

The mechanical and structural properties of Si doped diamond-like carbon prepared by reactive sputtering

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Silicon doped diamond-like carbon (Si-DLC) thin films were synthesized on silicon substrates using a reactive sputtering system. A plasma composed of the decomposition of a CH₄ and SiH₄ gas mixture and RF magnetron sputtering of a graphite target by Ar gas was used. The Si content in the films was controlled by adjusting the α -ratio (input fraction of SiH₄) ranging from 0 to 15 at.%. The Raman spectra revealed that the G peak position shifted to a lower wavenumber and the I_D/I_G ratio decreased with increasing Si content, indicating that Si incorporation reduced the average size of sp²-bonded clusters and promoted sp³ bond formation. It was found that the hardness increased and residual stress decreased as the Si content was increased. The changes of the structural and mechanical properties might be explained by the existence of 5 nm β -SiC crystallites embedded in an amorphous matrix.

Key words: Si-DLC, thin films, deposition, reactive sputtering, microstructure.

Introduction

It is well known that silicon doping of DLC has the advantages of reducing the residual compressive stress, giving high hardness, and a low friction coefficient [1, 2], a high thermal stability [3] and improved biocompatibility [4]. The most widely used method for doping DLC films with silicon is the plasma enhanced chemical vapor deposition (PECVD) technique, which uses silicon containing precursors such as silane (SiH₄) and tetramethyl silane (TMS) [3-5]. These studies have focused on the tribological, structural, chemical and surface properties of Si doped DLC (Si-DLC) films as a function of various experimental parameters and compositions. Also the doping of DLC with silicon using the sputtering process has been widely studied. In this case, silicon doping is reactive [6], in which Si-DLC films are prepared by sputtering from a pure graphite target in Ar and gaseous compounds containing both silicon and carbon. This technique has advantages over the PECVD methods in that it is more readily adapted to industrial-scale applications because of its versatility, widespread use and scalability [7]. From the above two methods, it has generally been found that silicon is bonded to four carbon atoms. There is also evidence of substantial changes in surface and bulk properties from fine silicon or silicon carbide nano-crystallites embedded in an amorphous

carbon cross-linked structure [8, 9]. However, the changes in structure and properties with the deposition conditions have not yet revealed enough information about reactive sputtered Si-DLC films.

In this present paper we report on the mechanical and structural properties of Si-DLC films prepared by the reactive sputter deposition technique with a graphite target in an Ar and CH₄/SiH₄ plasma.

Experimental

Si-DLC films were deposited on a p-type Si (100) substrate using a reactive sputtering system, which is composed of the plasma decomposition of a CH₄ and SiH₄ (5% in Ar) gas mixture and RF magnetron sputtering of a high purity (99.99%) graphite target through Argon. The substrates were RCA cleaned and placed on the lower electrode of the reactor. Prior to deposition, the chamber was evacuated to less than 6×10^{-4} Pa, the substrate was then cleaned by an Ar plasma. After that, Si-DLC films were deposited onto the substrates using RF generated CH₄/SiH₄ plasma and a magnetron sputtered graphite target. The working pressure and the sputter power was kept at 10 Pa and 150 W, respectively.

The Si content in the film was controlled by adjusting the ratio of SiH₄ to Ar. The gas flow ratio $\alpha = [\text{SiH}_4(\text{sccm}) / ([\text{SiH}_4(\text{sccm})] + [\text{CH}_4(\text{sccm})] + [\text{Ar}(\text{sccm})])]$ was varied from 0 to 0.04 and the CH₄ gas flow ratio was kept at 0.1. Pure DLC films were also prepared by RF magnetron sputtering of a graphite target in Ar or an Ar/CH₄ gas mixture. The substrates were not heated or biased during the deposition

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under all conditions, but the deposition time was varied to achieve about 300 nm thick films.

The film thickness was measured by a cross-sectional FESEM view. Micro-Raman spectroscopy using an Ar laser, with an excitation wavelength of 532 nm was performed to analyze the carbon bonding structure. The spectra in the 1000 to 1800 cm^{-1} wavenumber range were fitted by so-called D and G peaks using a Gaussian-curve function. The microscopic structure and chemical bonding state within the films were investigated by high resolution transmission electron microscopy (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 deposition rate of the sputtered a-C, pure DLC and reactive sputtered Si-DLC films. As can be seen from the figure, the deposition rate of the sputtered a-C is relatively low because of the low sputter yield of graphite and is increased remarkably with the addition of CH_4 . The deposition rate of the reactive sputtered Si-DLC films increases linearly with the α -ratio (input fraction of SiH_4 in the gas mixture). This behavior may have originated from the fact that the threshold electron energy, cross-section and dissociation energy of SiH_4 is low, causing SiH_4 to more easily dissociate and incorporate into the films, which leads to an increase in the deposition rate [4, 10]. Under the various deposition conditions used above, the deposition time was varied to fix the film thickness to about 300 nm.

The dependence of the Si content of the Si-DLC films to the α -ratio is shown in Fig. 2. The atomic percentage of Si in the Si-DLC films was determined by the ratio under the C 1s and Si 2p peaks in the XPS core-level spectra neglecting the hydrogen contribution, which could not be measured [11]. It can be seen from the plot that the Si content in the Si-DLC films varies linearly with the

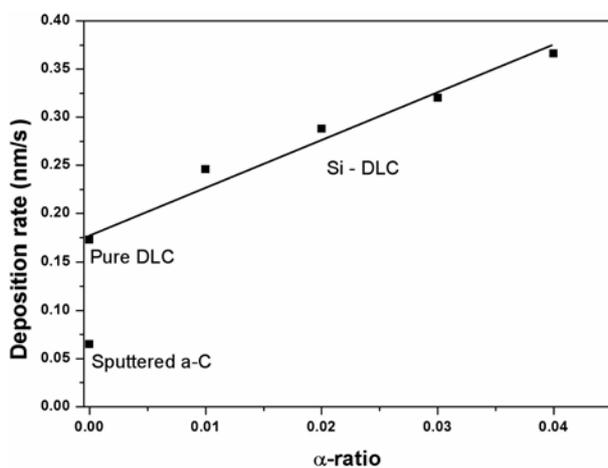


Fig. 1. Deposition rate as a function of the α -ratio.

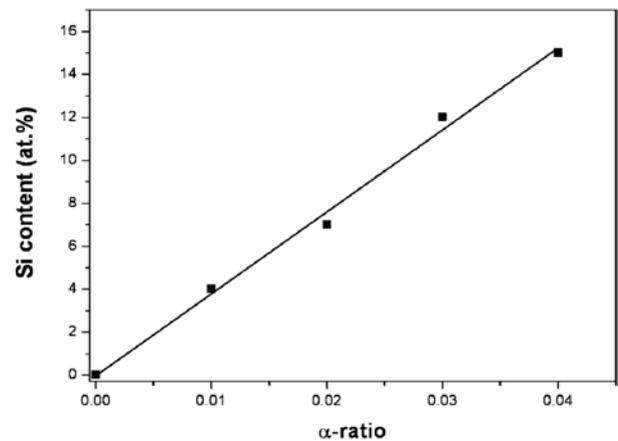


Fig. 2. Si content as a function of the α -ratio.

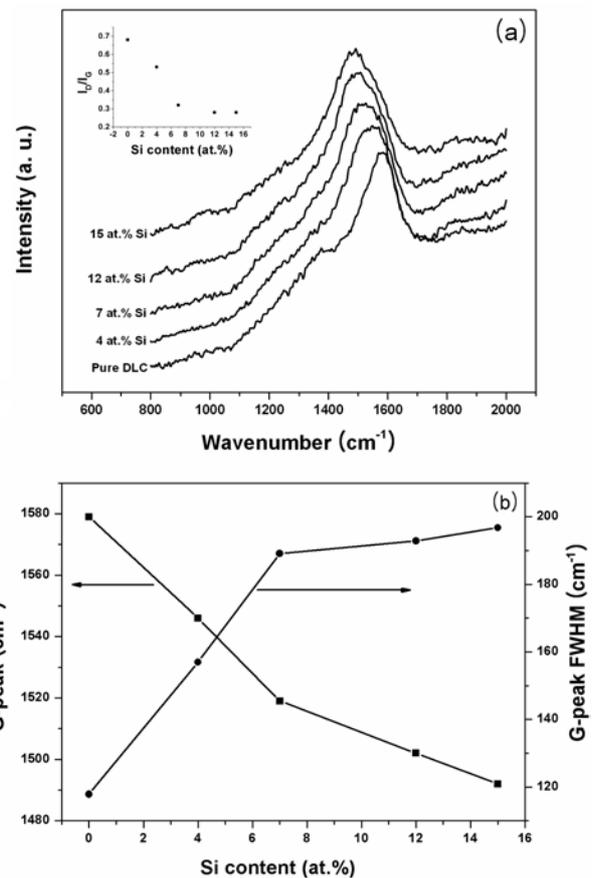


Fig. 3. (a) Raman spectra of DLC films as a function of Si content. Inset shows the dependence of I_D/I_G on the Si content. (b) G peak position and G peak FWHM as a function of Si content.

α -ratio and ranges from 0 to 15 at.%, which is consistent with the study reported by Bendavid *et al.* [4].

The microstructure of the DLC films was determined using Raman spectroscopy, which is frequently applied to measure the microstructure of carbon-based materials. Fig. 3(a) shows the Raman spectra for films with different Si contents and their corresponding I_D/I_G value as an inset. As the silicon content increases, the G peak becomes more

pronounced relative to the D peak and is shifted to a lower wavenumber. Additionally, the I_D/I_G intensity ratio decreases with increasing Si content. Fig. 3(b) reveals that the full width at half maximum (FWHM) of the G peak increases and the G peak position shifts linearly to a lower wavenumber when increasing the Si content in the films. This observation is similar to those in previous investigations of the preparation of Si-doped DLC films using the PECVD method [4, 8]. It is well known that this trend, such as the simultaneous downshift of the G peak and decrease in the I_D/I_G ratio, can account for the reduction in the average size of the sp^2 -bonded clusters and the promotion of sp^3 bond formation in the Si-DLC films [12]. Moreover, it is reported that the presence of Si-C bridging bonds can weaken the adjacent C-C bonds, resulting in a shift downward and a decrease in I_D/I_G ratio upon Si incorporation [13], which will be discussed with the results of the HRTEM microstructure.

Fig. 4 shows the mechanical properties of the pure and Si-DLC films. The hardness increases until the Si content is 12 at.%. However, it shows a saturated behavior when the Si content is more than 12 at.%, which seems to be related to the increasing number of Si atoms incorporated into the carbon network as well as the total hydrogen content as the silane fraction is increased. On the other hand, the residual stress decreases with increasing Si content.

It has been recognized that the effects of Si addition into DLC films, such as lower stress and higher hardness, are generally attributed to the Si-C bond formation. To give direct proof of the existence of SiC nanocrystallites, we carried out an HRTEM observation of the 15 at.% Si-DLC film. The results are presented in Fig. 5. The microstructure shows that the crystallites are about 5 nm in size and are embedded in an amorphous matrix. The interplanar spacing corresponding to (111) taken from a fast Fourier transform (FFT) is about 0.245 nm, which is attributed to the cubic β -SiC phase. Consequently, the behavior of the structural (downshift of the G peak and decrease in the I_D/I_G ratio) and mechanical properties (lower stress and higher hardness)

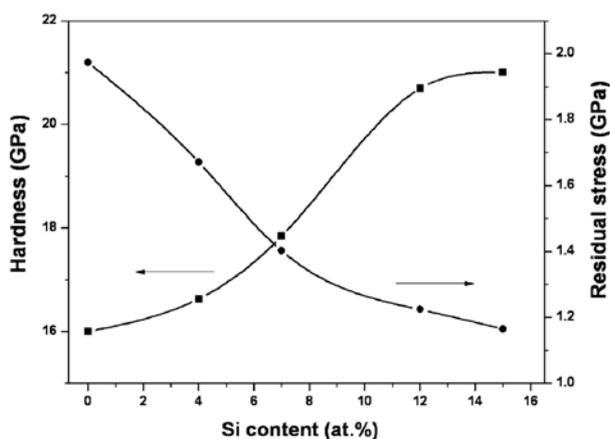


Fig. 4. Hardness and residual compressive stress as a function of Si content.

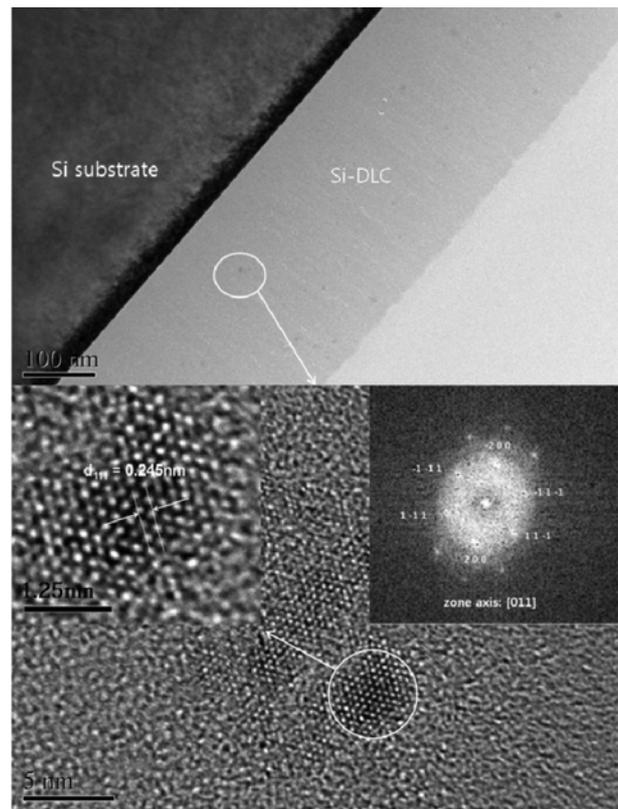


Fig. 5. HRTEM image of a 15 at.% Si-DLC film.

can be explained by SiC nanocrystallite formation when Si is incorporated in DLC films. Due to the difference in bond length (0.189 nm for Si-C, 0.154 nm for C-C), the extension of bond length may reduce the residual compressive stress. Furthermore, since Si atoms stabilize sp^3 -bonded carbon, the hardness is likely to increase with increasing Si content.

Conclusions

In this study, we have investigated the reactive sputtered growth of Si-DLC films with Si contents in the range of 0-15 at.%. As the Si content in the films increased, the deposition rate increased and the simultaneous downshift of the G peak and decrease in the I_D/I_G ratio appeared. Also, the hardness increased and the stress decreased when Si was incorporated. This might be explained by structural changes, such as the formation of the β -SiC nanocrystalline phase, which could clearly be observed from HRTEM image of a 15 at.% Si-DLC film.

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