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On the upper limit of sp^3 content in tetrahedral amorphous carbon film

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Abstract. The morphological properties of the tetrahedral amorphous carbon (ta-C) films deposited by the filtered cathodic vacuum arc (FCVA) technique have been studied over the carbon ion energy range 15 to 200 eV. All the films studied are very smooth with a roughness below 0.6 nm. The minimum roughness ($\sim$0.12 nm) occurs at the highest sp^3 content. The lateral feature size increases with ion energy. There appear to be two different growth mechanisms before and after the peak sp^3 content. The morphological result suggests an upper limit sp^3 content of about 89% in the ta-C films deposited by FCVA technique.

Recently, a highly sp^3 bonded form of amorphous carbon denoted tetrahedral amorphous carbon (ta-C) film deposited by the filtered cathodic vacuum arc (FCVA) technique has been intensively studied [1–6]. The FCVA deposition system employs a magnetic filtering technique to remove unwanted macro-particles and neutral atoms. The properties of ta-C films have been correlated to the energy of the incident carbon ions during deposition [6–9]. A different FCVA system yields different optimal energy for the formation of sp^3 bonds while the mass selected ion beam deposition (MSIBD) data of several laboratories indicate a broad optimal energy region [10, 11]. A recent study of the various deposition conditions used to obtain ta-C films shows that the predominant factor determining the optimal ion energy is the deposition rate [12]. The high sp^3 content in ta-C films results in unique properties that include extreme hardness, chemical inertness and high electrical resistivity. It has been shown that the variation of the mechanical properties exhibits a linear dependence on the variation in sp^3 content [13]. The maximum hardness, Young's modulus, stress, critical load and minimum friction coefficient all coincide with the highest sp^3 fraction [13]. There is an interesting question of how high an achievable maximum sp^3 content in the tetrahedral amorphous structure would be. The present paper reports surface morphological measurement of ta-C films and its relation to the sp^3 content in the films. An achievable maximum sp^3 content is derived from the measurement results.

The ta-C films were deposited by a FCVA system described elsewhere [6]. The system incorporates the off-plane double-bend (OPDB) filter [14, 15] to effectively remove all macro-particles. During deposition the C plasma leaves the self-sustaining arc spot, and then C$^+$ ions are accelerated with a DC bias to the out-of-sight highly doped silicon substrate. The arc current was kept constant at 60 A. A toroidal magnetic field around 40 mT was employed to produce the axial and curvilinear fields to steer the plasma. The substrate temperature was kept at room temperature for all deposition. The ion beam sputtering (600 eV and 20 mA Ar ions) with a pre-fixed duration was used to remove the native oxide layer on the silicon wafer surface

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and to create a constant substrate morphology with a RMS roughness about 0.35 nm over an area of 1 μm^2. The silicon substrate after ion beam bombardment exhibits fine periodic texture on the surface [16]. Films with thickness of about 60 nm were deposited for all samples, and the deposition rate was kept at about 1.0 nm s^{-1}. The film surface morphology was observed using the Digital Instruments Dimension 3000 SPM system. An etched silicon cantilever tip with a curvature radius of 10 nm was used for tapping mode AFM measurement. The RMS roughness was obtained using the digital image-processing package attached to the SPM system over the image area of 1 μm^2. The lateral feature size was obtained by averaging the distance between adjacent crest points along a series of parallel cross-sectional lines in the image area using the digital image-processing package. Given that the AFM roughness measurements are very sensitive to both the tip and surface structure, more than five tips were used to measure the same series of samples and the results are reproducible.

Ion energy is known to be a crucial parameter in the determination of film properties deposited by the FCVA technique. For samples fabricated at deposition rate of 1.0 nm s^{-1}, the dependence of the sp^3 fraction on the carbon ion energy was reported in previous work [13]. The sp^3 fraction increases from about 75% at 15 eV to the maximum of about 87% at 95 eV. Then, it decreases to about 80% at about 195 eV. The sp^3 content is more than 80% in a wide range of carbon ion energy from 50 to 195 eV.

The ta-C films deposited at various ion energies exhibit different morphology. Figure 1 shows the AFM pictures of ta-C films deposited at 35, 75, 115 and 175 eV respectively. The image of the film deposited at 35 eV is very similar to that of silicon substrate after ion beam cleaning. The only difference is that the film has a larger RMS roughness of 0.45 nm. This may be due to the fact that the morphology of ta-C film follows the shape of the silicon substrate at low carbon ion energy. Comparing the four pictures in figure 1, it is clearly seen that the film deposited at 35 eV has a smaller lateral feature size and a higher RMS roughness; the film deposited at 175 eV has a larger lateral feature size and a higher RMS roughness; the films deposited at 75 and 115 eV have an intermediate lateral size and a lower RMS roughness. The lateral feature size increases from 40 to 185 nm as the carbon ion energy increases from 15 to 195 eV. The surface RMS roughness, however, first reduces to a minimum value of 0.14 nm at the ion energy of 95 eV and then increases with ion energy. All films are in general very smooth with RMS roughness below 0.6 nm.

In order to correlate the surface morphology properties to the sp^3 content in the ta-C films, the dependences of the lateral feature size and film RMS roughness upon the sp^3 content are plotted in figures 2 and 3, respectively. The lowest RMS roughness occurs at maximum sp^3 content. Two straight lines are observed in each plot. The data along the solid lines are of the samples deposited at ion energies below 95 eV, and the data along the dashed lines are of those deposited at ion energies above 95 eV. The solid and dashed lines intersect at an sp^3 content of about 89% both in figures 2 and 3. The two linear regions shown in figures 2 and 3 indicate that the growth mechanism of the ta-C films is different before (first region) and after (second region) reaching the maximum sp^3 fraction. In the first region (solid line), the lower the ion energy, more surface growth occurs and therefore, the roughness increases as ion energy decreases. Similar phenomena were observed by Lifshitz using MSIBD [10]. However, the excessive ion energy in the second region (dashed line) causes surface damage and thus an increase in the roughness. The surface growth and surface damage coexist during the deposition which is in agreement with the sub-plantation model [17], and this results in the minimum roughness at the optimal ion energy (corresponding to the maximum sp^3 content). In addition, an increase in ion energy will in general enhance the aggregation of atoms and thus increase the lateral feature size. The convergence of the two growth regions, or the intersection of the solid and dashed lines in figures 2 and 3 implies that for ta-C film deposited by FCVA

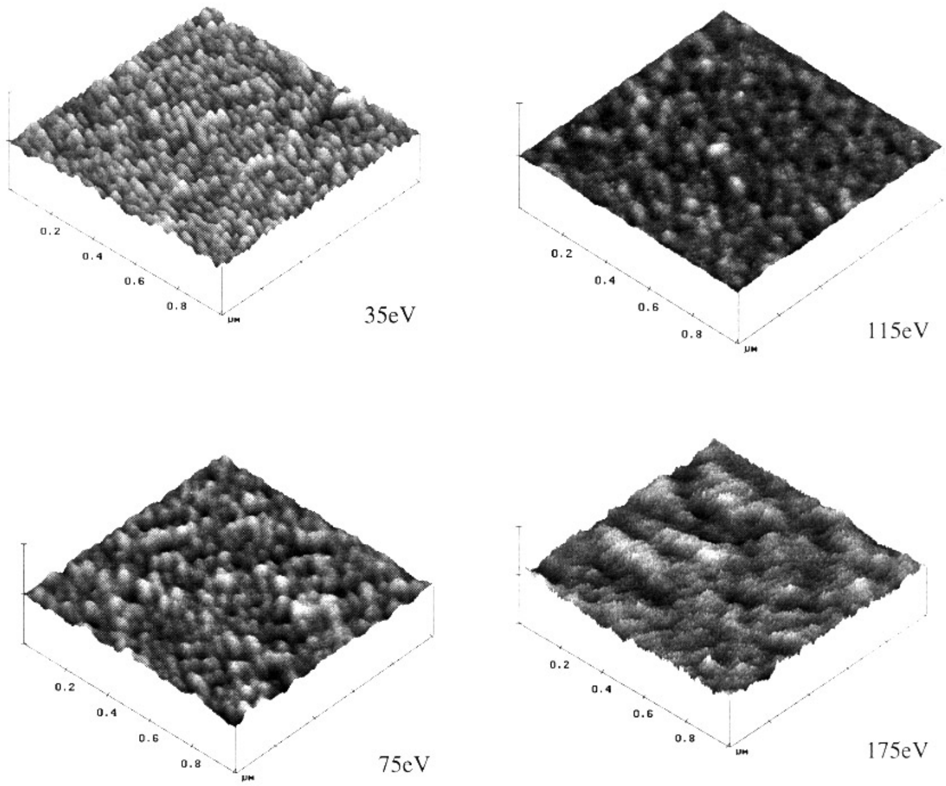

Figure 1. Surface morphology pictures with ion energy of 35, 75, 115 and 175 eV. The vertical scale is 10 nm/div.

technique the maximum sp^3 achievable could be around 89%. It can be qualitatively argued that a small amount of sp^2 is inevitable in the ta-C atomic structure in which sp^2 serves as the 'lubricant' among the rigid sp^3 structures. However, the quantitative analysis is still not available.

A similar phenomenon was observed in previous Raman measurement [13]. For the visible argon-ion laser with a 488 nm line, the Raman spectrum monitors the sp^2 bonded component within the sp^3 matrix. The Raman spectra were quantitatively analysed by fitting the Raman spectra with a Breit–Wagner–Fano (BWF) line shape and a linear background using a least-squares fit [18] in the range of 1100 to 1950 cm^{-1}. Figure 4 shows the variation of Q skewness parameter with the change of sp^3 content [13]. The Q factor remains constant around -3.0 over a wide range of sp^3 content from 10% to 70%. When the sp^3 content is more than 70% (or sp^2 content below 30%), the Q factor noticeably increases in magnitude and approaches a large negative value -36 at the maximum sp^3 content. For a small magnitude of skewness parameter Q, the spectrum could also be fitted with two Lorentzian shape lines corresponding to a large G peak and a very small D peak of graphite. For a large magnitude of Q, the spectrum becomes more symmetrical so that there is only G peak; the D peak is effectively zero. At higher sp^3 fraction (more than 80%), the sp^2-bonded material could form isolated sites within the amorphous sp^3 matrix. The sharp increase in the magnitude of Q with higher sp^3 content shown in figure 4 indicates that there is an upper limit of sp^3 content in ta-C films.

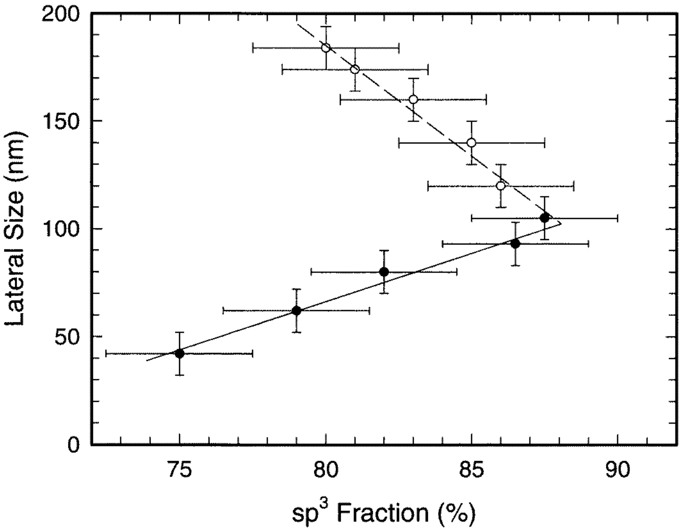

Figure 2. Lateral feature size against sp^3 fraction. The black and open circles represent the data for ion energy below and above 95 eV, respectively.

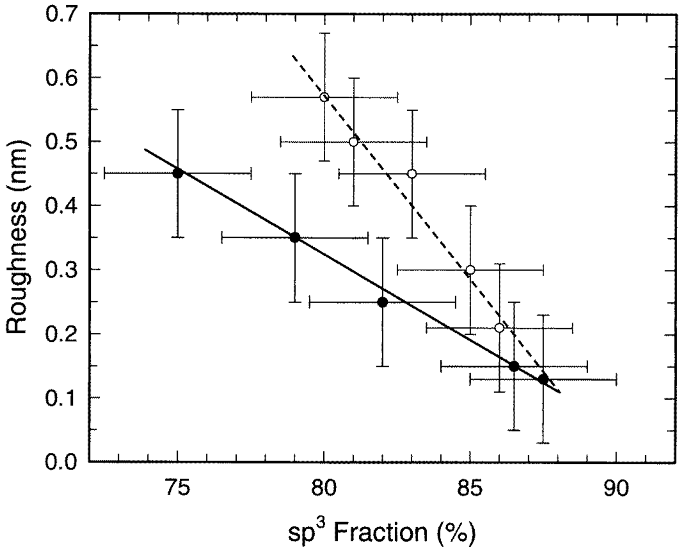

Figure 3. RMS roughness against sp^3 fraction. The black and open circles represent the data for ion energy below and above 95 eV, respectively.

In summary, all the films studied are very smooth with a roughness below 0.6 nm. The minimum roughness (~0.12 nm) occurs at the highest sp^3 fraction. There appear to be two different growth mechanisms before and after the peak sp^3 fraction. The surface growth and surface damage coexisting during deposition result in the minimum roughness at the highest sp^3 fraction. The fact that the lateral feature size increases with ion energy results from that higher ion energy enhances aggregation of atoms. The BWF skewness parameter Q of the

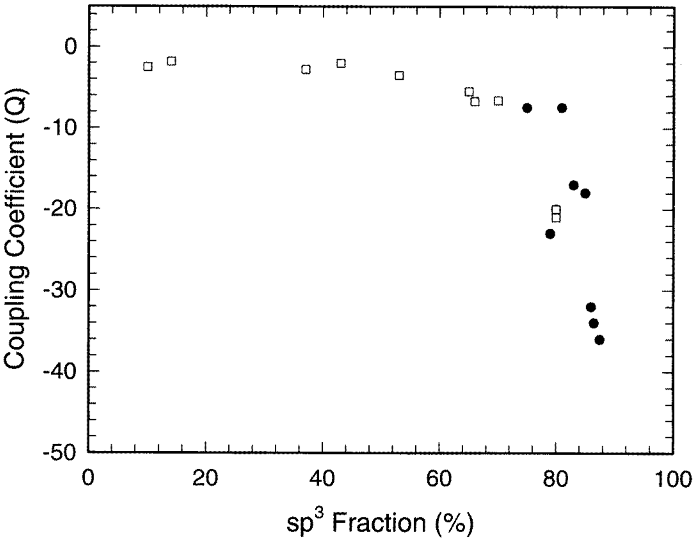

Figure 4. The skewness parameter Q as a function of sp^3 fraction (after [13]). The open squares and black circles are for films deposited by the MSIBD and FCVA technique, respectively.

Raman spectrum sharply decreases as the sp^3 content is larger than 80%. The morphological and Raman scattering results suggest an upper limit sp^3 content of about 89% for the ta-C films deposited by the FCVA technique.

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