

Mechanical properties of diamond-like carbon composite thin films prepared by pulsed laser deposition

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Abstract

We have investigated the mechanical properties of diamond-like carbon (DLC) thin films that contain foreign atoms. The DLC films were prepared by pulsed laser deposition. A novel target design was adopted to incorporate foreign atoms into the DLC films during film deposition. Copper, titanium and silicon are chosen as the dopants. The chemical composition of the doped films was determined using Rutherford backscattering spectrometry, X-ray photoelectron spectroscopy and calibrated extrapolation. Experimental results of both visible and UV Raman are presented and discussed in terms of peak shape and position. The effect of dopants on the Raman spectrum is also analyzed. Optical microscopy of the pure DLC of a certain thickness showed severe buckling. A brief review of the theoretical background of adhesion is given and the possible mechanisms of adhesion that may work in DLC coatings are discussed. Qualitative scratch tests on the specimens show that pure DLC has quite poor adhesion due to the large compressive stress, while the doped DLC films exhibit much improved adhesion. Wear tests show improved wear resistance in the doped DLC coatings. Nanoindentation results give an average hardness above 40 GPa and effective Young's modulus above 200 GPa for pure DLC. The copper doped DLC films showed slightly decreased hardness and Young's modulus as compared to pure DLC films. Ti and Si can reduce the hardness and Young's modulus more than Cu. All these can be understood by analyzing the internal stress reduction as derived from Raman G-peak shift to lower wavenumbers. A preliminary model of the stress reduction mechanism is discussed. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbon manifests itself in several different phases such as diamond [1], graphite, fullerenes [2] (recent advancements in this field may be found in Refs. [3,4]), nanotubes [5–8] and diamond-like carbon [9] etc., due to its ability to hybridize in several forms such as tetrahedral (sp^3), trigonal (sp^2) and linear coordinations (sp^1) [10]. Diamond-like carbon (DLC) is an important form of amorphous carbon consisting of a mixture of both sp^3 and sp^2 coordinated carbon. With a large fraction of sp^3 bonded sites, DLC can exhibit properties close to those of diamond [11]. The attractive properties of this novel structure include high values of hardness, transparency in the infrared range, chemical inertness, low coefficient of friction and high wear resistance, small electron affinity that leads to field emission effect, etc. Unlike diamond films produced by, for example, hot filament chemical vapor deposition, DLC films are synthesized at

much lower temperatures and are usually very smooth. As a result of their unique properties, DLC films have found applications as hard protective coatings for magnetic disk drives, as antireflective coatings for infrared windows [12], as field emission source, and so on.

The beneficial properties of DLC are due to the sp^3 bonding constituents. DLC films of high quality can rival diamond films in terms of mechanical performance such as wear resistance, very low coefficient of friction, high hardness and elastic modulus, etc. It has been found that both the mechanical properties, such as hardness, Young's modulus, adhesion to the substrate and internal stresses, etc., and important electronic properties, such as the optical gap (Tauc gap), photoluminescence, conduction behavior, etc., of DLC films could be tailored to a certain extent by the $sp^3:sp^2$ ratio [9].

The interesting aspect of pulsed laser ablation is that it is a nonequilibrium process and the species produced in the laser plasma possess very high kinetic energy. For instance, the kinetic energy of atomic species produced by electron beam evaporation is around $\sim kT$ (~ 0.025 eV) (k is the Boltzmann constant and T is the absolute temperature)

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whereas those produced by pulsed laser may be as high as 100–1000kT (~ 2.5 – 25 eV) or even higher [13]. The photon energy might help promote one of the 2s electrons to the 2p orbital and lead to the formation of sp^3 hybridization that is the precursor of diamond-like carbon constituents. Also, pulsed laser deposition could produce hydrogen free DLC films. Upon optimization, PLD produces DLC films superior to filtered cathodic vacuum arc (FCVA) [14] deposition and mass selected ion beam (MSIB) deposition [15].

However, successful preparation and application of DLC films have long suffered by a large internal compressive stress in the films regardless of the film growth technique employed [16–18]. This internal stress could be as high as 10 GPa [14]. Traditional explanation for the presence of the large internal stress is based upon the assumed subimplantation mechanism of DLC deposition. In this mechanism, incident energetic carbon species bombard the existing DLC film and since usually it takes place at room temperature where mobility of atoms is quite limited, it will give rise to large compressive stress [16,19]. McKenzie et al. [20] even argued that large compressive stress is a prerequisite for the formation of high quality DLC films. Adhesive failure of thin films occurs when the internal stress σ exceeds a critical value. A film of thickness h delaminates when the mechanical energy density exceeds the energy needed to create two new surfaces, such as

$$2G_1 \left(\frac{1 + \nu}{1 - \nu} \right) hf^2 < 2\gamma, \quad (1)$$

where γ is the surface/interfacial energy, ν the Poisson's ratio, G_1 the shear modulus of the film and f the strain in the film. If we write the equation in terms of strain, we can have

$$h < \frac{\gamma}{G_1 f^2} \left(\frac{1 - \nu}{1 + \nu} \right). \quad (2)$$

This equation sets the upper limit on film thickness. Thus, a film of certain thickness would bulge when the mechanical energy density exceeds the energy required to create two fresh surfaces.

In the past, some efforts have been directed toward improving the adhesion of DLC films by depositing an interlayer or several interlayers between the DLC film and the substrate [21–23]. For example, Bentzon et al. [22], used metallic interlayers to study the enhancement of the adhesion of DLC on steel. It was found that Cu/Cr appeared to provide the best adhesion. However, the authors did not provide a convincing explanation for their observations, in light of the fact that there is a weak chemical bonding between carbon and copper, which leads to poor adhesion of diamond films to copper substrates. Therefore, a better understanding of the mechanism of adhesion improvement by metallic interlayers needs to be developed. A possible mechanism may be related to the accommodation of the compressive stress by copper to provide stress relief in DLC films, thus copper providing a compliant layer. More

recently, functionally gradient DLC coating design has been proposed to produce adherent DLC protective coatings.

In this paper, we present results on several aspects of the mechanical properties of pure DLC films and those containing various types of dopants prepared by PLD. A novel target configuration will be adopted so as to in situ incorporate foreign atoms into the DLC films. The DLC coatings are characterized by Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), visible and ultraviolet Raman spectroscopy, optical microscopy, scratch test for adhesion assessment and wear test for comparison of tribological properties among the specimens. The internal stress reduction is analyzed by observing the Raman peak shift. A preliminary model will be proposed to explain the experimental observations. Nanoindentation measurements are carried out to obtain the Young's modulus and the nanohardness of the DLC thin films.

2. Experimental procedure

The novel target configuration was described elsewhere [24]. The p-type silicon (100) wafers were used as substrates. Copper, titanium or silicon was incorporated into the growing films. The Si wafers were cleaned in acetone and methanol ultrasonic baths followed by HF dip to remove the native oxide layer before loading into the laser deposition chamber. The laser beam source used was pulsed excimer laser ($\lambda = 248$ nm, $t_s = 25$ ns) at a repetition rate of 10 Hz, with an energy density close to 3.0 J/cm². All the depositions were conducted at room temperature in a high vacuum exceeding 10^{-7} torr.

The surface morphology of the films was observed using an optical microscope. Visible Raman spectra were collected using 514 nm coherent photon (laser) beam. The Raman spectra were deconvoluted into two Gaussians to study the peak shift so as to get information about the internal stress reduction due to the presence of foreign atoms. Ultraviolet Raman spectroscopy on some specimens was conducted in an attempt to acquire more information about the chemical characteristics of the films. Both RBS and XPS were used for chemical composition determination. Fundamental scratch tests were performed on the specimens to study the adhesion of DLC films on the substrate. The scratches were observed and compared via optical microscopy. A "crater grinding method" based upon microabrasion was used to measure the wear rate and to study the wear characteristics of the samples. Nanoindentation measurements were conducted to gain knowledge of the Young's modulus and nanohardness of the undoped and doped DLC coatings.

3. Results and discussion

Standard profilometry on the doped and undoped DLC specimens showed consistently that the film thickness lies

Table 1
Geometric (apparent) and true concentration of dopants in DLC films

Dopant	Copper			Titanium			Silicon		
	Cu-1	Cu-2	Cu-3	Ti-1	Ti-2	Ti-3	Si-1	Si-2	Si-3
Apparent values	15	16	27	14	21	40	14	28	35
True values	1.4	1.5	2.5	2.7	4.0	7.7	–	–	–

in the range of 400–600 nm. Both RBS and XPS were used to acquire the chemical composition of the doped DLC films. Table 1 give the chemical composition of the DLC films that containing various types of foreign atoms.

Fig. 1 is the visible Raman spectra for several samples with different dopants and for the pure DLC film. For disordered materials such as amorphous Si and Ge that possess the same short range order as their crystalline counterparts, the Raman spectroscopy might be understood on the basis of the selection rule breakdown concept developed by Shuker and Gammon [25].

In a simple approach, the first-order Raman scattering of the amorphous covalent state corresponds to the broadened vibrational density of states. This simple model has been verified in the case of amorphous semiconductors such as Si and Ge [26]. In addition, a Raman peak shift, which can sometimes be observed, is usually attributed to a change of the force-constant values and the broadening of the lines is caused by the relaxation of the \mathbf{k} -selection rules. Since the wavevector \mathbf{k} corresponds to the eigenvalues of the translational operator in a crystal lattice, therefore it is a good quantum number only for a perfect crystal lattice. The strict selection rules for electronic transition set by the transla-

tional symmetry of the crystal lattice are relaxed in amorphous state and therefore, more modes could contribute to the Raman scattering and results in broadened Raman spectrum. There is also a general resemblance between the Raman spectrum of pure DLC, DLC + Cu and DLC + Si samples. It was argued that a visible Raman spectrum with a relatively symmetrical G-band corresponds to high quality DLC film, i.e. high $sp^3:sp^2$ ratio [27]. Apart from the G-band, the spectra also exhibit a small shoulder at around 1350 cm^{-2} associated with disorder-allowed zone edge mode of graphite and it is thus designated as D-band (A_{1g} mode). It appears that the DLC film doped with Ti shows more asymmetry and an increased D-band in the Raman spectrum. There is a general tendency in Fig.1 that all the peak positions of the G-band of the doped samples have been shifted toward smaller wavenumber. The shift of Raman peaks will be used to analyze the internal stress reduction later in this paper. We have found out that the incorporation of Ti is very efficient in this matter.

The majority of the reported Raman studies of DLC have used visible lights, mostly 514.5 nm line of an argon ion laser, to acquire the Raman spectra. It has been generally observed that a relatively sharper Raman band occurs at 1560 cm^{-1} , and a broad shoulder band at around 1400 cm^{-1} , in the spectra excited by a 514.5 nm line [28,29]. Actually, the major features of the visible Raman spectra of a-C films appear to be derived from corresponding features in the spectrum of graphite [30]. The so-called G-peak corresponds to the G-line associated with the optically allowed E_{2g} zone center mode of crystalline graphite and the D-peak roughly corresponds to the D-line associated with disorder-allowed zone-edge mode (A_{1g} mode) of graphite.

Theoretical calculations show a peak at $\sim 1200\text{ cm}^{-1}$ due to sp^3 carbon [31]. Raman scattering from MeV-ion implanted diamond beyond a critical ion dose that turned the surface diamond into amorphous diamond showed a broad peak at 1200 cm^{-1} [32], in good agreement with the approximate one-phonon density of states for sp^3 amorphous carbon.

More recently, direct observations of sp^3 bonding in DLC films have come into practice by the utilization of ultraviolet Raman spectroscopy [27,33,34]. Shorter wavelengths, such as violet light are used to enhance the resonance of the $\sigma-\sigma^*$ electronic transitions. A Raman peak at around 1200 cm^{-1} has been observed for largely sp^3 bonded DLC films. EELS measurements have been used to calibrate the UV-Raman

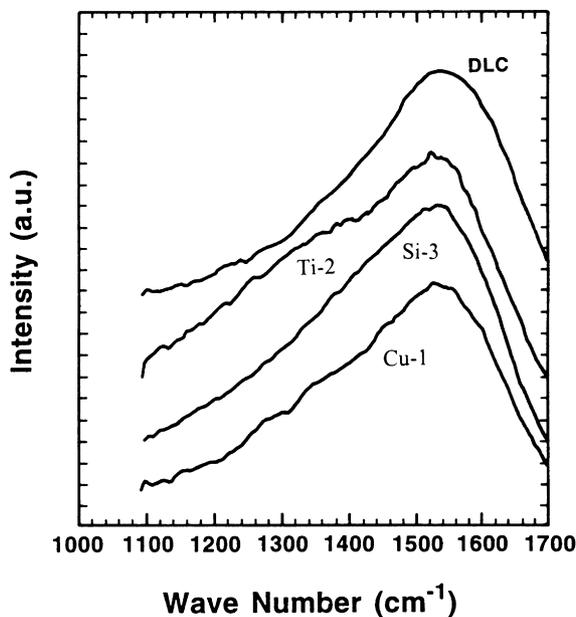


Fig. 1. Visible Raman spectra of pure DLC, DLC doped with Cu, DLC doped with Ti and DLC doped with Si. The labeling of specimens is referred to Table 1.

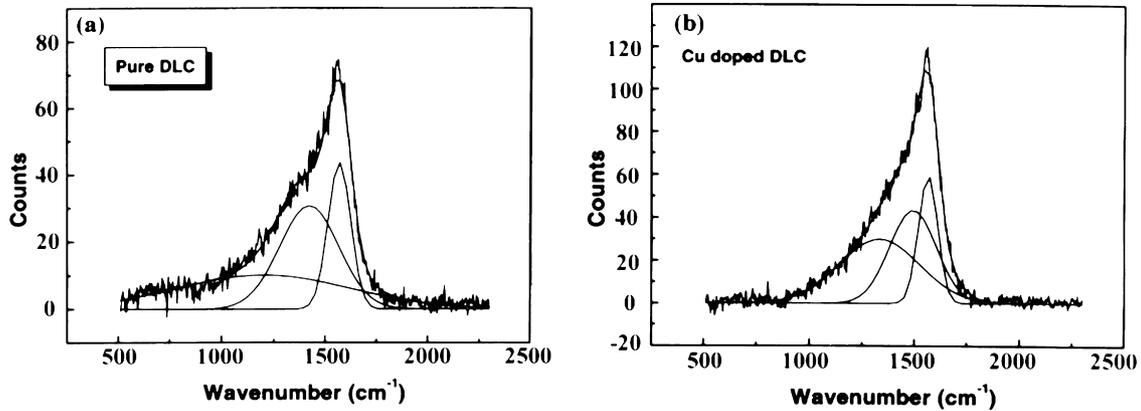


Fig. 2. Ultraviolet Raman spectra of (a) pure DLC and (b) DLC + Cu. Deconvolutions of the spectra with multiple Gaussians are also shown in the spectra.

studies. The experimental results are found to be in excellent agreement with theoretical predictions and contributed to an improved understanding of the mechanism by which the diamond-like fraction develops within the amorphous carbon network.

Fig. 2 is the UV-Raman spectra obtained from pure DLC (a) and DLC + Cu (b). The samples were irradiated with about 25 mW of 262 nm light (4th harmonic of Nd:YLF)-focused to a diffuse line on the sample. The laser is pulsed at 300 Hz with a pulse width of a few nanoseconds. The spectra were collected with a SPEX triple spectrograph-CCD combination at 25 cm^{-1} resolution. No distinct features are visible from UV-Raman spectra assumed for sp^3 carbon. However, unlike visible excitations where a single shoulder part is centered at 1350 cm^{-1} , one can see another shoulder located at about 1200 cm^{-1} in the case of DLC and DLC + Cu. This shoulder is quite small presumably because part of the sp^3 -bonded carbon had been converted into sp^2 bonded carbon due to the irradiation of the incident laser beam.

The insignificant effect of Si on the general shape of Raman spectrum could be understood in the light that Si itself is of sp^3 hybridization, being covalently bonded and its presence might not greatly affect the short range environment of DLC structure (bond length and bond angle, for example) that contributes to the Raman spectrum of DLC. In

the case of Cu, since its d shell is fully occupied and it has been recognized that Cu has little chemical bonding with carbon [35], it might be expected that Cu would not contribute much to changing the short range environment of DLC either. The outer shells of a Ti atom is $2\text{d}^22\text{s}^2$, and it might be envisaged that this shell configuration could contribute to the change of short range electronic structure of DLC and thus give rise to the change of Raman spectrum.

Fig. 3 shows the optical micrographs of DLC films containing Cu, Ti and Si. While in the Cu doped DLC only a few particulates are present, in the Ti and Si doped DLC, a relatively large particulate density exists. This can be discussed based upon heat equilibrium consideration. In addition to this observation, it is seen that all the doped DLC films sticks well to the substrate. No buckling has been observed in these specimens.

However, buckling occurred in the pure DLC films. At lower magnification, the sinusoidal shape of the buckling pattern would be more obvious, as shown by Fig. 4. Usually, buckling would not spread over the whole surface but start from edges of the specimen. The bright contrasts of the sinusoidal wrinkles correspond to the ridges of the buckling.

While it is clear from the occurrence of the buckling patterns that pure DLC films have a very large internal compressive stress, the buckling phenomenon is absent at

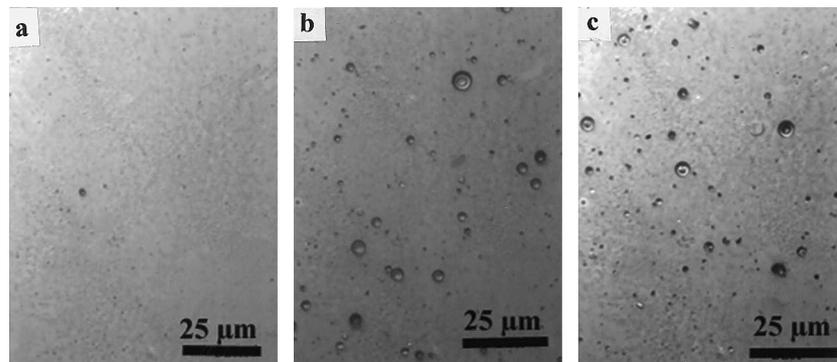


Fig. 3. Optical micrographs of (a) DLC + Cu, (b) DLC + Ti and (c) DLC + Si. It shows that the particulate density of the Cu doped DLC is much smaller than those of Ti and Si doped DLC.

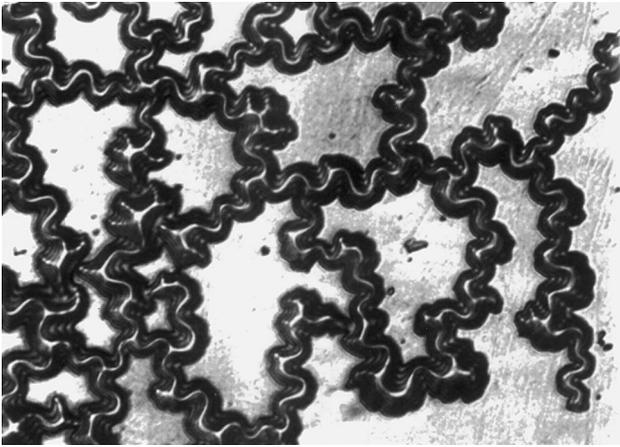


Fig. 4. Buckling patterns taken from pure DLC film. The buckling exhibits sinusoidal shape. See text for detailed discussions.

all in all the doped DLC films. Therefore it appears that the presence of dopants can reduce the internal compressive stress in DLC films and much thicker DLC films can be prepared with doping.

In order to have a better understanding of how the presence of dopants enhances the adhesion of DLC films, we carried out qualitative scratch tests on pure DLC and some doped DLC films.

In fact, the term adhesion covers a wide variety of concepts and ideas, depending on whether the subject is discussed from a molecular, microscopic, or macroscopic point of view or whether one talks about formation of the interface or failure of the formed system [36,37]. The term adhesion is therefore ambiguous, meaning both the establishment of interfacial bonds and the mechanical load required to break an assembly. Because of this, researchers from different fields of study have proposed many theoretical models of adhesion. These models together are both complementary and contradictory. They include: (1) mechanical interlocking, (2) electronic theory, (3) theory of boundary layers and interphases, (4) adsorption (thermodynamic) theory, (5) diffusion theory, (6) chemical bonding theory. Among these models, we can usually distinguish rather arbitrarily between mechanical and specific adhesion,

the latter being based on the various types of bonds (electrostatic, secondary, and chemical) that can develop between two solids. In practice, each of these theoretical considerations is valid to some extent, depending upon the nature of the solids in contact and the conditions of formation of the bonded system.

It is easy to understand that chemical bonds formed across the coating–substrate interface can greatly participate to the level of adhesion between both materials. These bonds are generally considered as primary bonds in comparison with physical interactions, such as van der Waals, which are called secondary force interactions. The terms primary and secondary stem from the relative strength or bond energy of each type of interaction. The typical strength of a covalent bond, for example, is on the order of 100–1000 kJ/mol, whereas those of van der Waals interactions and hydrogen bonds do not exceed 50 kJ/mol. It is obvious that the formation and strength of chemical bonds depends upon the reactivity of both coating material and substrate material. In the case of thin film deposition *in vacuo*, one of the key parameters that would considerably affect the chemical bonds between the thin film and the substrate is the surface cleanliness of the substrate prior to deposition and the vacuum condition of the deposition chamber. For instance, if the native oxide of the silicon wafer has not been completely removed prior to DLC deposition, poor adhesion will usually be observed. On the other hand, fresh Si surface would usually result in good adhesion since Si and C have strong covalent bonding. This is the reason that some investigators tried to bombard the substrate surface with energetic ions such as Ar or N ions so as to achieve fresh and chemically active substrate surface.

A direct measure of adhesion may be obtained by applying a force normal to the interface between film and substrate [38]. Tensile tester, ultracentrifuge, and ultrasonic vibrations have been utilized to apply the required force but with inconsistent results.

In this study, unlike the purpose of achieving a quantitative critical load, we used a constant normal load of 10 g for all the films and drew the indenter across the film. Qualitative comparison could be made between the films by studying the scratch morphology using optical microscopy. Fig. 5

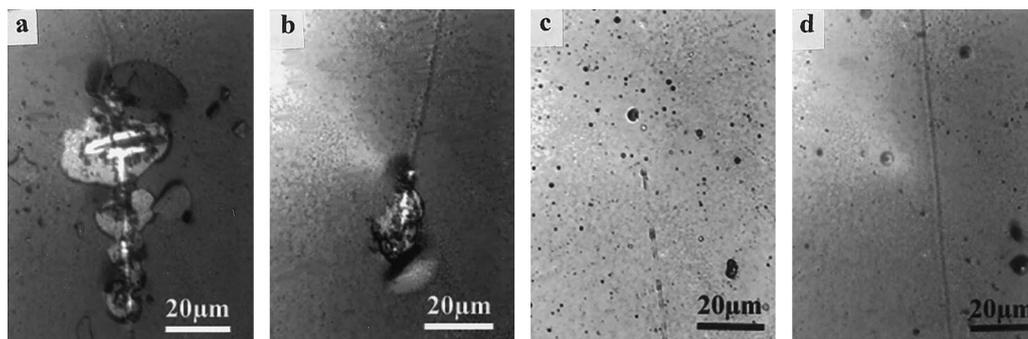


Fig. 5. Optical micrographs of scratches made on (a) pure DLC, (b) DLC + Cu, (c) DLC + Ti and (d) DLC + Si showing different adhesion properties of these films.

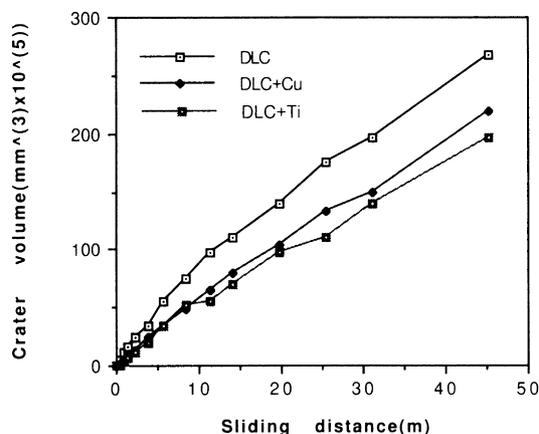


Fig. 6. Wear test results of pure DLC, DLC + Cu and DLC + Ti.

shows the scratches made on different diamond-like carbon films. It can be seen that in the case of pure DLC (Fig. 5(a)), the film is easily stripped off from the substrate, indicating poor adhesion. This is consistent with the optical microscopy studies of the buckling patterns of pure DLC film. In all the doped DLC samples, the films adhere well to the substrate (Fig. 5(b) and (c)), with no buckling patterns. This is particularly so for DLC films containing Ti (Fig. 5(c)) and Si (Fig. 5(d)).

From our results, we conclude that diamond-like carbon films that contain a small content of foreign atoms can have significantly improved adhesion. In the pure DLC films, buckling can be frequently observed and the buckling patterns exhibit sinusoidal shape, implying large internal compressive stress in the as deposited film. The geometry and mechanism of the formation of buckling patterns might be described in connection with theories pertaining to the buckling of thin plates or shells. Qualitative scratch tests on the specimens show that DLC films containing foreign atoms exhibit much better adhesion than pure DLC.

Since at present the primary application of diamond-like carbon is related to tribological performance and wear resistance, we carried out studies on the wear resistance of doped DLC coatings and compared these results with pure DLC coatings.

The most common form of wear is the so-called adhesive wear [39]. It takes place whenever one solid material is slid over the surface of another or is pressed against it. The removal of material takes the form of small particles, which are usually transferred to the other surface but may come off loose depending on the geometry and material of the specific case. Generally, the tendency of contacting surfaces to adhere arises from the attractive forces that exist between the surface atoms of the two materials. If two surfaces are brought together and then separated, either normally or tangentially, these attractive forces act in such a way as to attempt to pull material from one surface on to the other. Whenever material is removed from its original surface in this way, an adhesive wear fragment is created.

There have been several theoretical models regarding the mechanisms of adhesive wear since the pioneering work of Archard [40], whose study on the quantitative aspect of sliding wear has been corroborated by extensive study on different materials combinations without lubrication. Basically, the following is concluded: a) The amount of wear (adhesive removal of material) is generally directly proportional to the load L . b) The amount of wear is generally proportional to the distance slid, x . c) The amount of wear is generally inversely proportional to the hardness H of the surface being worn away. Therefore, the volume worn away can be written as

$$V = \frac{kLx}{H}, \quad (3)$$

where k is a dimensionless constant dependent on the materials in contact and their exact degree of cleanliness. Eq. (3) is also called the Holm–Archard equation. The constant k is also called wear coefficient analogous to the coefficient of friction. The quantity $k/3$ can be taken as the probability that any junction leads to the formation of a transferred fragment. It has been verified that k is always below unity [39], which suggests that the probability of forming an adhesive wear particle is, in most cases, quite low.

Many different experimental designs have been explored to study sliding wear [41]. In our study, we use a “crater grinding method” based on microabrasion mechanism to acquire experimental results of the wear resistance of diamond-like carbon coatings. A nominal load of 5 g was applied to create the craters.

Fig. 6 shows the wear test results for the DLC, DLC + Cu and DLC+Ti films on silicon. The plots contain the volume worn off (in mm^3) as a function of sliding distance (in m). Improvement of wear resistance of the DLC films through incorporation of metal is very significant, especially during the initial stages of the wear test. It is also observed that the effect of titanium is stronger than that of copper. One possible reason may be that titanium is a strong carbide former and it produces relatively stronger bonding with carbon in the film, whereas Cu is a very weak carbide former and it is doubtful whether it exists in carbide. What is also apparent from Fig. 6 is that the sliding wear of DLC films follows the Holm–Archard law.

The improvement of wear resistance by incorporating foreign atoms into the DLC films is consistent with the enhancement of adhesion of these films by doping. It appears based on our discussions that this improvement might most probably be due to reduction in the internal compressive stresses. This will be discussed in more detail later.

Since the vital properties of DLC for tribological applications are, among others, hardness and Young’s modulus, the effect of doping on these properties should be crucial.

Nanoscale mechanical characterizations of both hydrogen free DLC and hydrogenated DLC have been reported [42,43]. Again, the nanohardness and Young’s modulus of

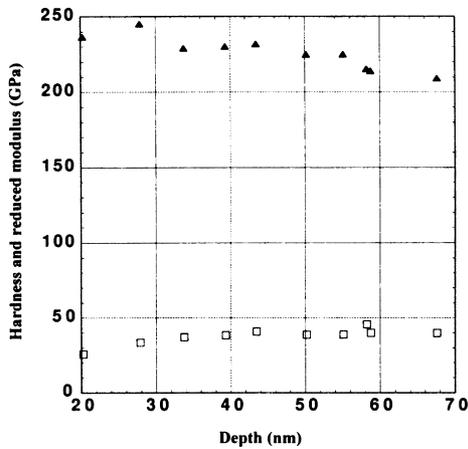


Fig. 7. Nanohardness (squares) and Young's modulus (pyramids) of undoped diamond-like carbon films as a function of indentation depth.

diamond-like carbon can be tailored with the $sp^3:sp^2$ ratio. Hoshino et al. [43], used ultramicroindentation method (in other word, nanoindentation) to measure the hardness and Young's modulus of DLC films. They reached an unrealistic hardness value of 200 GPa (compared to natural diamond). The documented hardness value of natural diamond falls in the range 56–102 GPa [44], but these authors reported for a-C:H films hardness values of 200–500 GPa. In their studies of structure and properties of DLC produced by PLD, Voevodin et al. [45] showed that the presence of hydrogen reduced film hardness from 60 GPa for a-C films to 14 GPa for a-C:H films. Hydrogen was also associated with dependence of a-C:H films friction coefficient on environment and with higher wear rates of a-C:H films in comparison to a-C films. Savvides and Bell reported a somewhat detailed investigation on the hardness and Young's modulus of diamond and DLC films [42] by means of force–displacement curves (nanoindentation). The DLC films were prepared by low energy ion-assisted unbalanced magnetron

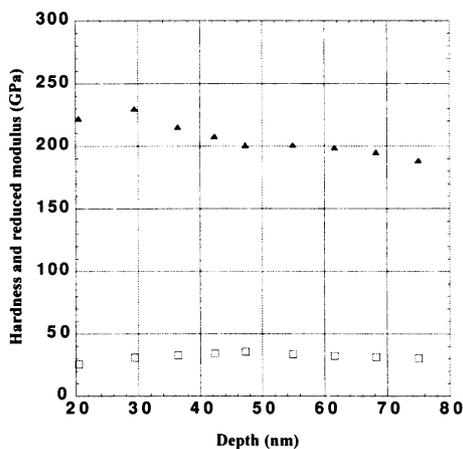


Fig. 8. Nanohardness (squares) and Young's modulus (pyramids) of diamond-like carbon film containing 1.4 at.% Cu as a function of indentation depth.

sputtering. By varying the bombarding ion energy, five films were prepared having different $sp^3:sp^2$ bonding ratio (3–6), optical gaps (1.2–1.6 eV), and hydrogen concentrations (4–20 at.%). The force–displacement measurements are characterized by substantial elastic recovery, and individual films show a very narrow range of hardness and modulus values. It is found that high hardness and improved modulus in DLC films correlate with increasing ion energy, $sp^3:sp^2$ bonding ratio, and energy gap. Individual films have mean values of hardness and elastic modulus in the range 12–30 GPa and 62–213 GPa, respectively.

We have measured the nanohardness and Young's modulus as a function of indentation depth. Fig. 7 shows the reduced Young's modulus and hardness for undoped pure DLC. It shows Young's modulus above 200 GPa and hardness around 40 GPa. The values of nanoscale mechanical properties represented by Fig. 7 imply good film qualities of DLC. It is worth noting that diamond has a Young's modulus of around 1000 GPa and hardness 80–100, and most of the hard ceramic materials have hardness around or below 20 GPa. It is then clear that our DLC films should consist of high percentage of sp^3 bonded carbon. Fig. 8 gives the nanohardness and Young's modulus of Cu doped diamond-like carbon film as a function of indentation depth. It can be seen that, in comparison to undoped DLC, both the Young's modulus and the hardness of the Cu doped DLC film are slightly reduced.

Fig. 9 is the nanohardness and Young's modulus of diamond-like carbon film that contains 2.7 at.% Ti. The Young's modulus shows insignificant change as compared to the Cu doped specimen. However, the nanohardness exhibits slight reduction, with the average value of 25 GPa.

Fig. 10 shows the nanoindentation results for Si doped DLC film as a function of indentation depth. As compared to pure DLC, DLC containing Cu and Ti, respectively, both the hardness and Young's modulus are considerably decreased.

It is interesting to recall the scratch test shown in Fig. 5. There it shows that pure DLC exhibits very poor adhesion, indicative of very large internal compressive stress in the film. It has long been recognized that high quality DLC films always possess large internal compressive stresses. Fig. 5 also shows that the adhesion of DLC containing Cu is not as good as DLC containing Ti and Si. In one sense, it might be presumed that the level of residual stresses in the Cu doped DLC film is still quite high, while the Ti and Si doped DLC films have substantially reduced internal compressive stresses. However, quantitative information about the internal stress reduction would necessitate further consideration. In the following, analysis will be performed on this problem based on Raman spectroscopy results.

Raman spectroscopy has been used to probe the stress–strain conditions of materials with quite consistent results [46,47]. This is because of the fact that the stress–strain dependent property is the frequency of the atomic vibrations in a material that can be characterized with the spectroscopic technique of laser Raman spectroscopy. The principle by

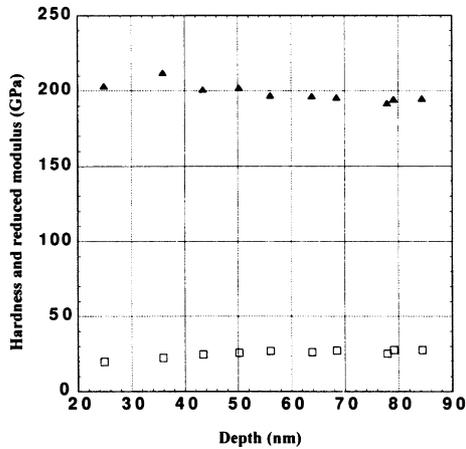


Fig. 9. Nanohardness (squares) and Young's modulus (pyramids) of diamond-like carbon film containing 2.7 at.% Ti as a function of indentation depth.

which this technique works is that when a material is stressed, the equilibrium separation between its constituent atoms is altered in a reversible manner. As a result, the interatomic force constants that determine the atomic vibrational frequencies also change since they are related to the interatomic separation. In general, as the bond lengths increase with tensile load, the force constants and, hence, the vibrational frequencies decrease, while the reverse effect is present when the material is subjected to hydrostatic or mechanical compression.

Robinson et al. [48] examined the effect of axial tensile strain on the Raman spectrum of PAN based, pitch based and rayon based carbon fibers. They found that the strain dependence of the G line (E_{2g} zone center mode) of the carbon fiber Raman spectrum obeys a linear relationship up to fiber fracture. Melantis and Galotis [49] investigated the dependence of the Raman vibrational frequencies of carbon fibers on axial compression. In their study, the single

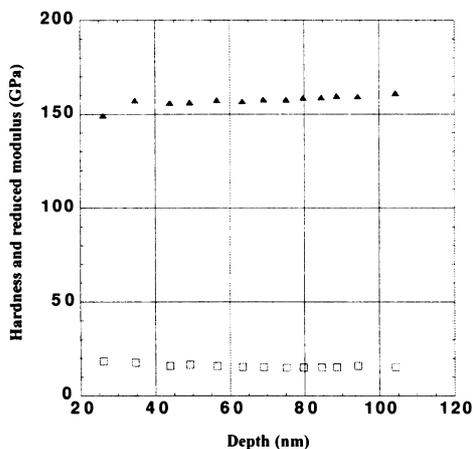


Fig. 10. Nanohardness (squares) and Young's modulus (pyramids) of diamond-like carbon film containing silicon as a function of indentation depth.

filaments were bonded to the top surface of a polymer cantilever beam which could be flexed up or down to subject the specimens to compression or tension, respectively. By monitoring the Raman frequencies along the fibers with a small laser probe of a Raman microscope, the critical strain to compressive failure was measured. The relationship between the Raman frequency of the E_{2g} vibrational mode and the applied compressive strain was again found to be linear for high modulus fibers. Yang and Young [50] reported results in SiC- and C-glass composites. They measure the residual strain due to processing and also found good agreement between predicted and measured values if there was no crystallization of the matrix around the fiber.

Accordingly, the magnitude of the Raman shift can be related to the residual stress, σ , by the following equation

$$\sigma = 2G \left(\frac{1 + \nu}{1 - \nu} \right) \frac{\Delta\omega}{\omega_0}, \quad (4)$$

where $\Delta\omega$, ω_0 , G and ν are the shift in the Raman wavenumber, the wavenumber of a reference state (not necessarily the stress free state), the shear modulus of the material and the Poisson's ratio of the material, respectively.

We have presented both visible Raman spectra and UV Raman spectra of some DLC films that are either dopant free or contain some foreign atoms such as Cu, Ti and Si. In the case of UV Raman spectra, it is observed that the G -peak positions located by deconvolving the Raman spectra by multiple Gaussian fitting are 1568.3 cm^{-1} for pure DLC, 1563.6 cm^{-1} for Cu-1, 1560 cm^{-1} for Ti-1 and 1551 cm^{-1} for Si-1 (the labeling of specimen is shown by Table 1). The trend is clear that the presence of dopant leads to shift of the G -peak to smaller wavenumbers, indicating that the internal compressive stress of the films is decreased. More detailed analysis is done on the visible Raman data since the Raman spectra can generally be resolved into two Gaussians to achieve the best possible fit. However, the peak positions may be different from those via UV Raman spectroscopy since different experimental routes are used in that case. By so doing, we also found significant shift of the G -peak of the doped DLC films towards lower wavenumber relative to the undoped DLC. If we use pure DLC as the reference, and use the mechanical properties of DLC as measured by nanoindentation given in the last section, the internal stress reduction can be calculated according to Eq. (4). The results are tabulated in Table 2.

It appears that Ti has the strongest effect on internal stress reduction. This might be due to the unique electronic structure of titanium atoms as discussed previously. Another possibility might be that the concentration of Ti is generally higher than Cu. Table 2 also shows that the effect of Si is somehow constant. This could be understood in terms of the fact that the real concentration of Si has not been changed significantly with the increase in the nominal concentration (based on geometrical considerations) since the density of particulates also increased rapidly. Another reason might be

Table 2

G-peak position (cm^{-1}) and internal compressive stress reduction (GPa) as obtained from Raman shift analysis. (The G-peak of pure DLC = 1556.83 cm^{-1})

Dopant	Copper			Titanium			Silicon		
	Cu-1	Cu-2	Cu-3	Ti-1	Ti-2	Ti-3	Si-1	Si-2	Si-3
$\Delta\sigma$ (GPa)	0.77	1.80	2.31	1.64	4.11	7.2	1.54	1.64	1.67
$\omega_G - 1500$ (cm^{-1})	52.03	45.64	42.44	46.60	31.23	11.99	47.24	46.60	46.44

that Si is tetrahedrally bonded, and might not be able to contribute significantly to the internal stress reduction in the films. This argumentation seems not quite consistent with UV Raman results that showed Si doped DLC films do have much smaller wavenumber for the G-peak. It also appears to be at odds with adhesion and nanoindentation measurements. It has been observed in previous context that Si doped DLC exhibits good adhesion, reduced Young's modulus and hardness. For the time being, we presume that the DLC films containing Si might have more defects such as microvoids, etc., which make them more compliant as compared to other systems.

The general reduction of internal compressive stress through incorporation of dopants might be understood by invoking the atomic structure of DLC. By far, three models for the atomic structures of DLC have been developed, i.e. the strained layer model, the domain model and the continuous rigid random network (CRN) model [9]. It has been recognized that the CRN model, which is analogous to that of tetrahedrally bonded amorphous silicon, is the most realistic, as justified by various experimental and theoretical studies. The reduction of the internal compressive stresses arising during preparation of DLC films through the in situ introduction of dopants can then be understood on the basis of the effect of these dopants on the CRN of DLC. It is known that transition metals like Cu and Ti are usually more compliant as compared to covalently bonded materials like DLC. The substitution of metal dopants for carbon atoms in the CRN might be able to accommodate or take up the strain by distortion of the electron density distribution since the outer shell electrons of transition metals are loosely bound to the atom. The effect of Si can also be interpreted by the same token. Also, in the case of Ti and Si doped DLC films, the nanoparticles produced through the "splashing" mechanism can be deformed and accommodate the compressive stress in the DLC film.

Sullivan et al. [18], reported the stress relaxation and thermal evolution of film properties of highly tetrahedrally bonded amorphous carbon. They proposed a model for the stress relaxation. The onset of stress relaxation in these materials occurs following thermal annealing at temperatures as low as 100°C , and near full stress relaxation occurs after annealing at 600°C . The stress relaxation is modeled by a series of first order chemical reactions which lead to a conversion of some fourfold coordinated carbon atoms into threefold coordinated carbon atoms.

Observations similar to ours have been reported by

Monteiro et al. [51], of significant internal stress reduction in DLC films doped with Ti and W. The films were produced by dual-source vacuum arc plasma immersion technique. The authors found evidence of nanocrystal TiC and WC by high-resolution transmission electron microscopy. This would not be surprising considering the film preparation technique they used. Neto et al. [52], studied the relation between mechanical and structural properties of silicon-incorporated a-C:H films and they also found reduction in the residual internal compressive stress due to the presence of silicon.

It is now apparent that appropriate dopants can be used to produce DLC films with reduced internal stresses. The film adhesion can thus be considerably enhanced. Detailed theoretical modeling is needed, however, to elucidate the underlying mechanism that leads to the stress reduction. Also important is the information of how the dopant atoms are distributed in the CRN of DLC.

4. Summary and concluding remarks

In this paper, attempts are made to reduce the large internal compressive stresses in the diamond-like carbon films by in situ doping the DLC films with various types of foreign atoms, such as copper, titanium and silicon. Experimental results of both visible and UV Raman are presented and discussed in terms of peak shape and peak position, etc. Optical microscopy of the pure DLC of a certain thickness showed severe buckling of the DLC film and the sinusoidal buckling pattern. A brief review of the theoretical background of adhesion is given and the possible mechanisms of adhesion that may work in DLC coatings are discussed. Preliminary qualitative scratch tests on the specimens show that pure DLC has quite poor adhesion due to the presence of large compressive stress, while the doped DLC films exhibit much improved adhesion. Wear tests show improved wear resistance in the doped DLC coatings. Nanoindentation results show that pure DLC is of quite good quality, with an average hardness above 40 GPa and reduced Young's modulus above 200 GPa. It implies that the DLC films are predominantly composed of fourfold coordinated carbon atoms. The copper doped DLC films showed slightly decreased hardness and Young's modulus as compared to pure DLC film. Ti and Si can reduce the hardness and Young's modulus more than Cu. All these can be understood by analyzing the internal stress reduction as

acquired from Raman G-peak shift to lower wavenumbers. A preliminary understanding of the stress reduction mechanism is proposed based on outer shell electron distribution distortion as a means of accommodating the internal stress relief.

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