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Nanoindentation measurements on modified diamond-like carbon thin films

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ABSTRACT

In the present study, we explored the effect of metallic interlayers (Cu and Ti) and indentation loads (5–20 mN) on the mechanical properties of plasma produced diamond-like carbon (DLC) thin films. Also a comparison has been made for mechanical properties of these films with pure DLC and nitrogen incorporated DLC films. Introduction of N in DLC led to a drastic decrease in residual stress (*S*) from 1.8 to 0.7 GPa, but with expenses of hardness (*H*) and other mechanical properties. In contrast, addition of Cu and Ti interlayers between substrate Si and DLC, results in significant decrease in *S* with little enhancement of hardness and other mechanical properties. Among various DLC films, maximum hardness 30.8 GPa is observed in Ti-DLC film. Besides hardness and elastic modulus, various other mechanical parameters have also been estimated using load versus displacement curves.

1. Introduction

Diamond-like carbon (DLC) or hydrogenated amorphous carbon (a-C:H) films consisting of carbon and hydrogen, possessing both diamond-like sp^3 and graphite-like sp^2 sites, are known for their outstanding mechanical and tribological properties together with excellent biocompatibility and chemical inertness coatings [1–6]. Presence of sp^2 site makes it also a material of great utility in electrical and optical applications [7,8]. Recently, some work has been explored for the development of DLC based superhard coating [9,10]. All these properties and various applications of DLC films such as hard and protective coating on cutting tools, automobile parts, solar cells and magnetic storage media can be limited because of high level of residual stress, which causes poor adhesion of DLC film with substrate. Thus, reduction of residual stress in DLC film is very important to enhance its industrial applications. Nevertheless, stress minimization in DLC films is still a technological challenge. Kumar et al. have explored various possible solutions for the reduction of residual stress in DLC films using very high frequency (VHF) power and pulse power deposition, etc. [11,12]. Other way to improve the adhesion of DLC with substrate along with improvement of mechanical properties can be the use of bilayer and multilayer structures as well as incorporation of foreign elements in DLC films [13–16]. Among various foreign elements, nitrogen was found to be most suitable element that minimize the stress but with sacrifices of hardness [16]. We have also obtained considerable reduction in residual stress of DLC films (grown in low base vacuum system) through nitrogen incorporation but with expenses of hardness [13]. On the other hand introduction of sandwich metallic layer between DLC and substrate may reduce the stress without affecting hardness of DLC films. However, the selection of proper metal sandwich layer was also found be an essential requirement to obtain desired properties from modified DLC films. Cu and Ti interlayers seems to be appropriate interlayers due to fact that Cu does not form carbide so avoid the formation of mixed layer at interface and reduce the interfacial stress. And Ti itself is very hard material and form very strong TiC bonding when reacts with carbon and therefore, enhances the hardness. Recently, we also observed reduction in stress in Cu/DLC multilayer structure grown in low base vacuum systems [14]. The improvement in hardness and other mechanical properties along with reduction in stress is very essential to make DLC as tremendous engineering material for mechanical and tribological applications. Further, the mechanical property such as hardness of thin films strongly depends on indentation load and increase in load modifies the hardness due to substrate influence [17–23]. Thus, optimization of indentation load is also a basic requirement to perform proper experiments that can be obtained by measurements at different loads.

The aim of present study is to improve the mechanical properties of DLC films by incorporation of foreign elements and by placing metallic interfacial layers such as Cu and Ti between Si and DLC. We also explored the effect of indentation load on various mechanical parameters of four different types of DLC films such as pure DLC film, nitrogen-DLC (N-DLC) film, copper-DLC (C-DLC) film and titanium-DLC (T-DLC) film. The mechanical parameters estimated in present study are: hardness (*H*), elastic modulus (*E*), plastic resistance parameter (*H*/*E*), elastic recovery (*ER*), ratio of residual displacement after load removal with displacement at maximum

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load (d_{res}/d_{max}), plastic deformation energy (U_r), hardness per unit stress (H/S) and contact stiffness $(dP/dh)_{max}$.

2. Experimental details

DLC and N-DLC films have been grown in asymmetric capacitive coupled radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD) technique, on Si ⟨1 0 0⟩ substrate, at a base pressure of 1×10^{-5} Torr. The electrode (power electrode) on which the substrate is placed is made much smaller than other electrode (anode). The whole body of process chamber is acted as anode. Prior to deposition, Si substrates are cleaned first ultrasonically with trichloroethylene followed by their treatment with isopropyl alcohol and finally by deionized water. Again Si substrates have also been cleaned by argon plasma, generated at negative self bias 300 V, to eliminate any remaining contamination from the surface. The deposition of DLC film is carried out at negative self bias of 125 V with maintaining working pressure of 1×10^{-3} Torr, which is achieved by feeding C_2H_2 gas in the process chamber that changes pressure from 1×10^{-5} Torr (base pressure) to 1×10^{-3} Torr. Similarly, the deposition of N-DLC film is done at negative self bias of 125 V with maintaining working pressure of 12×10^{-3} Torr, which is achieved by feeding both C_2H_2 and nitrogen gases into the process chamber. For deposition of N-DLC film, first C_2H_2 gas is incorporated into process chamber that changes the pressure from 1×10^{-5} Torr (base pressure) to 1×10^{-3} Torr followed by simultaneous incorporation of nitrogen gas into chamber that further changes pressure from 1×10^{-3} Torr to 12×10^{-3} Torr. C-DLC and T-DLC films have been prepared using hybrid system involving RF-PECVD and RF-sputtering units on Si substrate at the same base pressure. The description as well as schematic representation of this hybrid system can be found elsewhere [14]. The deposition of Cu and Ti layers are carried out at a negative self bias of 400 V while maintaining working pressure of 20×10^{-3} Torr which is achieved by feeding Ar gas into process chamber that changes the pressure from 1×10^{-5} Torr to 20×10^{-3} Torr. Further, successive DLC layer is grown on Ti and Cu layers and process parameters for their growth have been kept same as was kept for the growth of pure DLC film without interlayers as well as without nitrogen incorporation.

Due to its depth sensing ability, nanoindentation is found to be an appropriate indentation tool to measure mechanical properties of thin films. Mechanical properties of these films have been measured at various indentation loads of 5, 10, 15 and 20 mN by IBIS-Nanoindentation (M/S Fisher-Cripps laboratories Pvt. Limited, Australia), equipped with Berkovich indenter. The details of IBIS nanoindentation along with working principle can be found elsewhere [13]. The residual stress in these films deposited on silicon wafer has been determined from the change in the radius of curvature of the wafer, before and after deposition, using 500TC temperature controlled film stress measurement system (M/s FSM Frontier Semiconductor, USA). The substrate curvature method generally relies on the Stoney formula relating the film average stress to the substrate curvature under the assumption that the film is much thinner than the underlying substrate. The Stoney formula which is used to estimate residual stress (S) is given in Eq. (1).

$$S = \frac{E_s {d_s}^2}{6(1-\nu_s)d_f}\left(\frac{1}{R_f} - \frac{1}{R_0}\right) \tag{1}$$

where E_s, ν_s and d_s are Young's modulus, Poisson ratio and thickness of the substrate, respectively and R_0 and R_f are the radii of substrate curvature before and after film deposition. The thicknesses of these films are measured by Taylor–Hobson Talystep instrument. In order to measure the thickness using this technique, a step between the film and the substrate is required. Therefore, prior to deposition of the films we masked some area of the substrate so that a step between the films and the substrate could be created. Once the film is deposited and step is created, by moving stylus either from film to substrate or from substrate to film a thickness of the film can be estimated by measuring the height of the film with respect to substrate surface. The thicknesses of DLC, N-DLC, C-DLC and T-DLC films were measured to be 310 nm, 280 nm, 337 nm and 324 nm, respectively. Prior to deposition of DLC films on Cu and Ti coated substrates, the thickness of these metallic layers were measured separately and found to be ∼27 nm and ∼14 nm for Cu and Ti, respectively. In addition these values were also estimated indirectly by subtracting thicknesses of combined metal (Cu or Ti)/DLC to DLC only. Since DLC layer in C-DLC and T-DLC were deposited at identical deposition conditions, hence, the thicknesses of Cu and Ti layers as measured and estimated values were found to be same.

3. Results and discussion

3.1. Residual stress

The residual stress (S) in DLC films is a very serious problem because higher S leads to detachment of the films from the substrates, which results in limitation of its widespread applications [24]. Although, much efforts have already been made both fundamentally as well as practically to resolve the problem of S in DLC films but its minimization is still a very challenging task for the researchers. It is expected that the binding energy of carbon atoms, making the DLC film, be poor at edges due to more interfacial mismatch between the films and the edges and other unavoidably flaws. Hence, the initiation of detachment of film from substrate start from edges and remain detachment of film done with the help of driving forces which is related to strain energy release rate [24–26]. The variation of S versus various DLC films is shown in Fig. 1. The S in all the films is found to be compressive in nature. It is evident from figure that the maximum value of S of 1.8 GPa is observed in DLC film. However, nitrogen incorporation in DLC (N-DLC) reduces S considerably and it becomes minimum as 0.7 GPa. It is worth noting that introduction of Cu and Ti interfacial layers also reduces S significantly and the values in C-DLC and T-DLC films are found to be 0.95 and 1.1 GPa, respectively. Observed significant reduction in S in N-DLC film are due to the following reasons, which are (i) nitrogen incorporation in DLC enhance the soft graphite-like sp^2 bonding, (ii) promote hard sp^3 C–C debonding and (iii) reduces average coordination number [27]. On the other hand observed decrease in S in C-DLC and T-DLC films can be explained on the basis of bilayer and multilayer concept where Cu and Ti interlayers

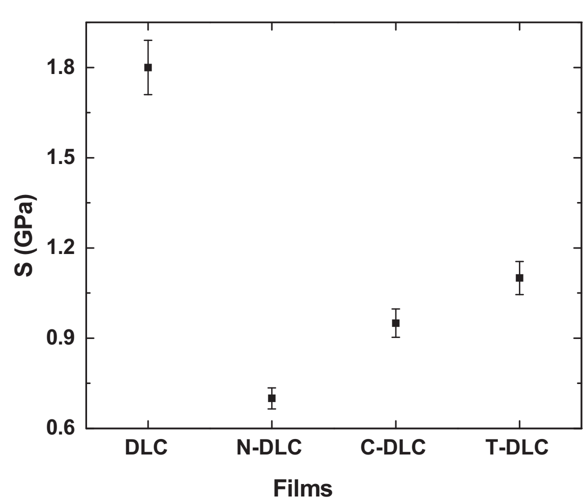

Fig. 1. Variation of stress for DLC, N-DLC, C-DLC and T-DLC films.