

Defect density and atomic bond structure of tetrahedral amorphous carbon (ta-C) films prepared by filtered vacuum arc process

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Defect density of tetrahedral amorphous carbon (ta-C) film prepared by filtered vacuum arc process was investigated in a wide range of fraction of sp^3 hybridized bond. We could observe a close relationship between unpaired spin density measured by electron spin resonance spectroscopy and their atomic bond structure: the defect density was proportional to the content of sp^3 hybridized bond in the film. Near edge x-ray absorption fine structure analysis further showed that the content of the surface C-H bonds presumably due to the absorption of hydrocarbon to the surface dangling bond also increased with increasing content of sp^3 hybridized bond. The observed dependence was discussed in terms of the degree of clustering or pairing of the isolated sp^2 sites. © 2004 American Institute of Physics. [DOI: 10.1063/1.1699481]

I. INTRODUCTION

Amorphous carbon films deposited by filtered vacuum arc process are known to have a high fraction of sp^3 hybridized bond of up to 80%, which results in a unique combination of physical and chemical properties. The films, also referred to as tetrahedral amorphous carbon (ta-C) film, have high hardness, high wear resistance, optical transparency in wide range of the wavelength, and excellent chemical inertness.¹ It is generally accepted that the properties of the film are governed by the fraction of the sp^3 hybridized bond that is strongly dependent on the kinetic energy of the deposited carbon ion. Since the ionization ratio in the vacuum arc plasma is as high as 90%, applying a negative bias voltage to the substrate is known to be an effective way to control the kinetic energy of the deposited carbon ion.²

Although the main interest of ta-C film has been centered on their mechanical applications, recent investigations are also focused on the possibility of its use for electronic devices. ta-C film exhibits the properties of a p -type semiconductor with a band gap in the range 2.0–2.5 eV.³ As in other amorphous semiconductors, dangling bonds in the ta-C structure can lead to trap states in the mobility gap resulting in deterioration of the device properties. Therefore, systematic control of the defect would be one of the major concerns for their electronic applications. The purpose of the present work is to characterize the formation of the dangling bonds in ta-C film for various deposition conditions.

Defect density in the ta-C film has been characterized by electron spin resonance (ESR) method as the defect results in

unpaired spin.⁴ However, the relationship between the defect density and the atomic bond structure is to be clarified yet. Amaratunga *et al.* reported that the spin density decreased with increasing fraction of sp^3 hybridized bond in the ta-C film.⁵ On the other hand, Gerstner *et al.* reported a gradual decrease in the defect density as the fraction of sp^2 hybridized bond increased up to 50%.⁶ However, abrupt decrease in the defect density was observed when the fraction of sp^2 hybridized bond was 75%.⁶ This discrepancy can be hardly understood, considering that their experimental conditions were almost identical. This indefinite relationship should be resolved to characterize the defect generation behavior in ta-C films. In the present work, we could observe that the defect density is proportional to the content of sp^3 hybridized bond in the film, which can be understood in terms of the clustering and pairing of sp^2 hybridized bonds.

II. EXPERIMENT

ta-C films were prepared by filtered vacuum arc (FVA) deposition method. Figure 1 shows the schematic of the deposition system used in the present work. Arc plasma generated at the graphite cathode was introduced to the reaction chamber via magnetic filtering duct in which the macroparticles were removed from the plasma beam. A water-cooled substrate holder was placed normal to the arc plasma beam at a distance of 300 mm from the exit of the FVA source. In order to apply DC bias voltage, the substrate holder was electrically isolated from the reaction chamber. The base pressure of the vacuum system was less than 10^{-4} Pa. The film was deposited at a pressure of 10^{-2} Pa. Si(100) wafers of thickness 510 μm were used for the substrate. Stripes of thin Si(100) wafer of thickness 100 ± 5 μm were also used to measure the residual stress of the film. Before the film deposition, the substrate was precleaned by using the carbon arc plasma beam mixed with Ar ion at the negative bias voltage of -700 V. During carbon film deposition, a DC bias voltage

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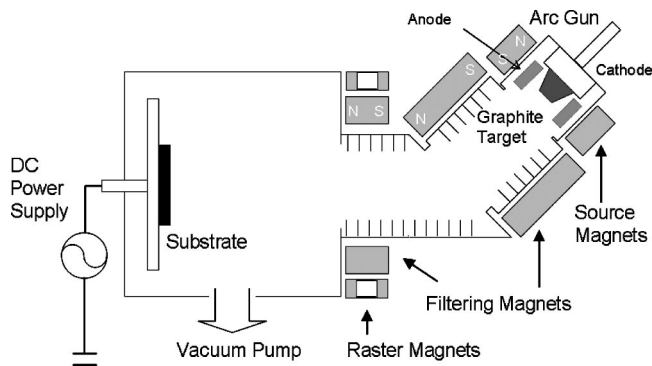


FIG. 1. The schematic of filtered vacuum arc deposition system used in the present work.

ranging from 0 to -500 V was applied to obtain films of various atomic bond structures. No impurities or hydrogen were observed in the film as could be characterized by Rutherford backscattering spectrometry (RBS) and Fourier transformation infrared (FTIR) spectrum analysis. In the present experimental condition, atomic bond structure and corresponding mechanical properties of the film varied in a wide range from graphitic to dense diamondlike carbon. A film of more graphitic structure was prepared by thermal annealing of the deposited film at 900°C for 5 min in Ar environment.

The residual stress of the film was obtained from the curvature of film/substrate composite using Stoney equation.⁷ Nanoindentation in the continuous stiffness measurement mode was employed to characterize the hardness and the elastic modulus of the film. The atomic bond structure was analyzed by using near edge x-ray absorption fine structure (NEXAFS). NEXAFS spectra were obtained in a beam line of Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The paramagnetic defect density of the sample was measured at room temperature with an X-band (9.5 GHz) electron spin resonance (ESR) spectrometer.

III. RESULTS AND DISCUSSION

Figure 2 shows the dependence of hardness on the applied negative bias voltage. Data of filled circles are those of as deposited films, and the open circle represents that of the annealed film. The hardness increased with increasing negative bias voltage and reached a maximum value of 54 ± 2 GPa at the negative bias voltage of about -50 V. In the range of the negative bias voltage larger than -100 V, the hardness decreased with the bias voltage. The plane strain modulus and the residual stress also showed the same dependences on the negative bias voltage. Maximum values of the elastic modulus (364 ± 12 GPa) and the residual stress (7.2 ± 0.8 GPa) were obtained at the negative bias voltage of about -50 V. Similar dependence of the mechanical properties on the negative bias voltage was reported in the previous experimental works.^{8,9} High temperature annealing of the film significantly degraded the mechanical properties. Open circle in Fig. 2 shows that the hardness of the film decreased from 47 ± 2 to 30 ± 2 GPa after the annealing at 900°C for 5 min.

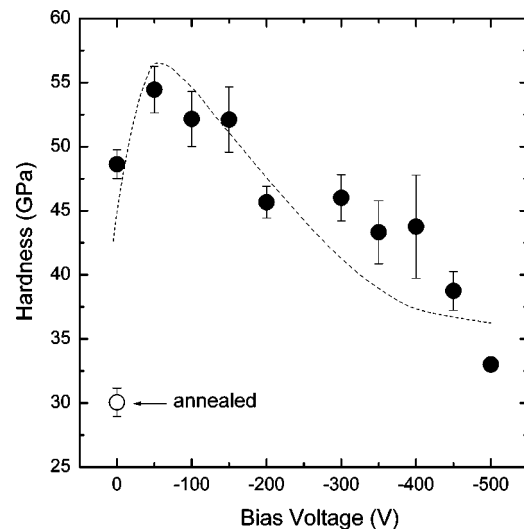


FIG. 2. Dependence of hardness of ta-C film on the negative bias voltage applied to the substrate during deposition. Open circle data represents the hardness of annealed ta-C film at 900°C for 5 min.

Freidmann *et al.* reported the thermal stability of ta-C film in a vacuum environment.¹⁰ They showed that dense diamondlike ta-C film was transformed to nanocrystalline graphite when the annealing temperature was higher than 800°C . It can be thus said that the decrease in the hardness after the annealing at 900°C is associated with significant graphitization of the ta-C film.

NEXAFS spectroscopy can be used to estimate the concentration of sp^2 hybridized carbon atoms, because the π^* resonance is well separated in energy from the rest of the resonance in the carbon K edge spectra.^{11,12} Figure 3 shows NEXAFS spectra of ta-C films for various bias voltages. All spectra were normalized to the maximum peak at about 300 eV and shifted upward for ease of comparison. For comparison, those of graphite and the annealed ta-C film are also presented in Fig. 3. The spectra of as deposited films have a peak around 284 eV corresponding to the transition from

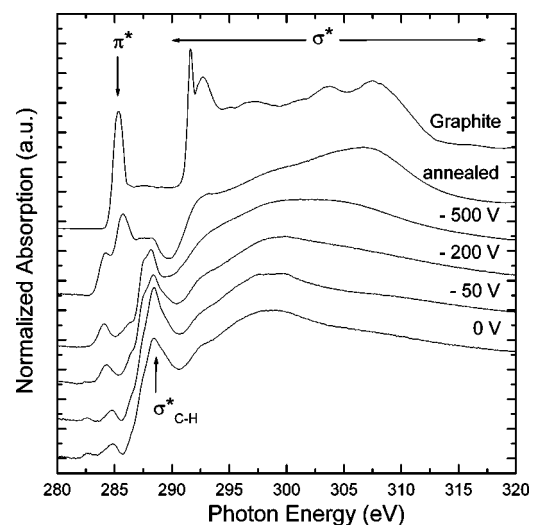


FIG. 3. NEXAFS spectra of the ta-C films for various values of the applied bias voltages. For comparison, those of annealed ta-C film at 900°C for 5 min and pure graphite are also included.

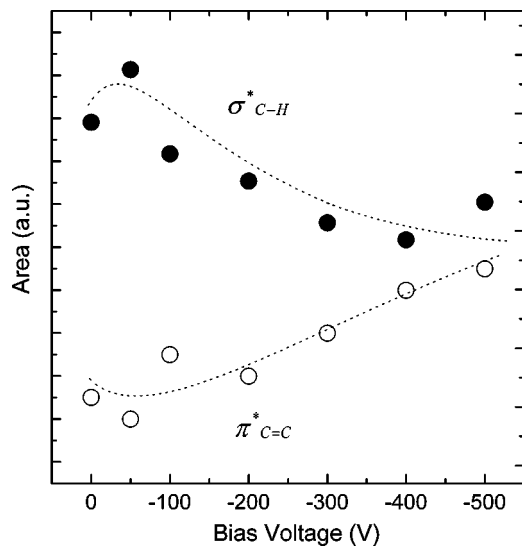


FIG. 4. Variation of $\pi_{C=C}^*$ and σ_{C-H}^* peak intensities in NEXAFS spectra as a function of applied negative bias voltage. The lines are only to guide the eyes.

C 1s level to unoccupied π^* state of sp^1 and sp^2 sites of carbon-carbon bond.¹¹ In most ta-C films, content of $C\equiv C$ bond corresponding to sp^1 hybridization is so small that the peak near 284 eV can be considered to be of only $C=C$ bonds or sp^2 sites.^{13,14} Hence, the peak intensity can be used to estimate the content of sp^2 hybridized bond of the film. The peak near 287 eV corresponds to the σ_{C-H}^* transition of the C-H bonds that would originate from the absorption of hydrocarbon to the surface dangling bonds.¹⁵ The broad band between 290 and 310 eV results from overlapping C 1s $\rightarrow \sigma^*$ transition at sp^2 or/and sp^3 sites. Amorphous structure of the ta-C film would cause the broadening of the σ^* resonance.

When the negative bias voltage was less than -100 V, $\pi_{C=C}^*$ peaks near 284 eV were much smaller than that of graphite, showing that the deposited films have high content of sp^3 hybridized bond. However, as the negative bias voltage increased beyond -100 V, the intensity of the $\pi_{C=C}^*$ peak increased with slight peak shift to lower energy. Even if the reason for the peak shift is yet to be fully addressed, Diaz *et al.* suggested that the delocalization of the π bond could induce the downward shift of the π^* resonance.¹⁵ This result shows that the increase in the negative bias voltage beyond -100 V increases the content of sp^2 hybridized bond and decreases unpaired sp^2 sites. In the annealed sample, well-defined another peak at 285 eV appeared in addition to the peak near 284 eV. Comparing the peak shape with that of graphite reveals that the peak at 285 eV is correlated with the crystalline graphitic phase in the film. Furthermore, the broad feature in the energy region from 290 to 320 eV became more similar to that of graphite. This change in NEXAFS spectrum confirms that the significant graphitization occurred in the annealed film.

Figure 4 shows the dependence of the peak intensity of $\pi_{C=C}^*$ and σ_{C-H}^* resonance on the negative bias voltage. The intensities were obtained by deconvolution of the spectrum with $\pi_{C=C}^*$ and σ_{C-H}^* peaks of Gaussian shape after correct-

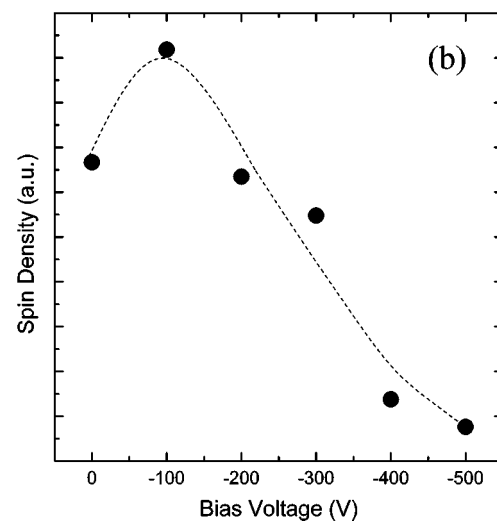
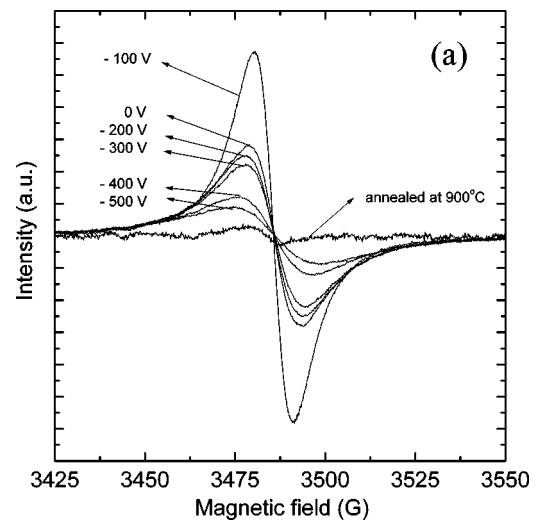


FIG. 5. ESR spectra (a) and spin density (b) of the ta-C films for various values of the applied negative bias voltage. The line is only to guide the eyes.

ing the background. The broad feature between 290 to 320 eV was considered as σ^* states corresponding to the overlapping of sp , sp^2 , and sp^3 sites. In spite of the scattering of the data, it is evident that the peak intensity of $\pi_{C=C}^*$ resonance has a minimum at the negative bias voltage near -50 V, which shows that the film deposited at the negative bias voltage of -50 V has a maximum fraction of sp^3 hybridized bond. This analysis is consistent with the dependence of the mechanical properties on the negative bias voltage. On the other hand, the peak intensity of σ_{C-H}^* resonance shows an opposite behavior to that of $\pi_{C=C}^*$ resonance. This behavior will be discussed later in conjunction with the ESR measurement data.

Figure 5(a) shows the ESR spectra for various values of the negative bias voltage. The spectra were normalized with respect to the volume of the carbon film for comparison between the samples. The g factors of the spectra were 2.0028 ± 0.0001 , similar to the values for other forms of carbon.⁶ As shown in Fig. 5(b), the intensity of ESR spectra had a maximum when the negative bias voltage was about -100 V. Beyond -100 V, the intensity monotonically decreased with

the negative bias voltage. It must be noted that this behavior is the same as those of hardness (Fig. 2) and the fraction of sp^3 hybridized bond (Fig. 4). In the annealed sample where significant graphitization occurred, the ESR peak almost disappeared due to the formation of ordered sp^2 clusters [Fig. 5(a)]. These results definitely show that the paramagnetic defect density is proportional to the content of sp^3 hybridized bond in the film.

The surface C–H bonds characterized by NEXAFS analysis is also consistent with this conclusion. Figure 4 shows that the intensity of σ_{C-H}^* resonance at 287.8 eV has a maximum when the negative bias voltage was -50 V. Because hydrogen was not included in the deposition environment, this C–H bond would be due to the surface absorption of hydrocarbon in ambient air. If one reasonably assumes that the absorption is enhanced by the surface dangling bond, the intensity of the σ_{C-H}^* resonance would represent the content of the surface defects. Intensity of σ_{C-H}^* peak showed an opposite behavior to that of $\pi_{C=C}^*$ peak, which means that the surface defect or dangling bond is proportional to the content of the sp^3 hybridized bond. This behavior is in good agreement with the previous report by Gutierrez *et al.*¹⁶

In a mixed sp^3 and sp^2 hybridized bond network like ta-C films, sp^3 hybridized dangling bond tends to be relaxed to threefold-coordinated sp^2 site as proposed by Robertson.¹⁷ He showed that the defects in ta-C film are mostly isolated sp^2 sites, which have not paired up to form π bonds.¹⁷ The first principle calculation by Drabold *et al.* showed that the pairing of the sp^2 sites to form π bonds is energetically much more favorable.¹⁸ Therefore, if other unpaired sp^2 sites exist nearby, they are likely to pair each other to form π bond. When the number of sp^2 site increases in the film, therefore, most unpaired sp^2 sites would not act as the defects but form carbon double bonds via π electrons.

This strong tendency of pairing would explain the present experimental observation. In the case of high content of sp^3 hybridized bonds, the possibility for pairing the unpaired sp^2 sites is low because they are isolated far from each other in the sp^3 rich network. Furthermore, the isolated sp^2 sites are under constraint of the cross-linked rigid sp^3 network. High defect density observed in the sp^3 rich network stems from the unpaired sp^2 sites. On the other hand, when the content of sp^2 hybridized bond increased, the distribution of sp^2 sites would become closer. The sp^2 sites would form carbon–carbon double bonds, resulting in low defect density. This behavior becomes significant in the annealed ta-C film that has high content of sp^2 bonds with larger sp^2 clusters and ordered atomic structure. Furthermore, when annealing at high temperature, thermal activation would enhance the pairing of the sp^2 sites.

IV. CONCLUSIONS

The present work showed that the defect density of ta-C films deposited by FVA process is proportional to the fraction of sp^3 hybridized bond in the film. Hence, the same behaviors were observed in both the mechanical properties and the defect density on the applied negative bias voltage. Decreasing defect density with increasing content of the sp^2 hybridized bond was due to the pairing of unpaired sp^2 sites that would be relevant when the content of sp^2 hybridized bond was large. This result was also consistent with the NEXAFS analysis showing that the content of sp^3 hybridized bond is proportional to the intensity of the surface σ_{C-H}^* peak that stems from the absorption of hydrocarbon in ambient air to the surface dangling bonds.

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