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Pull-Test Adhesion Measurements of Diamondlike Carbon Films on Silicon Carbide, Silicon Nitride, Aluminum Oxide, and Zirconium Oxide*

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ABSTRACT

Hydrogenated amorphous carbon films or diamondlike carbon (DLC) films were formed by deposition of 400 eV methane (CH_4) ions on several smooth and rough ceramics, as well as on ceramics coated with a layer of Si and Ti. Adhesion was measured by the pin-pull method. Excellent adhesion was measured for smooth SiC and Si_3N_4 , but adhesion of DLC to Al_2O_3 and ZrO_2 was negligible. The use of a Si bonding interlayer produced good adhesion to all the substrates, but a Ti layer was ineffective because bonding between the DLC film and Ti was poor. The presence of surface roughness appeared to greatly increase the measured adhesion in all cases.

Bulk thermodynamic calculations are not directly applicable to bonding at the interface, because the interface is two dimensional and the compositions of interfacial phases are generally not known. If the standard enthalpy of formation ΔH_f° for the reaction between CH_4 and the substrate material is calculated under the assumption that a carbide or carbon phase is produced, a relationship is seen between the reaction enthalpy and the relative adhesion. Large positive enthalpies are associated with poor adhesion; negative or small positive enthalpies are associated with good adhesion.

This relation between enthalpy and adhesion was also observed for DLC deposited on Si. The lack of adhesion to the Ti was attributed to inadvertent formation of a surface oxide layer that

rendered the enthalpy for the reaction with CH_4 strongly positive and similar in magnitude to that for Al_2O_3 and ZrO_2 .

I. INTRODUCTION

Carbon coatings that are hard and exhibit low friction and wear are being intensively investigated because of recent progress in deposition methods. That diamond has favorable tribological properties has been known for many years^{1,2}, but until the advent of low-pressure chemical vapor deposition (CVD) methods³⁻⁵, no practical means of depositing diamond films had been available. Cubic diamond with sp^3 bonding can be produced by many methods but, until now, only at temperatures much higher than can be tolerated by most engineering materials⁵⁻⁸. At room temperature, deposited films tend to be amorphous and contain variable amounts of H. In applications where the optical and thermal properties of crystalline diamond are not critical, diamondlike carbon (DLC) coatings are attractive alternatives to diamond because of their low-friction properties and resistance to wear⁹. DLC is an amorphous form of carbon with a density and hardness approaching that of diamond, but its precise atomic structure and properties are not as well characterized as those of crystalline diamond.

DLC coatings can be hard, wear resistant, and have low static and dynamic friction against many materials⁹, yet they can be formed at low temperatures. The first DLC films were produced at room temperature by ion-beam deposition (IBD) more than 20 years ago¹⁰. Recently, considerable progress has been made in producing these films economically by various CVD and ion-beam methods¹¹⁻¹³. In IBD, a beam of C^+ ions is directed at a substrate. Although possessing smaller heat conductivity than diamond, DLC films produced with low-energy beams of C^+ ions exhibit hardness and density similar to that of diamond¹⁴. Alternately, beams of hydrocarbon molecules can be used; sometimes films produced by this means are referred to as hydrogenated amorphous C films ($a-C:H$). Carbon films deposited on ceramics by a low-energy beam of CH_4 ions exhibit low friction and wear when slid against ceramics¹⁵. The carbonaceous coatings produced in the work presented here will be referred to as DLC films.

There is interest in depositing DLC coatings on ceramics, which offer chemical inertness, hardness, and strength, but often exhibit poor tribological performance. If DLC films can be successfully applied to the sliding surfaces of ceramics, the favorable mechanical properties of the ceramic (strength and stiffness) will be retained and good tribological properties of the DLC film will be added. Good adhesion of the coating to the substrate is necessary for any practical application; a coating that is rapidly removed will be useless. Tribological properties of DLC films have been reported^{5, 9, 15-19}, but little work has been done on the adhesion of DLC films to underlying substrates, although a Si bond layer was found to dramatically increase the adhesion of a DLC film to M-50 steel¹⁵, and a bond layer of SiC was necessary for successful deposition of DLC on a Ti alloy²⁰.

In this paper we report measurements of the adhesion of DLC films formed by IBD of CH₄ on alumina (Al₂O₃), zirconia (ZrO₂), silicon nitride (Si₃N₄) and silicon carbide (SiC). Adhesion was measured by the pin-pull method. Films were deposited on the ceramic substrate by 400 eV ion deposition with CH₄ and Ar ions, with or without bonding interlayers of Ti and Si.

II. EXPERIMENT

Specimens measuring 25.4 x 6.4 x 1 mm were coated in the highly polished condition, or were roughened prior to coating by grinding with a 200- μ m diamond wheel (Table I). Specimens were ultrasonically cleaned in acetone and ethanol and dried with hot air before insertion into a vacuum chamber. Carbon films were deposited directly on the specimens, or on specimens which had been coated with thin bonding layers of Ti or Si (50 nm). An 11:2 mixture ($2.2 \times 10^{-7} \text{ m}^3 \cdot \text{s}^{-1}$ total flow rate) of CH₄ and Ar was used in a Kaufman-type ion source to produce the DLC coatings. For sputter cleaning of the specimens prior to CH₄ bombardment, Ar gas was used at the same flow rate. The accelerating voltage was 400 V and the plasma discharge voltage was 45 V. The current density measured with a Faraday cup was nominally $1.6 \text{ A} \cdot \text{m}^{-2}$ and the dynamic chamber pressure was $\approx 1 \times 10^{-2} \text{ Pa}$. Typical base pressures in the cryopumped system were 10^{-5} Pa . Substrate temperatures attained were 150-200°C.

For deposition, specimens were sputter cleaned with Ar ions for 300 s and then the ion composition was changed from Ar to CH₄/Ar. For specimens with a bonding layer, specimens were sputter cleaned with Ar ions for 300 s, the beam was turned off, and the metal was allowed to deposit on the cleaned specimen to a thickness of 50 nm, whereupon the deposition was stopped and CH₄/Ar film deposition was started.

The adhesion of the films was tested with a commercial pin-pull-type testing machine. Tapered Al pins (2.69-mm head diameter) were bonded to the film with an epoxy adhesive that was cured for 1800 s at 150°C. We took the "adhesion strength" to be the force required to pull a pin from the specimen divided by the area of the pin. Usually each specimen was tested five times. When the film is successfully pulled from the substrate, a coin-shaped section of film is removed, and this type of pull is referred to as a "coin pull." When the adhesion of the film to the substrate is high and it is not possible to pull the film off, the epoxy breaks first and this is referred to as "epoxy failure." In the case of epoxy failure or specimen fracture, the actual adhesion of the film to the substrate cannot be precisely determined, but it is greater than the nominal value.

III. RESULTS AND DISCUSSION

Before production of the films for adhesion testing, test depositions on polished Si wafers were made at various ion energies and hardness measurements were obtained (Table II). A Knoop indenter was used to minimize indenter penetration and measurements were obtained with either 10- or 25-g loads, calibrated with a steel standard. Hardness was 2500 for 400-eV deposition and lower for 250- and 750-eV depositions. The low hardness at 750 eV was attributed to incorporation of Ar into the film.

Okada et al.²¹ studied the properties and structure of IBD films deposited from CH₄. Measured hardnesses were a function of substrate deposition temperature and were inversely proportional to H content. For the lowest temperature deposition (200°C) Vickers hardness was $\approx 3000 \text{ kgf}\cdot\text{mm}^{-2}$, similar to the values obtained in this work. Hydrogen content was near 30 at.%. At 300°C and with a -800 V bias, a Vickers hardness of $6000 \text{ kgf}\cdot\text{mm}^{-2}$ was attained. Anttila et

al.²² evaluated the hardness of IBD coatings formed from accelerated C and hydrocarbon ions. Hardness of the films formed from accelerated C⁺ was twice that of any of the films formed from the accelerated CH₃⁺, CH₄⁺, and C₂H₂⁺ ions. For films produced from the hydrocarbon beam, the H content was 25-30 at. %. It is thus believed that the films deposited in this work contained appreciable quantities of H.

In most cases, the DLC films appeared black or gray, and the surfaces of films deposited on smooth substrates were also smooth. Film thickness was nominally 300 nm, although, in some cases, the thickness was smaller because of experimental difficulties. Table III shows the measured adhesion of DLC to smooth substrates. Adhesion for films on ZrO₂ and Al₂O₃ is vanishingly small. Test pins fell off at the slightest touch. In contrast, bonding to Si₃N₄ and SiC was excellent and the actual adhesion of the DLC film to the substrate could not be quantitatively be determined.

Several difficulties present themselves when attempting to assign thermodynamic values to interfacial formation. 1) The interface is a two-dimensional region and little information exists on surface energies of solid interfaces or thermodynamic values of interfacial compounds. Baglin et al.²³ studied the effect of 0.5 A·m⁻² 500-eV Ar-ion bombardment on the adhesion of Cu to O-annealed Al₂O₃ as a function of sputtering time. Peel strength was low for sputtering times of a few minutes. For longer sputtering times, large adhesion increases occurred, but these were followed by decreases to nearly zero after much longer sputtering times. The peak adhesion was attributed to the production of an optimal surface Al:O ratio during sputtering that allowed the formation of a stable Cu-Al-O compound at the interface. This finding reinforces the need to regard interfaces as two-dimensional structures, for which the equilibrium properties, such as stoichiometry, differ from those of bulk material, but depend on the electronic configurations of the interfacial atoms and the atoms on either side of the interface. Baglin²⁴ proposed that the arrangement of atoms at the boundary between film and substrate can be described as an "interface phase." Evidence was found for a stable ternary interfacial Cu-O-Al compound²³. Although a

bulk Cu-O-Al compound exists, the bonding configuration for the spinel was different from that found for the interface phase. 2) Although thermodynamic data exist for common organic materials, no thermodynamic data seem to be available for the amorphous hydrogenated C compounds that are produced by IBD. 3) Locher et al.²⁵ studied DLC deposited with a Kaufman type ion source. Measurements showed that 60% of the ion impacts that contribute to film growth were found to be CH_3^+ , and it was believed that the other 40% were CH_4 . Thus it is a problem determine the properties of the particular molecular species that are impinging on the substrate. 4) During the formation of the first few monolayers of material, substantial collisional energy is delivered to the substrate material and growing film. The energy dissociates the arriving molecule and disrupts the substrate bonding. Atoms and molecules released from the surface may not attain equilibrium composition, or remain in excited states. Although collision of ions with substrate atoms is a nonequilibrium ballistic process, some investigators now think that equilibrium thermodynamic considerations play a much larger role than was previously assumed in determining which phases and microstructures will form during irradiation²⁶. Despite the uncertainties, in this case, simple thermodynamic considerations seem to be useful to understanding DLC film adhesion.

Table IV shows values of ΔH_f° calculated from Ref. 27. In calculating these values, it was assumed that the most thermodynamically favorable volatile species are formed, and that no H is present in the interlayer compound. Reaction enthalpies were normalized to the number of moles of CH_x in the reaction. If the enthalpies are not normalized, or are normalized to the number of moles of solid product, the ranking is unchanged. Although compounds with H exist for elements such as Si, the molecules are generally gaseous and with modest enthalpies.

A strong correlation of DLC adhesion with the relative enthalpies of compound formation was noticed. Although mechanical bonding has never been shown to be directly associated with enthalpies of compound formation, the correlation is suggestive. If instead of ΔH_f° , values of ΔG_f° are calculated, the numbers are very similar and the ranking is unchanged. As mentioned above, it is thought that a large fraction of the ions are CH_3 . Because CH_3 has a positive enthalpy,

use of CH_3 essentially shifts ΔH_f° to more negative values so that the enthalpies of reaction for SiC and Si_3N_4 are negative. Because the ions strike the substrate at effectively a very high temperature ($>4 \times 10^6 \text{ K}$), dissociation will occur, and the reactivity will be high despite positive enthalpies. These results are consistent with the work by Kustas et al.²⁰ in which it was found that a bond layer of SiC was necessary for successful adhesion of DLC to a Ti alloy.

Table V shows the measured adhesion of DLC to rough substrates. The presence of roughness increased the measured adhesion substantially for all materials, suggesting that a mechanical interlocking (of the film or perhaps of the bonding agent) is occurring. It appears that adhesion is better to Al_2O_3 and SiC than to Si_3N_4 and ZrO_2 . It should be noted that the smooth Al_2O_3 has a roughness substantially above that of the other group of materials.

Table VI shows the measured adhesion of DLC to substrates that incorporate a Si bonding layer. Bonding is generally excellent and failure occurred in the epoxy or as a result of specimen fracture. Table VII shows the measured adhesion of DLC to substrates that incorporate a Ti bonding layer. In contrast to Si, adhesion was generally poor. The degree to which Ti itself bonds to ceramic substrates could not be determined, because failure always occurred at the DLC-Ti interface and not at the Ti-substrate interface. Again, adhesion to rough substrates was generally greater than to smooth. These results are consistent with work by Erdemir et al.¹⁵.

The bonding of DLC to the Si but not the Ti surfaces is more difficult to explain. Table VIII shows values of ΔH_f° for some reactions of interest. If correlation exists between enthalpy and adhesion, DLC should adhere well to both Si and Ti (Table VIII, Reaction 1 and 2). Because the reactivity of Ti is high, it might be expected that the coating would adhere better to Ti, but this was not observed. This explanation, however, assumes that the surface is unreacted Ti, and, because the reactivity of Ti with oxygen is extremely high, it is believed that the surface of the Ti-coated specimen was contaminated in these experiments. Ti will react rapidly with any water that is present in the vacuum environment or the oxygen present in the CH_4 to form an oxide (Table VIII, Reaction 4 or 5). For the experimental conditions used, oxygen absorption into Ti has been observed²⁸. The oxide has a large positive enthalpy of reaction with CH_4 or CH_3 (Table VIII,

Reaction 6 or 7). In this case TiO_2 should exhibit poor adhesion to DLC, similar to that experienced on ZrO_2 and Al_2O_3 . In contrast, the enthalpy of silicon with respect to ambient water is large and positive, and no surface reaction should occur (Table VIII, Reaction 7) in a vacuum environment.

IV. SUMMARY

1. DLC film hardness was 2500 Knoop for the 400-eV deposition and lower for the 250- and 750-eV depositions. The low hardness values at 750 eV were attributed to incorporation of Ar into the film.
2. Adhesion of DLC to smooth Al_2O_3 and ZrO_2 was vanishingly small, but adhesion to Si_3N_4 and SiC was very good.
3. The presence of surface roughness enabled the attainment of substantial adhesion in some cases.
4. Although mechanical bonding has never been shown to be directly associated with enthalpies of compound formation, a consistent correlation between enthalpy of reaction and film adhesion was noted.
5. DLC bonds extremely well to Si. In all cases, the epoxy failed before the DLC film could be pulled from the Si bond coating, or the Si coating could be pulled from the substrate.
6. DLC was found to bond poorly to Ti. It is not known how well Ti itself bonds to ceramic substrates, because failure always occurred at the DLC-Ti interface and not at the Ti-ceramic interface. The lack of adhesion to the Ti was attributed to inadvertent formation of a surface oxide layer that made the enthalpy for reaction with CH_4 strongly positive and similar in magnitude to that of Al_2O_3 and ZrO_2 .
7. In all cases DLC adhered better to rough than to smooth Ti, suggesting that some type of mechanical interlocking is occurring. This trend was also observed for Al_2O_3 , but not for Si_3N_4 .

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TABLES

TABLE I. Average roughness of smooth and roughened specimens

Substrate	Average Roughness Ra (μm)	
	Smooth	Rough
Al ₂ O ₃	0.033	0.050
ZrO ₂	0.009	0.051
Si ₃ N ₄	0.010	0.066
SiC	0.009	0.045

Table II. Hardness of test films deposited on Si at various ion energies and a gas flow of 10 CH₄, 2.5 Ar sccm.

Ion Energy (eV)	Knoop Hardness (kgf·mm ⁻²)
250	2250
400	2400
750	600

TABLE III. Measured adhesion of DLC to smooth substrates

Substrate	Adhesion (MPa)	Appearance of Film
Al ₂ O ₃	≈0 ^a	shiny brown
ZrO ₂	≈0 ^a	shiny brown
Si ₃ N ₄	> 85 ^b	shiny black
SiC	> 86 ^b	shiny black

^a Pins fell off at the slightest touch, coin pull.

^b Epoxy failure.

TABLE IV. ΔH from Ref. 27, per incident methane molecule ($\text{kJ}\cdot\text{mol}^{-1}$)

Reaction	ΔH_f° for CH_4	ΔH_f° for CH_3
$2 \text{ Al}_2\text{O}_3 + 3 \text{ CH}_4 \Leftrightarrow \text{Al}_4\text{C}_3 + 3 \text{ H}_2\text{O}$	637	584
$\text{ZrO}_2 + \text{CH}_4 \Leftrightarrow \text{ZrC} + 2 \text{ H}_2\text{O}$	488	273
$\text{Si}_3\text{N}_4 + 3 \text{ CH}_4 \Leftrightarrow 3 \text{ SiC} + 2 \text{ N}_2 + 6 \text{ H}_2$	197	-2
$\text{SiC} + \text{CH}_4 \Leftrightarrow \text{SiC} + \text{C} + 2 \text{ H}_2$	51	-164

TABLE V. Measured adhesion of DLC to rough substrates

Substrate	Adhesion (MPa)	Appearance of Film
Al ₂ O ₃	>66 MPa ^a	matte brown
ZrO ₂	50 MPa	matte brown
Si ₃ N ₄	26 MPa	matte gray
SiC	>78 MPa ^b	matte gray

^a Epoxy failure

^b Because the substrate broke, the actual adhesion strength is greater than the value shown.

TABLE VI. Adhesion Tests of DLC with Si interlayer

Substrate	Failure Mode	Adhesion (MPa)
Al ₂ O ₃ Smooth	epoxy fail	>39 ^a
Al ₂ O ₃ Rough	-	>43 ^a
ZrO ₂ Smooth	epoxy fail	>85
ZrO ₂ Rough	epoxy fail	>82 ^a
Si ₃ N ₄ Smooth	epoxy fail	>84
Si ₃ N ₄ Rough	epoxy fail	>76
SiC Smooth	epoxy fail	>90
SiC Rough	-	85

^a Because the substrate broke, the actual adhesion strength is greater than the value shown.

TABLE VII. Adhesion Tests of DLC with Ti interlayer

Substrate	Failure Mode	Adhesion (MPa) ^a
Al ₂ O ₃ Smooth	coin pull	≈0 ^c
Al ₂ O ₃ Rough	coin pull	.80
ZrO ₂ Smooth	coin pull	<6.2 ^b
ZrO ₂ Rough	coin pull	<9.1 ^b
Si ₃ N ₄ Smooth	coin pull	<11 ^b
Si ₃ N ₄ Rough	coin pull	<6.9 ^b
SiC Smooth	coin pull	≈0 ^c
SiC Rough	coin pull	56

^a All failures occurred at the interface between DLC and the Ti.

^b Some of the bonded pins fell off at the slightest touch, and are not included in the numerical average.

^c Bonded pins fell off at the slightest touch.

TABLE VIII. ΔH_f° for selected reactions

Reaction No.	Reaction	ΔH_f° (kJ·mol ⁻¹)
1	$\text{Si} + \text{CH}_4 \rightleftharpoons \text{SiC} + 2 \text{H}_2$	-20
2	$3\text{Ti} + \text{CH}_4 \rightleftharpoons \text{TiC} + 2 \text{TiH}_2$	-233
3	$\text{Si} + 2 \text{H}_2\text{O} \rightleftharpoons \text{SiO}_2 + 2 \text{H}_2$	+386
4	$\text{Ti} + 2 \text{H}_2\text{O} \rightleftharpoons \text{TiO}_2 + 2 \text{H}_2$	-459
5	$\text{Ti} + \text{H}_2\text{O} \rightleftharpoons \text{TiO} + \text{H}_2$	-276
6	$\text{TiO}_2 + \text{CH}_4 \rightleftharpoons \text{TiC} + 2 \text{H}_2\text{O}$	+554
7	$\text{TiO} + \text{CH}_4 \rightleftharpoons \text{TiC} + \text{H}_2\text{O} + \text{H}_2$	+283

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