Effect of nanocrystalline silver impregnation on mechanical properties of diamond-like-carbon films by nano-indentation

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Received 16 January 2012; revised 27 January 2012; accepted 8 February 2012

Nano-crystalline silver was embedded in diamond-like-carbon films by capacitatively coupled plasma chemical vapour deposition. Films with different nanocrystallite sizes and volume fractions of silver, deposited on glass and silicon (100) substrates have been studied by nano-indentation to evaluate the modulation of mechanical properties caused by silver incorporation into the diamond-like-carbon. Raman, atomic force microscopy, energy dispersive X-ray studies and X-ray diffractions have been utilized to determine the structural properties as well as the bonding environment in these films. Mechanical properties have been seen to be modulated significantly by nanocrystalline silver incorporation.

Keywords: Diamond-like carbon, Nano-crystalline silver, Hardness, Frictional coefficient

1 Introduction

Use of pure diamond-like-carbon (DLC) films having promising mechanical, optical and electrical properties are retarded due to inherent high compressive stresses induced by the sp³ carbon bonding during the synthesis. Researchers are trying to deposit metal-DLC composite coatings that would combine high hardness, elevated ductility and toughness since pure DLC films lacked toughness and resistance to cross-sectional crack propagation. Incorporation of nanoparticulated silver (Ag) in different dielectric matrix has been reported by a number of groups and the effect of adding silver to DLC coatings has been tested to be beneficial in a variety of applications utilizing its remarkable surface plasmon resonance, antibacterial and surface enhanced Raman spectroscopic characteristics.

Numerous techniques that include precipitation, physical vapour deposition (PVD), chemical vapour deposition (CVD), thermionic, vacuum arc, plasma immersion ion implantation and organic encapsulation were used in the past to incorporate silver in DLC matrix. But, the main hurdle to the widespread application of metal nanoparticles is their agglomeration due to high surface energy. In recent times, silver nanoparticles in DLC matrix (nAg-DLC) was incorporated by Ahmed et al. for the enhancement of field emission properties of DLC films. Silver incorporation in DLC matrix by CVD cum sputtering technique and related surface plasmon resonance effect were reported by Paul et al. Wang et al., Lungu et al. and Zhang et al. reported the effect of silver incorporation in DLC films and associated modulation of tribological properties. But, incorporation of lb metal nanoparticles with homogeneous dispersion in DLC matrix by CVD technique seemed to be still a challenge to the scientists. The surface and nano-tribological properties of these films are not yet completely understood.

In the present paper, the mechanical properties of nAg-DLC composite films deposited by CVD-cum-sputtering technique have been studied. Films have been characterized by atomic force microscopy (AFM) and transmission electron microscope (TEM). Raman and glancing incidence X-ray diffraction (GIXRD) studies have been carried out to obtain information on the bonding environment in these films. Mechanical properties of these films have also been studied by nano-indentation characterization. The results are reported here.

2 Experimental Details

nAg-DLC films were deposited by capacitatively coupled radio frequency (13.56 MHz) plasma enhanced chemical vapour deposition, details of which had been reported in Ref. 9. In short, plasma
was generated between two circular aluminium discs (2.54 cm in diameter), the top one holding a 1.0 mm thick silver disc. The whole assembly was housed in a stainless steel CVD chamber which could be evacuated to a level of 0.133 mPa before deposition. The nAg-DLC were deposited at 100 W rf power onto glass and Si (100) substrates kept at room temperature (300 K) by using pre-mixed methane+argon gas mixtures with argon in four different proportions (50%, 60%, 70% and 80%). Pure DLC film without silver incorporation was deposited by replacing the top disc with a pure aluminium disc.

Micro-structural studies were carried out by a TEM (Hitachi, Japan). For surface characterization, AFM (Nanosurf Easy Scan2) was used and the images were recorded in contact mode. GIXRD studies were carried out by Bruker D8 advance X-ray diffractometer at grazing a constant incidence (3 degree). Compositional information was obtained by using an energy dispersive X-ray (EDX) instrument (AMETEK EDAX\textsuperscript{TM} analyzer). Renishaw inVia micro-Raman spectrometer (514 nm Argon laser) was used to record Raman spectra. Mechanical properties have been determined by nano-indentation (tetrahedral diamond Berkovich tip) characterization using a Tribo Indenter 700 UBI, Hysitron, USA, having load range between 0.1 and 12,000 µN. Thermal drift was lower than 0.05 nm/s during the measurement. The resolution of measurement was 1 mN (Force) and 0.4 nm along Z axis (Depth).

The hardness and Young’s moduli of the present DLC and nAg-DLC films have been calculated from the experimentally measured load depth plots using the well established Oliver and Pharr\textsuperscript{17} method. For a given peak load, at least four nano-indents have been made at a given fixed loading rate at each of the five randomly chosen different locations of the sample. Thus, each reported value of hardness was an average of at least 20 or more individual data points. The same is true of the Young’s moduli data. Further, to evaluate the depth dependence of the hardness and Young’s moduli data; the partial unloading experiments of 53 cycles were conducted on both DLC and nAg-DLC films at a constant peak load of 1000 µN keeping the loading rate fixed at 0.09 µNs\textsuperscript{-1}. This variation of load or normal force with time during the indentation experiment is shown in Fig. 1(a) for a typical partial unloading condition.

For the evaluation of the tribological properties of the DLC and nAg-DLC films, single pass nano-scratch experiments have been conducted at a constant load of 100 µN with the same Berkovich indenter. The variations of normal force (load) as well as x-displacement with time during tribology experiments are shown in Fig. 1(b). The lengths of the scratches have been kept fixed at 8 µm. At least five scratches have been made at each of the five randomly chosen different locations of the sample at a given loading rate for a given peak load. Thus, each reported value of friction coefficient was an average of at least 25 or more individual data points.

3 Results and Discussion

In the CVD cum sputtering technique, introduction of increased amount of argon in the argon-methane gas mixture would culminate in higher incorporation of silver nanocrystallites in the DLC films due to enhanced sputtering of the silver target by the argon ions in the plasma. All the depositions have been carried out at a chamber pressure ~25 Pa. It may be noted here that in this high pressure regime, the ejected silver particles from the target would undergo numerous collisions with the argon gas atoms leading to fragmentation of the silver particles. These silver nanoparticles would nucleate on the substrate and grow by rapid condensation to form ultra-fine particles along with the DLC deposition by plasma CVD leading to a composite film of nAg-DLC.

3.1 Micro-structural studies

The AFM images for the four representative films are shown in [Fig. 2(a-d)] and the insets show the corresponding TEM micrographs. One may observe that the size and distribution of the silver nanocrystallites changed with increased silver
incorporation in the DLC matrix. The number density of the particles increased with increasing amount of argon in the plasma during deposition. Formation of larger agglomerates in films deposited with higher silver content is apparent from Fig. 2. The shape and the size distribution were narrower for the films deposited with lower concentration of argon in the plasma [Fig. 2(a,b)] than those deposited with higher amount of argon in the plasma [Fig. 2(c,d)]. Average grain size varied between 11 and 36 nm (Table 1). Fig. 3(a) shows the EDX spectra of a representative film deposited with 80% Ar in the plasma. The peaks of energy corresponding to O, Na, Mg, Si and Ca might have arrived from the substrate. The EDX spectra showed that the silver content in the films increased from 6 at % to 15.4 at % (Fig. 3b) with the increase in argon content in the methane+argon plasma.

### 3.2. XRD analysis

Glancing incidence angle XRD traces of the nAg-DLC films deposited with four different proportions of argon (50%, 60%, 70% and 80%), in argon and methane gas mixtures are shown in Fig. 4.

![Fig. 2 — AFM micrographs of four representative nAg-DLC films deposited with different amount of argon in methane+argon gas mixtures: (a) 50%, (b) 60%, (c) 70% and (d) 80%. Insets show the corresponding TEM micrographs](image)

<table>
<thead>
<tr>
<th>% of Ar</th>
<th>Thickness of DLC (nm)</th>
<th>Thickness of nAg-DLC (nm) from TEM</th>
<th>nAg-DLC size (nm) from XRD</th>
<th>Strain from XRD</th>
<th>$I_D/I_G$ for pure DLC Film</th>
<th>FWHM of G-peak for pure DLC film (cm$^{-1}$)</th>
<th>$I_D/I_G$ for nAg-DLC film</th>
<th>FWHM of G-peak for nAg-DLC film (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>65</td>
<td>50</td>
<td>11</td>
<td>1.56</td>
<td>0.113</td>
<td>0.809</td>
<td>112</td>
<td>0.771</td>
</tr>
<tr>
<td>60</td>
<td>68</td>
<td>70</td>
<td>21</td>
<td>1.12</td>
<td>0.028</td>
<td>0.807</td>
<td>114</td>
<td>0.721</td>
</tr>
<tr>
<td>70</td>
<td>70</td>
<td>88</td>
<td>18</td>
<td>2.07</td>
<td>0.102</td>
<td>0.802</td>
<td>128</td>
<td>0.717</td>
</tr>
<tr>
<td>80</td>
<td>75</td>
<td>105</td>
<td>36</td>
<td>5.87</td>
<td>0.165</td>
<td>0.791</td>
<td>134</td>
<td>0.671</td>
</tr>
</tbody>
</table>
Predominant peaks arising out of reflections from (111), (200), (220) and (311) are visible in the XRD traces. Intensity of the strongest (111) peak increased for films deposited with increasing amount of argon in the plasma. Insets of Fig. 4 show the glancing angle XRD traces for the corresponding pure DLC coatings.

It may be noted here that the XRD traces of pure DLC films resembled that for an amorphous material.

Line profile analysis (LPA) was adapted to characterize the nAg-DLC films deposited. It is customary to assess the size-strain relationship and correlate them with physical properties (mechanical) of the resulting materials. We have utilized the Scherrer relation\(^\text{18}\) to extract the size of the coherent diffracting domains from diffraction peak. The apparent domain size, a volume-weighted quantity, is given by:

\[ t = \left( \frac{K}{\text{FWHM}} \right) \cos \theta \quad \ldots(1) \]

where \( K \) is a constant close to unity, \( \lambda \) is the wavelength of the X-ray used and FWHM corresponds to the full width at half maximum of the peak and \( \theta \) the Bragg angle of the \([h k l]\) reflection. Then, Wilson\(^\text{19}\) defined an “integral breadth apparent size” that is also a volume-weighted quantity:

\[ (D)_v = \left( \frac{K}{\text{FWHM}} \right) \cos \theta \quad \ldots(2) \]

where, the integral breadth \( \beta = \frac{A}{\sqrt{I_0}} \), \( A \) being the peak area and \( I_0 \) the height of the observed line profile. In both the relations, the peak broadening was attributed to the effect of the diffracting coherent domain size. When the broadening is solely due to the strain effect, the following Stokes and Wilson\(^\text{20}\) may be applied:

\[ \eta = \beta \cot \theta \quad \ldots(3) \]

\[ e = \frac{\eta}{4} = \left( \frac{\beta}{4} \right) \tan \theta \quad \ldots(4) \]

where \( \eta \) is the “apparent” strain and \( e \) is the maximum strain. In all practical cases, line broadening occurs due to simultaneously size and lattice distortion effects. In such cases, Williamson-Hall plot\(^\text{21}\) may conveniently be utilized to separate these two effects. In this technique, plots of \( \beta \) for all the reflections of the sample are expressed in terms of reciprocal unit \( [\beta^\alpha = \beta \cos(\theta)/\lambda_0] \), as a function of \( d^\alpha \) \( [d^\alpha = 2 \sin(\theta)/\lambda_0] \).

It is apparent that the plot of \( \beta^\alpha \) versus \( d^\alpha \) would be a straight line and the intercept would give the particle size \( [K/(D)_v] \) while the slope would give the strain \( (2\eta) \). Fig. 5 shows that such plots for all the nAg-DLC films deposited here. The variation of particle size and strain in these films are presented in Table 1. It could be seen that the crystallite size determined from the above calculations is lower than that obtained from the TEM studies. This is basically due to conglomeration of such crystallites forming
polycrystallites which are apparently visible in the TEM micrograph. Increase in particle size (and associated polycrystallite size) with increased argon content in the plasma is apparent from XRD and TEM studies.

3.3 Raman measurements

Typical Raman spectra of four representative pure DLC and nAg-DLC films deposited with different amount of argon in the plasma, are shown in Figs 6 (a and b), respectively which indicates the presence of two broad peaks located at ~1373-1388 cm$^{-1}$ (D-line) and ~1581-1587 cm$^{-1}$ (G-line). The D-lines indicated a shift in the peak positions towards lower wave number with the incorporation of nanocrystalline silver in them (Fig. 6b). It is known that the bond length of rings are higher than that of chains (olefins) and this would result in shift in vibrational frequency to lower wave number. Thus, the Raman studies indicate that these films are composed of sp$^2$ bonded carbons dispersed in a sp$^3$ bonded carbon matrix.

The DLC films are established to consist of a mixture of tetrahedral (sp$^3$) and trigonal (sp$^2$) bonding structures$^{22}$. Thus, one would expect the appearance of all possible forms of graphite and diamond (amorphous, microcrystalline and crystalline), distinguished from each other by the structure degree of disorder. This will be reflected in the observed shape of the Raman spectrum. It is known that one of the most important parameters characterizing the microstructure of disordered graphite is the $I_d/I_G$ ratio. This ratio is roughly proportional to the ratio of momentum non-conserving-to conserving phonons that contribute to the Raman spectrum$^{23}$.

It might be noted that no obvious bands originating from sp$^3$-bonded carbon at 1332 cm$^{-1}$ was present in our experimental Raman spectra. This would not necessarily mean that domains with a tetrahedral structure are absent in the deposited nAg-DLC films. The phonon-confinement effect is known to play a substantial role, leading to the shift and to the strong broadening of a fundamental diamond mode, usually observed at 1332 cm$^{-1}$. The G (graphite) peak is mainly sensitive to the configuration of sp$^2$ sites because of their higher cross-section. Thus, $I_d/I_G$ would be a measure of the size of sp$^2$ phase organized in rings and is roughly phonons that contribute to the Raman spectrum. But the full width at half maximum (FWHM) of the G-peak is mainly sensitive to structural disorder, which arises from bond angle and bond length distortions. FWHM of the G-peak would be small if the clusters were defect free, unstrained or molecular. Thus, for a given cluster size, a higher FWHM would lead to higher bond length and bond angle disorder and hence higher sp$^3$ content and higher band gap. Although, the intensity ratio between the D and G peaks ($I_D/I_G$) is a very useful parameter in Raman study but in many published data, the ratio of the integrated areas under the D and G peaks is presented to indicate the
bonding environment. It may be noted here that ratio of the areas under the D and G peaks may not be the best parameter to use since it is essentially equivalent to the product of the intensity ratio \(I_D/I_G\) and FWHM. Thus, it will be interesting to study the dependence of sp\(^2/sp\(^3\) ratios on \(I_D/I_G\) and FWHM separately, since they contain different information.

The integrated intensity ratios of \(I_D/I_G\) of all the films deposited here are presented in Table 1. The \(I_D/I_G\) values for the pure DLC films did not indicate any significant change when the films were deposited with increasing amount of methane in the plasma. But, nAg-DLC films showed a decrease in the integrated intensity ratio that would correspond to an increase in the graphite particle size with increasing silver content. The FWHM of the G-peak for DLC films was seen to decrease for films deposited with increasing amount of methane in the plasma indicating sp\(^3\)-rich ambience. But the FWHM of the G-peak for nAg-DLC films indicated significant change when deposited with increasing amount of methane in the plasma. It could be observed that the FWHM of the G-peak for nAg-DLC films increased when deposited with increasing amount of methane in the plasma. Thus, nAg-DLC films are rich in sp\(^3\) bonded carbon with larger bond-angle disorder when the films contained lesser amount of silver in the DLC matrix. Thus, inclusion of nanocrystalline silver in DLC matrix would culminate structural change and render the DLC matrix to be more graphitic in nature. It should be noted here that there is a small shoulder arising to be prominent, around 2928 cm\(^{-1}\), for the nAg-DLC films deposited with higher Ag content. This peak position is little higher compared to that of so called 2D Raman band generally observed for graphitic carbon films but could have been occurred due to red shift as described by Das et al\(^{24}\) for the increment of defects due to nanoparticulated Ag incorporation. This also confirms the graphitic nature of nAg-DLC films deposited with higher Ag content.

3.4 Mechanical properties

At this juncture, it would be interesting to study the modulation of the mechanical properties of the DLC films with the incorporation of silver nanoparticles in them. One may also try to correlate the observation with the \(I_D/I_G\) ratio or precisely sp\(^2/sp\(^3\) content in the films.

Typical in-situ SPM images of the impression of Berkovich indentation array of a typical pure DLC and nAg-DLC nanocomposites are shown in Figs. 7(a and b), respectively. The image scan size is 3.5 \(\mu\text{m}\). There is no visible damage in the nanoindented impressions of the base DLC50 and nAg-DLC nanocomposite films. A comparison of the nanoindent impressions in DLC50 and nAg-DLC50 nanocomposite films show that at the same comparable load, the area of the impression was much larger in nAg-DLC50 in comparison to that in DLC50. The hardness is automatically calculated by the computer, based on the areas of indentations. Fig. 7(c and d) shows typical in-situ SPM images for the tribology experiments on a typical pure DLC film and a nAg-DLC nanocomposite film. The image scan size is 10 \(\mu\text{m}\). The surface imaging by in-situ SPM imaging after the nano-scratching experiments did not yield any identifiable evidence of permanent deformation, suggesting that the scratching was predominantly elastic. The results from the micro scratch tests reveal that the scratch resistance is mainly dependent on the film thickness of the DLC layer as well as on the deposition parameters.

Figure 8 (a and b) shows the variation of the measured hardness and frictional coefficient, respectively of pure DLC and nAg-DLC films deposited with different argon content in the plasma. The hardness value of the nAg-DLC films sharply increased from the hardness of 1.8 GPa at 6 at % Ag
to a maximum value of approximately 4.2 GPa at 10 at % Ag. It then decreases to 1.5 GPa approximately at 15.5 at % Ag. This implies nAg-DLC films with the Ag content ~10 at % are harder than pure DLC film. This is in conformity with the observation by Wang et al.\textsuperscript{7} who also observed a sharp increase in hardness with ~10 at % silver inclusion in the DLC matrix. Adding Ag tends to relax the intrinsic strain in DLC films. XRD studies indicated (Table 1) that the intrinsic strain value would drop with silver inclusion up to 10 at % and then tend to increase with further silver inclusion. The coefficient of friction measured by nano-scratch tests for DLC and nAg-DLC films is shown in Fig. 8(b). It may be seen that pure DLC films have lower coefficient of friction and coefficient of friction increased significantly with silver inclusion in the DLC matrix. This observation is in conformity with that observed by Zhang et al\textsuperscript{10}. It may also be worth while to refer to the work of Lungu et al\textsuperscript{15} who observed that carbon inclusion as DLC phase in silver matrix led to the reduction of coefficient of friction.

At this juncture it will be prudent to observe that no regular dependence of the tribological properties with sp\textsuperscript{2}/sp\textsuperscript{3} ratios in the nAg-DLC films deposited here. We, thus, support the observation by Zhang et al\textsuperscript{10} and Wang et al\textsuperscript{7} who observed that hardness and the intrinsic stress on the Ag content is rather a complex phenomena. The hardness of DLC films is usually a result of the balance between the local increase in the mass density of the film and the lattice relaxation due to the thermal spikes in formations of sp\textsuperscript{3} hybridization. The process of doping Ag nanoparticles in the amorphous DLC matrix would possibly lead to two competing and contradicting effects. On one hand, the local density and the intrinsic stress of the nAg-DLC films would be enhanced due to the difference in sizes of Ag and C atoms. On the other hand, energy transfer to the growing film from the plasma stream will be greater. The final condition of a film would depend on the compromise of these two effects. Thus, one may incorporate suitable amount of Ag nanoparticles of suitable sizes in the amorphous carbon matrix which may increase the hardness and reduce the intrinsic stress of nAg-DLC film.

4 Conclusions

nAg-DLC nanocomposite films with various volume fractions of silver were prepared by using capacitatively coupled plasma (CCP) chemical vapour deposition technique (CVD). Silver nanocrystallite size increased from 2.7 nm to 3.5 nm for films deposited with increasing amount of silver in the DLC matrix. Raman studies indicated the presence of two broad peaks located in the range of ~1373 and 1388 cm\textsuperscript{-1} (D-line) and ~1583 cm\textsuperscript{-1} (G-line). Both the D- and G-lines indicated a shift in the peak positions towards higher wave number with the incorporation of nanocrystalline silver in them. The attempt to use nano-indentation was successful to evaluate the nanomechanical and nanotribological properties of the nAg-DLC nanocomposite films wherein in-situ SPM imaging was utilized to depict the details of the deformation features in static and dynamic contacts. The nAg-DLC nanocomposite films showed lower nanohardness and elastic moduli compared to those of the DLC films as expected, because Ag incorporation increased the ratio of sp\textsuperscript{2}/sp\textsuperscript{3} hybridization affected through the increase in the percentage of argon from 50% to 80%.

![Fig. 8 — Variation of (a) Hardness*, (b) Young’s modulus* and (c) coefficient of friction values of pure DLC and nAg-DLC films as a function of Ar % in the plasma during deposition. (*measured at 30 nm depth)](image)
Acknowledgement

The authors like to thank the University Grants Commission (UGC), New Delhi, Government of India, for extending financial assistance in carrying out this programme.

References