Correlation between sp^2/sp^3 Ratio or Hydrogen Content and Water Contact Angle in Hydrogenated DLC Film

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Water contact angle has been measured to indirectly assess the sp^2/sp^3 ratio and hydrogen content of DLCH film under post N₂ annealed treatment with O₂ content under 100 ppm. XPS spectrum is used to measure the C1s bonding type and calculate the sp^2/sp^3 ratio. The surface morphology of DLCH film was examined by SEM and AFM. From experimental results, it seems the surface morphology was not a critical factor on water contact angle value, at least for DLCH film. A quantitative correlation between water contact angle and sp^2/sp^3 ratio of DLCH film is established from which the hydrogen content can be estimated by the sp^2/sp^3 ratio as well as Angus equation.

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1. Introduction

The material characteristics of hydrogenated diamond-like carbon (DLCH) film can be varied from different manufacturing processes, such as ion beam deposition, plasma-assisted CVD, sputtering and filtered cathode arc (FCA) method. The advantages of DLCH film such as high hardness, high thermal conductivity, low thermal expansion, low friction coefficient and high chemical stability and high wear resistance have made it an excellent candidate in many fields.^{1,2)} Previous studies have shown that the hydrogen contents can strongly affect the growth status of DLCH film where hydrogen atom can passivate the dangling bonds during growth mechanism.³⁾ The hydrogen is mainly bonded to sp^3 sites, and partially bonded to sp^2 sites.⁴⁾ It is believed that the hydrogen content is closely related to the material characteristics. The conventional way to measure the hydrogen content is via elastic recoil detection (ERD), Rutherford backscattering (RBS) and nuclear reaction analysis (NRA) method. These methods are often time consuming and expensive. From the correlation of material characteristics and hydrogen content, there seems to other method to measure the hydrogen content. For material characterization, the amorphous hydrogenated carbon film is often hybridized with three kinds of bonding structure: diamond-like (DLCH, sp^3 site), graphite-like (GLCH, sp^2 site) and polymer-like (PLCH, sp^1 site). For DLCH film, the sp^1 part can be neglected due to its low content. Therefore, the sp^2/sp^3 ratio is the primary factor to characterize the DLCH film property. To our knowledge, there are at least nine methods to quantitatively measure the sp^2/sp^3 ratio of DLCH film, such as UV Raman spectroscopy,⁵⁻⁷⁾ x-ray photoelectron spectroscopy (XPS),⁸⁻²¹⁾ Fourier transform infrared spectrometry (FTIR),^{22,23)} nuclear magnetic resonance (NMR),²⁴⁾ Auger electron spectroscopy (AES),²⁵⁾ x-ray reflectivity (XRR),^{26,27)} electron energy loss spectroscopy (EELS),²⁸⁾ spectroscopic ellipsometry & spectroscopic reflectometry (SE & SR)²⁹⁾ and

near-edge x-ray absorption spectroscopy (NEXAFS).³⁰⁾ The sp^2/sp^3 ratio had been shown to be correlated with many material properties. One interesting observation was made by Ostrovskaya *et al.* for the qualitative correlation between water contact angle and various sp^3/sp^2 ratio with diamond (100% sp^3 site, more polar component), amorphous carbon film (a-C, up to 90% sp^3 sites), amorphous hydrogenated carbon film (a-C:H, up to 60% sp^3 sites) and graphite (100% sp^2 site, more dispersive component).³¹⁾ Furthermore, Mattia *et al.* have shown there exists an correlation between different degree of graphitization and water contact angle of DLCH film by post vacuum annealing treatment.³²⁾ Based on these two observations, we try to establish an quantitative relationship between water contact angle and sp^2/sp^3 ratio. Such relation can be used quantitatively to assess the sp^2/sp^3 ratio by simple water contact angle measurement.³³⁾ With this result and Angus equation, the hydrogen content of DLCH film can be obtained easily.³⁴⁾ Surface roughness from AFM analysis and surface cluster of DLCH film from SEM measurement are also examined to explore the surface roughness effect on sp^2/sp^3 ratio.

2. Experimental Procedure

The DLCH film was deposited on 6" bare Si wafer with ion beam deposition (IBD) method (Dash 700 model). The reactive chamber was pumped to 5×10^{-4} Pa, and Ar and hydrogen gas were poured into chamber until the background was reached at 0.1 Pa. The wafer temperature was kept at 200°C and DLCH thickness was 1.0 μm. The more detailed experimental of DLCH film deposition procedure can be found elsewhere.¹⁾ N₂ gas oven was used to anneal the DLCH film for one hour and at 300°C, 350°C and 400°C, respectively. The oxygen content in the oven was controlled under 100 ppm during full heating step in order to avoid the DLCH oxidation. XPS apparatus (Escalab 210) with Al Kα radiation (1486.6 eV) was used to measure C1s bonding type and sp^2/sp^3 ratio of DLCH film. The pre-clean treatment by Ar⁺ gas sputtering step was skipped in order to avoid the

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Fig. 1 SEM images of DLCH film at different state: (a) as-deposited, (b) 300°C, (c) 350°C and (d) 400°C as-annealed.

thermal hybridization transformation for DLCH film, and the detected depth of XPS was about 5 nm. The 100% Gaussian and three assigned peaks (sp^2 , sp^3 and CO) are used to deconvolute C1s XPS line by curve fitting. The water contact angle was measured by AST VCA 2000 with de-ionized water where CCD can automatically catch the contact angle in left and right side. The contact angle was defined as the average of these two values, and the idle time is 30 seconds for stabilization of the water droplet with 1 mm diameter on DLCH film surface. The ESEM (FEI Quanta 400F, magnification 100,000X) was used to inspect the surface morphology of DLCH film and AFM (NT-MDT/P47E10 P7LS (dry type)) was used to measure the surface roughness, the scanned area is about $5\ \mu\text{m} \times 5\ \mu\text{m}$.

3. Results and Discussion

Figure 1 exhibits the SEM images of DLCH film under different annealed temperature, in order to get clear contrast

of images taken under 100,000X magnification, all these SEM images have been treated with maximum improvement on image contrast. The surfaces are rather smooth and the size of these surface cluster (or grain boundary) for as-deposited, 300°C, 350°C and 400°C are estimated smaller than 50 nm. These surface morphologies are not noticeably different, and these near nano-structured amorphous carbon (NAC) films with nano-scale clustering surface structure observed by SEM are similar to the report of Henley *et al.* without surface roughness consideration.³⁵⁾ Figure 2 shows the AFM images of DLCH film under different annealed temperature, and the surface roughness Rms (Root mean square) of these samples for as-deposited, 300°C, 350°C and 400°C are estimated as 1.531 nm, 1.267 nm, 1.175 nm and 1.707 nm, respectively. These surfaces did not show a monotonic trend in roughness in these nano-structured DLCH films. The small variation in surface roughness (the mechanical anchoring effect) among these DLCH samples indicates the surface roughness might not be the critical

Fig. 2 AFM images of DLCH film at different state: (a) as-deposited, Rms: 1.531 nm (b) as-annealed, 300°C, Rms: 1.267 nm (c) as-annealed, 350°C, Rms: 1.175 nm and (d) as-annealed, 400°C, Rms: 1.707 nm.

Fig. 3 XPS survey spectra of DLCH film at as-deposited and as-annealed states.³⁸⁾

factor for wettability between de-ionized water and DLCH film. Uelzen *et al.* mentioned that surface roughness even with micrometer level could not affect the water contact angle, and film property was the critical factor.³⁶⁾ Kaibara *et al.* proved that plasma modification of diamond film could affect water contact angle behavior on diamond film. The hydrogen plasma treatment could cause hydrophobic surface and increase water contact angle whereas the oxygen plasma treatment could result in hydrophilic surface and reduce water contact angle.³⁷⁾

XPS was used to measure the chemical bonding of DLCH film, and the sp^2/sp^3 ratio for as-deposited state as well as different annealed temperature. Figure 3 shows the XPS survey spectra of as-deposited and as-annealed states.³⁸⁾ In addition to the carbon peak, the oxygen peak is also apparent.

The CO bond percent of as-deposited, 300°C, 350°C and 400°C are 16.1%, 29.4%, 27.4% and 29.6%, respectively. CO bond with hydrophilic property could reduce the water contact angle.³⁷⁾ There is no nitrogen element peak at 400 eV under 400°C annealing treatment with N₂ atmosphere, in comparison with the XPS spectra of a-C:H (N) film.³⁹⁾ It is obvious that N₂ gas did not react with DLCH film under post annealing treatment during this study. Nitrogen atom could chemically bond with carbon to form C-N, C=N, and C≡N bonds during a-C:H(N) film deposition, and these CN bonds increase the polar part of DLCH film and reduce the water contact angle on the Si and N doping DLCH film.⁴⁰⁾ The sp^2/sp^3 ratios for as-deposited state, annealed temperature 300°C, 350°C and 400°C are 1.98, 3.07, 5.46 and 7.34, respectively, as shown in Fig. 4. The positive correlation trend between the sp^2/sp^3 ratio and annealed temperature is similar to the report by Diaz, Franta and Mattia *et al.*^{9,29,32)} For contact angle measurement, water has stronger polar component than its disperse component, i.e. the polar/disperse ratio is 2.62 (52.2/19.9) for de-ionized water and is 5.07 (60.3/11.9) for pure water.^{40,41)} Figure 5 shows that the water contact angles of DLCH film are as a function of annealed temperature, and the water contact angle for as-deposited state, 300°C, 350°C and 400°C is 37.0°, 52.6°, 55.6° and 62.0°, respectively.⁴²⁾ This trend shows the higher the annealed temperature, the larger the water contact angle (i.e. the more hydrophobic of DLCH film), which might result from the thermal treatment leading to graphitization for DLCH film. This finding is in agreement with the report by Mattia *et al.* for CVD-carbon films under post vacuum annealing treatment at higher temperature (1200°C~2000°C) without surface roughness consideration.³²⁾ It is reasonable to combine Figure 4 and

Fig. 4 sp^2/sp^3 ratio of DLCH film as a function of annealing temperature.

Fig. 6 sp^2/sp^3 ratio of DLCH film as a function of water contact angle on DLCH film surface.

Fig. 5 Optical images of water contact angle of DLCH film at different state: (a) as-deposited, water contact angle: 37.0° (b) 300 °C as-annealed, water contact angle: 52.6° (c) 350 °C as-annealed, water contact angle: 55.6° and (d) 400 °C as-annealed, water contact angle: 62.0°. ⁴²⁾

Figure 5 together to get the quantitative correlation between water contact angle and sp^2/sp^3 ratio of DLCH film, as shown in Fig. 6. It is well known that the a-C:H film properties are determined by versatile deposition methods and variable parameter process controls, the concept could be used to explain that the water contact angle measurement difference of as-deposited a-C:H film from Ostrovskaya study is near 55°, but is 37° from our experimental result prepared by IBD method. The similar curve trend of Fig. 6 is that sp^2/sp^3 ratio increases with increasing water contact angle due to thermal treatment cause transformation from more sp^3 part (diamond-like) into more sp^2 part (graphite-like) of a-C:H film from the view point of chemical graphitization mechanism based on some reports.^{1,2,31)} The physical mechanism could be attributed to the polar water droplet with hydrophilic property wetting on dispersive surface with hydrophobic property of

annealed DLCH film, the higher the annealed temperature, the worse the wettability with higher water contact angle. Furthermore, in DLCH film, the hydrogen content and sp^2/sp^3 ratio are correlated. Therefore, if the sp^2/sp^3 ratio is obtained, then the hydrogen content of DLCH film can be estimated by Angus equation.³⁴⁾ This will relinquish the complex measurements for hydrogen contents, such as elastic recoil detection (ERD), Rutherford backscattering (RBS) and nuclear reaction analysis (NRA) when those analysis tools are not available. Figure 7 shows the hydrogen content in DLCH film deposited by IBD method is among the normal range 20~40 at.%,^{2,43)} From the trend between hydrogen content and sp^2/sp^3 ratio under different annealed temperature, it seems the mechanism of hydrogen content reduction resulted from thermal desorption and mass loss reaction during annealed treatment. This result is similar to the report

Fig. 7 Hydrogen content of DLCH film as a function of sp^2/sp^3 ratio.

of Neyts and Vuppuladhadiam *et al.*^{44,45} Initially, the correlation did not show a clear trend between the sp^2/sp^3 ratio and hydrogen content of Angus equation. However, in this study, these two factors are established in an inverse correlation. For DLCH film, when the sp^2/sp^3 ratio is obtained by water contact angle measurement at any annealed temperature, the hydrogen content can be estimated by fitting this ratio with Angus equation. This is one indirect and simple method to evaluate the hydrogen content of DLCH film when hydrogen analysis tools are not available.

4. Conclusion

For as deposited DLCH film, the roughness effect is negligible, even though the nitrogen and oxygen bond possibly react with carbon to form CO and CN bonds with hydrophilic property during annealing treatment. However, in our experimental result the water contact angle was increased with increasing annealing temperature under N_2 atmosphere and low oxygen control below 100 ppm. The potential mechanism might be the sp^3 sites transformation to sp^2 sites during N_2 annealing treatment because of thermal graphitization. On the other hand, a quantitative correlation between water contact angle and sp^2/sp^3 ratio is established. From which, the hydrogen content of DLCH film can be obtained along with Angus equation. Based on this finding, the hydrogen content of DLCH film can be indirectly evaluated by water contact angle measurement when the complex measured tools are not available.

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