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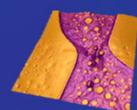
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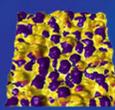
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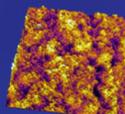


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Stress reduction dependent on incident angles of carbon ions in ultrathin tetrahedral amorphous carbon films

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We presented the combined experimental and simulation study on stress evolution as a function of incident angles of carbon ions for the ultrathin tetrahedral amorphous carbon films (ta-C). The residual stress was found about 3.6 ± 0.1 GPa for the incident angle of C ions with range of 0° – 30° , while it decreased significantly to 2.8 GPa with the incident angle of 60° . Different with the previous reports, noted that in this case both the sp^3 content and mechanical properties of film were not deteriorated. Taking molecular dynamics simulation, it was in particularly concluded that the critical relaxation of distorted C- sp^3 bond lengths and bond angles played key role on the unusual stress reduction mechanism. The results provide a route to fabricate the ultrathin ta-C films with low stress and high hardness for the precision wear resistant applications. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4870968>]

Owing to the high hardness, smooth surface, low friction coefficient, and good corrosion resistance, ultrathin tetrahedral amorphous carbon films (ta-C) have been widely used as a protective coating in industrial fields of microelectromechanical systems (MEMS), data storage, precision moulds/dies, etc.^{1–3} However, the compressive residual stress formed due to the heavy bombardment of energetic carbon ions causes the subsequent film delamination and/or specimen deformation, which is considered as the current key barrier for the extensive applications of ultrathin ta-C films. Many efforts have been recently carried out to reduce the residual stress such as decreasing the sp^3 atomic content by applying substrate bias during film deposition,⁴ introducing the pivot relaxation for distorted sp^3 bonds by incorporating third metal elements into amorphous carbon matrix,^{5,6} as well as conversing distorted fourfold coordinated carbon atoms to threefold preferentially oriented ones by using post-annealing process to 600°C .⁷ However, if one takes into account that both the residual stress and hardness are closely related to the sp^3 content and the obtained limited reduction of stress without hardness deterioration, an alternative method to prepare the ultrathin ta-C films with required high performance is to take full advantage of the incident energetic ions during deposition.^{8–10} In particularly, Hawkeye and Brett reported that the columnar structures of amorphous carbon films were changed by the atomic-scale ballistic shadowing and surface diffusion by varying the incident glancing angle of ions during film deposition.¹⁰ Recently, Joe *et al.* investigated the morphology evolution of amorphous carbon film growth with various incident angles of energetic carbon atoms by molecular dynamics (MD) simulation⁸ and found that the surface roughness was mediated by the uphill/downhill transport and shadowing effect of carbon atoms under various incident angles. However, the effect of incident angle of carbon atoms on the atomic bonds and

properties of ultrathin ta-C films, in particularly the residual stress evolution, has yet to be clarified in the atomic scale.

In the present work, we performed experiments combined with MD simulation to study the evolution of atomic bond structure and residual stress of the ultrathin ta-C films as a function of the incident grazing angle of carbon ions ranging from 0° to 60° . It was found that increasing incident angles of C ions significantly relaxed the highly distorted structure of amorphous carbon matrix, in agreement with the experimental results where the ta-C films with low stress and high hardness were obtained due to the un-deteriorated sp^3 hybridized content in the matrix.

Ultrathin ta-C films were deposited using a home-made 45° double-bent filtered cathodic vacuum arc (FCVA) technique. P-type silicon (100) wafers of thickness $290 \pm 15 \mu\text{m}$ and $545 \pm 15 \mu\text{m}$ were used as substrates and in particularly the thinner one was used for the accuracy of residual stress measurement. Graphite with purity of 99.999% was used as the cathodic target. Before deposition, the substrates were etched in the chamber using Ar^+ ions and the etched thickness was about 10 nm. During deposition, the films were deposited at bias voltage of -80 V and -140 V alternately and the arc current was fixed at 60 A. The grazing incidence of carbon ions was changed from 0° to 60° . The film thickness was kept around 50 nm by varying deposition time for each case. The residual stress was calculated from the curvature of the film/substrate composite using Stoney's equation. Nano-indentation in the continuous stiffness measurement (CSM) mode was employed to characterize the mechanical properties of ta-C films. A characteristic hardness of the films was chosen as being the depth where the measured values were not affected by the mechanical properties of the Si substrate. Ten indentations were made for each specimen in order to accurate the hardness value. Visible Raman and UV Raman spectroscopy, as well as the XPS were conducted to analyze the microstructure and composition of films.

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We performed the MD simulation with three-body empirical potential Tersoff to characterize the interaction between the deposited carbon atoms. For simplicity, energetic atoms of carbon impacted on a diamond (001) single crystal substrate of $25.2210 \times 25.2210 \times 24.0758 \text{ \AA}^3$ in the x , y , and z directions, which contained 2800 carbon atoms with 100 atoms per layer and was equilibrated at 300 K for 100 ps before deposition. The incident carbon atoms were introduced at 10 nm above the substrate surface at a random $\{x, y\}$ position. While the positions of atoms in the bottom two layers were frozen to mimic the bulk substrate, all the other atoms were unconstrained. The periodic boundary conditions were applied in x and y directions, and the time step was fixed at 1 fs. The time interval between two sequential deposited carbon atoms was 10 ps.

Fig. 1 shows the evolution of residual compressive stress and hardness of deposited ta-C films as a function of incident angles of C ions. When the incident angle of carbon ions is 0° , in the form of normal incident state, the residual stress is observed at 3.7 GPa and followed by a slight decrease as the incident angle increases to 30° . However, a significant stress reduction is presented beyond of the angle range of 30° . For the case of incident angle of 60° , the stress is reduced about 25% to 2.8 GPa. Of particular interest is that, in contrast to the residual stress behavior, the hardness of deposited ta-C films is almost independent of the incident angle from 0° to 60° and remains constant at 31.5 ± 1.5 GPa. Therefore, the results indicate it is possible to fabricate the ta-C film with a reduced residual stress without any associate degradation of the film's mechanical properties.

To elucidate the dependence of atomic bond structure on the incident angle, Fig. 2(a) presents the visible Raman spectra (inset in Fig. 2(a)) and the fitted data of the G-peak position and I_D/I_G ratio of the deposited ta-C films with various incident angles of C ions. The peak around $900\text{--}1000 \text{ cm}^{-1}$ on the Raman spectra is the second-order signals of the silicon substrate, indicating the increased transparency of deposited films as the incident angle increases. The broad asymmetric Raman peak in the range of $1100\text{--}1800 \text{ cm}^{-1}$ can be deconvoluted into a G-peak centered at 1560 cm^{-1} and a D-peak centered at 1360 cm^{-1} , showing the typical characteristic of tetrahedral amorphous carbon films.^{11–13} From Fig. 2(a), a significant result is that

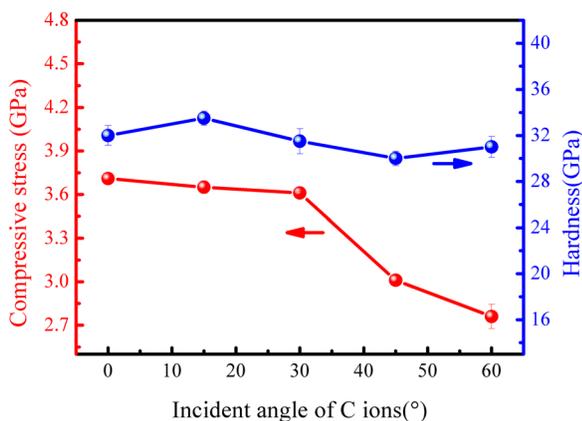


FIG. 1. Compressive stress and hardness of ultrathin ta-C films as a function of incident angles of C ions.

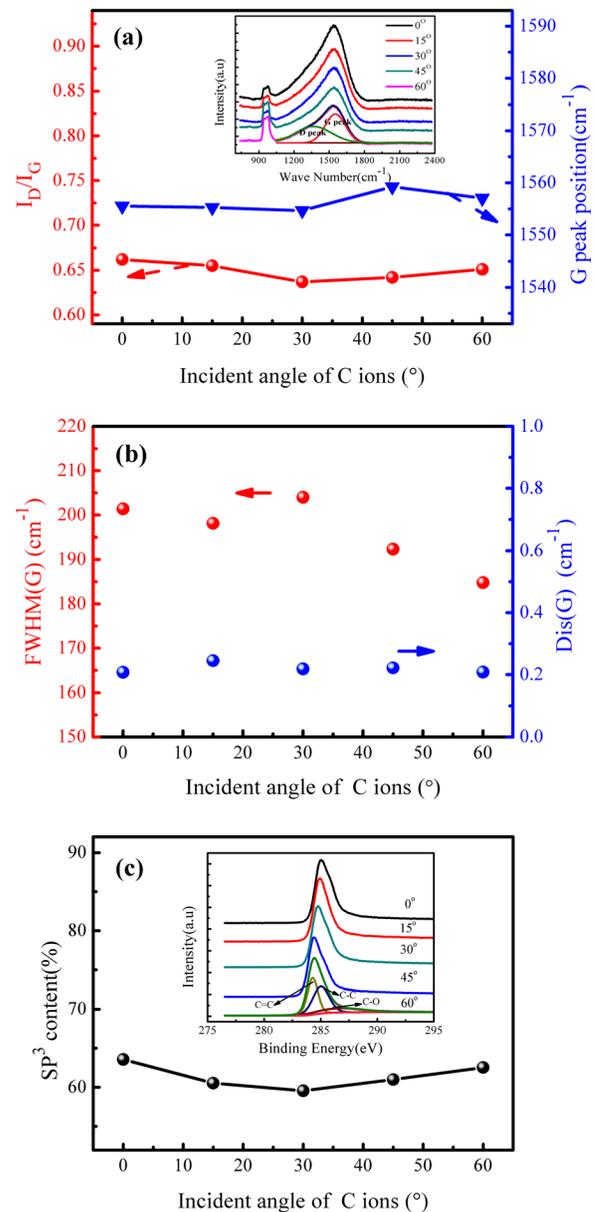


FIG. 2. (a) G peak position and I_D/I_G ratio, and inset of visible Raman spectra, (b) FWHM(G) and Dis(G), and (c) fitted sp^3 content in deposited ta-C films, and inset of XPS C1s spectra, with increasing incident angle of C ions.

both the G-peak position and the I_D/I_G ratio show independence on the changes of incident angle from 0° to 60° , and keep constant at $1557 \pm 2 \text{ cm}^{-1}$ and 0.65 ± 0.02 , respectively, implying that the sp^3 content and sp^2 clustering are not changed.^{14–16} However, as a sensitive measure of localized structural disorder, the Full Width at Half Maximum of G peak, $FWHM(G)$, reduces from 201.4 to 184.8 cm^{-1} with the increase of incident angle from 0° to 60° (Fig. 2(b)), indicating the certain changes of structure disorder emerge. However, the G peak dispersion at visible and UV Raman spectra with, Dis(G), as a measure of topological disorder in localized structure, almost keeps constant at $0.21\text{--}0.24 \text{ cm}^{-1}$ regardless of the variety of incident angle (Fig. 2(b)). If one keeps in mind that the optical properties are mainly dominated by the sp^2 content and sp^2 localized structure, it can thus be proposed that the increased transparency of deposited ta-C films is attributed to the changes of sp^2 localized

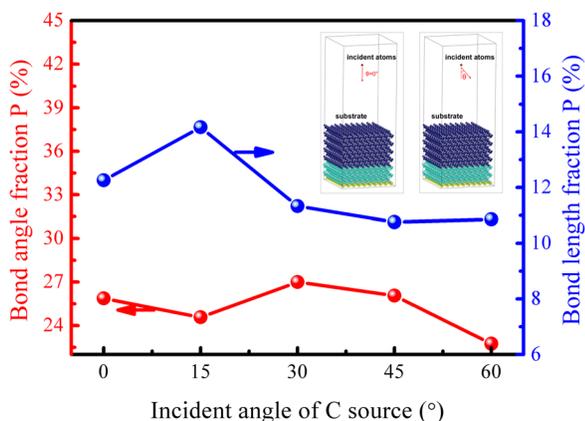


FIG. 3. Fraction dependence of distorted bond angle ($<109.471^\circ$) and bond length ($<1.42 \text{ \AA}$) upon the incident angle of carbon ions by MD simulation.

structure disorder, which generally arises from the bond angle and bond length distortion.¹⁵ Fig. 2(c) presents the combined XPS measurement on the microstructure of the deposited ta-C films. As illustrated in inset of Fig. 2(c), by deconvoluting all the XPS C1s spectra into three peaks: C=C (sp^2) around $284.3 \pm 0.2 \text{ eV}$, C-C (sp^3) around $285.2 \pm 0.2 \text{ eV}$, and C-O around $286.5 \pm 0.2 \text{ eV}$,¹⁷ the C- sp^3 and C- sp^2 content in the films can thus be quantitatively estimated from the related peaks area. Similar to the Raman results, the XPS data reveal that no obvious change is visible for the hybridized C- sp^3 bond content in the deposited ta-C films, and the C- sp^3 content is nearly keeps constant at $62 \pm 2\%$, regardless of the changes of incident angle with range of 0° – 60° . As a result, it can be said that, from the combined Raman and XPS data, the hardness of deposited ta-C film is mainly dominated by the C- sp^3 content while the residual stress should be discussed in terms of other key factor, specifically the structure disorder predicated by the transparency behavior.

Since the residual stress is closely related to the microstructure distortion during film deposition, we perform the MD simulation to understand the mechanism of stress reduction in atomic scale by characterizing the dependence of atomic bond structure on the incident angle of carbon ions. The schematic drawing of the deposition model can be seen in the inset of Fig. 3, where the normal and grazing incidence are corresponding to the incident angle of carbon atom at 0° and a certain angle between 0° and 60° . Generally, the equilibrium bond angle of graphite is 120° and the diamond is 109.471° , while the equilibrium bond length of graphite and the diamond is 1.42 \AA and 1.54 \AA , respectively. Previous

study has revealed that the high compressive stress of diamond-like carbon (DLC) film is mainly originated from the distortion of bond angles and/or bond lengths, which were less than 109.471° and 1.42 \AA , respectively.¹⁸ In order to gain the fractions of distorted bond angles and bond lengths, we calculated the distributions of both the bond angles and bond lengths using code. Fig. 4 presents the bond angles and bond lengths distributions for ultrathin ta-C films at the incident angle of 0° , 15° , 30° , 45° , and 60° , respectively. By integrating the bond angles distribution and bond lengths distribution (shaded area in Fig. 4), the fractions of bond angles ($<109.471^\circ$) and bond lengths ($<1.42 \text{ \AA}$), are thus deduced separately, as illustrated in Fig. 3. Increasing the incident angles from 0° to 30° leads to the opposite changes in the fraction of distorted bond angle and bond length, and as a consequence which leads to the experimental mediate change in the residual stress (Fig. 1). Nevertheless, as the incident angle further increases from 30° to 60° , both the fraction of distorted bond angle and bond length decrease simultaneously, and this combined contribution agrees well with the experimental results where a significant reduction of residual stress is visible.

Based on the growth mechanism of ta-C films, the compressive residual stress is generally considered as an intrinsic property of ta-C films arising from the highly distorted C- sp^3 bonds, which mean the higher C- sp^3 content in films, the higher stress is achieved. However, Ferrari *et al.* revealed that there was no linear relationship between residual stress and C- sp^3 fraction in the ta-C film. The reason for stress release was a rearrangement within the C- sp^2 phase.^{19,20} In this work, we presented the significant stress reduction by increasing the incident angles of C ions without obvious degradation of the film C- sp^3 content. The MD simulation reveals that the distortions of bond length and bond angle dominate the mediate stress behavior with changes in the incident angle. Our results suggest that, in addition to the dominant effect of C- sp^3 content, an alternative distorted structure factor is important to understand the reduction mechanism of residual stress in ta-C films.

In summary, the compressive residual stress of ultrathin ta-C films is significantly dependent upon on the incident angles of carbon ions. As the incident angle varies from 0° to 30° , the opposite evolutions of the distorted bond angle and bond length lead to the mediate small change in residual stress. While beyond the incident angle from 30° to 60° , the observed significant stress reduction about 25% is attributed to both the simultaneously decrease of distorted bond angle and bond length. Of particular, our interested result is that

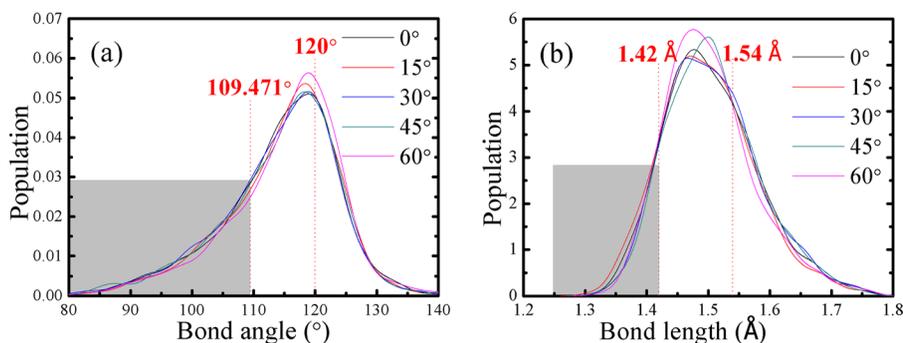


FIG. 4. Bond angle distribution (a) and bond length distribution (b) with various incident angles of carbon ions.

regardless of the changes in incident angle of carbon ions from 0° to 60° , the C- sp^3 content in the deposited ta-C films almost keeps constant at $62\% \pm 2\%$, leading to the undeteriorated mechanical properties but a significant stress reduction. This provides a promising route to fabricate the ultrathin ta-C films with high performance for the plethora of data storage and precision component applications.

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