

Structural modifications of SiO_x/DLC films by thermal annealing

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SiO_x/DLC films were deposited on Si substrates using CH₄/(C₂H₅O)₄Si/Ar gas mixtures by PECVD. The films deposited were identified as atomic-scale composite networks consisting mainly of diamond-like a-C:H and silica-like a-Si:O structures with a smaller contribution of Si-C and C-O bonds. Structural modifications of SiO_x/DLC films were monitored under thermal annealing in an Ar atmosphere. The structural transitions of the amorphous carbon matrix in the SiO_x/DLC films were investigated by a Raman spectrometer. The relationships between the microstructural modifications and mechanical properties are discussed.

Key words: SiO_x/DLC, Microstructure, Thermal annealing, Raman, Hardness.

Introduction

In the past several years, carbon-based materials have been widely studied and, in particular, polycrystalline diamond films and amorphous carbon or hydrogenated amorphous carbon films [1-5]. The amorphous carbon (a mixture of sp²-bonded carbon and sp³-bonded carbon which may be partially hydrogenated) films have been a special issue among the carbon-based materials because they have many attractive properties such as high hardness, low coefficient of friction, high wear resistance and optical transparency. Therefore, they have the potential for application as tribological and optical protective coatings. Diamond-like carbon (DLC) has been used as a representative terminology to describe these amorphous carbon films. DLC films have been prepared by various techniques such as RF-PECVD (Radio Frequency Plasma Enhanced Chemical Vapor Deposition), IBAD (Ion Beam Assisted Deposition), magnetron sputtering and pulsed laser deposition [6-9].

Although DLC films have many interesting properties, they have some limitations for industrial coating applications. High residual stresses, usually several GPa, is a significant problem, which inhibits the good adhesion, especially on steel substrates and limits the thickness of the film. A pronounced increase of the coefficient of friction with an increase of the environmental humidity also limits the coating applications of DLC films. During the actual industrial application of DLC films, a localized heating on the film surface could happen by a friction process, resulting in the

structural transitions of films. Also, structural transitions of the films occur when the films are exposed to a high temperature environment. These structural transitions are characterized by two features: hydrogen loss and graphitization (the growth of sp² bonded carbon). This thermal degradation under a high temperature environment would limit the industrial applications of DLC films.

The addition of Si into DLC films has been extensively studied as a means to remedy the drawbacks of DLC films [10-13]. The different bond lengths between Si-C of 1.89 Å and C-C of 1.54 Å [14] relieve the ordered structure stress because the extension of bond length can reduce the compressive strain in a longer range. The fourfold coordination (sp³ configuration) of silicon stabilizes the sp³-bonded carbon and thus can increase the sp³ to sp² ratio and inhibit graphitization.

In this study, the microstructure of DLC films was modified by adding Si-O structures into the amorphous carbon matrix. The resultant films were mainly composed of a-C:H and a-Si:O networks. The structural transitions of SiO_x/DLC films were monitored under thermal annealing in an Ar atmosphere. The relationships between the structural and mechanical characteristics were investigated as a function of the annealing temperature.

Experimental Procedures

A Plasma Enhanced Chemical Vapor Deposition (PECVD) system was employed to deposit the SiO_x/DLC films. The system consists of a capacitively-coupled, asymmetric plasma reactor driven by a 13.56 MHz r.f. power supply which is connected to the lower electrode. The substrates were located on the lower electrode where the negative self-bias voltages were

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developed due to an asymmetry between the upper and lower electrodes and also the large difference in the electron and ion mobilities. The negative self-bias voltages were controlled by the r.f. power and reactor pressure. The reactor was evacuated by a rotary pump followed by a turbo-molecular pump. The gaseous precursor was minutely controlled by a Mass Flow Controller (MFC). The bubbler system was used to deliver the liquid source to the reactor. A bubbler containing the liquid precursor was encapsulated with a band heater. The gas line was also taped with a band heater to prevent any condensation during the delivery of the vaporized precursor to the reactor.

The SiO_x/DLC films were deposited on Si substrates by the plasma-decomposition of methane (CH_4) and tetraethylorthosilicate (TEOS, $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$) which were used as precursors of C and Si, respectively. Before being loaded in the CVD reactor, the Si substrates were ultrasonically cleaned in acetone and ethanol. They were then rinsed in distilled water. The substrates were then placed on the lower electrode of the CVD reactor and then the reactor was evacuated to a base pressure less than 6.6×10^{-4} Pa. Before the deposition, the surface of the Si substrates was exposed to an Ar plasma for 10 minutes for the *in-situ* cleaning. The flow rate of CH_4 and Ar gas flowing directly to the reactor were set at 10 and 50 sccm, respectively. The flow rate of the liquid source was determined by a flow rate of carrier gas passing the bubbler, the temperature of the liquid container corresponding to the vapor pressure of the liquid source and an output pressure of mixed gaseous precursors (i.e. the mixtures of carrier gas and vaporized precursor) passing the gas line. The temperature of the bubbler was set at 50°C , keeping the vapor pressure of TEOS at approximately 3.3 kPa. The vaporized TEOS precursor was supplied to the reactor by the carrier Ar gas flow ranging from 10 to 20 sccm. The deposition was performed under a bias voltage of 200 V and a reactor pressure of 18 Pa. There was no additional substrate heating during the deposition.

After the deposition, the films were heated for 1 hr. in the furnace with a flow of Ar gas for the thermal annealing. After the films were loaded in the furnace, the furnace was evacuated by a rotary pump and then back filled with Ar gas at a flow rate of 0.5 l/minute to set the oxygen partial pressure at 10 Pa. The annealing temperature ranged from 200 to 500°C .

The chemical structure of grown films was investigated by a Fourier Transform Infrared Spectrometer (FT-IR) and X-ray Photoelectron Spectroscopy (XPS). FT-IR spectra were obtained in the wavenumber range from 4000 to 400 cm^{-1} . XPS measurements were carried out using Al K α radiation with energy of 1486.6 eV. A Transmission Electron Microscope (TEM) operated at 200 kV was employed to examine the crystalline phases in the films. A Raman spectrometer was employed to investigate the chemical structure of the amorphous

carbon matrix in the annealed films. An Ar ion laser with a wavelength of 514.5 nm was used as a power source for the Raman measurements. The Raman spectra in the wavenumber range of 1000 – 1800 cm^{-1} were fitted to the so-called D and G peaks using a Gaussian curve function. The position of the G peak and the integrated intensity ratio of D and G peaks were collected as Raman parameters. The thickness variation of annealed films was observed by cross-sectional views in a Scanning Electron Microscope (SEM). The thickness of the as-deposited films was approximately 650 nm. The chemical composition of annealed films was investigated by an Electron Probe Micro Analyzer (EPMA) using an acceleration voltage of 9 kV. The average values of the chemical composition measured at 5 different areas on the samples were determined to be representative data. There was no great deviation in the composition results when the acceleration voltages were changed between 8 to 15 kV. Therefore, it can be assumed that the probed regions in the samples were not affected by the Si substrate layer significantly. The hardness of annealed films was measured by the depth-sensing indentation technique. The indentation tests were performed under an applied load of 2 mN. The indentation was performed on 10 different areas in the samples and then each measured hardness value was averaged.

Results and Discussion

Electron diffraction patterns from SiO_x/DLC films showed that there were no crystalline phases in the films, implying the deposited films are consistent with an amorphous nature. A FT-IR spectrum of a SiO_x/DLC film is shown in Fig. 1. The main absorption bands are the Si-O stretching band in the 1100 – 1000 cm^{-1} range, the C-H stretching band in the 3100 – 2800 cm^{-1} range and the Si-C stretching band in the 800 cm^{-1} region. Also, a very weak C=C stretching peak appears

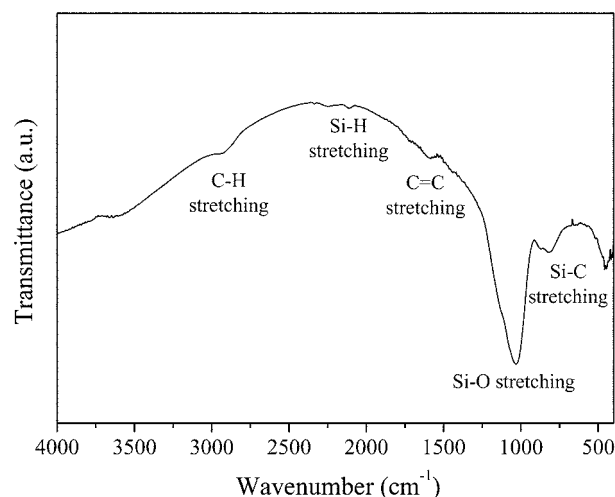


Fig. 1. FT-IR spectrum of SiO_x/DLC film deposited at 200 V.

in the 1580 cm⁻¹ region and a Si-H stretching peak in the 2100 cm⁻¹ region. The C-H absorption band in the 3100-2800 cm⁻¹ range is typical for sp³ and sp² bonded carbon. The FT-IR spectrum reveals that the deposited film consists mainly of C:H and Si:O networks with a contribution from Si-C bonds.

Figure 2 shows the XPS spectra relating to the coating elements of the SiO_x/DLC film. The survey

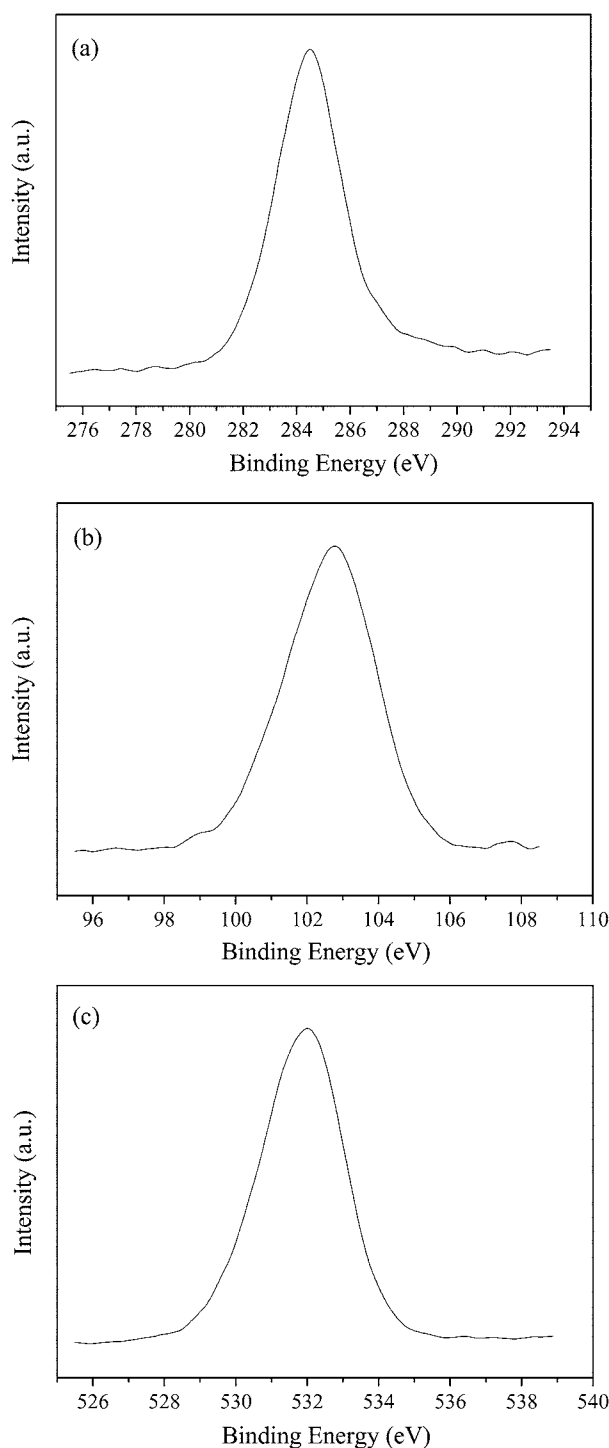


Fig. 2. XPS spectra of SiO_x/DLC film deposited at 200 V; (a) C 1s, (b) Si 2p and (c) O 1s.

spectrum showed that the film consists of carbon, silicon and oxygen, neglecting hydrogen. It should be noted that the films described here contained hydrogen as revealed in the FT-IR spectrum because the films were deposited by the plasma-decomposition of a hydrocarbon source. The C 1s spectrum exhibited a nearly symmetric line shape revealing the presence of C-C bonding at about 284.5 eV [15] which came from carbon matrix in the coating. There are no peaks relating to the carbide bond (C-Si) with a binding energy of 283 eV [15], not even the possibility of a minor contribution, nor from the O-C-O bond with a binding energy of 288.6 eV [16]. The Si 2p spectrum exhibited an asymmetric line shape centered at around 102.8 eV, which is assigned to Si-O bonding [15]. A tailing towards a lower binding energy is attributed to Si-C bonding centered at around 100-101 eV [17]. Thus, the Si 2p spectrum revealed that the Si-O bond predominates with a minor portion of Si-C bonds. The O 1s spectrum also exhibited an asymmetric line shape centered at around 532 eV, which is assigned to Si-O bonding [15]. A tailing towards a lower binding energy is attributed to C-O bonding centered at around 530.5-531.5 eV [17]. The XPS results imply that carbon with C-C and silicon with Si-O bonds dominate in the coating, while C-Si and C-O bonds contribute less. Therefore, the chemical structure of the films described here can be predominantly described as a network structure independently consisting of a-C:H and a-Si:O.

The annealed SiO_x/DLC films showed no remarkable change in their thickness until annealing at 500°C. The film thickness had a tendency to a slight decrease with increasing annealing temperature. However, the film thickness reduction was in the 5% range for most annealing temperatures. Figure 3 shows the composition ratio of the SiO_x/DLC films as a function of annealing temperature. The chemical composition of as-deposited SiO_x/DLC film was about 57.9 at.% of carbon, 32.8 at.% of oxygen and 9.3 at.% of silicon, neglecting

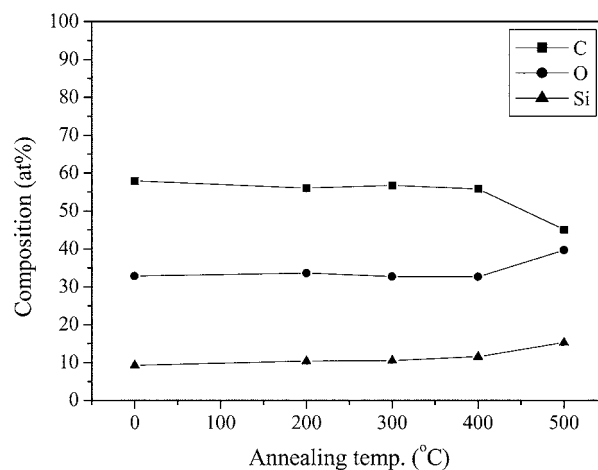


Fig. 3. Composition ratio of SiO_x/DLC films as a function of annealing temperature.

hydrogen. The chemical composition of SiO_x/DLC films was not significantly changed by annealing up to 400 °C. The slight decrease of carbon content in the film was observed above 400 °C with a corresponding slight increase of oxygen and silicon contents. During the annealing processes at higher temperatures, the residual oxygen in the annealing furnace could react with carbon in the film and form CO_2 which could then diffuse/effuse out from the film surface. Thus, the slight reduction of film thickness might be caused by the effusion of CO_2 and/or hydrogen loss which happened at 500 °C, and which will be later described in the Raman results. It has been reported that the annealing of amorphous carbon films with polymeric characteristics resulted in a significant thickness decrease with an increase of annealing temperature due to the effusion of hydrocarbons from the films [18]. It should be noted that the films described here showed no remarkable thickness reduction up to an annealing temperature of 500 °C.

Figure 4 shows the Raman spectra of SiO_x/DLC films annealed at different temperatures. There was no large change in the shape of Raman spectra until above 350 °C. However, an observable peak separation appeared above 400 °C and then this apparent separation into two peaks became more pronounced with an increase of annealing temperature. These two peaks are termed D and G peaks where G means graphitic and D means disordered. In the Raman analysis of disordered graphite, i.e. polycrystalline and amorphous carbon, a G peak appears in the 1580 cm^{-1} region of the Raman shift and a D peak in the 1350 cm^{-1} region. The Raman spectra showed a decline in the background luminescence because of hydrogenation. However, the film annealed at 500 °C showed no decline in the background luminescence, indicating significant hydrogen loss. Detailed structural information on the amorphous carbon matrix in the SiO_x/DLC films with the thermal annealing is obtained from the Raman parameters derived from the Gaussian

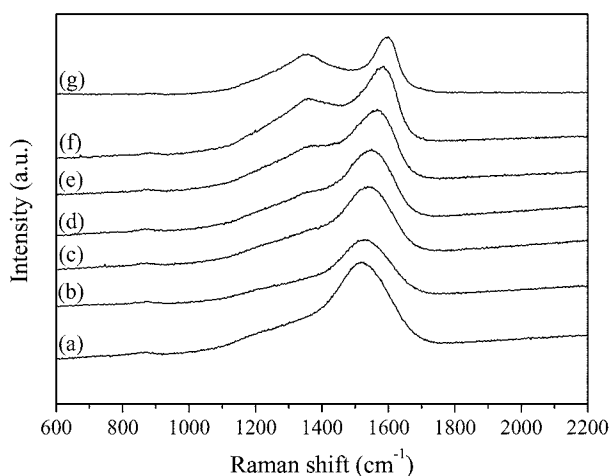


Fig. 4. Raman spectra of SiO_x/DLC films annealed at different temperatures; (a) as-deposited, (b) 200 °C, (c) 300 °C, (d) 350 °C, (e) 400 °C, (f) 450 °C and (g) 500 °C.

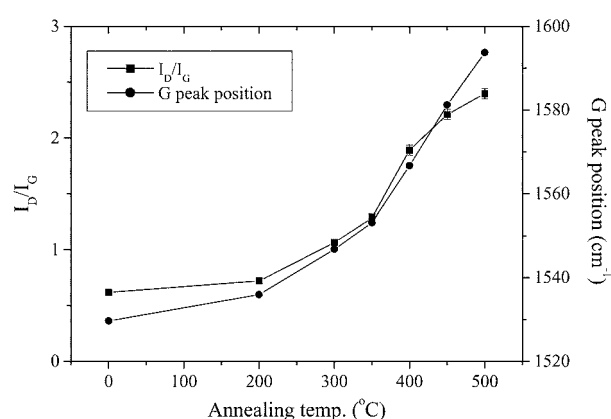


Fig. 5. I_D/I_G ratio and G peak position derived from the Gaussian curve fitting in Raman spectra of SiO_x/DLC films.

curve fitting of Raman spectra. Figure 5 shows the Raman parameters of the integrated intensity ratio of D and G peaks (I_D/I_G) and G peak position. The analysis of Raman parameters must be an indirect but sufficiently useful measure of the sp^3 -related structure based on the well-known structural model of amorphous carbon with small sp^2 -bonded clusters embedded in a sp^3 host matrix which may be partially hydrogenated [19]. The I_D/I_G ratio in the annealed SiO_x/DLC films showed an increase with increasing annealing temperature, implying that the graphitic component in the amorphous carbon matrix increased. Also, the variation of the G peak position showed a similar tendency as the I_D/I_G ratio. With increasing annealing temperature, the structural transitions of the amorphous carbon matrix are understood in terms of the growth of sp^2 -bonded carbon clusters and/or the transfer of sp^3 -bonded carbon to sp^2 -bonded carbon combined with hydrogen loss. Since the Si atoms, with a bond type of Si-O and Si-C in the films described here, do not form any sp^2 -related bonds (π bonds), the stabilizing of sp^3 -bonded carbon sites was expected by the surrounding Si atoms. However, the Raman findings showed that the structural transitions of the amorphous carbon matrix in the SiO_x/DLC films described here happened from 200 °C, which is unusual compared with our recently published article [20].

Figure 6 shows the hardness values of SiO_x/DLC films annealed at different temperatures. The hardness of SiO_x/DLC films showed a constant value until 200 °C with a slight decrease of the hardness value until 400 °C. Then, the hardness value decreased significantly with increasing annealing temperature. The variation of hardness value associated with the annealing does not accord with the predictions of the Raman findings. The significant decrease of hardness values above 200 °C could be predicted by the Raman findings because of the relatively severe structural transitions of the amorphous carbon matrix. However, the hardness values showed a less significant decrease until 400 °C, which

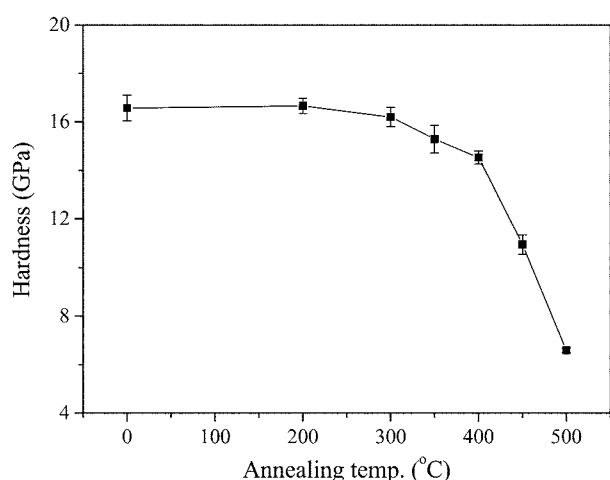


Fig. 6. Hardness values of SiO_x/DLC films as a function of annealing temperature.

was different from the Raman predictions. Although the Si atoms with a bond type of mainly Si-O and partly Si-C in the films could not inhibit the structural transitions of the amorphous carbon matrix, a significant decrease of hardness value in the SiO_x/DLC films described here was not observed until 400°C.

The reduction of hardness can be related to the amount of low energy bonds related to hydrogen bonds, or with the appearance of a higher number of low energy carbon bonds associated with sp² sites, or with the presence of low energy C-O bonds. The structural transitions associated with the larger number of sp²-bonded carbon atoms in the annealed films described here are obviously related to the reduction of hardness. However, the hardness results obtained provide a less significant decrease, indicating the Si-O and/or Si-C bonds might contribute to reduce the hardness reduction. Then, it can be suggested that the sp³ carbon sites were not mostly surrounded by the Si-related structures (Si-O and/or Si-C), implying the amorphous hydrocarbon matrix remains independent of the Si-related structures because the Si atoms could not inhibit the structural transition of the amorphous carbon matrix. The atomic rearrangements associated with the Si and O atoms in the films by thermal annealing thus deserve a detailed investigation.

Conclusions

The microstructure of SiO_x/DLC films was investigated by TEM, FT-IR and XPS. The SiO_x/DLC films were composed of two amorphous materials and it was shown that the amorphous silica phase was independently interconnected with the amorphous hydrocarbon. The SiO_x/DLC films annealed at different temperatures showed no remarkable thickness reduction up to an annealing temperature of 500°C and a nearly constant composition ratio. The amorphous carbon in the films

started to be graphitized easily from 200°C, which was confirmed from the Raman findings. Although the Si-related structures (mainly Si-O and partly Si-C) in the films could not inhibit the structural transition of the amorphous carbon matrix, a significant decrease of hardness values was not observed until 400°C, implying that the Si-related structures are able to thermally stabilize the films in terms of mechanical properties.

Acknowledgements

This study was financially supported by the Korean Science and Engineering Foundation (KOSEF) through the Ceramic Processing Research Center (CPRC).

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