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Interface tailoring for adhesion enhancement of diamond-like carbon thin films

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ABSTRACT

We have explored the suitability and characteristics of interface tailoring as a tool for enhancing the adhesion of hydrogen-free diamond-like carbon (DLC) thin films to silicon substrates. DLC films were deposited on silicon with and without application of an initial high energy carbon ion bombardment phase that formed a broad Si–C interface of gradually changing Si:C composition. The interface depth profile was calculated using the TRIDYN simulation program, revealing a gradient of carbon concentration including a region with the stoichiometry of silicon carbide. DLC films on silicon, with and without interface tailoring, were characterized using Raman spectroscopy, scanning electron microscopy, atomic force microscopy and scratch tests. The Raman spectroscopy results indicated *sp3*-type carbon bonding content of up to 80%. Formation of a broadened Si:C interface as formed here significantly enhances the adhesion of DLC films to the underlying silicon substrate.

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1. Introduction

Diamond-like carbon (DLC) is a synthetic material [1,2] with properties similar to diamond [3] and is an excellent material for many tribological coating applications [4,5]. High quality, hydrogen-free DLC thin films can be deposited by a technique employing a filtered vacuum arc carbon plasma source in conjunction with a suitably pulse-biased substrate so as to control the ion deposition energy, sometimes referred to as Metal Plasma Immersion Ion Implantation and Deposition (MePIIID) [6,7].

An inherent characteristic of DLC thin films is their high internal stress [8], a feature that leads to delamination for all but the thinnest of films [9]. Various approaches have been explored for ameliorating this behavior, including modifying the deposition parameters to reduce sp^3:sp^2 ratio (ratio of diamond-bonded carbon atoms to graphite-bonded carbon atoms) or introducing various chemicals into the film composition [9], but in both cases the film quality is reduced [7]. Thus there is a compromise between the hardness of the DLC film and other material characteristics, and its thickness. An alternative approach to diminishing this serious limitation of DLC coatings is to use an initial high energy carbon ion bombardment phase prior to a lower energy carbon ion deposition phase [10]. In this way the film–substrate interface can be controlled over a fairly wide range, creating a relatively gradual variation of carbon atom concentration in the direction perpendicular to the substrate surface, before the deposition of pure carbon at the optimum (for maximizing the sp^3:sp^2 fraction) ion energy. It is possible to choose deposition parameters that yield the highest quality DLC film with also much better adhesion to the substrate. The interface between the DLC film and substrate is not abrupt, but has a carbon concentration gradient.

In the work described here we formed DLC films with and without an initial high energy carbon ion implantation phase that formed a broad Si–C interface of gradually changing Si:C composition. The films were characterized using Raman spectroscopy, scanning electron microscopy, atomic force microscopy and scratch tests. The Raman spectroscopy results indicated *sp3*-type carbon bonding content of up to 80%. The interface depth profile was calculated using the TRIDYN simulation program, revealing a gradient of carbon concentration including a region with the stoichiometry of silicon carbide. The results of our work show that formation of a broadened Si:C interface significantly enhances the adhesion of DLC films to the underlying silicon substrate while yielding a high quality surface DLC film.

2. Experiment

Hydrogen-free DLC thin films were deposited by filtered vacuum arc plasma deposition in conjunction with substrate biasing for control of ion deposition energy. The carbon plasma source was a repetitively pulsed vacuum arc plasma gun utilizing a carbon cathode. The substrate was repetitively pulse-biased to a chosen negative voltage for control of the carbon ion energy during the deposition. This technique has been called Metal Plasma Immersion Ion Implantation and Deposition (MePIIID) [6,7]. The base vacuum pressure was about 10^{-6} Torr. The vacuum arc plasma gun generates carbon plasma in pulses of (here) 5 ms duration at a rate of 1 pulse per second. The

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carbon plasma streams from the gun with a drift energy of about 10 eV and is passed through a 90° bent solenoid for macroparticle (particulate cathode debris) filtering, and the filtered carbon plasma is directed to the silicon substrate. The substrate is biased by the application of a pulsed voltage train of negative-going pulses of 10 μs duration and 50% duty cycle; i.e., for the 5 ms plasma pulse duration, the substrate is biased with a 50 kHz negative square wave of experimenter-chosen amplitude. Thus the carbon ion deposition energy can be selected. During the (10 μs) pulse-off time there is no substrate bias and the carbon plasma deposits on the silicon substrate as a surface film, while during the (10 μs) pulse-on time the substrate is biased so as to accelerate the ions and the carbon flux is implanted into the silicon substrate at the selected ion energy. For each 5 ms plasma gun pulse there are 250 bias pulses applied to the substrate, and the carbon ions are alternately, in 10 μs packets, deposited at low energy (~10 eV) and implanted at the chosen high ion energy. Importantly, note that the super-thin surface layer of carbon (less than a monolayer) that is deposited during each pulse-off period is subsequently implanted via knock-on collisions with high energy ions in the next pulse-on period ("recoil implantation"). Thus the expected carbon depth profile is not that of two discrete regions, a surface layer and an implanted profile, but rather a complex profile that is a resultant of mixing of the two regions and that is fully buried below the surface.

Computer simulations of the resultant carbon atom depth profile in the silicon substrate were carried out using the TRIDYN program [11,12]. TRIDYN is a Monte Carlo simulation program based on the earlier TRIM (Transport and Range of Ions in Matter) program [13]. This program takes into account compositional changes in the substrate due to two factors: previously implanted dopant atoms, and sputtering of the substrate surface. The TRIDYN program is appropriate when the substrate composition changes significantly during the implantation process.

Raman spectroscopy was used to evaluate the DLC quality. The Raman spectra were obtained using Jobin Yvon T64000 equipment with exciting radiation $\lambda_0 = 514.5$ nm generated by a coherent Ar^+ laser with an output of 20 mW. Spectra were obtained with exposure time of 50 s, summing over five accumulations. Scanning electron microscopy (SEM) was used for measuring the films thickness; the micrographs were obtained on a FEG-SEM JEOL JSM-7401 with original magnification of 20 k×. Atomic force microscopy was also used for measuring films thickness; the equipment used was a NanoScope IIIA, Bruker. Scratch tests were used to evaluate the adhesion of the DLC films on silicon with and without the graded interface; the equipment used was a CETR UMT Multi-Specimen Test System with a

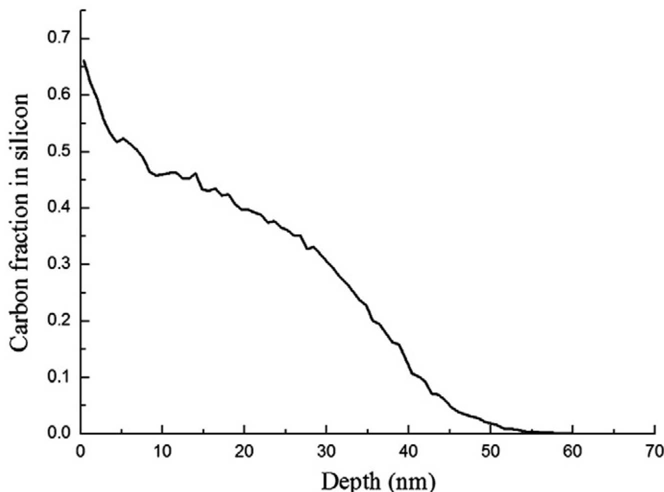

Fig. 1. Carbon atomic fraction as a function of depth below the Si surface; TRIDYN simulation results.

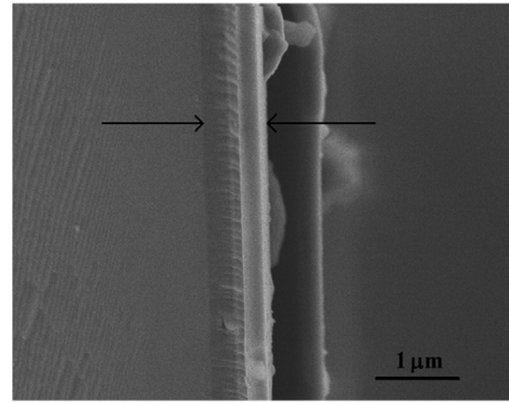

Fig. 2. Cross-section scanning electron micrograph of the DLC film for the case with interface broadening. The film thickness is 670 nm.

Rockwell C diamond tip (cone of 120° and hemispherical tip 200 μm in diameter). For inspection of the scratch test tracks, a scanning electron microscope JEOL 6460LV was used in backscattering compositional signal detection mode.

3. Results and discussion

It is known that a pure silicon substrate (without a carbon-containing interface) does not provide good DLC film adhesion [9], and that on the other hand an interface with an excess of carbon can lead to surface graphitization, also causing low adhesion. Thus we carried out a range of TRIDYN simulations, adjusting the carbon implantation dose and energy so that the interface contained a near-surface region with the stoichiometry of silicon carbide (SiC), i.e. 50% carbon in silicon. These simulation explorations led us to choose a carbon implantation dose of 1.2×10^{17} atoms cm^{-2} with energy 5 keV and 50% duty factor as the experimental conditions employed to form our DLC films.

Next we carried out simulations that mimicked to some extent the repetitive pulse biasing feature of the experiment. With the aim of approximating the conditions arrived at above (dose 1.2×10^{17} cm^{-2}, energy 5 keV) and also the switching between surface deposition and energetic ion bombardment of the repetitively pulse-biased substrate, we divided the carbon dose of 1.2×10^{17} cm^{-2} into four equal parts and simulated the implantation/deposition in four sequential steps:

- ¼ of the total dose depositing with zero energy,
- ¼ of the total dose implanting with energy of 5 keV,
- ¼ of the total dose depositing with zero energy, and
- ¼ of the total dose implanting with energy of 5 keV.

In the experiment, alternate deposition/implantation steps were done 250 times each 5 ms. Our simulation procedure is an approximation designed to mimic this process in a computationally manageable way.

The results of the simulation are shown in Fig. 1, where the calculated carbon depth profile is plotted—the fractional atomic carbon concentration as a function of depth below the silicon surface. There is a gradual transition of carbon concentration from approximately 50% at and near the surface reaching zero at about 50 nm depth. Thus the expected interface is a broad region of about 50 nm width and with the stoichiometry of SiC close to the surface, as desired.

DLC films were deposited, in the first place without forming the broad interface; i.e., the high voltage pulse biasing was not applied. We estimated the maximum thickness of the DLC film that could be formed in this way without the film delaminating from the substrate. For this purpose we mounded a silicon sample near a viewing window in the vacuum chamber in which the plasma deposition was

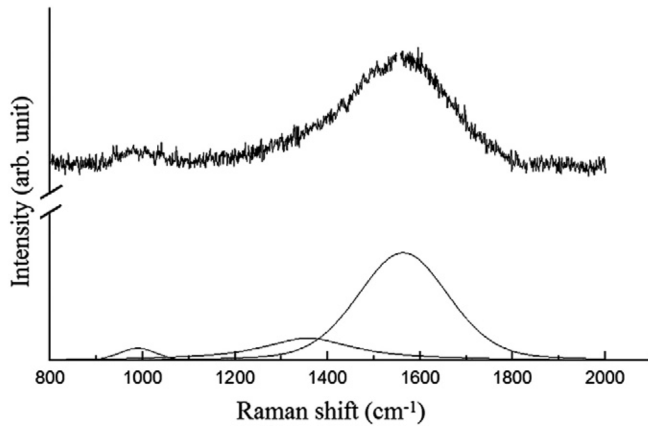

Fig. 3. Raman spectrum of DLC samples. The upper curve is the measured spectrum and three lower curves are fitted deconvolutions.

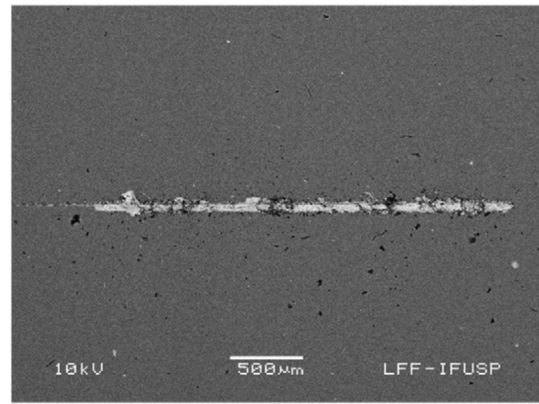

Fig. 5. Typical SEM backscattering compositional image for a DLC film without broadened interface, showing adhesion failure and consequent exposure of the silicon substrate. The lighter regions are the silicon substrate. The image shows just a part of the adhesion test line.

carried out. The deposition parameters were: plasma gun pulse length 5 ms and repetition rate 1 Hz; substrate bias −100 V at a pulse repetition rate of 50 kHz with 50% duty cycle (i.e., 20 μs period or 10 μs pulse-on duration). The substrate bias of −100 V was chosen to optimize the DLC quality (maximum sp^3 content), as has been shown [14]. The deposition was continued until the DLC film was seen visually to peel off from the substrate, and the deposition was then immediately discontinued. The film thickness was subsequently determined by removing in an ultrasonic bath the loose (delaminated) parts of the film and measuring the step formed between the remaining film and the substrate by atomic force microscopy, obtaining a thickness of 150 nm. We thus find that the maximum DLC thickness before delamination occurs is 150 nm.

Films were then formed with interface broadening as described in the preceding. The deposition parameters used were similar to those described above, but now included a preliminary phase in which −5 kV pulsed biasing was applied to the substrate (an implantation phase), followed by a deposition phase precisely as just described. The sample was again positioned near a viewing window. The deposition proceeded for several hours without any visible delamination of the film from the substrate. The deposition was discontinued and the film, with interface, was cleaved and its cross section imaged by scanning electron microscopy. A micrograph obtained in this way is shown in Fig. 2. The measured film thickness was 670 nm. We did not continue the deposition to the point of delamination; however we can state that the maximum film thickness without delamination, with interface broadening applied, is more than four times the maximum thickness possible without delamination, without interface broadening applied.

For Raman spectroscopy characterization a similar DLC sample was prepared with broadened carbon interface, of lesser thickness for simplicity. Fig. 3 shows a typical Raman spectrum of the DLC samples formed in this work. The upper curve shows the measured Raman spectrum and the lower curves show three fitted deconvoluted peaks. The peak centered at 1550 cm^{-1} corresponds to the G-band, related to sp^3 bonds, and the peak centered at 1360 cm^{-1} corresponds to the band D, related to sp^2 bonds. The third peak is related to the silicon substrate. Here, $I_d/I_g = 0.20$, which corresponds to about 80% sp^3-type bonds, demonstrating the excellent quality (high diamond content) of the DLC formed in our experiments.

For scratch test characterization [15–17] we deposited DLC films with and without the broadened interface and compared them. Scratch testing provides a means of evaluating the adhesion between the film and the substrate. The indenter scratches the sample horizontally at constant speed while an increasing compressive load is applied vertically, until adhesion failure of the film is observed. The films used here were 110 ± 10 nm thick (with and without broadened carbon interface)—all films were of thickness greater than 100 nm as is required for this test [15]. Two samples with broadened interface and two without interface were prepared, and three scratch tests were performed on each sample. A normal pre-load of 1.5 N was first applied for 10 s, followed by a continuous increase of normal load from 1.5 N to 2.0 N over a 10 s period. Then, for the DLC film

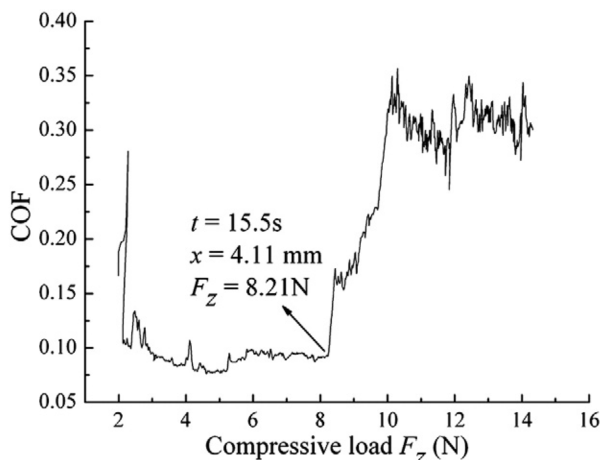

Fig. 4. Typical measured coefficient of friction as a function of compressive load for a DLC film without interface broadening. Film failure occurs at a normal load of 8.21 N.

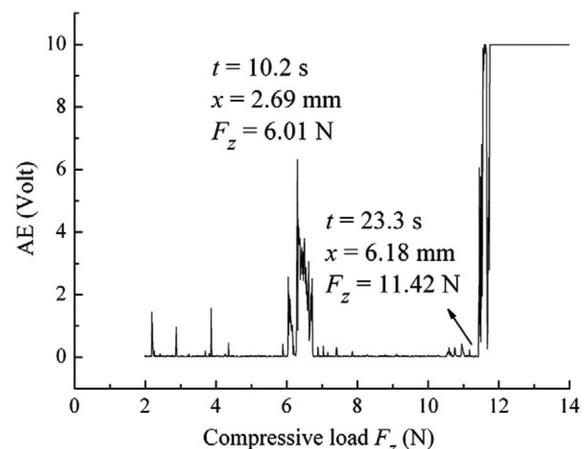

Fig. 6. Acoustic emission (AE) signal as function of compressive load for a DLC film without interface broadening, showing premature adhesion failure.

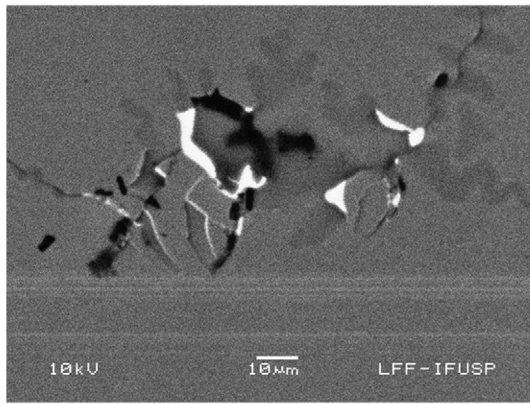

Fig. 7. SEM backscattering composition image showing premature adhesion failure of DLC deposited on silicon without interface broadening.

prepared without interface broadening, a horizontal scratch was generated with the tip moving at a constant speed of 0.266 mm s^{-1} and a continuous increase of normal load from 2.0 N to 15.0 N over 30 s, resulting in an 8 mm scratch length. For the case of the DLC films prepared with interface broadening, the final load of the test had to be increased to 20.0 N to obtain adhesion failure; in this case the tip was moved at a constant speed of 0.266 mm s^{-1} with a continuous increase of normal load from 2.0 N to 20.0 N over 30 s, resulting in an 8 mm scratch length.

During the scratch tests, an acoustic emission (AE) sensor was used and its signal monitored as a function of time t and horizontal position x of the tip. Also, the scratch normal force F_z and the scratch tangential force F_x were monitored, allowing determination of the coefficient of friction (COF) from the ratio F_x/F_z.

Fig. 4 shows typical COF results as function of time for a DLC film prepared without interface broadening. A drastic increase in the COF occurs at a normal load of 8.21 N, corresponding to film failure. The mean value of the force F_z for which the COF indicates film failure was 9.04 N, averaged over all six scratch tests performed. Fig. 5 shows a typical SEM backscattering compositional image for a DLC film without broadened interface, showing adhesion failure and consequent visible exposure of the silicon substrate. For these films, without interface broadening, some premature adhesion failure was revealed by the AE signal prior to final adhesion failure, as can be seen in Fig. 6. Fig. 7 is an SEM backscattering compositional image showing premature adhesion failure of a DLC film deposited on silicon without interface broadening.

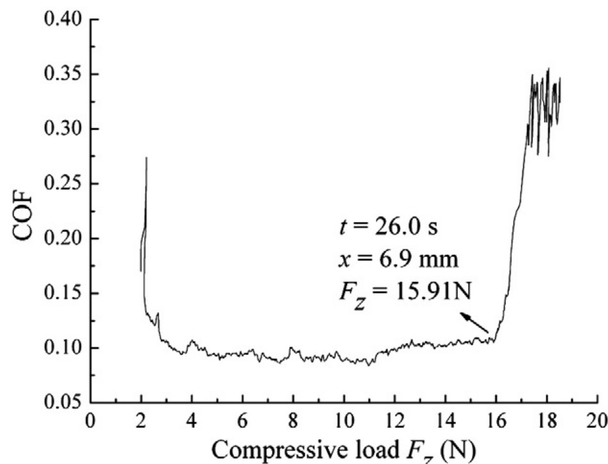

Fig. 8. Typical measured coefficient of friction as function of compressive load for a DLC film with interface broadening. Film failure occurs at a normal load of 15.91 N.

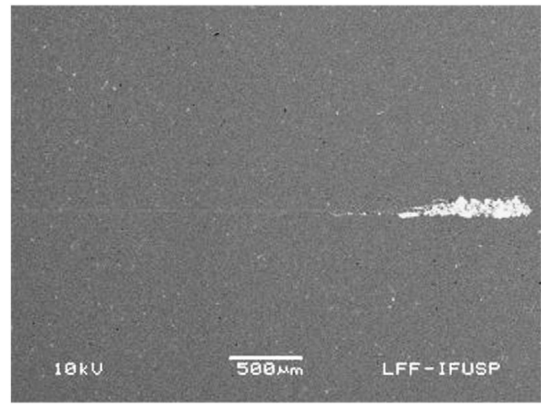

Fig. 9. Typical SEM backscattering compositional image for a DLC film with broadened interface, showing adhesion failure and consequent exposure of the silicon substrate. The lighter regions are the silicon substrate. The image shows just a part of the adhesion test line.

Fig. 8 shows typical COF results as function of time for a DLC film prepared with interface broadening. Here the force F_z for which the COF changes drastically, indicating film failure, is 15.91 N. The mean value of the force F_z for which the COF indicates film failure was 15.45 N, averaged over all six scratch tests performed. Fig. 9 shows a typical SEM backscattering compositional image for a film with interface broadening, showing adhesion failure and exposure of the underlying silicon. For all films with broadened interface, no significant premature failure was observed during the scratch tests.

The scratch test results indicate that the broadened interface results in an enhancement of the adhesion between the DLC film and the silicon substrate, increasing the normal force at adhesion failure from 9.04 N to 15.45 N. (Failure load measurements were all made on films of the same thickness, 110 ± 10 nm thick, with and without broadened carbon interface.)

4. Conclusion

We have demonstrated a technique for forming a substantially broadened interface between vacuum arc deposited DLC thin films and the underlying silicon substrate, resulting in enhanced film–substrate adhesion. The interface was formed by introducing a preliminary carbon ion implantation phase to create a sub-surface region of slowly graded carbon concentration in the direction normal to the substrate surface. DLC films deposited with and without the broadened interface were characterized using Raman spectroscopy, scanning electron microscopy, atomic force microscopy and scratch tests. TRIDYN computer simulations were performed to determine the appropriate ion implantation dose and energy so as to yield an interface with the stoichiometry of silicon carbide at the surface. Non-delaminating DLC films thicker than 670 nm were formed with interface broadening, while films without interface broadening delaminated at 150 nm thickness. Raman spectroscopy showed that the DLC formed here had about 80% *sp3*-type carbon bonds, indicating excellent diamond-like quality. Scratch tests showed that the broadened interface resulted in enhancement of the film–substrate adhesion, increasing the normal force necessary for adhesion failure from 9.04 N up to 15.45. We conclude that the broad, graded interface significantly enhances the film adhesion and allows for significantly thicker films before delamination occurs.

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