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Role of base pressure on the structural and nano-mechanical properties of metal/diamond-like carbon bilayers

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ABSTRACT

The influence of base pressure on the structural and nano-mechanical properties of plasma produced metal (Cu and Ti)/diamond-like carbon (DLC) bilayers is reported. All of these samples show the formation of micro and nano-structured morphology with very low average roughness (less than 1 nm). The Cu/DLC and Ti/DLC bilayers deposited at low base pressure exhibit comparatively higher hardness and better nano-mechanical properties than the ones grown at higher base pressure. Highest hardness as ~49 GPa is obtained in Ti/DLC bilayer grown at low base pressure condition. Several other nano-mechanical parameters are also examined and correlated with each other. Present investigation will be useful to understand the role of base pressure on the properties of DLC coatings and may enhance its industrial application in term of hard and protective coatings.

1. Introduction

Diamond-like carbon (DLC) is an interesting form of carbon as it contains multiple phases including diamond-like sp^3 and graphite-like sp^2 phases. It is a metastable material and has high degree of disorder owing to distortion in bond angle and bond length. Despite having high degree of disorder, DLC films have shown excellent mechanical, electrical and optical properties [1–9]. The properties of DLC films strongly depend on sp^3/sp^2 ratio, which is predominantly controlled by deposition parameters. By varying sp^3/sp^2 ratio, its hardness, optical band gap and conductivity can be tuned over wide range. Recently, Dwivedi et al. [10] have explored the correlation of sp^3/sp^2 ratio with electrical, optical and nano-mechanical properties of DLC films. The DLC films can be deposited at low temperature, even room temperature, which allows its deposition on glass and flexible plastic substrates. Hence, DLC has been considered as an excellent engineering material for the past few years.

There are several parameters for the deposition of DLC thin films including ion energy or self bias, gas pressures, deposition temperature, gas flow rates, etc. All of these parameters influence the sp^3/sp^2 ratio, structure and bonding environment of DLC film and tailor its properties. Singh et al. [11] have evaluated the effect of bias on properties of DLC films. Piazza et al. [12] have examined the properties of DLC films as a function of acetylene gas pressure. Fallon et al. [13] and Maitre et al. [14] have explored the influence of bias on the properties of amorphous carbon films. Recently, we have also examined the properties of DLC and modified DLC films as the function of pressure and bias [15–17]. So, all these parameters have already been widely explored for the deposition of DLC films. Apart from these parameters, the base pressure is also found to be a crucial parameter that can directly affect the properties of DLC films. The base pressure influences the gas phase kinetics and structure of the deposited films. Under a high base pressure condition, atmospheric oxygen added into the structure. However, an amount of atmospheric oxygen gets reduced when the base pressure becomes lower. So it would be very exciting to see how the nano-mechanical properties of DLC gets change upon changing the base pressure from high to low base pressure regimes, as DLC is hard material. It would be worth mentioning that despite of this important parameter no significant research pertaining to evaluation of properties of DLC films as a function of base pressure has been conducted.

Although DLC films have excellent properties, they also show poor adhesion to the substrates due to high residual stress. In order to solve stress issue, various foreign elements have been incorporated in DLC matrix. Damasceno et al. [18] have incorporated Si into DLC to minimize stress. Freire [19] has reduced the stress of amorphous carbon film by adding nitrogen. Chen and Hong [7] have minimized the stress of carbon films by copper incorporation. All of these foreign elements although lowers the stress, they also reduce the hardness. Hence, alternative approach is required to reduce the stress and improve the adhesion of DLC film without affecting its

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hardness. In this context, metal/DLC bilayer structure can play vital role. Also, metal interlayer may transform amorphous phase of carbon layer to their micro- and nano-structured phases. Therefore, in this work rather taking single layer DLC film, we have taken Cu/DLC and Ti/DLC bilayers and explored the effect of base pressure on their structural and nano-mechanical properties.

2. Experimental details

Cu/DLC bilayers (CD bilayers) and Ti/DLC bilayers (TD bilayers) are deposited on well cleaned Si substrate using hybrid system involving RF-sputtering and RF-plasma enhanced chemical vapor deposition (RF-PECVD) techniques. The base pressure is varied from 1×10^{-3} Torr to 1×10^{-5} Torr, whereas self-bias of -100 V is kept constant for the deposition of DLC over layer. The base pressure of 1×10^{-3} Torr is acquired by rotary and roots pumps combination, whereas the base pressure of 1×10^{-5} Torr is obtained by rotary and turbo molecular pumps combination. We call the CD and TD bilayers grown at high base pressure of 1×10^{-3} Torr as samples CDHBP and TDHBP, respectively. When CD and TD bilayers are deposited at low base pressure of 1×10^{-5} Torr; we call these samples as CDLBP and TDLBP, respectively. The Cu and Ti disks of 50 mm diameter are used as the target, and the substrate to target distance is kept constant as ~6 cm The detailed description along with schematic of hybrid system as well as extensive study of samples CDHBP and TDHPB can be found elsewhere [20,21].

The thicknesses of deposited bilayers are measured using Taylor-Hobson Talystep instrument and are found to be 56 nm, 331 nm, 227 nm and 318 nm in CDHBP, CDLBP, TDHBP and TDLBP samples, respectively. Scanning electron microscope (SEM, model JEOL, JSM-35) and atomic force microscope (AFM, model Veeco V) are used for investigating the morphology, topography and roughness of the deposited bilayers. High resolution and depth sensitive nanoindentation (IBIS-nanoindentation equipped with Berkovich indenter, M/S Fisher Cripps Lab., Australia) is employed for measuring the nano-mechanical properties of CD and TD bilayers at maximum indentation load of 10 mN.

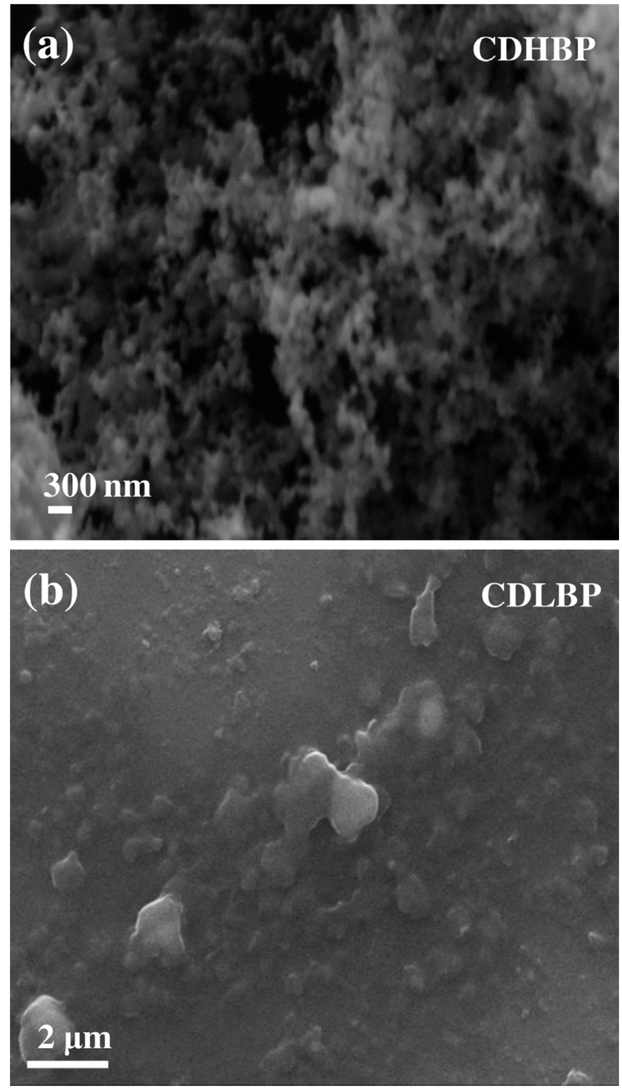

Fig. 1. SEM images of the samples (a) CDHBP and (b) CDLBP.

3. Results and discussion

Fig. 1a and b shows the SEM micrographs of samples CDHBP and CDLBP, respectively, which clearly reveal the formation of nanostructured morphology. Sample CDHBP shows nano-agglomerates that are interconnected and form chain-like structure throughout the surface. The morphology of this sample looks fibers like. We feel that such nanostructures may be carbon nanofibers because they are grown over Cu layer at high base pressure, which is essential condition for the growth of carbon nanofibers. However, when the base pressure is made to lower the morphology is changed significantly and agglomerates converts into the microcrystalline structure (CDLBP). The surface morphology of sample CDLBP looks very rigid and shows generation of transparent spots on many locations. The Cu having low affinity with carbon acts as a catalyst for the generation of agglomerates and microcrystalline structure. Fig. 2a and b shows the AFM 2D and 3D micrographs of sample CDHBP and Fig. 2c and d are the AFM 2D and 3D micrographs of the samples CDLBP. AFM micrographs are in good agreement with the SEM pictures and confirm the creation of carbon nano and micro-structures. By AFM technique, average roughness (R_a) of these two samples are also calculated and found to be 0.37 nm and 0.23 nm in the samples CDHBP and CDLBP, respectively. This infers that high base pressure growth enhances the R_a of CD bilayer. Fig. 3a and b shows the SEM pictures of samples TDHBP and TDLBP, respectively. The formation of nano-structured morphology in these bilayer samples is evident from the figures. The sample TDHBP exhibits the formation of carbon nanospheres, whereas the sample TDLBP shows the clustering of very small (nano) carbon nuclei. Here Ti having high affinity with carbon acts as a catalyst for forming nanostructures. The modification in the morphology with the changing interlayer material and altering base pressure can be ascribed to the change in the surface reactivity of interlayer material with carbon over layer and change in the average energy of the carbon ions. Fig. 4a and b shows the AFM 2D and 3D images of the sample TDLBP, which confirms the formation of uniform and dense carbon nanostructures. The R_a of the sample TDLBP is also estimated and found to be 0.217 nm. This can be seen that R_a of the sample TDLBP is lowest among all bilayer samples. The SEM and AFM results are further correlated with the nano-mechanical properties, which will be discussed in a subsequent section.

Load versus displacement (P–h) curves of the bilayer samples CDHBP, CDLBP, TDHBP and TDLBP; reference sample fused silica (FS) and the substrate silicon are shown in Fig. 5. The evaluation of hysteresis of P–h curves can provide an idea about expected mechanical behaviour of the coatings. Large hysteresis of P–h curves is associated with high plastic deformation and hence, less hard characteristic of the coating. Fig. 5 shows that the hysteresis is negligible in the sample TDLBP and is highest in the sample CDHBP. Hence, based on the P–h curves, it is inferred that former sample should be harder than the later sample. Fig. 6a shows the bar plot of