G peak is shifted in comparison to that in the sample produced at 300 W (see Table 2). This means that more six-fold rings are present in the film produced at 300 W. Such shifts are observed for both excitation energies. The analysis of the I(D)/I(G) ratio shows that at a laser excitation of 514 nm, this ratio increases, whereas one decreases at 633 nm. This phenomenon could be explained by the resonance nature of the G peak in amorphous carbons [14]. Thus, the electron band structures of the two films are different, which agrees with the band gap values determined from the UV-Visible spectra of the films. The I(D)/I(G) ratio is situated between 0.7 and 1.8, which suggests that there is a high portion of

Table 2. The peak positions, intensities, FWHMs, and I(D)/I(G) ratio resulting from the Gaussian fitting of the Raman spectra taken at two laser excitation energies of the films obtained by fullerene magnetron sputtering at 130 and 300 W

Plasma power	E_{ex}, nm	G			D			I(D)/I(G)
		ν, cm^{-1}	I	FWHM cm^{-1}	ν, cm^{-1}	I	FWHM cm^{-1}	
130	514	1579	0.82	104	1381	0.59	246	0.71
130	633	1565	0.61	85	1367	1.05	288	1.73
300	514	1570	0.65	125	1393	0.67	299	1.03
300	633	1558	0.63	124	1373	0.86	266	1.37

aromatic rings in both type of films [15].

The analysis of the Raman spectra is useful for comparing our films with the carbon films produced by other techniques [14]. Based on the position and dispersion of the G mode, the structure of both kinds of our films produced at 130 and 300 W plasma powers is similar to tetragonal hydrogenated amorphous carbon (ta-C : H), which was grown by an electron cyclotron resonance source from C_2H_2 with subsequent annealing between 500-600 °C. The I(D)/I(G) ratio of the carbon films produced by the sputtering of C_{60} at 130 and 300 W increases with increasing energy and is similar to those of ta-C : H annealed at 600 and 1,000 °C, respectively. It is known that at such temperature hydrogen released from tetragonal hydrogenated amorphous carbon films and partial graphitization take place with transfers of tetragonal sp^3 carbon to sp^2. Based on the above analysis, one can conclude that the structure of the amorphous carbon film produced by the RF magnetron sputtering of C_{60} does not fully match known carbons, but is closest to that of annealed ta-C : H. It should be mentioned that in our case high temperature does not need to be applied to produce such films.

3. Scanning Electron Microscopy of the Sputtered Deposits

Fig. 5 shows the surface morphology of the films resulting in both sputtering of C_{60} and graphite at 130 W plasma power. The surface of both films looks similar and consists of grains sized between 10 to 40 nm without pores. The surfaces of the films produced at other plasma power are the same as presented on Fig. 5 both for the originated from fullerene and graphite. Such surface morphology is desirable for covering silicon electrodes in the lithium secondary batteries because a coated carbon sector is small enough that has led to a longer cycle performance as was reported in our previous work [2].

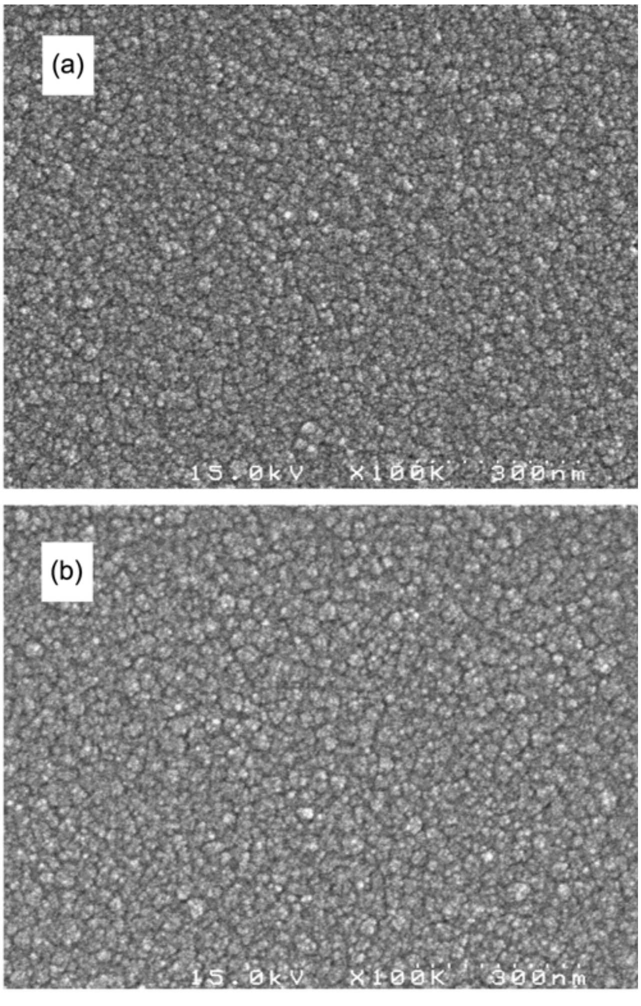

Fig. 5. The SEM images of the a-C films produced by RF magnetron sputtering at plasma power of 130 W of (a) C_{60} target, (b) graphite target.

The thicknesses of 20, 80, and 200 nm were determined from the cross section for films originating from fullerene sputtered at 50, 130, and 300 W plasma power, respectively. The thicknesses of the films produced by graphite sputtering were 96 and 220 nm at plasma power of 130 and 300 W, respectively. All films were produced by sputtering during 30 min that indicates that the sputtering rate of graphite is slightly higher than that of fullerene.

4. Electrochemical Application

Fig. 6 shows the change of the discharge capacities of the cells with a-Si : H electrode, which is coated by a-C originated form sputtering of C_{60}. The electrochemical curve of the a-Si : H thin film electrode without the a-C coating that is also presented on Fig. 6 drastically decreases with increasing number of charge-discharge cycles. This may be due to the structure disintegration of a-Si : H caused by the large volume changes which occur during the repeated lithium ion insertion and extraction processes. However, all of the a-C coated a-Si : H thin film electrodes showed higher cycle performance than that of the bare a-Si : H electrode. The effect of the carbon coating on the a-Si : H electrode was similar for all of the samples, but the capacity fading of the samples slightly depended on the coating condition of the a-C film. The capacity for the electrodes covered by the carbon films produced at 130 and 300 W is close to the theoretical value. The a-C film covered Si electrode, which was prepared by C60 sputtering at 300 W for 30 min, exhibited higher electrochemical performance than the other electrodes prepared with different plasma powers. The electrochemical performance does not depend on the thickness of the covering a-C films proving that the diffusion of the lithium during the charge-discharge cycling take place along the grain boundaries.

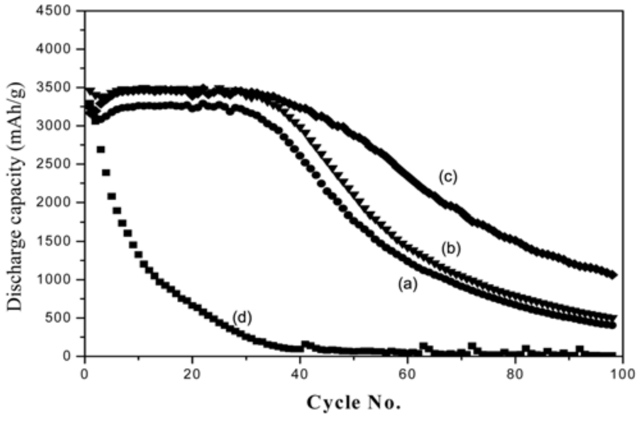

Fig. 6. The electrical capacity of the a-Si films electrode covered by a carbon film produced by the sputtering of a C_{60} target at plasma powers of (a) 50, (b) 130, (c) 300 W and (d) bare a-Si film electrode.

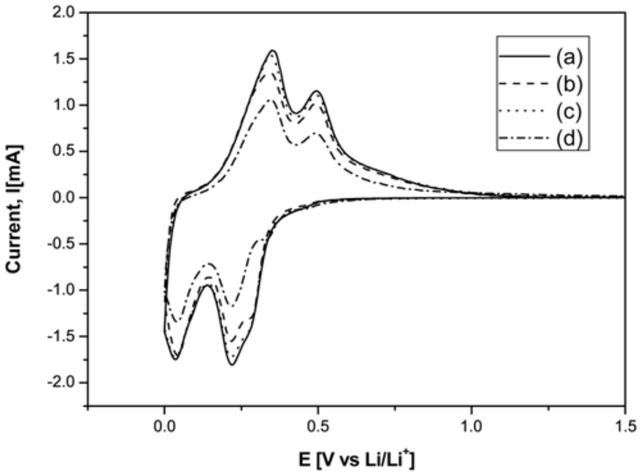

Fig. 7. Comparison of cyclic voltammetry between a bare a-Si film and Si electrode covered by carbon films produced by the sputtering of a C_{60} target at plasma powers of (a) 50, (b) 130, (c) 300 W and (d) uncovered a-Si film electrode.

Fig. 7 shows the cyclic voltammetry diagram for the cells prepared from the bare a-Si : H electrode and ones that are coated by a-C produced by C_{60} sputtering at various plasma powers. Evidence of Li_xSi alloy formation can be found in Fig. 7. Comparing the cyclic voltammetry behavior of the pristine a-Si : H electrode and ones covered by a-C films originated from C_{60}, we see that no new oxidation and reduction peaks are observed after the a-C coating. These results can be explained by assuming that the a-C film acts as a passivation layer, which maintains the physical structure of the electrode during the charge-discharge reactions. As to the a-C coated silicon electrodes, the deintercalation peaks of the Li ions are higher than those of the bare silicon electrode. This result can be explained by the increase in the discharge rate afforded by the a-C coating.

CONCLUSIONS

Carbon films were produced by the sputtering of a C_{60} target in RF plasma at different powers. The films were classified as amorphous carbon films, and differ from those produced by the sputtering of a graphite target. The UV-Visible adsorption and Raman scattering spectra of these films did not reveal any features of the fullerene molecule. The analysis of the G and D peaks in the Raman spectra shows that the films are similar to tetragonal hydrogenated amorphous carbon film annealed at 600-1,000 °C. The electron band structure of the carbon films originating from the sputtering of C_{60} depends on the plasma power.

The coating effect of the produced carbon films on the capacity performances of the Si-film electrode of lithium secondary batteries is significant. For the electrodes covered by the carbon films produced at 130 and 300 W, the capacity is close to the theoretical value. On the basis of the number of effective cycles, the most effective film is the one formed at a plasma power of 300 W.

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