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Effects of thermal annealing and Si incorporation on bonding structure and fracture properties of diamond-like carbon films

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ABSTRACT

The effects of thermal annealing and Si incorporation on the structure and properties of diamond-like carbon (DLC) films were investigated. As-deposited DLC film (DLC) and Si incorporated DLC film (Si-DLC), both with and without thermal annealing, were analyzed for bonding structure, residual stress, film thickness, elastic modulus and fracture properties using Raman spectroscopy, wafer curvature, nanoindentation, four-point bend fracture testing, and X-ray photoelectron spectroscopy (XPS). Raman spectroscopy clearly showed that thermal annealing of DLC films promotes more sp^2 bonding character, whereas Si incorporation into the films promotes more sp^3 bonding character. Interfacial fracture energies, film hardness and elastic modulus, and residual film stress were all found to vary strongly with the degree of sp^3 bonding in the DLC film. These changes in mechanical properties are rationalized in terms of the degree of three dimensional inter-links within the atomic bond network.

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1. Introduction

Diamond-like carbon (DLC) films are of great interest as a protective coating in industrial tools and medical implants due to their low coefficient of friction [1], excellent wear resistance properties [2] and their extremely good chemical inertness and biocompatibility [3,4]. However, the reliability of systems in which DLC films are used is strongly dependent on the adhesion of DLC films coating to the underlying substrate. If sufficiently high compressive residual stress is present in the DLC film, spontaneous delamination of weak interfaces can occur through, e.g., buckling or peeling off of the DLC coating [5,6]. Such challenges threaten to limit the lifetime of DLC-coated implants with initiation of inflammatory response leading to osetoclast cells activation resulting in bone resorption [7]. This instability is closely related to the poor adhesion of DLC coating. The film spontaneously buckles when the strain energy release rate supplied through residual stress exceeds the interfacial toughness. Accordingly, many adhesion-promoting strategies have been investigated for DLC coatings, such as increasing of Ar cleaning time, adjusting bias voltage during Ar cleaning [8,9], Si incorporation into DLC film [10], and Si buffer layer deposition [11] between the substrate and DLC film.

Several methods have been employed to characterize the adhesion of DLC coatings, such as Scotch tape test [12], delamination test [5,6,13,14], tensile testing [15,16], and four-point bend testing [17–19]. The Scotch tape test is only semi quantitative and cannot be used to extract a reliable adhesion value [12]. Alan Lee et al compared delamination test results with four-point bend results on thin films with low adhesion values and high compressive residual stress [6]. On such films, their work indicated that it may be possible to extract quantitative interfacial adhesion values using telephone cord delamination method. However, application of this approach is limited when considering DLC films used in industrial applications that have comparatively good adhesion and low residual stress. Ohmura and Matsuoka proposed the tensile test to evaluate adhesion strength of TiN coatings on stainless steel. If the tensile strength and elastic modulus of the film are accurate, this technique will provide a simple and reliable method to assess the adhesion of the film/substrate interface. However, application of this method is limited when the mechanical properties of the film are difficult to determine accurately, as is often the case with DLC films. Furthermore, for films with poor adhesion, the cracking normal to the strain axis is combined with cross-linked cracking or spallation of the coating that may considerably affect the stress environment. Thus, one should carefully consider these factors when evaluating the interfacial strength using crack spacing. One widely used method to evaluate the interfacial fracture energy is the four-point bending test. This technique has been applied to thin film structures sandwiched between elastic substrates and has been shown to give very consistent and reliable data [17]. This technique is applicable to a wide range of thin-film structures and allows for reproducible and accurate quantitative measurements over a wide range of adhesion values than other methods. Additionally, the constraint of the elastic substrates prevent residual stress in the thin

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films from contributing to the debond driving energy. Thus, in contrast to some of the aforementioned technique, the applicability of the four-point method is not dependent on the amount of residual stress present in the thin-film stack.

The present work focuses on the use of four-point bend testing to characterize the interfacial fracture energy of DLC films that have been modified through thermal annealing and/or the incorporation of Si into the film. The intent is to gain more fundamental understanding of the relationship between film structure and mechanical properties.

2. Experimental

As-deposited DLC (DLC) film and Si incorporated DLC (Si-DLC) films were prepared by a radio frequency plasma-assisted chemical vapor deposition (r.f. PACVD) method using benzene and a mixture of benzene and diluted silane as the reaction gases. Before deposition, the Si (100) substrates with thickness of 650 µm were cleaned by Ar plasma generated by r.f power at the bias voltage of −400 V for 5 min. Following this cleaning step, a 5 nm thickness of Si buffer layer was deposited on the Si substrate and then 650 nm of DLC film or Si-DLC film was synthesized on the Si buffer layer respectively. All of films were deposited at the bias voltage of −400 V. For structure modification, a portion of the DLC and Si-DLC films were thermally annealed at 300 °C in N_2 gas for 30 min. For the residual stress measurements using a curvature method, thin (200±2 µm thick) Si strips of size 3 mm×40 mm were used as the substrates.

The thickness of the deposited film was measured using an α-step profilometer employing a step made using a shadow mask. The composition of the film was analyzed using Rutherford backscattering spectrometry (RBS) analysis employing a 2 MeV collimated $^4He^{2+}$ ion beam. 2 MV Pelletron accelerator of National Electrostatic Corporation was used for the He ion acceleration. A homemade analysis chamber was used to collect the RBS data. A micro-Raman spectroscope with a spectra physics Ar-ion laser (Jobin-Yvon 64000, France) was used to characterize the chemical bonding structure of the DLC and Si-DLC film. Nanoindentation in continuous stiffness measurement (CSM) mode was used to characterize the hardness and elastic modulus (Hysitron, U.S.A.) using a Berkovich diamond tip. The measured hardness and elastic modulus of the films chosen as being the depth at 35 nm where the measured values were not affected by the mechanical properties of the substrate.

For the four-point bend interfacial fracture energy measurements, the DLC or Si-DLC films were first coated with 25 nm of Ti followed by 175 nm of Al (see Fig. 1), and the resulting thin-film structure was bonded to bare silicon using previously reported epoxy method [20]. The bonded wafers were sectioned using a high speed diamond wafering blade into individual four-point bend specimen with nominal dimensions of 1.3 mm thickness, 3.8 mm width, and 40 mm length. A diamond scribe was to create the initial pre-notch. The specimens were loaded in four-point flexure at a constant displacement rate of 0.5 µm/s using the delaminator adhesion test system (DTS Company, Menlo Park, CA) in a laboratory air environment (~25 °C and ~45% relative humidity). At least four specimens were tested for each experimental condition. The interfacial fracture energy, G_c can be expressed in terms of the critical applied load at which crack growth occurs, P_c the dimension of specimens width, b, and half-thickness, h, the distance between the inner and outer loading pins, L, and the plane strain elastic modulus of Si substrate, E [21]:

$$G_c = \frac{21P_c^2L^2}{16Eb^2h^3} \quad (1)$$

Following fracture, XPS (Surface Science Instrument, S-probe, Mountain View, CA) was used on the fracture surfaces to determine the location of fracture within the thin-film structure. For the four-

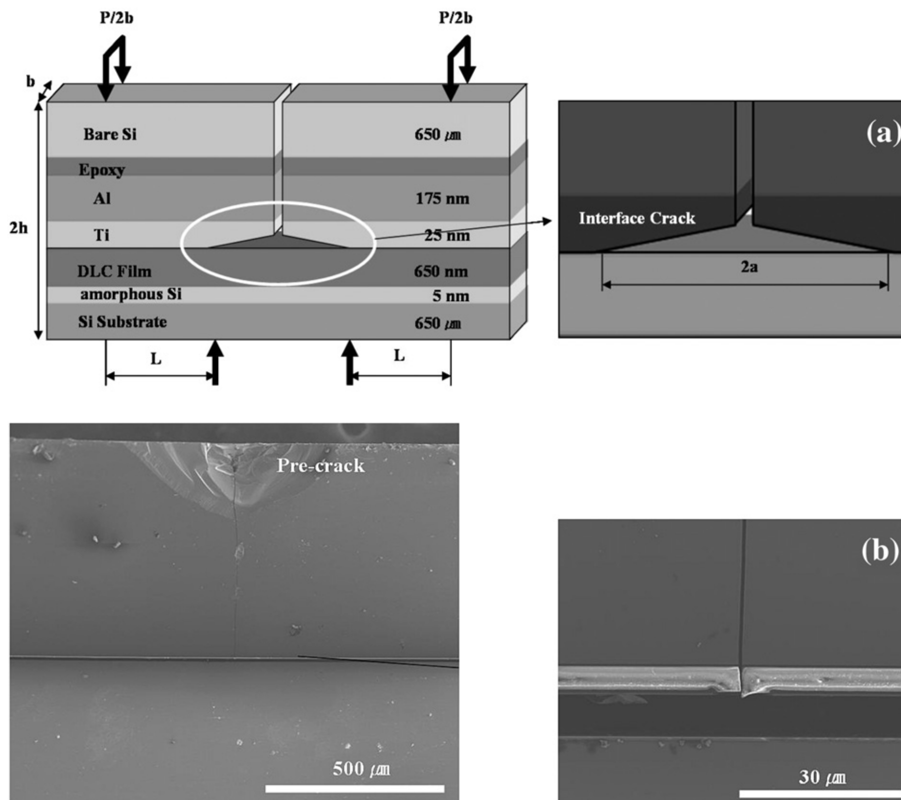

Fig. 1. A schematic diagram of (a) the four-point flexure sample and (b) detail observation of the multilayer stack including the weak interface under the initial notch using scanning electron spectroscopy (SEM).

point data presented in this paper, failure occurred within the DLC or Si-DLC film but very near to (within ~few nm) of the DLC/Ti interface.

3. Results and discussion

Using a proper mixture of diluted silane and benzene gases, DLC films were prepared both with (Si-DLC) and without (DLC) 2 at.% of Si incorporation revealed by RBS. Results of Raman spectroscopy of these films, both with and without thermal annealing, are shown in Fig. 2. Raman spectra of DLC films can be resolved by two Gaussian peaks which are associated with D and G peaks of solid carbon materials respectively [22,23]. An increase in the ratio of D intensity to G intensity, I(D)/I(G), along with G peak shift to higher wave number and the narrowing of G peak, indicate an increase in graphite-like sp^2 bonding [22]. As shown in Fig. 2, the incorporation of 2 at.% of Si within the DLC film decreased the I(D)/I(G) ratio from 0.37 to 0.33. On the other hand, for both the DLC and the Si-DLC films, thermal annealing increased the I(D)/I(G) ratio from 0.37 to 0.42 and from 0.33 to 0.40, respectively. These results are in good agreement with previous studies on the effects of thermal annealing [24,25] and Si incorporation [26,27]. Our results clearly show that the thermal annealing promotes graphitization and greater sp^2 bonding, whereas the Si incorporation leads to an increase in the number of sp^3 sites.

The measured values of residual compressive stress, film hardness, and elastic modulus for the different film conditions are shown in Fig. 3. The incorporation of Si into the non-annealed DLC film increased the film residual compressive stress from 0.885 GPa to 1.037 GPa. This can be explained by structure analysis already reported by previous investigations [28,29]. Lee et al reported that the stress value and the hardness of Si-DLC films are greater than those of pure DLC film and the values are independent of the Si concentration [28]. In contrast to carbon, Si can have only sp^3 hybridized bonds which increase the degree of three dimensional inter-link. Thus higher hardness and higher residual stress are expected when Si is incorporated into the DLC film [30]. Upon thermal annealing, the stress values of the DLC and Si-DLC film were decreased from 0.885 to 0.616 GPa and 1.037 to 0.777 GPa respectively. Thermal annealing is one of well known methods to reduce DLC film stress through transformation toward graphitization which is associated with increased sp^2 content [24]. Therefore, low residual stress is expected when the DLC film is thermally annealed. Hardness and elastic modulus values followed the same trends as with the residual compressive stress values and can also be explained by structure analysis of the films [31,32]. Robertson reported a structure model of DLC films that suggested the hardness is proportional to the degree of sp^3 bonding in amorphous carbon matrix. By incorporating of Si into DLC film, the ratio of I(D)/I(G) decrease from 0.37 to 0.33 with a slight G peak position shift to low wave number, indicating more sp^3 bonding and leading to an increase in hardness and elastic modulus. On the other hand, thermal annealing leads to less sp^3 bonding character and thus lower hardness and elastic modulus values.

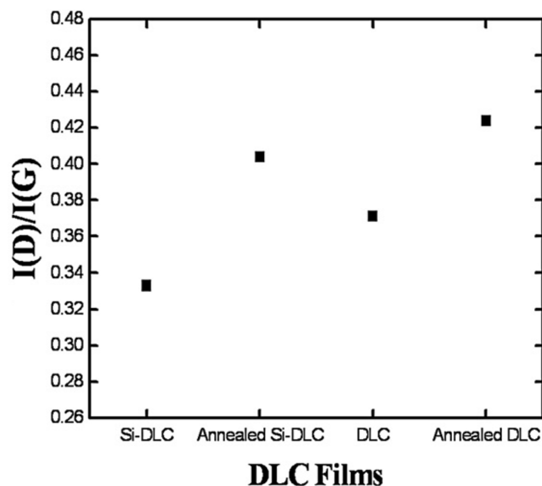

Fig. 2. Variation of micro Raman I(D)/I(G) ratio with structure modified DLC film and DLC film.

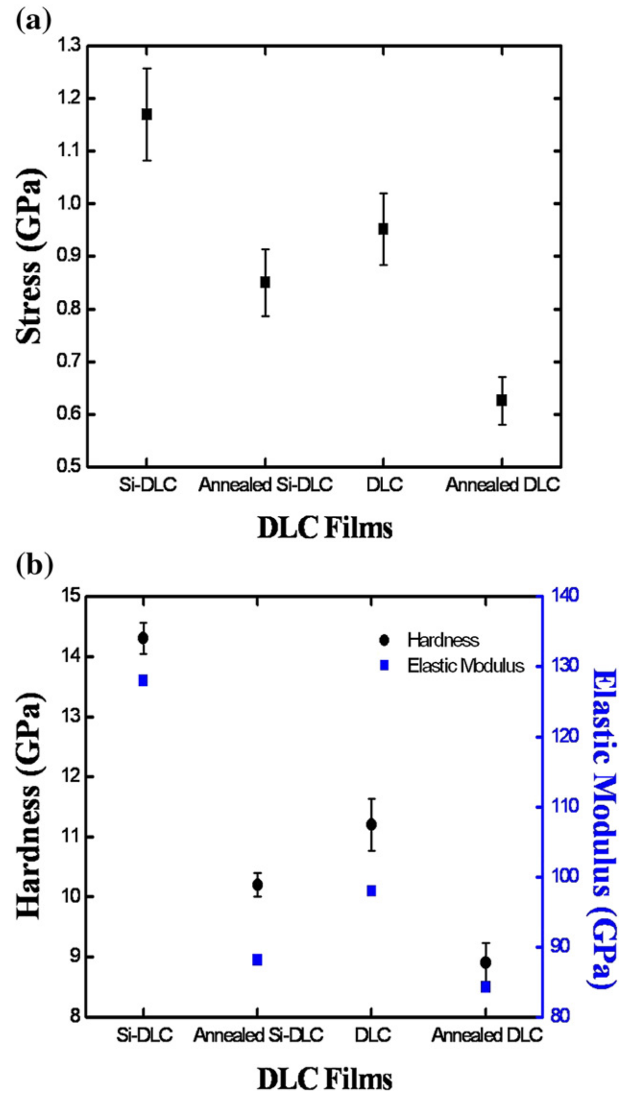

Fig. 3. (a) Compressive stress value and (b) film hardness and elastic modulus values of structure modified DLC film and Si-DLC film.

All of the DLC four-point specimens tested failed near-interfacially between the DLC film and the Ti capping layer, as revealed by XPS of the fracture surfaces (Fig. 4). The oxygen peaks are there because the fractured specimens are exposed to air before they are analyzed under XPS. Therefore, the fracture surfaces undergo oxidation, and this oxidation results in the oxygen peaks in the XPS spectra. The interfacial fracture energies, G_c, for the different film conditions are shown in Fig. 5. As was the case with the residual stress and film hardness values, the fracture energies systematically scale with bonding structure: the film with greater sp^3 bonding character also have higher fracture energies. The incorporation of 2 at.% Si into the non-annealed DLC film, which promotes greater sp^3 bonding, increased the fracture energy from 9.29 J/m^2 to 12.16 J/m^2. In contrast, upon annealing the DLC and Si-DLC films, which promotes less sp^3

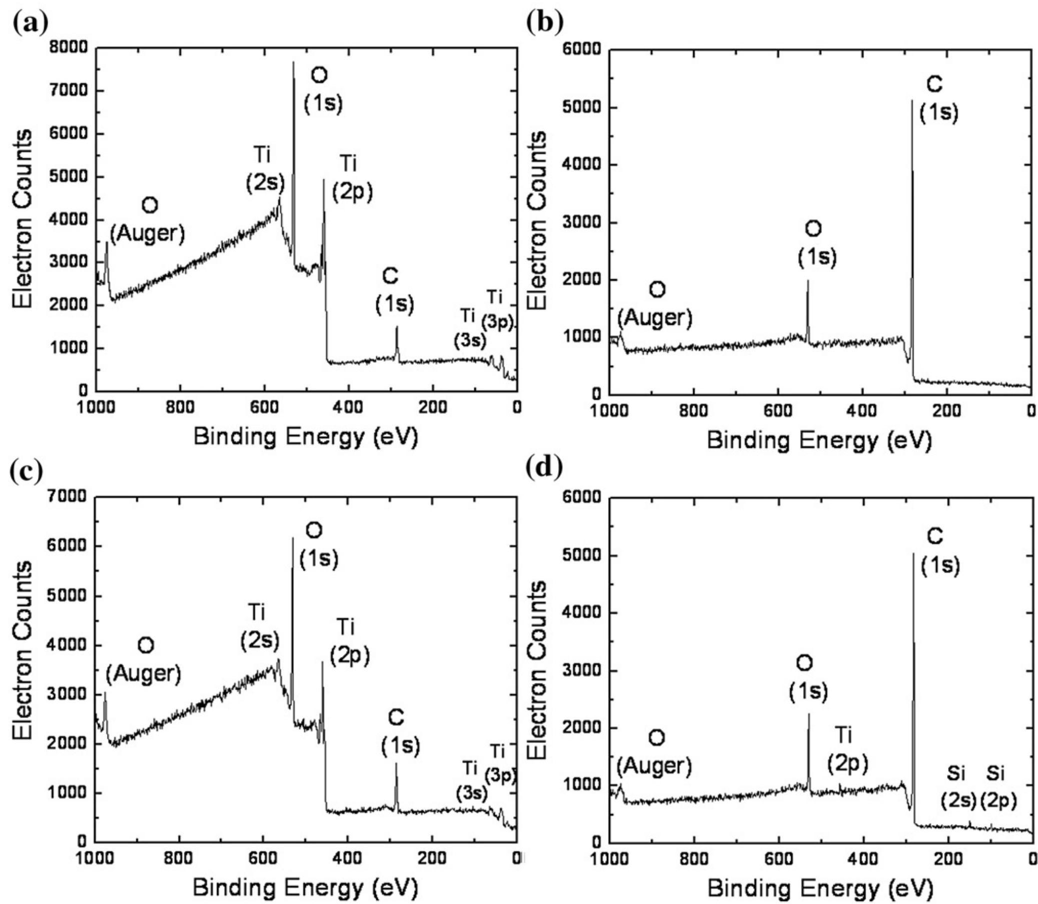

Fig. 4. XPS analysis of four-point bend fracture surfaces showing near-interfacial failure between DLC and Si-DLC films and Ti capping layers: (a) top and (b) bottom fracture surfaces of representative DLC film specimen (c) top and (d) bottom fracture surfaces of a representative Si-DLC film specimen.

bonding, the fracture energies decreased substantially from 9.29 J/m^2 to 1.22 J/m^2 and from 12.16 J/m^2 to 4.37 J/m^2, respectively. Thus the fracture energies scaled proportionally with the degree of sp^3 bonding in the DLC film. In sp^3 configuration, a carbon atom's four valence electrons are each connected to a tetrahedrally directed sp^3 orbital, which makes a strong σ bond to a neighbor atom. However in the sp^2 configuration, three of the four valence electrons enter trigonally directed sp^2 orbitals and fourth electron of sp^2 atom lies in pπ orbital, which lies normal to the σ bonding plane. This π orbital forms a weaker π bond with a π orbital on one or more adjacent atoms [22]. Therefore, we expect the fracture energy to scale with the degree of sp^3 bonding, and this explains why Si incorporation increase the amount of energy needed to drive fracture whereas thermal annealing reduces it.

For a thin film on a substrate, the strain energy release rate, G, for cracking is given by

$$G = Z\frac{\sigma_f^2 h}{E_f}, \tag{2}$$

where σ_f is the film stress, h is the film thickness, E_f is the plane strain elastic modulus of the film, and Z is a dimensionless parameters that depends on the cracking pattern and elastic mismatch between the film and substrate [13]. The parameter Z is a unifying dimensionless number that yields insight into possible decohesion modes. The practical significance of the number is explained in detail in the following reference [33]. The strain energy release rate therefore has strong dependence on film stress and elastic modulus, both of which may be influenced significantly in DLC films with structure modifications such as Si incorporation. When G in Eq. (2) is equated with the relevant fracture resistance, G_c, a critical film thickness below which a specific cracking pattern is inhibited can be predicted:

$$h_c = \frac{G_c E_f}{Z\sigma_f^2} \tag{3}$$

Although Si incorporation does increase the film stress, the improvements in fracture energy and elastic modulus leads to a net benefit in reducing probability of failure of the DLC film. This is

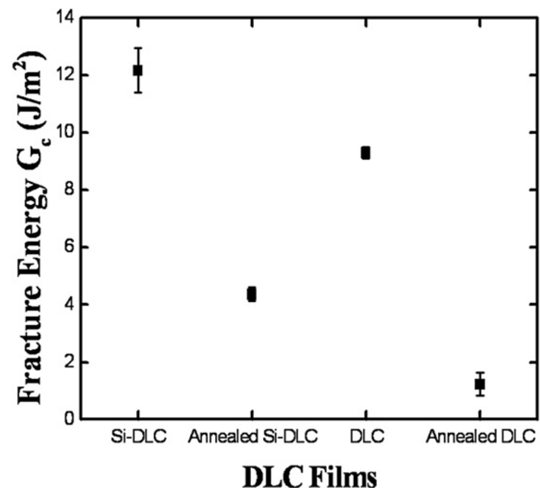

Fig. 5. Fracture energy values for the different DLC film conditions.

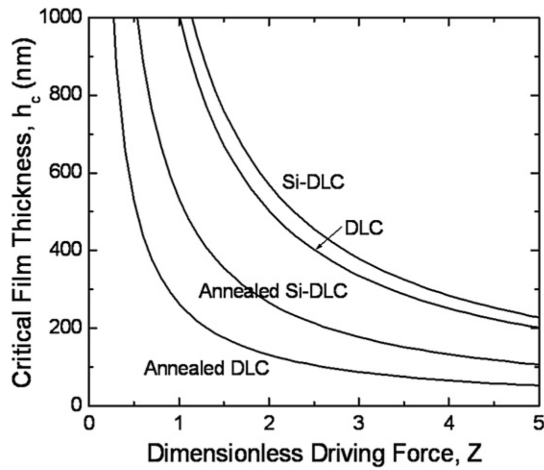

Fig. 6. Critical film thickness versus dimensionless driving force for the different DLC films. The incorporation of Si reduces the propensity for cracking for a given cracking pattern, whereas thermal annealing has the opposite effect.

demonstrated in Fig. 6 where the critical film thickness, h_c, is plotted versus the dimensionless driving force, the Si-incorporated DLC films resulted in increasing of sp^3 bonding have higher critical film thickness values than their pure DLC counterparts while in increasing of sp^2 bonding induced by annealing resulted in the lowest critical film thickness. This indicated that for a given cracking pattern, the Si incorporation yields a net benefit and inhibits failure of the DLC film.

4. Conclusions

We synthesized pure DLC film and Si incorporated DLC film using R.F. PACVD system, and thermally treated some of the samples to modify their structure and mechanical properties. The Si incorporation alters the microstructure of DLC film by increasing the number of sp^3 bonding sites, while thermal annealing increase the degree of sp^2 bonding. The changes in film structure that occur during Si incorporation and thermal annealing were found to greatly affect film properties, such as residual compressive stress, hardness, elastic modulus and interfacial fracture energy. In general, these properties were found to scale in proportion with amount of sp^3 bonding in the DLC film. In particular, the Si incorporation was found to significantly improve film hardness, elastic modulus and adhesion and to inhibit the propensity of film failure and cracking, whereas thermal annealing had the opposite effect.

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