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Surface & Coatings Technology 200 (2006) 6405 – 6408

SURFACE & COATINGS TECHNOLOGY

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Control of stress and delamination in single and multi-layer carbon thin films prepared by cathodic arc and RF plasma deposition and implantation

Peter C.T. Ha [a,d,*], D.R. McKenzie [a], M.M.M. Bilek [a], E.D. Doyle [b],
D.G. McCulloch [c], P.K. Chu [d]

[a] *School of Physics, University of Sydney, Sydney, NSW, Australia*
[b] *Swinburne University of Technology, Melbourne, Australia*
[c] *Department of Applied Physics, RMIT, Melbourne, Australia*
[d] *Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China*

Abstract

The build-up of intrinsic stress in carbon thin films deposited by vapour deposition is a major cause of delamination. The delamination issue is one of the main reasons preventing wider applications of carbon vapour deposited films. In this work, we studied single and multilayer thin films of carbon and found that under certain deposition conditions, we were able to produce thin films free from delamination. Furthermore, we were able to stop film delaminating by adding a control layer. Two methods were used to deposit the carbon films: (1) filtered cathodic arc deposition with both negative DC and pulsed bias applied to the substrate and (2) RF plasma CVD with negative pulse bias up to 30 kV, 60 Hz, 100 µs. Both single and multilayer structures of carbon with different sp^2 and sp^3 ratios were deposited and it was found that, under controlled conditions, the overall stress was maintained at acceptable levels. Moreover, it was found that an additional control layer stopped ongoing delamination of the film. The structures of these multilayers were studied using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

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1. Introduction

Diamond-like carbon (DLC) films have excellent features such as high hardness and low friction coefficient, and have applications to cutting tools, metallic molds and machine parts [2–9]. Unfortunately, they generally exhibit low adhesion strength [1], resulting in peeling off from a substrate due to the high internal compressive stress. Various approaches have been tried to reduce the internal stress including, incorporating additional elements such as silicon and nitrogen [3,4], metal, ceramic and DLC [5–7], pulsed bias Plasma Enhance Chemical Vapor Deposition (PECVD) [8] and Filtered Cathodic Vacuum Arc (FCVA) [9]. In this work, we present a comparison between the intrinsic stress values achieved from two methods of deposition, FCVA and Radio Frequency (RF) Plasma Chemical Vapor Deposition (CVD). In both methods, the Plasma Ion Immersion and Implantation (PIII) mode was employed with the bias applied to the substrate holder.

2. Experimental

2.1. Carbon films prepared by cathodic arc with PIII

Carbon films were prepared in a FCVA fitted with a 1D rotational substrate holder connected to a high voltage feed-through, PIII. During the FCVA operation, the PIII voltage power supply is operated at 20 keV with pulse bias of 20 µs duration and a repetition rate of 200 Hz. The deposition results in a film with an sp^2 fraction of 95–98%, using electron energy loss quantification of the carbon K-edge. This compares with the sp^2 fraction of less than 20% for a film prepared by cathodic arc deposition with no additional bombardment [9]. We have taken the advantages of the range of sp^2 fractions to construct the multilayer structures.

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* Corresponding author. School of Physics, University of Sydney, Sydney, NSW, Australia.
E-mail address: peterha@physics.usyd.edu.au (P.C.T. Ha).

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doi:10.1016/j.surfcoat.2005.11.011

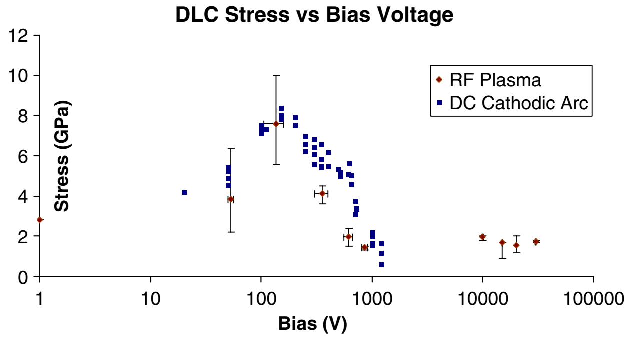

Fig. 1. The intrinsic stress value of carbon films obtained from the DC cathodic arc and RF plasma as a function of bias voltage applied during pulsed bias.

2.2. Carbon films prepared by RF plasma with PIII

The single and multilayer carbon films were prepared using RF plasma CVD and a substrate bias power supply that operated at high voltage, 30 kV with pulse bias of 400 μs duration and repetition rate of 60 Hz.

2.3. Intrinsic stress measurement

The silicon wafers of (100) orientation of 300 μm thickness and double side polished were cut into 25 × 25 mm pieces and surface-scanned with the Tenco P10 profilometer for the initial radius of curvature R_0. The surface-scan parameters were 2 mm/s scan rate, 20 mm in length for curvature measurement while 50 μm/s rates and 500 μm in length for film thickness measurement. The radius of curvature R of the sample is repeatedly measured after deposition and Stoney's equation (1) was used to calculate the intrinsic compressive stress, σ, for the deposited film

$$\sigma = \frac{1}{6}\frac{E_s}{1-v_s}\left(\frac{1}{R}-\frac{1}{R_0}\right)\frac{t_s^2}{t_f}, \tag{1}$$

where E_s is Young's modulus, v_s is Poisson's ratio and t_s and t_f is the thickness of the substrate and the coated film, respectively.

3. Results and discussion

3.1. Film growth rate

There were two factors that influenced the FCVA deposition rate: (1) Argon flow rate which helped the arc stabilize and (2) the bias voltage applied to (filter strength) the duct-filter coil attached to the cathodic arc. For an argon flow rate of 2 sccm and duct-filter current of 10 A (20 mT), the carbon deposition rate in the FCVA system was 1 nm/s. While in the RF plasma system at 500 W forward and 100 W reflected and argon flow rate of 10 sccm and C_2H_2 of 20 sccm, the deposition rate was 1 nm/min. Based on Eq. (1), any uncertainties in the measurement of the film: thickness, roughness and uniformity, affect the intrinsic compressive stress value, σ.

3.2. DLC stress

The surface curvatures of silicon wafers were measured before and after deposition and their differences were assumed

Fig. 2. A demonstration of typical DLC films delaminating; (a) a highly stressed film freshly produced by RF plasma, (b) a typical high stress film delaminated after 24 h, and (c) a similar high stress film as to (b) but a control layer was added after 12 h of delamination. Both (a) and (b) was taken simultaneously after 24 h.

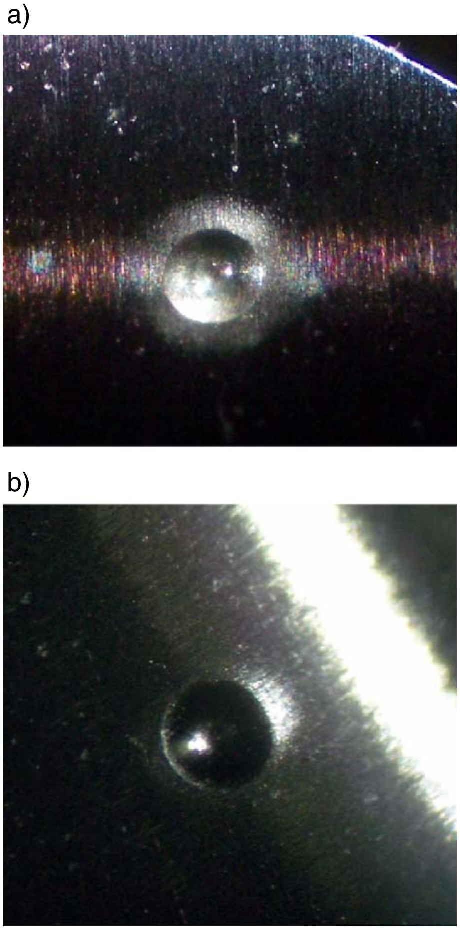

Fig. 3. A view from optical microscope to determine film adhesion strength; (a) film delaminated around the indented area showing signs of poor adhesion strength, (b) good adhesive film on top of GPT drill.

to be resulting from the intrinsic compressive stress of the deposited film. For both deposition methods, we deposited carbon films of approximately 200–300 nm in thickness and the calculated intrinsic stress values for the deposited films are presented in Fig. 1. The uncertainties in the stress values obtained from the films deposited by the FCVA system were to a lesser extent due to film uniformity and roughness. The film thickness values were easily obtained from the films deposited with the FCVA system, while it was difficult to determine the film thickness of the DLC films of similar thicknesses deposited by the RF plasma system. However, in both methods of deposition, the stress values showed a trend in which it first increased and then decreased with a peak at approximately 150 V negative bias.

From the relationship between the intrinsic stress versus applied bias voltage as shown in Fig. 1, we were able to tailor a multilayer structure consisting of a layer that absorbs the excessive internal stress of the other layers. Fig. 2a shows a typical high stress film that delaminates almost instantly after deposition. Fig. 2b and Fig. 2c shows a high stress film, similar to that of Fig. 2a; however, after 12 h of delamination, an additional absorbing layer was added and the additional absorbing layer had stopped it from further delaminating as demonstrated in Fig. 2c. In a test of 6 untreated high stress films, delamination continued to occur until all the stresses had been released as highlighted in Fig. 2b which the film was delaminated for 24 h. The DLC films were darker in color and delamination usually took place from the outermost edge and then moved slowly toward the center of the sample. The top section of the pictures in Fig. 2 was taken at the edge of the sample and the bottom section at the center of the sample.

3.3. Wear resistant and adhesion test

The performance of the structure has been previously assessed by impact-enhanced pin-on-disc wear test and indentation hardness [9]. However, here we present wear, adhesion and hardness results by performing pin-press and Rockwell hardness indentation tests. The optimized structure was deposited on to 25 TiN General Purpose Twisted (GPT) drills and the results from adhesion, Rockwell hardness indentation and life performance test were compared to untreated TiN GPT drills. The Rockwell hardness increased from 50 HRC to 70 HRC between uncoated and coated DLC, respectively.

As shown in Fig. 3, based on the deformation made when a spherical diamond indenter tip was pressed into the carbon film coated on top of GPT drills observed by optical microscopy, the adhesion strength of the film onto the drill can be determined by the delaminating ring around the deformed edge. The thicker the ring, the more serious is film delamination and the poorer is the adhesion strength, as shown in Fig. 3a. Therefore, for strong adhesion strength and high hardness, the film must show as little delamination around the indented area as possible, as shown in Fig. 3b.

4. Conclusion

We have investigated the intrinsic stress of single and multilayer film prepared by both filtered cathodic arc and RF plasma deposition system. Although there were differences in the rate of deposition, a similar trend was observed in both methods in which the intrinsic stress peaked at approximately 150 V. A high tress film produced from 150 V of substrate bias delaminates instantly, however, with the additional control layer of low stress this problem can be overcome. Evidence from indentation and performance tests show that stress control in DLC coating lead to strong adhesion strength and better life performance.

Acknowledgement

This project was funded by the Australian Postgraduate Award in Industries 2001–2004, Hong Kong RGC CERG CityU 1120/04E and the Endeavour Australia Cheung Kong Award 2005.

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