

Improvement of wear resistance of pulsed laser deposited diamond-like carbon films through incorporation of metals

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Abstract

We have investigated the characteristics of diamond-like carbon (DLC), DLC doped with Cu, and DLC doped with Ti deposited by a sequential pulsed laser ablation of two targets. The composition of these films was determined by Rutherford backscattering spectrometry and X-ray photoelectron spectroscopy (XPS). Raman spectroscopy and transmission electron microscopy studies showed typical features of DLC with a high fraction of sp^3 bonded carbon in the doped films as well as in the undoped films. Wear resistance measurements made on the samples by means of the 'crater grinding method' showed that DLC + 2.75% Ti has the highest wear resistance, while that of pure DLC has the lowest amongst the samples. Careful analysis of the Raman data indicates a significant shift to shorter wavelength with the addition of metal, which means that the compressive stress in the DLC films has been reduced. We envisaged that the reduction in the compressive stress promotes the wear resistance of the coatings. The XPS studies showed evidence for the formation of Ti–C bonding in the Ti doped sample. Thus metal-doped DLC coatings are expected to improve the tribological properties and enhance the performance of components coated with metal-doped DLC. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Wear resistance; Pulsed laser deposition; Diamond-like carbon films; Metal incorporation

1. Introduction

Diamond-like carbon films (DLC) have found a wide range of applications owing to their unique properties [1]. High quality DLC films can have hardness and coefficient of friction comparable to that of diamond [2,3], lending themselves to exciting applications pertaining to tribological surface coatings [4]. Pulsed laser ablation (PLA) has been used by a number of researchers to deposit high quality DLC films on various substrates [5]. Unfortunately, there is a very large compressive stress in DLC films that exists irrespective of thin film growth technique, such as magnetron sputtering, pulsed laser deposition (PLD), ion beam deposition, etc. [6]. This large compressive stress, when accumulates to a certain level, causes the film to bulge and peel off from the substrate, thus restricting the applications for

thin DLC films. Several studies have been carried out to understand the stress relief patterns (buckling patterns) formed in DLC films deposited on various substrates by different deposition techniques [7–10]. Anttila et al. [11], for example, achieved considerably high adhesion of DLC on silicon by pretreating the silicon surface with 'high energy' (140 eV) carbon plasma ions. However, the compressive stress of the

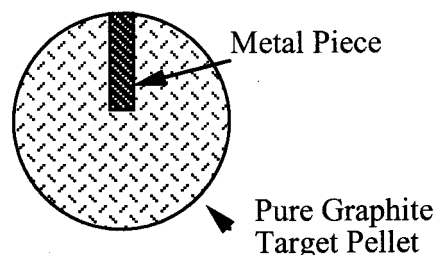


Fig. 1. Schematic illustration of the target configuration used in this study.

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films introduced during their deposition caused the silicon surface layer to peel off including up to 25 μm thick silicon substrate. Therefore, elimination or minimization of compressive stresses in DLC films offers a major challenge for technological applications of DLC coatings.

In the past, some efforts have been directed toward improving the adhesion of DLC films by depositing an interlayer between the DLC film and the substrate [12,13]. For example, Bentzon et al. [13], used metallic interlayers to study the enhancement of the adhesion of DLC on steel. It was found that DLC–Cu–Cr appeared to improve adhesion. However, the authors did not provide convincing evidence for their observations, in light of the fact that there is a weak chemical bonding between C and Cu, which leads to poor adhesion of diamond films to copper substrates. In their work, no consideration for stresses in their films, which can influence adhesion, was given. Therefore, a better understanding of the mechanism of adhesion improvement by metallic interlayer needs to be developed.

This paper is an attempt to enhance the wear resistance possibly by means of reducing the compressive stress in DLC films deposited by PLD through incorporation of a low concentration of metal in the films, without affecting the DLC bonding characteristics of the films.

2. Experimental

We used a target configuration schematically illustrated in Fig. 1. Since the target was spinning during deposition, the focused laser beam would impinge alternatively on graphite and metal portions to ablate the target materials to form a composite film. We used copper and titanium because a Cu interlayer between a silicon substrate and the DLC film has been considered to improve adhesion of the film even though Cu is not a carbide former, while Ti is a strong carbide former. The silicon (100) wafers were used as substrates, which 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.

A pulsed excimer laser was used to ablate the graphite target with a small metal piece covering a part of the target, as shown in Fig. 1. All depositions were done at room temperature in a high vacuum exceeding 1×10^{-7} Torr. High power, pulsed laser ($\lambda = 248$ nm, time of duration $t_s = 25$ ns) was used for ablation at a repetition rate of 10 Hz. The depositions lasted for 40 min, producing a film thickness of ~ 240 nm [2,3]. The energy density used in these depositions was close to 3.0 J cm^{-2} . The films were then analyzed using Raman spectroscopy and X-ray photoelectron spectroscopy for bonding characteristics and Rutherford backscattering

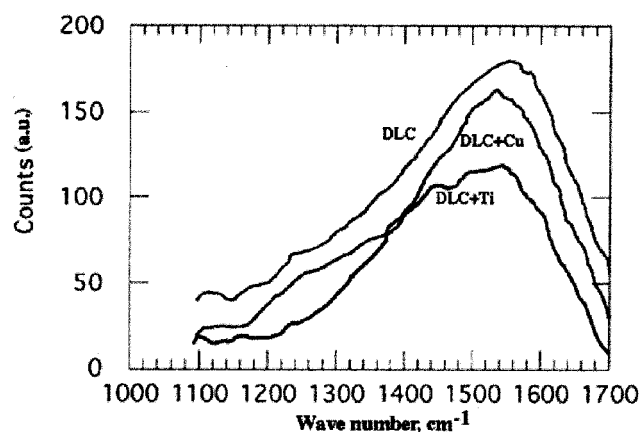


Fig. 2. Raman spectra of undoped DLC, Cu doped DLC and Ti doped DLC.

spectroscopy (RBS) for chemical composition. A ‘crater grinding method’ [6] based upon microabrasion was used to measure the wear rate and to study the wear characteristics of the samples.

3. Results and discussions

Fig. 2 shows Raman spectra for pure DLC, DLC + Cu and DLC + Ti films. All the spectra show a broad hump centered in the range 1525 – 1555 cm^{-1} , which is typical of DLC films [14]. There is a general resemblance between the Raman spectrum of pure DLC and the Cu doped DLC in terms of the spectrum shape. However, the lower wavenumber shoulder part of the

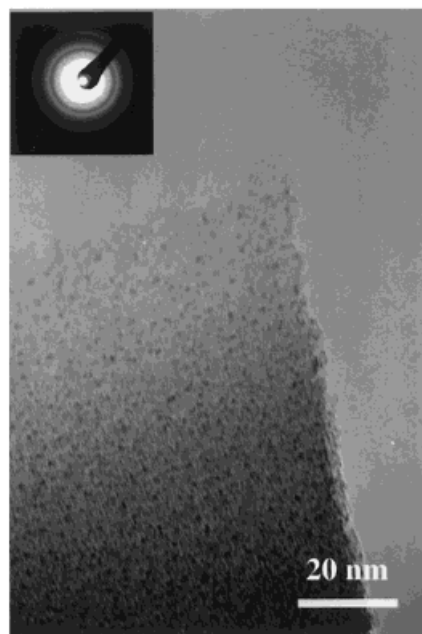


Fig. 3. Transmission electron micrograph of DLC + Cu film with the insert showing two diffuse rings corresponding to the first and second correlation lengths of a diamond tetrahedron.

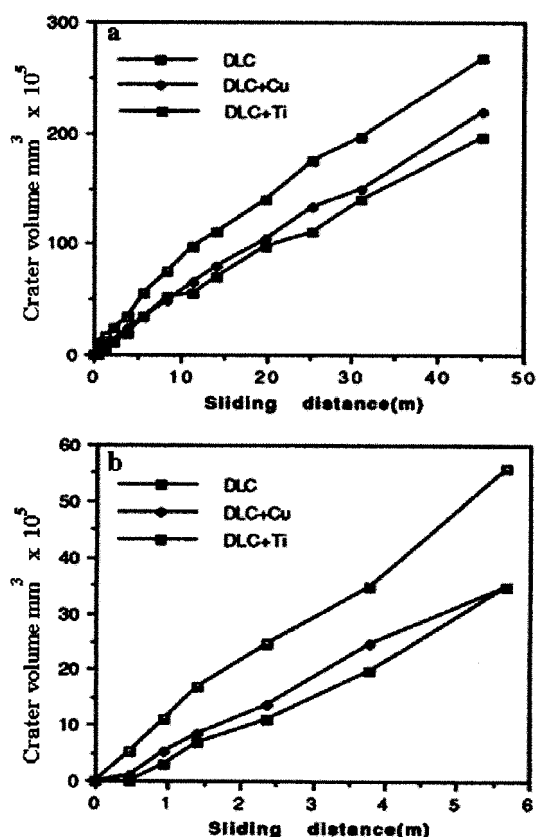


Fig. 4. Wear test results for the DLC, DLC+Cu and DLC+Ti coated samples for the whole range of sliding distance tested (a) and for the short sliding distance regime (b).

Ti doped DLC Raman spectrum is apparently larger than that of pure DLC, presumably because of the increased contribution from the D-peak (disordered carbon) constituents in the film [15]. Fig. 3 shows a transmission electron micrograph of the DLC+Cu film with an insert of the electron diffraction pattern taken from the film showing two diffuse rings with the indexed correlation lengths [16] roughly corresponding to the features inferred from the lattice parameters of diamond. This suggests that a large fraction of the film is composed of the tetrahedral sp^3 bonded structure, which is consistent with Raman results in Fig. 2.

Simulations of the RBS results showed that the fraction of Cu in the DLC+Cu film is 1.2% and the content of Ti in the DLC+Ti film is 2.75% (both in atomic fraction). The XPS analysis of the same samples consistently gives 1.44% Cu for the DLC+Cu film and 2.66% Ti for the DLC+Ti film, respectively. It should be noted that the composition of the film can be changed by changing the laser beam position or by changing the position of the circular target since this will change the perimeter of the circle made by the laser beam on the target surface and the fraction of the metal in the circle is thus changed. It should also be noted that the ablation yields of Cu and Ti are different because they have different reflectivities and will hence

result in different composition even though the target configurations are the same.

Fig. 4 is the wear test results for the DLC, DLC+Cu and DLC+Ti films on silicon. The plots contain the volume worn off (mm^3) as a function of the sliding distance (m). Fig. 4(b) is a replot of the short sliding distance regime of Fig. 4(a) to illustrate the differences during the initial stages of the wear test. From these figures the improvement in 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 Ti is more pronounced than that of Cu. One possible reason may be that Ti is a strong carbide former and it produces relatively stronger bonding with C in the film, whereas Cu is a very weak carbide former and it is doubtful whether it exists in carbide form [17]. To investigate this point we performed XPS studies on these samples. Fig. 5(a) shows an XPS spectrum from a DLC+Cu film. Two peaks due to $\text{Cu}(2\text{p}_{1/2})$ and $\text{Cu}(2\text{p}_{3/2})$ are shown with binding energies of 952.6 and 933.3 eV [18], respectively, with no evidence of carbide formation. On the contrary, in the XPS of the DLC+Ti sample, apart from the peaks corresponding to Ti 2p orbital electrons at binding energies of 460 and 454 eV [18], respectively, two shoulders close to these peaks are also observed at 460.9 and 454.7 eV. These shifts in the binding energies of $\text{Ti}(2\text{p}_{3/2})$ (454 eV) and $\text{Ti}(2\text{p}_{1/2})$ (460 eV) towards higher binding energy side provide indications of Ti and C bonding [19]. There was no evidence for Ti–O

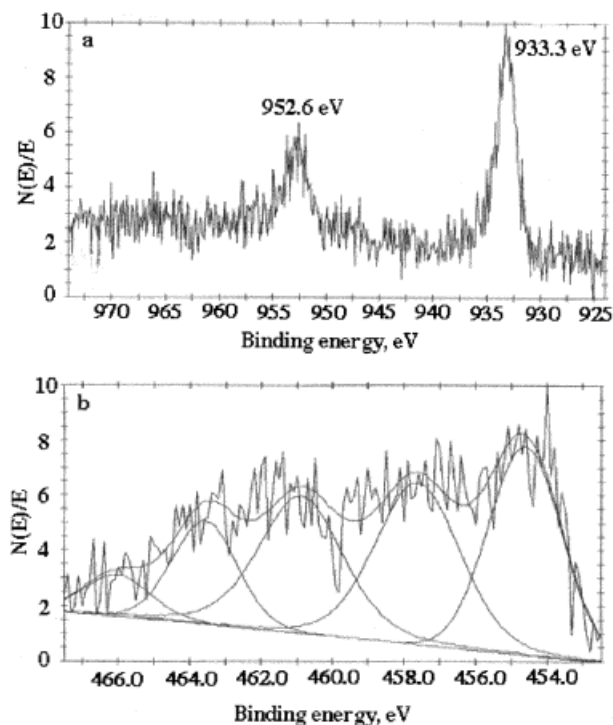


Fig. 5. XPS of Cu from the DLC+Cu film (a) and of Ti from the DLC+Ti film (b).

bonding and the films were also free from oxygen impurities.

The tribological behavior of materials with hard coatings depends critically on the adhesion of the coating to the substrate [2,3]. Many ideas have been proposed for the improvement of adhesion of thin films [20,21]. These include: (a) mechanical interlocking; (b) electronic potential near the interface; (c) formation of boundary layers and interphases; (d) adsorption (thermodynamic); (e) diffusion, and (f) chemical bonding. In the case of thin coatings, the internal stresses in the coatings will affect the mechanical load required to break the assembly, since the relaxation of the stressed state will decrease the free energy of the system. It has been observed that a large compressive stress in DLC films would cause spallation, suggesting that compressive stress in the films will decrease the adhesion and is, thus, detrimental to their tribological behavior. Changes in compressive stress resulting from the incorporation of the metals was investigated in this study. We analyzed the peak shifts that arise due to stresses present in the films [22]. Deconvolution of the Raman spectrum was carried out using the D-peak (around 1380 cm^{-1}) and G-peak (around 1550 cm^{-1}). The peak positions, the heights and widths of the two peaks were changed to provide the best fit to the observed spectrum given in Fig. 2. We find that the G-peak of the DLC sample is located at 1553 cm^{-1} , that of Cu doped DLC at 1540 cm^{-1} , while that of Ti doped DLC is at 1529 cm^{-1} . In the mean time, the position of the D-peak is relatively unchanged. The above shift in the G-peak position to a small wavenumber occurred in the doped samples with Cu and Ti. We have estimated the compressive stress reduction of the doped DLC films from the Raman G-peak shifts with respect to the undoped DLC film. The underlying principle for this estimation is that the vibrational frequencies in a material are proportional to the ‘spring constant’, or interatomic force, between the atoms. As the material is under strain, the interatomic distance changes which results in a change of the interatomic force, and thus a change in the vibrational frequency. The magnitude of the Raman shift is related to the residual stress, δ , as given by

$$\delta = 2G(1 + \nu)/(1 - \nu)(\Delta\omega/\omega_0),$$

where $\Delta\omega$, ω , G and ν are the shift in the Raman wavenumber, the wavenumber of a reference state (pure DLC in this study), the shear modulus of the material and the Poisson ratio, respectively. Taking 300 GPa for the value of $2G(1 + \nu)/(1 - \nu)$ for DLC, we estimated 2.5 and 4.6 GPa compressive stress reduction for Cu and Ti doped DLC films with respect to the undoped DLC film. This observation is in agreement with that achieved by Monteiro et al. [23] who doped DLC films with tungsten and Ti using dual-source vacuum arc

plasma immersion and produced DLC films with significantly reduced internal stresses.

4. Conclusions

In conclusion, we have deposited DLC, DLC + Cu and DLC + Ti films by pulsed laser ablation using a novel target configuration to incorporate metals into the film. Raman spectroscopy showed typical DLC feature for the film and electron diffraction indicated that the DLC + metal composite films are mostly composed of tetrahedron sp^3 structures. The composition of the films has been determined using Rutherford backscattering spectroscopy and XPS. The wear resistance measurements on the samples by means of the crater grinding method showed that DLC + 2.75% Ti has the highest wear resistance, and then DLC + 1.2% Cu, while that of pure DLC has the lowest amongst the samples. This is interpreted with the XPS results that showed evidence for formation of Ti–C bonding in the Ti containing film, as well as the observation of Raman peak shift to a smaller wave number for the samples containing metal, indicating a significant compressive stress reduction. From these results, we suggest a promising way to improve the tribological performance of DLC coatings.

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References

- [1] J. Robertson, Surf. Coat. Technol. 50 (1992) 185–203.
- [2] A.A. Voevodin, M.S. Donley, J.S. Zabinski, J.E. Bultman, Surf. Coat. Technol. 77 (1995) 534.
- [3] A.A. Voevodin, M.S. Donley, J.S. Zabinski, J.E. Bultman, Surf. Coat. Technol. 82 (1996) 199–213.
- [4] K.-H. Habig, Surf. Coat. Technol. 76-77 (1995) 540–547.
- [5] J. Krishnaswamy, A. Rengan, J. Narayan, K. Vedam, J. McHargue, Appl. Phys. Lett. 54 (1989) 2455–2457.
- [6] Q. Wei, J. Narayan, (to be submitted).
- [7] S.B. Iyer, K.S. Harshavardhan, V. Kumar, Thin Solid Films 256 (1995) 94–100.
- [8] G. Gille, B. Rau, Thin Solid Films 120 (1984) 109–121.
- [9] D. Nir, Thin Solid Films 112 (1984) 41.
- [10] N. Matsuda, S. Baba, A. Kinbara, Thin Solid Films 81 (1981) 301.
- [11] A. Anttila, J. Salo, R. Lappalainen, Mater. Lett. 24 (1995) 153.
- [12] M. Grischke, K. Bewilogua, K. Trojan, H. Dimigen, Surf. Coat. Technol. 74–75 (1995) 739–745.
- [13] M.D. Bentzon, K. Mogensen, J.B. Hansen, et al., Surf. Coat. Technol. 6869 (1994) 651–655.

- [14] J. Wagner, C. Wild, P. Koidl, *Appl. Phys. Lett.* 59 (1991) 779–781.
- [15] M. Yoshikawa, H. Fukuda, N. Nagai, G. Katagiri, H. Ishida, A. Ishitani, I. Nagai, in: J.D. Durig, J.F. Sullivan (Eds.), XII ICORS, Int. Conf. on Raman Spectra, 13–17 August 1990, Columbia, SC, USA, pp. 518–519.
- [16] J.M. Cowley, *Diffraction Physics*, chap. 5, North-Holland, Amsterdam, 1981.
- [17] P.M. Hansen, *Constitution of Binary Alloys*, Wiley, New York, 1958.
- [18] C.D. Wagner, W.N. Riggs, L.E. Davis, J.G. Moulder, G.E. Mullenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, MN, 1979.
- [19] L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman, C. Nordling, *J. Phys. Chem. Solids* 30 (1969) 1835–1847.
- [20] J. Schultz, M. Nardin, in: D.E. Packham (Ed.), *Handbook of Adhesion Science and Technology*, Wiley, New York, 1992, pp. 19–33.
- [21] J. Narayan, R.D. Vispute, K. Jagannadham, *J. Adhes. Sci. Technol.* 9 (1995) 753.
- [22] C. Galiotis, *Mater. Technol.* 8 (1993) 203.
- [23] O.R. Monteiro, M.P. Delplancke-Ogletree, I.G. Brown, J.W. Ager III, *Mater. Res. Soc. Symp. Proc.* 438 (1997) 599.