

Thermal annealing behavior of Si-doped diamond like-carbon films deposited by reactive sputtering

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Silicon doped diamond-like carbon(Si-DLC) thin films with Si contents in the range 0-15 at.% were deposited on silicon substrates using a reactive sputtering method. The thermal annealing behavior of the films was investigated by annealing the films using a rapid thermal process(RTP) system. X-ray photoelectron spectroscopy(XPS), Raman spectroscopy, Fourier transform IR(FTIR) spectroscopy, high resolution transmission electron microscopy (HRTEM) and micro-hardness testing were used to determine the structural and mechanical property changes of the annealed pure and Si-DLC films. It was found that the graphitization process as a result of the D-band and G-band splitting, the increase of I_D/I_G ratio and G-peak position shifting started from 400 °C in the pure DLC films, and from 500 °C in the 15 at.% Si-DLC films, respectively. Moreover, in the case of the 15 at.% Si-DLC films the intensity of the Si-C bond was detected even after annealing at 600 °C, which indicated the formation of a SiC phase embedded in the amorphous carbon matrix. This formation of SiC nanocrystallites with a size of 5 nm was confirmed by HRTEM images, and then they were stable even after high temperature annealing although the size was decreased slightly. Therefore, the mechanical properties and thermal stability of the reactive sputtered Si-DLC films could be improved by the existence of SiC nanocrystallites after thermal annealing.

Key words: Si-DLC thin film, reactive sputtering, thermal annealing, nanocrystallite.

Introduction

Incorporation of foreign atoms, such as nitrogen, boron, silicon, fluorine and transition metals, into diamond-like carbon (DLC) films has been reported to overcome the main problems of DLC films, which are the low thermal stability and the high compressive internal stress [1-3]. Among them, Si-doped DLC(Si-DLC) films have a great potential for many applications, since they may show reduced residual internal stress, high hardness and good adhesion to many substrates [4-5]. Si-DLC films can mainly be obtained by the PECVD technique of gaseous compounds containing both Si and C, or sputtering a graphite target into an Ar and Si containing atmosphere [4-7]. Much attention has been paid to enhance the mechanical and thermal properties by modification of the microscopic bonding structure of Si-DLC films using the PECVD process [8-10]. In the case of the effect of annealing on the stability of Si-DLC prepared by PECVD despite the various deposition conditions, a general finding is that silicon contributes to the increase of the temperature showing thermal degradation such as graphitization (sp^3 to sp^2 transformation) and hydrogen effusion for their long-term application at higher temperature [10].

On the other hand, there has been studies using magnetron sputtering, which can conveniently deposit hydrogenated as well as hydrogen-free DLC films by controlling the flow rate of hydrocarbon feed gas. However, the effects of the structure, composition, and chemical bonding on the mechanical properties of Si-DLC films prepared by the sputtering technique have not been examined systematically, yet. Furthermore, the effect of annealing on the stability of sputtered Si-DLC films has not been extensively studied. Recently, Ito *et al.* investigated the thermal stability of unbalanced magnetron sputtered DLC films with two different hydrogen contents. They showed that the thermal stability is higher for DLC films with lower hydrogen contents [11]. Evans *et al.* reported that mechanical properties of Si-aC : H films prepared by reactive sputtering with a varying tetramethyl silane(TMS) flow rate are dependent on Si and H contents [7]. However, little studies have investigated the effects of silicon contents on the thermal annealing behavior of hydrogenated sputtered Si-DLC films.

Therefore, in this study, a series of Si-DLC films with various silicon contents by varying the SiH_4 flow rate were deposited using magnetron sputtering. Film structures and mechanical properties of the Si-DLC films were studied as a function of input gas concentration and the thermal annealing behavior of the films was investigated by annealing the films using a rapid thermal process(RTP) system. The variation in microstructure of the films under post-deposition

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annealing was also studied by examining the HRTEM images after annealing.

Experimental

Si-doped DLC films were deposited on p-type Si(100) substrates by using a combined plasma assisted PVD/CVD technique and sputtering system. The combined system is composed of the plasma decomposition of a CH_4 and SiH_4 (5% in Ar) gas mixture and RF magnetron sputtering of a high purity (99.99%) graphite target by Argon. The substrates were RCA cleaned and then placed on the lower electrode of the reactor. Prior to deposition, the chamber was evacuated to less than 6.6×10^{-4} Pa, then the substrate was cleaned by an Ar plasma. After that, Si-DLC films were deposited onto the substrates using an RF generated CH_4/SiH_4 plasma and magnetron sputtering of a graphite target. The Si content in the film was controlled by adjusting the ratio of SiH_4 to Ar as the precursor gases. The SiH_4 flow was varied between 0 and 4 vol.% SiH_4 in Ar and CH_4 . Pure DLC films were also prepared by RF magnetron sputtering of a graphite target in Ar or a Ar/ CH_4 gas mixture. The substrates were not heated or biased during the deposition under all the conditions, while the deposition time was varied to achieve a thickness of about 300 nm. Subsequently, all films were annealed for 10 minutes at 6 Pa pressure in vacuum using the RTP system from 200 °C to 700 °C at intervals of 100 °C in order to study the thermal annealing behavior of the sputtered Si-DLC films and compared to that of pure DLC films.

The film thicknesses were measured by cross-sectional views in a FESEM. The structure of the films was analyzed by FT-IR and micro-Raman spectroscopy. FT-IR absorption spectra were obtained in the wavenumber range from 700 °C to 3000 cm^{-1} . Micro-Raman spectroscopy was excited using a beam of wavelength 532 nm from an Ar laser in the wavenumber range from 500 °C to 2000 cm^{-1} . The microscopic structure and chemical bonding state within the films were investigated by high resolution transmission electron microscope (HRTEM) and X-ray photoelectron spectroscopy (XPS). The residual compressive stress was obtained by the substrate bending method using a Stoney equation and the hardness was measured by a micro Vickers hardness tester with an applied load of 0.1 N.

Results and Discussion

Fig. 1. shows the correlation between the volume fraction of SiH_4 in the $\text{SiH}_4/\text{CH}_4/\text{Ar}$ gas mixture and the silicon atomic concentrations in the as-deposited Si-DLC films. With an increase in the SiH_4 flow rate, the silicon content is increased to 15 at.% at 4 vol.% SiH_4 . The silicon concentrations were measured by XPS and the deconvolution of XPS spectra was done using a software system with a Gaussian distribution function in order to estimate the fractional ratio of the sp^3 to sp^2 . It is well known that the estimation of the sp^3/sp^2 ratio is helpful to understand the

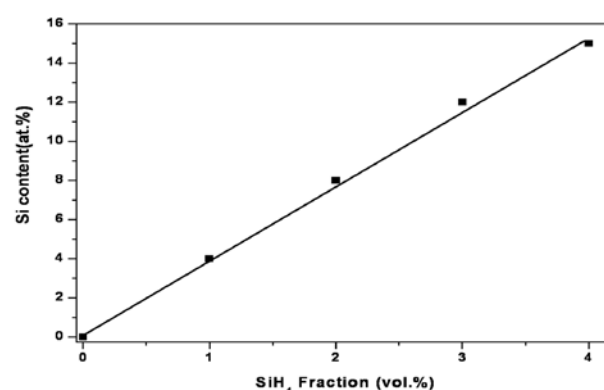


Fig. 1. Si content as a function of SiH_4 fraction.

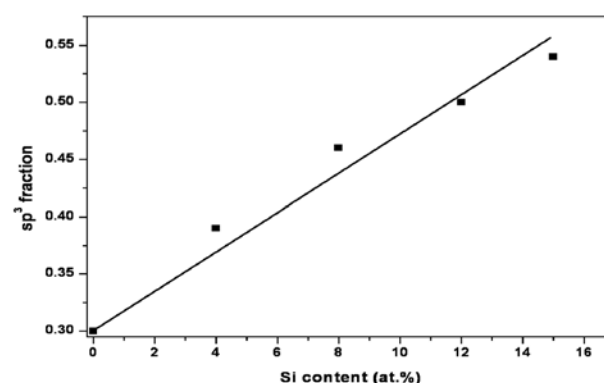


Fig. 2. sp^3 fraction as a function of Si content.

effects of silicon incorporation on the mechanical and structural properties of DLC films [12]. The dependence of the fraction ratio of sp^3 to sp^2 as a function of silicon content in the as-deposited Si-DLC films is shown in Fig. 2. The sp^3 fraction in the films increases with increasing silicon content. This result can be attributed to the Si-C bond formation when silicon is co-deposited into the DLC films. The fourfold coordination (sp^3 configuration) of silicon stabilizes the sp^3 -bonded carbon and thus can increase the sp^3/sp^2 ratio [13].

In order to study the thermal annealing behavior of Si-DLC films, a series of annealing treatments was performed using the RTP system, which is an apparatus with a rapid heating and cooling capability. After annealing, the pure DLC films (prepared by reactive sputtering without SiH_4) and Si-DLC films (prepared by reactive sputtering with SiH_4) were examined using Raman scattering to further compare their structures and properties. Fig. 3 presents the results of Raman spectra of the pure DLC and 15 at.% Si-DLC films annealed at different temperatures. For the pure DLC films, the D-band and G-band peak splitting occurs at an annealing temperature of 300 °C. The splitting is apparent at 400 °C and increases with the temperature, which indicates some degree of conversion of sp^3 -bonded carbon to sp^2 -bonded carbon. Instead, for the film with 15 at.% Si content the splitting is not significantly changed until annealing at 400 °C and becomes observable above 500 °C. This suggests

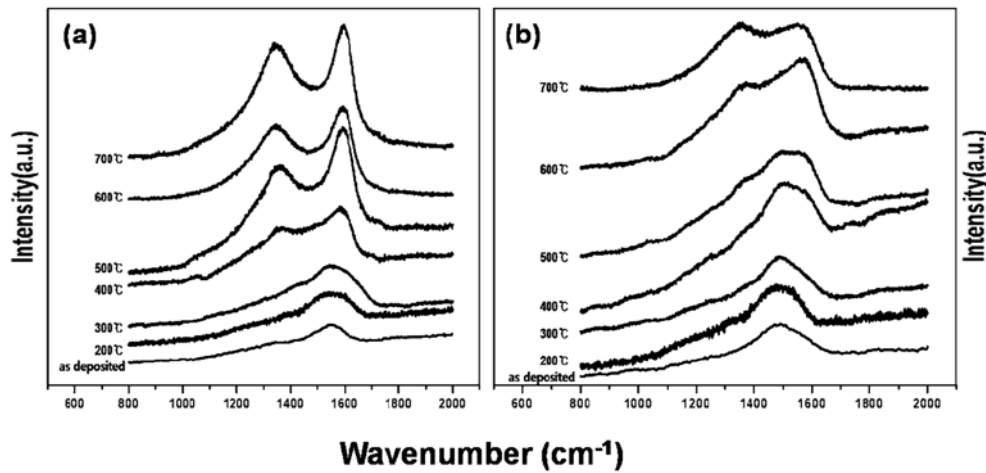


Fig. 3. Raman spectra of pure DLC and 15 at.% Si-DLC films as a function of annealing temperature; (a) Pure DLC, (b) 15 at.% Si-DLC.

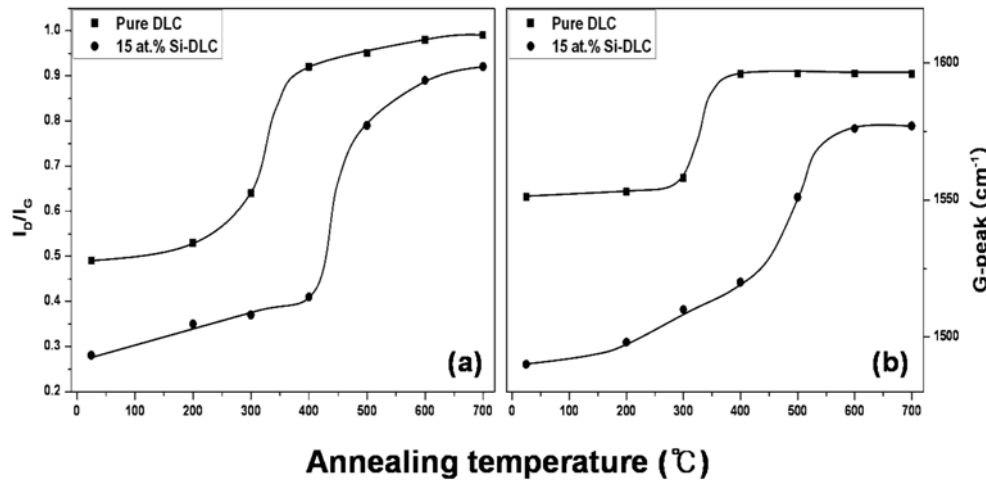


Fig. 4. Variation of the ratio of I_D/I_G and the G peak position calculated from pure DLC and 15 at.% Si-DLC films as a function of annealing temperature; (a) I_D/I_G , (b) G peak position.

that Si incorporation into diamond-like a-C : H leads to an increase in the number of sp^3 sites, which inhibits graphitization of the films. Therefore, it is assumed that the graphitization process of the films becomes clear from 400 °C in the pure DLC films and from 500 °C in the 15 at.% Si-DLC films, respectively. Fig. 4 reveals that the ratio of I_D/I_G and G-peak position of the pure DLC and Si-DLC films as a function of annealing temperatures. Fig. 4(a) shows that the I_D/I_G ratio of the pure DLC films starts to increase at 300 °C and then greatly increases above 400 °C whereas that of the 15 at.% Si-DLC films changes from 500 °C. This observation is consistent with the D-band and G-band splitting data shown in Fig. 3. Furthermore, as shown in Fig. 4(b), the G-peak position of all the samples shifts towards a higher wavenumber. Such an increase of the I_D/I_G ratio and the shift in the G-peak position to a higher wavenumber as a result of the observable separation of the D-band and G-band means a considerable transformation of the sp^3 bonds to sp^2 bonds, indicating an increase of graphite nano-crystallites in the volume as the annealing temperature increases. This tendency agrees with the results

in previous studies of the thermal stability of Si-DLC films [10, 14]. Therefore, by our results obtained from Raman spectra, it can be concluded that Si incorporation forms more sp^3 bonded carbon and stabilizes the structure, which leads to graphitization at a higher temperature than the pure DLC films, although the annealed films contain relatively larger amounts of sp^2 bonding. However, our results show that the graphitization temperature of both pure DLC and Si-DLC films is higher than that in a previous reported investigation [15]. This can be explained by the use of the RTP system in our study for the thermal annealing process.

Fig. 5 shows the mechanical properties of the annealed pure DLC and 15 at.% Si-DLC films. As-deposited Si-DLC films have a higher hardness than pure DLC films because the hardness is proportional to the degree of sp^3 bonding in the amorphous carbon matrix [16]. This result is consistent with the sp^3 fraction result shown in Fig. 2. The hardness and residual compressive stress of both pure DLC and Si-DLC films decrease as the annealing temperature increases, indicating that the transfer of the sp^3 bonds to sp^2 bonds increases with the annealing temperature [4, 14, 17].

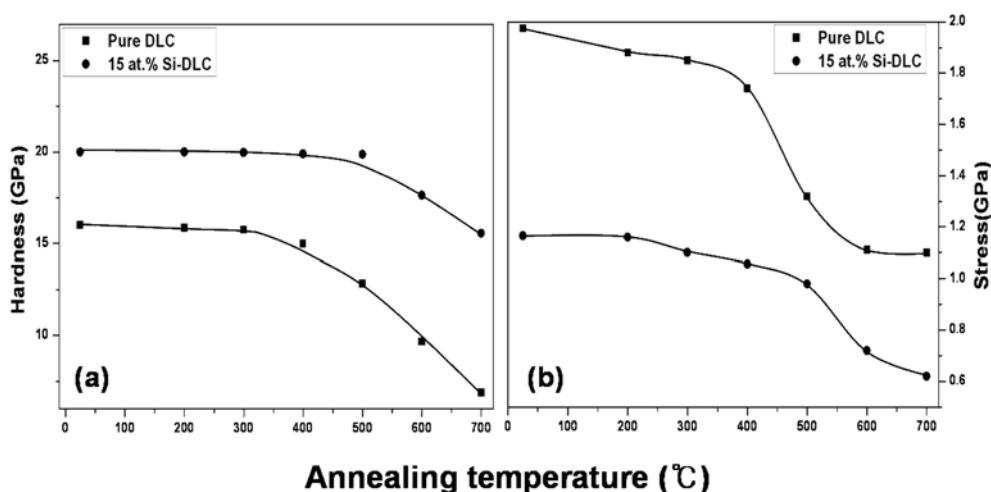


Fig. 5. Hardness and residual compressive stress values of pure DLC and 15 at.% Si-DLC films as a function of annealing temperature; (a) Hardness, (b) residual compressive stress.

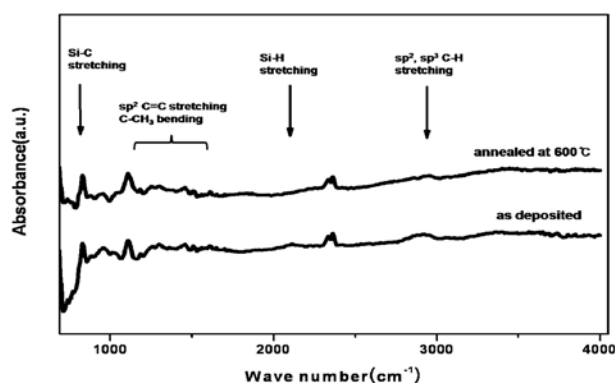


Fig. 6. FT-IR spectra of the as deposited and annealed at 600 °C, 15 at.% Si-DLC films.

However, the change in the decreasing hardness of the Si-DLC films is slight compared with that of the pure DLC films after higher temperature annealing, which indicates the improved thermal annealing behavior.

Fig. 6 shows the FT-IR absorption spectra of different vibration modes in the range 700–3000 cm⁻¹ for 15 at.% Si-DLC films before and after annealing at 600 °C. It is observed that the spectra of 15 at.% Si-DLC films have C-H bonds around 3000 cm⁻¹, Si-H bonds around 2100 cm⁻¹ and Si-C bonds around 750 cm⁻¹ irrespective of the annealing process. However, the intensity of the C-H and Si-H bonds decreases significantly after annealing, which indicates a structural change with hydrogen effusion [10]. It is also found that the intensity from Si-C bonds is detected even after annealing at 600 °C, indicating a SiC phase due to the increased content of Si-C bonds was formed when the Si concentration was 15 at.%. The formation of the SiC phase at a higher Si concentration is confirmed by the HRTEM image shown in Fig. 7. Fig. 7(a) shows the HRTEM image of a 15 at.% Si-DLC film before annealing. The microstructure shows that crystallites of about 5 nm size are embedded in an amorphous carbon matrix. The interplanar spacing corresponding to the (111) plane taken

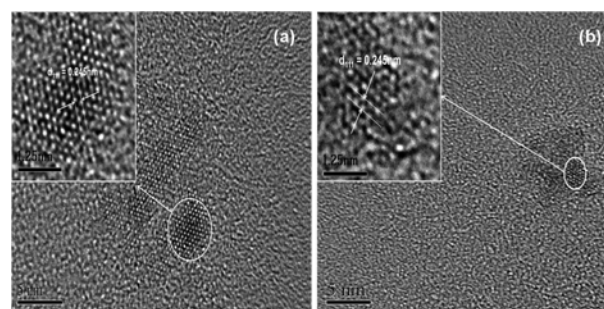


Fig. 7. HRTEM images of as deposited and annealed at 600 °C, 15 at.% Si-DLC films; (a) as deposited, (b) annealed at 600 °C.

from a fast Fourier transforms (FFT) is about 0.245 nm, which is attributed to the cubic β -SiC phase. After annealing, the β -SiC phase formed still exists in the matrix with a slightly decreased size as shown in Fig. 7(b). To our knowledge, there has not previously been a report on the observation of SiC nanocrystallites after thermal annealing. Therefore, it can be deduced that with an increasing Si content in the films, more Si-C bonds and sp³-bonded carbon form, resulting in the formation of the SiC phase in the amorphous carbon matrix. This SiC phase is stable even after annealing at 600 °C, thereby inhibiting the graphitization and maintaining the hardness of the Si-DLC films at high annealing temperatures.

Conclusions

We investigated the thermal annealing behavior of reactive sputtered Si-DLC using the RTP system. From the experimental results, the following conclusions can be deduced:

1. Si incorporation has large effects on the microstructure of the films, including the Si content, sp³ fraction and the formation of SiC nanocrystallites.
2. The more Si incorporated in the films, the higher the temperature of graphitization starts than for pure DLC films, which is confirmed by the results such as the D-band and

G-band splitting, the increase of I_D/I_G ratio and the G peak position shifting.

3. The Si atoms present in the films promote Si-C bonds, resulting in the formation of β -SiC nanocrystallites, which are stable even after high temperature annealing.

4. The mechanical properties and thermal stability of the reactive sputtered Si-DLC films can be improved by the existence of β -SiC nanocrystallites after thermal annealing.

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