Mechanical properties of gradient pulse biased amorphous carbon film

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Abstract

A new method to prepare compositional amorphous carbon (a-C) film termed gradient pulse bias is presented. The a-C film prepared this way showed outstanding mechanical and excellent tribological properties. The hardness and reduced modulus of the film are calculated to be 66 GPa and 320 GPa respectively. A wear rate of $1.3 \times 10^{-8}$ mm$^3$/N m and frictional coefficient of 0.1 was also recorded. The novel film is also compared with multilayered and single layer a-C film prepared using the same system.
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1. Introduction

Silicon (Si) based micro/nano-electromechanical systems (M/NEMS), especially those requiring extensive sliding and rolling contacts suffers from high infant mortality rate due to mechanical failures from wear and low hardness [1–3]. This is an intrinsic material drawback which can only be resolved by avoiding rubbing contacts altogether. However this is not a viable solution to micro mechanical assemblies (MMAs) such as micro gears and motors requiring energy transfer through forced contacts. An alternative solution is to use a different base material.

Amorphous carbon (a-C) is a disordered mixture of the various allotropes of carbon. Of which, two of the most prominent form are diamond (sp$^3$ hybridized) and graphite (sp$^2$ hybridized). A-C is a blend between the two hybridization and its properties is largely determined by the amount of each kind within its matrix. Higher sp$^3$ content generally gives a much harder and wear resistance material [4] which is good for MMAs. Although there are many methods to synthesise a-C, one of the best method is the Off Plane Double Bend Filtered Cathodic Vacuum Arc (OPDB-FCVA) technique [5–11]. This deposition method generally produces ultra high quality a-C films with high density (3.4 g/cm$^3$), high hardness (75 GPa), high Young’s modulus (700 GPa), low friction coefficient (0.08), low wear rate (0.7 $\times$ $10^{-8}$ mm$^3$/N m), low surface roughness (≈ 0.1 nm, r.m.s.) and negligible hydrogen content. The sp$^3$ content (≈ 85%) is so high that this form of a-C is sometimes termed as tetrahedral-amorphous carbon (ta-C).

However the as deposited a-C films produced by the OPDB-FCVA suffers from high intrinsic stress (≈ 9 GPa) which causes film delamination from the substrate after ∼ 100 nm of deposition [12,13]. This limited the potential applications of the film tremendously. A solution to reduce the stress and improve adhesion was to use a voltage pulse bias at the substrate holder during deposition [14]. This enables films in excess of 1 μm to be deposited in a single process with relatively lower compressive stress (≈ 500 MPa). However, this film has much lower sp$^3$ content (60%) and subsequently lower hardness and wear resistance.

This prompted the studies of composite multilayer a-C films that have discreet modulation of high sp$^3$ and low sp$^2$ content [15–18]. Multilayer a-C films has slightly better hardness and wear properties but still is not near as good as ta-C. In this paper, we propose a new modification technique that creates a unique non-discreet composite a-C film that has stress levels lower than multilayer films but with hardness and wear properties near that of ta-C. We term this technique, gradient pulse bias (GPB). Unlike the multilayer technique that uses a high/low pulse voltage bias at the substrate, which induces step layering to create a film, the GPB method uses a continuously varying pulse voltage to achieve low stress film growth.
2. Experimental

The film was deposited onto 4” n++ silicon wafers using a commercial OPDB-FCVA in conjunction with a substrate pulse voltage generator. A 99.999% pure graphite target was employed with an arc current of 80 A. Chamber deposition pressure was maintained at ∼3 × 10⁻⁵ Pa. To ensure uniformity, the substrate was rotated during deposition.

In order to deposit the GPB film, a continuously varying pulse voltage bias was employed at the substrate throughout the deposition. The voltage was set at negative 3000 V at the start of the deposition and reduced linearly to 0 V by the end of the deposition process. The substrate pulse voltage generator was set at pulse width 25 μm, frequency 600 Hz and voltage gradient of 5 V/s. The entire deposition took 600 s.

For properties comparison, different graded multilayer a-C samples as well as single layered samples were also fabricated. The same OPDB-FCVA under the same deposition environment was used and the details of the process has been described elsewhere [15]. The different types of films deposited are summarized in Table 1. Samples 1 to 3 represent the range of multilayer films tested. All the multilayer films are composed of 10 identical layers. Each layer consists of a hard and a soft sublayer. The hard and soft sub-layers are similar to a-C films prepared using the OPDB-FCVA with substrate bias (−3 kV) and without biasing respectively. The reason for the term hard and soft is because a-C films prepared by the OPDB-FCVA without bias have a hardness of ∼52 GPa while films deposited with a substrate pulse bias of −3 kV has hardness of only ∼25 GPa [19]. Sample 4 is prepared by pulse biasing the substrate with −3 kV throughout the deposition process and sample 5 is deposited under −100 V to create an ultra hard ta-C film [19]. The GPB film is represented as sample 6. All films studied were 1 μm thick with the exception of sample 5 which is 100 nm.

2.1. Film stress

The internal stress of the films were calculated by measuring the wafer curvature before and after deposition of the film, and applying Stoney’s equation [20] given by,

\[ \sigma_s = \frac{E_s t_s^2}{6(1 - \nu_s)} \frac{1}{t_c} \left(1/R - 1/R_o\right) \]

Where \(E_s\), \(\nu_s\), \(t_s\) and \(t_c\) are the Young’s modulus, Poisson ratio, thickness of the substrate and of the film, respectively. \(R_o\) and \(R\) are the radii of curvature of the bare and coated substrate, respectively.

2.2. Hardness and reduced modulus

To investigate the mechanical properties such as hardness and elastic modulus of the film, nanoindentations experiments, using a Hysitron triboscope with a Berkovich diamond tip was used. Calibration of the diamond tip was done using a fused silica standard periodically throughout the indentation experiments. No significant drift of the Young’s modulus was detected and therefore the area function of the tip could be approximated to be constant throughout all the tests. Creep and drift were minimized by keeping the loading rate (100 μN/s) and temperature (26 °C) constant throughout all the indentations. In order to extract the elastic and hardness properties of the samples, a software attached to the instrument, digitally records the load–displacement characteristic of the indentations and fit the unloading points by a power law curve.

The reduced modulus \(E_r\) could be gained from the contact stiffness \(S\) on any point on the unloading curve using the following relations [21].

\[ S = \frac{dF}{dh} \]

\[ E_r = 0.5 \left( \frac{S}{A_c/\pi} \right)^{1/2} \]

Where \(F\), \(A_c\) and \(h\) are the applied force, contact area and depth respectively. The depth of the indentation was always less than 100 nm (10% of film thickness) to minimize substrate effects associated with deep indentations. The hardness used in this paper is Meyer hardness \(H_M\), obtained by

\[ H_M = \frac{F}{A_c} \]

where \(F\) and \(A_c\) have the same meaning as above. The averages of 10 indentations were used for all properties extraction.

2.3. Tribology

To investigate the tribological properties of the films, a pin-on-disk tribometer was employed to measure the circular sliding resistance of the various films. A software recorded the coefficient of friction versus the wear cycles as the dynamic friction spectra. The coefficient of friction was extracted from the steady value of the spectra. The tests were all conducted under a controlled environment under ambient air with relative humidity (RH) ~50% and temperature at 26 °C. The static friction partner used was sapphire. The tests parameters were set at a constant load of 2 N, linear speed of 0.1 m/s and wear track of 2 mm for 30,000 cycles. The wear rate was then calculated from the cross-sectional area of the wear track, which was measured using a surface profile meter. To ensure better accuracy of the calculations, 4 different points on the wear track are used to find an average.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Soft sub-layer thickness (nm)</th>
<th>Hard sub-layer thickness (nm)</th>
<th>Total thickness of film (nm)</th>
<th>Ratio of soft to hard sub-layer thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (multilayer)</td>
<td>75</td>
<td>25</td>
<td>1000</td>
<td>3:1</td>
</tr>
<tr>
<td>2 (multilayer)</td>
<td>50</td>
<td>50</td>
<td>1000</td>
<td>1:1</td>
</tr>
<tr>
<td>3 (multilayer)</td>
<td>25</td>
<td>75</td>
<td>1000</td>
<td>1:3</td>
</tr>
<tr>
<td>4 (single)</td>
<td>–</td>
<td>–</td>
<td>1000</td>
<td>–</td>
</tr>
<tr>
<td>5 (single)</td>
<td>–</td>
<td>–</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>6 (GPB)</td>
<td>–</td>
<td>–</td>
<td>1000</td>
<td>–</td>
</tr>
</tbody>
</table>

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Lastly, a commercial atomic force microscope (AFM) was used to determine the r.m.s. surface roughness of the samples. The evaluation is done on an area of 5 μm².

3. Results and discussion

3.1. Stress

Table 2 shows the compressive stress of the various films.

The compressive stress of the multilayer films averaged at 3 GPa. The highest stress displayed among the 3 films was from sample 3 having a compressive stress of 4.2 GPa. Despite being relatively thin at 100 nm, the stress of the ta-C film is extremely high at 9 GPa and signs of delamination can be seen at the edge of the film. At only 1.5 GPa, the stress of the GPB film is significantly lower than any of the multilayer samples.

This represents a significant improvement in stress reduction of compositional a-C films prepared by the OPDB-FCVA. The nature of stress generation of the film is now different from those of discreet graded films. Instead of well defined layers adding up to a final film, the GPB a-C film does not have clear distinct “layers” but is instead made up of a film that is continually varying in internal composition. The stress properties would therefore likely be a result of both the total sp³/sp² fraction as well as the degree of change of sp³/sp² fraction or “gradient” of the film. Since the GPB film is deposited by linearly varying the bias during deposition from −3000 V to 0 V, a large portion of the composite a-C film is deposited while under high voltage bias. This in effect created a large low stress initial portion to offset the much higher stress portion near the top of the film. Due to this large initial low stress region, the overall stress value of the GPB film is therefore relatively low.

3.2. Hardness and reduced modulus

Except for the single layer samples, the rest of the films are composite in nature. The GPB film is no exception. The internal structure of the film varies across its thickness. Therefore some of its material properties, especially mechanical properties would be dependant on the depth of the sample. In order to study how the depth (or thickness) of the sample affect the indentation hardness, a range of indentation depth was investigated. The results are shown in Fig. 1. For comparison, a composite multilayer film (sample 1) was also tested in the same way.

From Fig. 1, the average hardness of the GPB film is ~66 GPa while the multilayer film is ~33 GPa. Both the GPB film and multilayer film were observed to be softer as the indentation depth increases. But this trend is far more pronounced in the case of the multilayer film. This could be due to the layering nature of the multilayer film. Since the top 25 nm of the film consists of the hard sub-layer it is not surprising that with shallow indents the film would show hardness close to 40 GPa. However with deeper indents, the much softer soft sub-layer starts to affect the hardness measurements more significantly causing the hardness to drop below 35 GPa. Although the GPB film is also compositional in nature, the degree of change throughout the film can be controlled by the differential gradient of the voltage pulse bias. Therefore a large portion of the top of the film could be “tune” to be hard while the bottom is low in stress. Moreover, since the change is gradual, the change of hardness with depth would be less pronounced.

For easy cross reference between the various samples, Table 2 summarizes the indentation hardness and reduced modulus obtained for an indentation depth of 50 nm for all samples except for sample 5. Since sample 5 is only 100 nm thick, the properties were obtained at an indentation depth of 10 nm. From the results it is clear that although the GPB film has hardness nearest to that of the pure ta-C film it also shows a 6 times decrease in compressive stress. These results are remarkable considering that the hardest multilayer film has a hardness of only 41 GPa but stress levels almost 3 times higher than the GPB film.

Coefficient of friction, wear rate and surface roughness of the films

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Film type</th>
<th>Coefficient of friction</th>
<th>Wear rate (10⁻⁸ mm²/N m)</th>
<th>Surface roughness (RMS), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Multilayer a-C</td>
<td>0.1</td>
<td>3</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>Multilayer a-C</td>
<td>0.15</td>
<td>2.1</td>
<td>0.17</td>
</tr>
<tr>
<td>3</td>
<td>Multilayer a-C</td>
<td>0.12</td>
<td>1.6</td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td>Single layer a-C</td>
<td>0.09</td>
<td>3.8</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>Single layer ta-C</td>
<td>0.1</td>
<td>1.2</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>Gradient Pulse</td>
<td>0.1</td>
<td>1.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Bias a-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
reduced modulus of the GPB film is also significantly higher than those of the multilayer films.

3.3. Tribology

The results from the various tribological tests are summarized in Table 3. The results shows that the GPB film has better wear resistance, frictional properties and surface roughness than any of the multilayer films. The most critical among these properties for MMAs is the wear rate. The GPB film has a wear rate of $1.3 \times 10^{-8} \text{ mm}^3/\text{N m}$ which is comparable to the wear rate of $1.2 \times 10^{-8} \text{ mm}^3/\text{N m}$ recorded for the ta-C film.

The wear properties exhibited is not surprising since the top portion (100 nm) of the GPB film is biased between 0 to $-300 \text{ V}$ which is known to create high sp$^3$ content a-C film [19]. However as the wear progresses towards the underlying portion of the film, the wear resistance may be lowered. This is because the bottom portion of the film is softer than the top.

4. Conclusion

The mechanical and tribological properties of the GPB a-C film have been studied. Comparing with current multilayer a-C films prepared using the OPDB-FCVA, it shows much better mechanical properties. The hardness of the GPB film is $\sim 66 \text{ GPa}$ at an indentation depth of 50 nm and has a reduced modulus of 320 GPa. The frictional characteristic of the film is similar to those of the multilayer film and comparable with that of ta-C. The wear rate of the film is also better than all the multilayer films studied in this paper.

Overall, the GPB a-C film have shown mechanical and wear properties close to those of ta-C but with only a fraction of the compressive stress associated with it. This material shows good prospect to be a base material for MMAs and other types of MEMS. Due to its high hardness, relatively low stress and simple deposition method, it could find applications in coating and surface protection as well.

References