Influence of copper content and nanograin size on toughness of copper containing diamond-like carbon films

Z. W. Ning¹, X. Yu*,¹, M. Hua² and C. B. Wang¹

Five copper containing diamond-like carbon films (Cu-DLC), each with a particular content of Cu, were deposited on Si (100) substrates in an ion beam assisted deposition system. The influence of Cu content and nanograin size on film toughness has been investigated along with verifying through the microstructural, mechanical and sliding tribological behaviours of the films. Variation of Cu content and nanocrystallites dispersing in DLC matrix induces corresponding modification in film toughness as well as hardness, intrinsic stress and sliding frictional behaviour, resulting in improvement of film toughness for the combined tribological performances. The film toughness was investigated by scratch crack propagation resistance from the critical load data obtained from scratch test. Results revealed that doping Cu with nanograin sizes, especially at a suitable content of 10-5 at-%, will significantly improve the crack initiation resistance and propagation resistance of crack during scratch test, demonstrating the improved toughness.

Keywords: Diamond-like carbon film, Copper incorporation, Toughness, Ion beam assisted deposition

Introduction

Owing to uniquely combined properties such as high hardness and surface smoothness, diamond-like carbon (DLC) films have drawn an extensive concern as good candidates in sliding components under various environments.¹,² The major drawbacks of DLC films are their poor adhesion property due to the high compressive stress induced during the formation of $sp^3$-C bond and lack of toughness to resist the propagation of cross-sectional cracks.³,⁴ Metal containing DLC (Me-DLC) films may enhance the adhesion of the films to their substrates by reducing the intrinsic stress in the films, and improve the toughness of the films via metal nanocrystals residing in the amorphous carbon matrix to release the strains in the films.⁵ As carbide formation elements are able to bond strongly with amorphous carbon which results in high hardness, existing literature in the synthesis and characterisation of Me-DLC films mainly focuses on doping carbide formation elements such as titanium (Ti),⁶ tungsten (W)⁷ and chromium (Cr).⁸ However, the formation of high inherent stress leads to brittleness which subsequently jeopardises their use as preferred incorporating element(s). On the other hand, there is neither a standard test procedure nor a standard methodology available for the toughness assessment of DLC films due to its small scale in thickness.⁹

Our previous researches¹⁰,¹¹ based on a medium frequency dual magnetron sputtering system indicated that embedding soft and ductile silver (Ag) nanocrystallites in DLC on silicon (Si) substrate could vary the Ag content and nanograin size and induce Ag-DLC films with various mechanical and sliding tribological behaviours as compared with those carbide formation elements such as Ti and W. Results of this preliminary research suggested a new methodology to improve the poor adhesion and toughness problem of DLC. Copper (Cu) is a typical ductile metal and is inert with respect to carbon, which is similar to silver.¹² This work has thus been initiated to investigate the influence of Cu contents and nanosizes on the toughness of Cu-DLC films for improving the combined tribological behaviours. Subsequently, it is hoped to provide knowledge of how to acquire suitable microstructures and compositional ranges of Cu for optimisation and evaluation of the toughness of the DLC films.

Experimental

Si (100) wafers were used as the substrate for Cu-DLC film deposition. In pretreatment, the substrate was ultrasonically cleaned in acetone bath for 20 min and blow dried with nitrogen. The IBAD system was employed for Cu-DLC film deposition and it consisted of four Kaufman ion sources with different energies: one high energy source for ion implantation before sputtering, two medium energy sources for sputtering copper (Cu) and graphite (C) targets respectively and one low energy...
source for ion bombardment resistance during deposition. The base vacuum and deposition pressure of the system were set at $2 \times 10^{-4}$ and $2.5 \times 10^{-5}$ Pa respectively. The substrate was sputter cleaned for a 10 min implantation with $Ar^+$ beam at 10 kV/20 mA. In order to improve the adhesion property of the films, a 0-2 μm thick Cu interlayer was first deposited on the substrate by a singular sputtering with Cu target at 1100 eV/40 mA. A DLC film containing x%Cu (a-C-Cux%) layer was deposited by the cosputtering of Cu and C targets together with a simultaneous $Ar^+$ beam bombardment at 100 eV/20 mA. The cosputtering was carried out with the Cu sputtering current varied from 0 to 100 mA (Table 1) with a fixed energy of 1000 eV. The C sputtering current and its energy were fixed at 50 mA and 1200 eV respectively. Five different Cu-DLC films with an approximated thickness of 1 μm (which were respectively denoted as A0–A4 in Table 1) were fabricated.

Cu content in the films was determined by an energy dispersive spectrometer attached to a scanning electron microscope. The Cu nanocrystallite sizes and structure characteristics in the amorphous carbon network were analysed and compared using X-ray diffractometer and Raman spectroscopy respectively. The film hardness was measured by a nanoindenter loaded under 2 mN. Intrinsic stress $\sigma$ in each film was determined using Stoney equation, in which the curvature radius of the substrate before and after deposition was measured by a surface profiler. Toughness of the Cu-DLC films was measured by a scratch tester under a progressive normal load ranging from 3 to 80 N; the value of each adhesion force was the averaged value of six measurements on each sample; scratch failure regions were further observed using an optical microscope. The tribological behaviour of the films in ambient atmospheric condition was evaluated using a ball on disc tester under a normal load of 2 N and slid at a speed of 0-65 m s$^{-1}$ for a distance of 1000 m.

<table>
<thead>
<tr>
<th>No.</th>
<th>Film</th>
<th>$I_{target}$/mA</th>
<th>Cu at-%</th>
<th>$D_{grav}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>a:C-Cu0%</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A1</td>
<td>a:C-Cu4%</td>
<td>18</td>
<td>5.4</td>
<td>7.2</td>
</tr>
<tr>
<td>A2</td>
<td>a:C-Cu10%</td>
<td>40</td>
<td>10.5</td>
<td>15.1</td>
</tr>
<tr>
<td>A3</td>
<td>a:C-Cu14%</td>
<td>60</td>
<td>16.2</td>
<td>26.3</td>
</tr>
<tr>
<td>A4</td>
<td>a:C-Cu18%</td>
<td>92</td>
<td>20.7</td>
<td>53.2</td>
</tr>
</tbody>
</table>

Table 1 Cu percentage and nanograin size of fabricated a:C-Cux% films

Results and discussion

The individual Cu atomic percentages and nanograin sizes as measured from the five deposited a:C-Cux% films were tabulated in Table 1, suggesting that the copper contents in the Cu-DLC films vary from 0 to 26-7 at-% and their corresponding Cu nanograin sizes span from 0 to 53-2 nm. A direct proportional relationship can be obtained by correlation of Cu atomic percentage and nanograin sizes in Table 1. It implies that the Cu ion flux is a dominating factor to control both Cu content and its grain size under the condition of fixed ion energy.

Raman spectra of the deposited Cu-DLC films were also investigated, generating two curves in Fig. 1 for behaviour change exhibition of G peak positions of Raman spectra and $I_D/I_G$ ratios with respect to various Cu contents. As metal atoms in the amorphous carbon matrix act as catalysts in the formation of $sp^2$ sites, $I_D/I_G$ ratio is also proportional to the fractional ratio of $sp^2$/($sp^2$ + $sp^3$) bonds within the DLC films caused by Cu content increase. The $I_D/I_G$ ratio is also proportional to the fractional ratio of $sp^2$/($sp^2$ + $sp^3$) bonds within the DLC films. Figure 1 indicates that the increase in Cu contents basically leads to the decrease in $I_D/I_G$ ratios and also the increase in G peak positions to its higher wave numbers. These characteristics obviously suggested that the graphite-like $sp^2$ bond increases when deposited with higher Cu content in the films. The property of C bonds ($sp^2$ or $sp^3$) determined the surface morphology and frictional characteristics of Cu-DLC films. Also, as the internal stress in DLC will decrease with the increase in $sp^2$ content, the internal stress of the Cu-DLC films may tend to decrease with increasing Cu content.

Both hardness and stress values of the coating are dependent on the accumulative effects of the deposition parameters. The present hardness measurements are accurate to ±5%. The variation of the measured hardness and intrinsic (compressive) stress of Cu-DLC films with the Cu content is shown in Fig. 2. Each Cu content corresponds to a hardness and intrinsic stress value. When the Cu content is increased, the hardness value suddenly increases from 24-2 GPa at 5-4 at-%Cu to a maximum value of ~36-7 GPa at 10-5 at-%Cu. It then gradually decreases to a minimum value of ~13-4 GPa at 26-7 at-%Cu. The trend of the intrinsic stress values shows an initial decrease from the maximum value of 3434 MPa at a:C-Cu0% to 2207 MPa at a:C-Cu4%.
followed by another slight decrease to 2146 MPa at a:C–Cu10–5%. Then the intrinsic stress value drastically reduces to 1078 MPa at a:C–Cu5–7%. The curves in Fig. 2 show that increasing Cu content at 10–5 at.% results in a significant increase in the hardness and a simultaneous decrease in the intrinsic stress for the highest film hardness. The dependence of the hardness and the intrinsic stress on the Cu content is rather complex with two competing and contradicting factors taking effect in Cu-DLC films. On the one hand, as the size of metal atoms such as Cu is much larger than C atoms, the addition of Cu to the film will cause an increase in intrinsic stress. On the other hand, the film hardness and intrinsic stress tend to decrease with increasing Cu content. The final condition of hardness and residual stress depends on the combined action of these two factors. Suitable content of Cu doped in amorphous carbon matrix and favourable size of the formed Cu nanograins are likely to optimise the mechanical property of the film, resulting in high hardness and low intrinsic stress for a good toughness.

During the scratch test, the ‘lower critical load’ ($L_{c1}$) represents the minimum load at which a failure or cracking occurs, and the ‘higher critical load’ ($L_{c2}$) represents the load at which the film will completely peel off. A scratch crack propagation resistance (CPRs) CPRs=$L_{c1} (L_{c2} - L_{c1})$ obtained from the critical load data has been proposed in literature to assess the toughness of nc-TiN/a-SiNx thin films. The lower critical load $L_{c1}$ represents the resistance to initiation of cracks. The difference between the higher and the lower critical load ($L_{c2} - L_{c1}$) refers to how long the film can stay between a crack initiation and a catastrophic failure. Therefore, higher CPRs indicates higher toughness of the film.

In this work, we estimated the CPRs values of Cu-DLC films in the scratch test as an indication of thin film toughness. Figure 3a and b shows the $Lc$ values and CPRs of the deposited Cu-DLC films as a function of Cu content. According to Fig. 3a and b, doping copper with nanograin sizes in DLC films significantly improves $Lc_1$, as well as the CPRs values of film, showing the improved cracking initiation resistance and the higher propagation resistance of the crack during the scratch test. Film of a:C–Cu10–5% has the highest CPRs as well as $Lc_1$ among the five films, which means that it has the best toughness.

Figure 3c presents the damage evolution of a:C–Cu10–5% film during scratch test under a progressively applied normal load from 3 to 80 N. Figure 3c-1 shows the change of scratch after the test. Figure 3c-2–c-4 shows the partially magnified images of Fig. 3c-1. The first damage mark on the scratch trace can be seen in Fig. 3c-2. The appearance of the first flaking shown in Fig. 3c-3 reveals the crack initiation resistance. The appearance of the complete failure of the DLC on the surface shown in Fig. 3c-4 reveals the film propagation resistance of the crack. Analysis of the morphologies suggests that the synthesised Cu-DLC films have good toughness to resist severe damages.

Results from the CPRs value and the damage evolution of the deposited film jointly reveal that doping Cu with nanograins sizes, especially at a suitable content of 10–5 at.% will significantly improve the crack initiation resistance and the propagation resistance of the crack during the scratch test, which demonstrates the improved toughness.

![Graph](https://example.com/graph.png)

3 a $Lc$ values and b CPRs of Cu-DLC film as function of Cu content and c optical observation of scratch trace for a:C–Cu10–5% film during scratch test

Figure 4 compares the steady state coefficient of friction (COF) $\mu$ with the wear rate as determined after a sliding distance of 1000 m for the Cu-DLC films deposited with the different Cu contents. The transient stage COF of the individual films exhibited an initial increase, followed by a drop and then another slow increase before stabilisation to a steady state $\mu$, which varies between 0–110 and 0–194. The COF of 0–194 for a:C–Cu0%, film is closer to the upper limit of the normal range of 0–10–0–20 for pure sputtered DLC films. When the Cu content starts to increase, the value of $\mu$ initially decreases from the maximum value of 0–194 for a:C–Cu0% to the minimum value of 0–110 for a:C–Cu10–5% and it then increases gradually to 0–187.
Effect of Cu content on frictional coefficient and wear rate of Cu-DLC films

for a:C–Cu26–7%. The values of wear rate (as shown in Fig. 4) were calculated by measuring the averaged worn cross-sectional area on the film specimen using a surface profiler at 20 equally spaced positions along the worn trace. The wear rates (within ±5% accuracy) are between 3–7% and 8.1 × 10⁻⁹ mm³ N⁻¹ m⁻¹ and assume a similar trend as µ with respect to Cu contents. The wear rates obtained from the measurements are low and well within magnitude order of 10⁻⁹ mm³ N⁻¹ m⁻¹.

Conclusions

Five Cu-DLC films were deposited on Si (100) substrate using an IBAD system. The influence of nanocrystalline Cu incorporation on the toughness was investigated as well as the microstructure, mechanical and sliding tribological behaviours of the Cu-DLC films. Within a suitable range of the Cu content and the nanograin size, the film toughness and hardness were increased while its compressive stresses and the COF of the Cu-DLC film were reduced. A Cu-DLC film of 10–5 at-%Cu with low compressive stress and high hardness exhibits the highest CPRs value, demonstrating the best toughness performance and resulting in the favourable combined tribological behaviours.

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