Diamondlike carbon films by rf plasma-assisted chemical vapor deposition from acetylene

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This paper is an overview of studies performed at the IBM Thomas J. Watson Research Center on diamondlike carbon (hydrogenated amorphous carbon) films, including some recent results on their tribological properties. The films were prepared by rf plasma-assisted chemical vapor deposition (PACVD) from acetylene. Their structure and composition were characterized by a variety of methods such as X-ray and TEM diffractometry, XPS, high-resolution ^{13}C NMR spectroscopy, and H(^{15}Nα,γ)C nuclear-reaction profiling. Their adhesion to various substrates, coefficients of static and dynamic friction, and wear resistance were also characterized. It was found that the films were essentially amorphous, reaching their bulk composition after 40 nm of growth above the initial growth interface. Their bulk composition included about 40% hydrogen. More diamondlike carbon bonding was obtained at the initial growth interface than in the bulk range. The ratio of sp^2 to sp^3 carbon atoms was found to be 1.6, with virtually all sp^3 carbon atoms bound to one or more hydrogen atoms. The diamondlike carbon films (DLC) displayed excellent adhesion to the surface of Si. Furthermore, the films could be bonded to films of otherwise nonbonding metals, provided the metals formed stable silicides. By using an interfacial Si film several atomic layers thick, adhesion to the metal films could be improved to the extent that attempts to detach the DLC films fractured the underlying metal films. The adhesive DLC films were found to have a very high resistance to sliding wear and chemical attack, and are therefore useful in various applications as very thin protective coatings.

Introduction

DLC films are metastable, amorphous materials which may contain a microcrystalline phase. The films must be differentiated from diamond layers, fabricated using plasma-based or hot-filament deposition, which are polycrystalline materials, with crystallites up to tens of microns in size, having the diamond structure. Since they were first deposited by Aisenberg and Chabot in 1971 [1], DLC films have been prepared by a variety of methods, including dc or rf plasma-assisted CVD, sputtering, and ion-beam deposition, from a variety of carbon-bearing, solid, or gaseous source materials [2–7].

All the means used for depositing DLC films are characterized by the interaction of energetic ions with the surface of the growing film. The metastable structure of the films most likely originates from the thermal and pressure spikes produced by impinging energetic species at the surface [8]. Thermal spikes of 3283 K and pressures of 1.3×10^{10} Pa (1.2×10^{5} atm), for about 7×10^{-11} s, have been calculated for impinging 100-eV ions [9]. The duration of the spikes is much longer than the vibrational period of 2.6×10^{-14} s for diamond, and is thus well beyond that required to allow bonding. The metastable DLC structure thus formed is conserved because of the extremely high quenching rates of the thermal spikes.

The films are characterized by a hardness measured to be 3000–9000 kg/mm^2 [10] and a generally low friction coefficient, between 0.01 [11] and 0.28 [12], but also very high internal stresses [4, 7, 11, 13]. They typically have high optical transparency over a wide spectral range [14], high electrical resistivity, and chemical inertness to both acids and alkalis. Their extreme hardness and chemical resistance make them good candidates for wear-resistant protective coatings for metals and optical or electronic components, particularly for applications requiring layers of about 100 nm or less. They are especially attractive for coatings which must be less than 50 nm thick, e.g. those used on high-density magnetic recording media.

Depending on the precursor materials used, many of the films contain a significant amount of hydrogen. For films deposited using various deposition methods, the hydrogen content has been determined to range from less than 10% [15] to 50% [16]. The films may contain sp^2, sp^3, and even sp^1 coordinated carbon atoms in a disordered network. It was found that the ratio between the carbon atoms in the different coordinations is to a great extent determined by the hydrogen content of the films. Hydrogen is also important for obtaining films having a wide optical gap (E_{opt}) and high electrical resistivity, because it passivates the dangling bonds in the amorphous structure [9]. This removes midgap defect states and stabilizes the network to prevent collapse into graphite.

Inevitably, if one wishes to understand the physical basis for properties of DLC films such as their hardness, resistance to chemical attack, or optical transparency, their atomic structure must first be characterized. Of importance is the ratio of carbon atoms in each bonding coordination and the hydrogen content, including its distribution in the bulk of the film.

Some characterization methods such as optical measurements [3, 4, 17] and NMR [18, 19] typically yield information regarding spatially averaged bulk properties of the films, although in reality film anisotropy can cause substantial variations of the properties of interest as a function of film thickness. This important liability of bulk characterization techniques is frequently ignored, yet its existence will be explicitly demonstrated by comparing results of NMR, nuclear activation, and XPS analyses of DLC films.

As mentioned above, the DLC films are typically found to have high internal stresses. In order to perform their protective role, the films must adhere well to their substrates; adhesive forces must overcome the internal stresses in the films, which would otherwise cause them to delaminate. Adhesion depends upon the material at the surface of the substrate and can be affected by the deposition method used. Means may have to be found to improve the adhesion of the DLC films to certain materials in order to facilitate their use.

The properties of DLC films have been found to depend strongly on the deposition method and on conditions used [14]. To understand the behavior of DLC films deposited in a specific manner (apparatus and precursor), one must characterize these films. This paper presents an overview of work at the IBM Thomas J. Watson Research Center on the deposition of DLC films from acetylene by rf plasma-assisted chemical vapor deposition (PACVD), their characterization, and the improvement in their adhesion to various substrates.

Experimental methods

The DLC films were prepared by the rf plasma decomposition of acetylene (C_2H_2). The plasma was sustained in a parallel-plate geometry by a capacitive discharge at 13.56 MHz, at a surface power density of 110 mW-cm^{-2}. The deposition was performed at a flow rate of 6 sccm and a pressure of 30 μm, on cathode-mounted substrates held at a deposition temperature T_d in the range $30°C < T_d < 300°C$. The cathode bias was held fixed at -90 V using an rf choke-isolated dc power supply. The deposition temperature was limited to the range given above because earlier work [20] showed that for deposition temperatures above 325°C, the films became graphitic in nature ($E_{\text{opt}} \rightarrow 0$ eV, $\sigma \rightarrow 10^2\ \Omega^{-1}\text{-cm}^{-1}$) and softened significantly.

Amorphous Si layers, used to improve adhesion, were deposited under similar conditions from a gas mixture of 1% silane in argon.

The substrates were either polished Si wafers or Si wafers coated with different metals and/or alloys; they were cleaned with electronic-grade acetone and ethanol and rinsed with 18 MΩ DI water. Additionally, they were sputter-cleaned *in situ* with an argon plasma prior to film deposition.

Grazing-angle X-ray diffractometry (XRD) and transmission electron microscopy (TEM) were used to determine the microstructure of the films. The index of refraction was measured by ellipsometry at a wavelength of 6238 Å, on films deposited on Si wafers.

High-resolution ^{13}C NMR spectroscopy [18, 21, 22] was used to determine the relative concentrations of sp^2- and sp^3-hybridized carbon, as well as the local atomic environment of carbon in each state. For this purpose, DLC films were prepared by deposition onto Si substrates from a gas mixture containing 10% $^{13}C_2H_2$. The films were then removed from the substrates by dissolving the Si in 7:2 HNO_3:HF etchant ("acid etch"), which did not attack the films. The ^{13}C NMR spectra were obtained at a center frequency of 48.29 MHz. Adequate peak separation was obtained using magic-angle spinning [23] at 3.5 kHz. Spectra were obtained both with and without the use of proton decoupling. This facilitated the identification of carbon atoms with bound hydrogen, because the C-H spin interaction causes the carbon peak to be broadened into the baseline of the spectrum, leaving only the signal from carbon atoms with no bound hydrogen [24].

Analysis by XPS was performed on as-deposited 40-Å-thick films using an Al K_α X-ray source. Spectra were taken at 5° and 75° from the surface normal in order to examine the variation of the C_{1s} binding energy as a function of sampling depth.

The hydrogen content and its profile through the thickness of the DLC films, up to 1200 Å thick, was measured using the $H(^{15}N\alpha,\gamma)C$ nuclear resonant reaction at 6.4 MeV, employing an ion dose of 0.6 μC. The method was used previously by Brodsky et al. [25] to determine the hydrogen concentration in amorphous silicon and by Angus et al. [26] to determine hydrogen concentration in DLC films. The profiles were determined by using nitrogen ions having energies in the range of 6.36–6.67 MeV. The depth scale was obtained from the energy loss of ^{15}N ions per unit path length, which was determined from sample density and stopping power of carbon. The thickness resolution was 4 nm. The following values were used for analysis: stopping power = 1.90 MeV/μm; density = 1.14×10^{23} C/cm^3.

The adhesion of the films to the substrates, or the adhesion between different layers, was determined with a Sebastian Adherence Tester (available from Quad Group, Inc., Spokane, WA) using the following procedure: Aluminum studs, having a head diameter of 0.25 mm, precoated with epoxy, were bonded to the surface of the film by curing at 150°C for 1 h. Glass backing plates were attached to the rear of the samples with Permabond 910 glue to prevent the deformation or fracture of the substrates while the studs were pulled. The aluminum studs were pulled in the adhesion tester with a continuously increasing load, applied normal to the surface, until fracture occurred. The fracture load is registered by the apparatus and is generally taken to be a measure of adhesion strength. In practice, however, many cases were observed in which imperfect bonding of the stud to the film surface had occurred, causing the load to be applied to an area significantly smaller than the actual stud head surface. As a result, the apparatus was employed solely to determine the location of the fracture, thus assigning only relative values for the adhesion of the layers to one another.

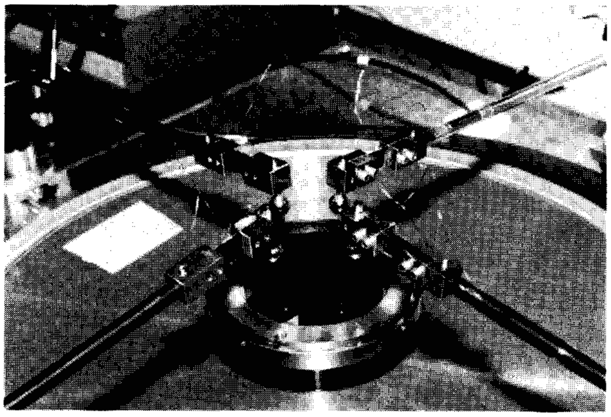

Figure 1

Wear test apparatus, showing disk and riders.

The wear resistance and friction coefficients of thin DLC films were investigated using a specially designed pin-on-disk-type tribotester [27]. The apparatus consists of a turntable on which the disks (i.e., substrates coated with the films) can be mounted. Thin substrates were attached to stainless steel support disks using low-temperature-melting wax. The pin, or rider, to which the load was applied was supported at the end of a low-mass stereo tone arm immobilized to travel only in a vertical plane. A close-up view of the disk and pin in the wear test apparatus is shown in **Figure 1**. The riders were either stainless steel ball bearings or sapphire balls cemented at the end of a small steel rod. The load was thus applied to the surface of the planar disk through a spherical contact surface, enabling the calculation of the Hertzian stress [28]. The wear test was performed by running the apparatus, under a constant load, for a number of rotations, and measuring the resulting wear tracks by using a profilometer. The

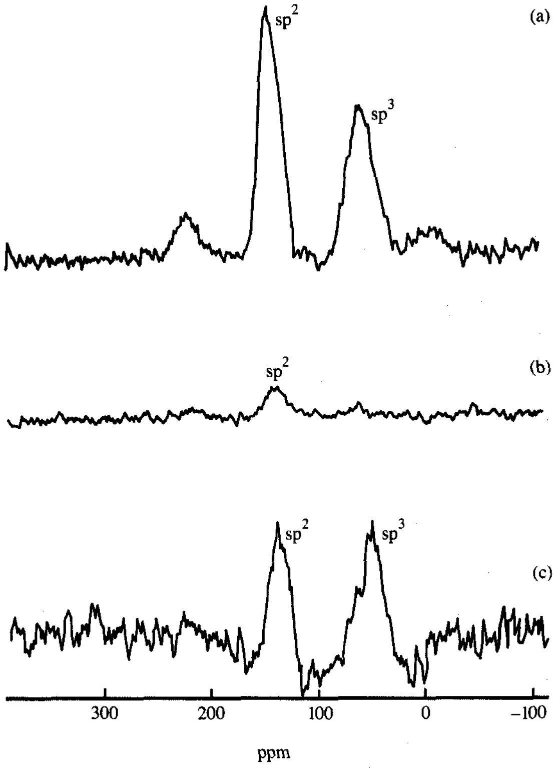

Figure 2

^{13}C NMR spectra of DLC film deposited at 250°C: (a) spectrum with proton decoupling; (b) spectrum without proton decoupling; (c) difference between spectra (a) and (b). From [13], reproduced with permission.

tribotester also made it possible to measure the friction coefficient between the surfaces of the rider and the films.

Results and discussions

- *General properties*

The PACVD-deposited DLC films were conformal and had nanometer-scale smoothness. They were found to have a Vickers hardness of approximately 5000 kg/mm^2 and exhibited a compressive stress of 2×10^{10} dyn/cm^2. The hardness values must be regarded as approximate, as they were obtained from films only 1 μm in thickness, only five times the depth to which the Vickers indenter that was used penetrated the films. Although approximate, this value is comparable to those commonly reported for such films. The DLC films were found to be electrically insulating, with resistivities in excess of 10^9 Ω-cm, and were resistant to chemical attack by both acids and hot alkali solutions.

Grazing-angle X-ray diffractometry and TEM measurements indicated that the films were essentially amorphous, although limited evidence of microcrystallites embedded in the amorphous matrix was observed. The higher degree of crystallinity of DLC films obtained by different authors [17, 29–31] is most probably a result of a much higher substrate bias used by them (up to 2 kV [30]), compared to the 90-V bias used in our work. It has been shown that the use of high-energy ion bombardment during deposition leads to enhanced crystallization in carbon films [7]. The index of refraction was found to be $n = 1.90 \pm 0.02$, for films deposited between 150 and 250°C. The values are within the range obtained by other authors [14].

- *Bonding*

Figure 2(a) presents the proton-decoupled NMR spectrum of a DLC film deposited at $T_d = 250°C$. The spectrum shows two well-resolved peaks representing both sp^2- and sp^3-coordinated carbon. The sp^2 ^{13}C peak is centered at 140 ppm, while the sp^3 peak is at 50 ppm, a condition similar to those observed previously for other carbon films [18, 19]. The integrated peak areas give a ratio of sp^2- to sp^3-bound carbon of 62:38. The peaks observed at 210 and 5 ppm are spinning side-bands generated as an artifact of the magic-angle spinning. **Figure 2(b),** obtained without the use of proton decoupling, shows the NMR signal from only those carbon atoms with no bound hydrogen [24]. No sp^3-bonded carbon is observed in this spectrum, indicating that virtually all of the sp^3-hybridized carbon atoms are bound to one or more hydrogen atoms. Thus, there is no detectable (≥2%) "pure diamond" (fourfold carbon-to-carbon bonding) in the DLC film. A significant amount of hydrogen was also found to be bound to sp^2 carbon, as indicated by the large decrease of the sp^2 peak in Figure 2(b). A different ratio of sp^2:sp^3 carbon and sp^3-coordinated carbon without attached hydrogen has been found by Kaplan and Dilks [21] in DLC films prepared from acetylene. Although the films were prepared under conditions apparently similar to those used in our work, neither power density nor substrate bias was reported [21]; different values of those parameters could be the reason for the different characteristics of the films prepared from the same precursor.

Similar results have been found by Jarman and Ray [18] for PACVD films deposited from methane and by Jansen et al. [19, 22] for ion-beam sputter-deposited films and PACVD films. Jarman and Ray found that hydrogen is bound to both sp^2 and sp^3 carbon, though primarily to sp^3 carbon, while Jansen et al. found that the sp^2 bonds in ion-beam sputter-deposited films remain to a large extent unsaturated up to a level of 35 at.% hydrogen.

- *Anisotropy with thickness*

The energy of the C_{1s} XPS peak is determined by the bound state of the carbon atom, i.e., incorporated in an

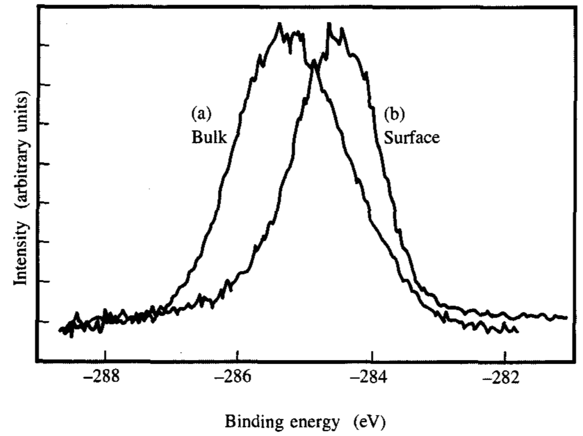

Figure 3

XPS carbon peak C_{1s} from 40-Å-thick film deposited at 250°C: (a) at 5° from surface normal; (b) at 75° from surface normal. From [13], reproduced with permission.

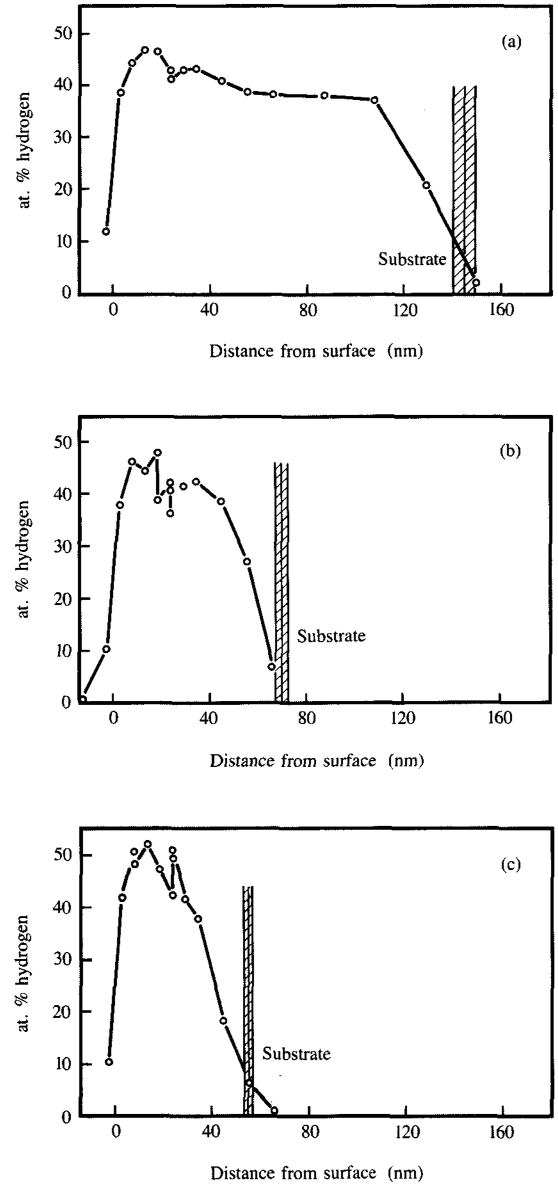

Figure 4

Hydrogen profiles of DLC films that were deposited at (a) 250°C, (b) 150°C, and (c) 30°C. From [13], reproduced with permission.

adsorbed hydrocarbon species, complexed as a carbide, or in its graphite or diamond state [29, 32]. There is a separation of at least 1 eV between the peaks associated with the different carbon states. Mori and Namba [29] used XPS techniques to argue that their carbon films had a diamond structure. The XPS spectra we have obtained at both normal and grazing incidence for a film deposited at T_d = 250°C are shown in **Figure 3**. An increase in binding energy is observed for the spectra taken close to the surface normal relative to the one taken at grazing incidence. The shift observed is consistent with the existence of a gradual change in carbon coordination as probing occurs nearer the initial growth interface, and the observed binding energy approaches that of tetrahedrally coordinated carbon (287.28 eV [29]). This effect is most likely related to several features common to all plasma deposition methods. When a highly insulating film is deposited onto a conductive substrate, the potential between the growth interface and the plasma varies with time as the insulating dielectric layer is deposited. Several workers have reported significant variations in resultant film morphologies with changes in bias [8], and this is likely the underlying cause of the depth anisotropy observed.

Hydrogen profiling was performed for DLC films deposited at three different temperatures. The results, to an accuracy of ±3%, are presented in **Figure 4**. As can be seen to the left of the substrate locations, there is a gradual increase of the hydrogen content at the beginning of the deposition of the film, i.e., from the film/substrate interface. Hydrogen contents characteristic of bulk values are not obtained until more than 400 Å of film has been deposited. Similar behavior was reported previously by Angus et al. [6] for films deposited by several methods.

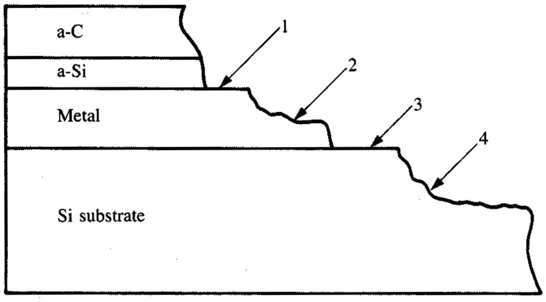

Figure 5

Cross section of layered structure. Numbers indicate possible fracture levels in adhesion test. From [39], reproduced with permission.

This behavior is likely also the result of a gradual decrease of the surface bias with increasing film thickness. An increase of the overall hydrogen concentration with decreasing bias has been reported by Weissmantel et al. [33] and Moravec and Lee [34]. As shown in Figure 4, the bulk hydrogen content increases from 38% to 50% when T_d decreases from 250°C to 30°C. It should be noted that for the films deposited at 150°C (b) and 30°C (c), holding the ion energy fixed, i.e., sampling at a constant depth, resulted in a decrease in the hydrogen content, pointing to an instability of those films under bombardment. Such an instability is characteristic of polymeric carbon materials, thus indicating that the films deposited at lower substrate temperatures contain a polymeric phase. It is estimated from the quenching of film instability with bombardment time that the polymeric phase contains about 8% carbon. In contrast, the carbon films deposited at 250°C were stable under ion bombardment, reproducing results on repeated measurements, indicating that no polymeric phase exists in such films.

A peak of hydrogen concentration in a surface layer about 20 nm thick was observed for all of our DLC films, though it is seen most readily in Figure 4(a) for the thicker film deposited at 250°C. A similar hydrogen peak has been observed in hydrogenated a-Si deposited by rf glow discharge [35].

The hydrogen content in DLC films has a key influence on their mechanical, electrical, and optical properties. Although the absolute hydrogen content of differently prepared DLC films may vary, those properties are a strong function of the hydrogen concentration. Significant hydrogen concentration is generally required to obtain the "diamondlike" properties [14]. Although very hard amorphous carbon films can be obtained without the presence of hydrogen [36], incorporation of hydrogen is required in order to obtain their diamondlike optical and electrical properties [37]. According to Angus and Hayman [37], diamondlike films are a form of hydrocarbon.

The spatially resolved measurements of hydrogen concentration as well as C_{1s} XPS data show clearly that the properties of the DLC films vary spatially over the first few hundred Å of thickness. XPS data imply that more diamondlike carbon bonding is obtained at the initial growth interface, while more graphitic carbon is found further into the bulk of the films. Not only do the dielectric properties of the growth interface vary with deposition time, but so also does the near-surface bias potential, which can account for the variation. The effects observed highlight the need to employ a variety of bulk as well as spatially resolved techniques to accurately characterize the local atomic coordination of carbon in DLC films.

• *Adhesion and tribological properties*

Good adhesion of DLC films has been found on silicon, quartz, and carbide-forming substrates such as iron alloys and titanium [7, 10, 38]. By the use of DLC films, numerous metals which are prone to corrosion or abrasion may be protected. However, not all metals form stable, adherent interfaces with DLC films, and the achievement of good adhesion can thus be the limiting factor in utilizing DLC films for protecting such surfaces.

Figure 5 is a cross section of an experimental layered structure formed on a Si wafer, with a DLC film as the uppermost layer. The numbers indicate the different possible fracture locations in the structure when it was subjected to the previously described adhesion test. The results of the adhesion measurements carried out are presented schematically in **Figure 6**, in which different layer configurations are indicated on the *x*-axis, while the *y*-axis presents the corresponding location of the fractures observed. The numbers in the brackets indicate deposition temperature in °C. A 0 value on the *y*-axis indicates that the DLC film had no adhesion to the underlying surface, and delaminated from the substrate upon removal from the deposition apparatus.

As indicated in Figures 6(a) and 6(b), the DLC films displayed a very good adhesion to the Si substrate, independently of deposition temperature. The adhesive force between the DLC films and the Si substrate is higher than the cohesion of the Si, as evidenced by the occurrence of fracture in the substrate. The same behavior was observed for the adhesion of metallic layers such as Co, Cr, Mo, Ni, or their alloys to the Si substrate [Figure 6(c)]. Figure 6(d) indicates that DLC films delaminate when deposited onto the same metallic layers, independently of the deposition temperature. In these cases, due to the lack of adhesion and high internal stresses, the DLC films crazed immediately after removal from the reactor, becoming a nonadherent powder which could be wiped off the substrate with a soft cloth.

It was previously observed [40] that amorphous silicon, a-Si, crystallizes in contact with certain metals at relatively low temperatures, forming silicides. For example, under thermal (nonplasma) conditions, chromium silicide forms at 500°C, while platinum silicide forms at 280°C [40]. Since the impact of energetic ions at a substrate surface yields a high surface energy [8], it was expected that silicidation reaction rates would be enhanced for a given bulk temperature by plasma immersion. Thus, silicon was an attractive candidate for use as a low-deposition-temperature adhesion layer.

As shown in **Figure 7(a)**, a-Si films behaved as expected. Such films deposited at room temperature fractured at the Si/metal interface, and in a few cases fracture occurred within the metallic film. In contrast [**Figure 7(b)**], a-Si films deposited at a substrate temperature of 250°C adhered well, and fracture occurred in the Si substrate, indicating that the a-Si/metal adhesive bond was stronger than the cohesive strength of the Si substrate. Attempts were therefore made to improve the adhesion of the DLC films to the metal layers by depositing an interfacial layer of a-Si, 20–40 Å thick, between the metal and the carbon film, at the same substrate temperature used during the deposition of the DLC film.

A layered structure [41] (Figure 5) that included a 20–40-Å-thick interfacial layer of a-Si was deposited at 250°C. For this structure, fracture occurred during the adhesion test in the Si substrate, as indicated in **Figure 7(c)**. Even the thinnest silicon interfacial layers, only several atomic layers thick (determined by Auger electron spectroscopy measurement), provided excellent adhesion of the DLC film to the metallic surface. Although silicide formation could not be detected directly, the significant improvement in adhesion when employing the a-Si interfacial layer indicated the formation of strong Si–C and Si–metal bonds.

When thicker (>100 Å) intermediate a-Si layers were used, adhesion test fracture occurred either in the silicon substrate or in the metallic film, or between the metallic film and the Si substrate, as shown in **Figure 7(d)**. The carbon/a-Si/metal interface was the only film junction which remained intact during all tests, indicative of substantially superior bonding at that junction. This was unexpected, as the metal was found to adhere well to the silicon substrate. It appears that the use of a thicker Si layer on the metallic film actually degraded the adhesion of the metallic film to the substrate material. It is known [42] that silicide formation is generally associated with large volume changes. When the thickness of the silicide layer is sufficiently large, these volume changes result in large internal stresses, which could cause degradation of the strength of the metallic layer [42]. In such a case the fracture in the adhesion test might be expected to occur in the metallic layer containing the silicides; this interpretation is speculative because the dimensions of the reacted layers could not be determined accurately enough to verify it.

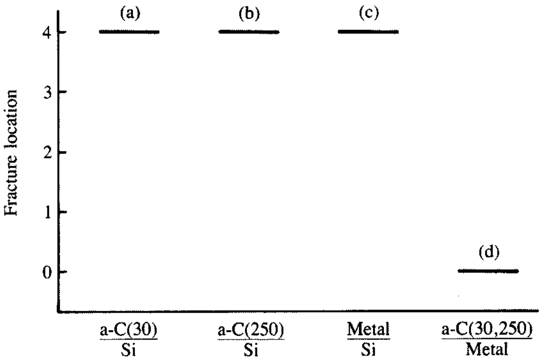

Figure 6

Adhesion fracture levels in layered structures containing DLC films. Numbers on the y-axis correspond to levels indicated in Figure 5; the numbers in brackets indicate deposition temperature in °C. From [39], reproduced with permission.

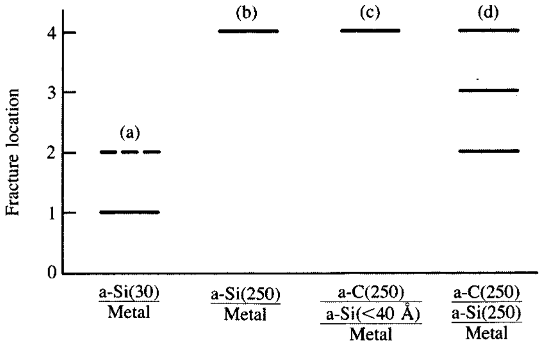

Figure 7

Adhesion fracture levels in additional layered structures containing DLC films. From [39], reproduced with permission.

The friction coefficient of the DLC films was found to be independent of relative humidity in the range of 5–50%, in contrast with the observation by other authors that it decreases with decreasing humidity [43]. It was found that the friction coefficient between stainless steel and DLC films, or between two DLC films, is about 0.15–0.22.

The wear testing showed that a 50-nm-thick DLC film, deposited either on Si or in metal/a-Si/DLC structures, could withstand 300 000 rotations in a pin-on-disk test, under an initial Hertzian load of 480 MPa. By applying an initial stress of 75 MPa for 5000 rotations on the pin-on-disk tribotester, significant amounts of wear were obtained both on a Ni disk and on a hard steel rider. Using a steel rider on a Mo disk resulted only in the wear of the rider. A significant amount of wear was obtained on the Mo disk by applying a stress of 350 MPa with a sapphire rider, but wear was also observed on the sapphire rider. Applying a protective DLC/a-Si structure to the Ni or Mo disks reduced the wear of disks to zero under identical testing conditions. In addition, when the wear test was performed on the disks coated with the protective structure, the wear of the pins was greatly reduced; i.e., no wear occurred on the sapphire ball, and very little wear (estimate from area of flat spot) was observed on the steel pin.

Applications

The special properties of DLC films make them suitable for a variety of applications. It has been suggested that they may be useful in semiconductor applications as gate dielectrics [44] or as passivating layers [45]. Because of their transparency in the infrared, they can be used for wear protection of infrared windows or lenses of Ge, ZnS, ZnSe. They can also be used to protect windows exposed to abrasion (as in passenger jets, copiers) [46]. The low deposition temperature of the DLC films permits their deposition onto products made of plastic materials to protect them against wear. The films may be especially useful where the protective coating must be very thin (100 nm or less); such applications include wear-protection of high-density magnetic storage media, such as hard disks, where they can prevent damage if the read/write head strikes the relatively soft metallic surface of the disks [46, 47]. The films may also be useful as a protective coating for optical storage disks.

Because of their chemical resistance, DLC films can be used as corrosion-resistant coatings. It has been found that corrosion currents decrease by two orders of magnitude to NiFe alloys and by four orders of magnitude to MnFe alloys when these are coated with a 500-Å-thick DLC film.* Similarly, such films may become useful as diffusion barriers for sealing optical fibers and optoelectronic devices against diffusion and degradation by oxygen and water vapor [46].

Summary

Hard, amorphous, and chemically inert diamondlike carbon films have been deposited by plasma-activated chemical vapor deposition from acetylene. It was found that the hydrogen content of films could reach 50% as a function of their deposition temperature. The films were found to contain sp^2- and sp^3-coordinated carbon in a ratio of 1.6:1, averaged through the bulk of the films, although no "diamond" clusters, i.e., fourfold bonded carbon clusters, were observed. The properties of the films were found to be spatially varying over their first 400 Å of thickness. More diamondlike carbon bonding was obtained at the initial growth interface, while more graphitic carbon bonding was found further into the bulk of the films. The studies described here highlight the need to employ a variety of bulk as well as spatially resolved techniques to accurately characterize the local atomic coordination of carbon in such films. The films displayed excellent adhesion to Si surfaces. By using an interfacial Si film several atomic layers thick, it was possible to obtain good adhesion between hard DLC films and silicide-forming metals. As a result of all of their attributes, very thin DLC films can be used as both wear- and corrosion-resistant coatings.

Acknowledgments

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