Atmospheric plasma deposition of diamond-like carbon coatings

Angela M. Ladwig a,b,⁎, Ronald D. Koch a, Edward G. Wenski a, Robert F. Hicks b

a National Nuclear Security Administration's Kansas City Plant, Kansas City, Missouri, United States
b Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, California, United States

ARTICLE INFO

Article history:
Received 28 January 2008
Received in revised form 4 February 2009
Accepted 21 February 2009
Available online xxxx

Keywords:
Atmospheric pressure plasma
Diamond-like carbon deposition
DLC
PECVD

1. Introduction

There is great demand for thin functional coatings in many industries, including semiconductors, medical devices, automotive and aerospace [1–13]. As fabricated components become smaller and more complex, the surface properties of the materials take on greater importance. Thin coatings play a key role in tailoring surfaces to give them the hardness, wear resistance, chemical inertness, and electrical characteristics needed in a desired application.

Diamond-like carbon (DLC) possesses an array of valuable properties: outstanding hardness, chemical inertness, electrical conductivity, and resistance to wear and impact. DLC can be made from a variety of methods, including ion beam sputtering, and plasma-enhanced chemical vapor deposition [14–22]. Diamond-like carbon is considered to be an amorphous material, containing a mixture of sp2- and sp3-bonded carbon. Based on the percentage of sp3 carbon and the hydrogen content, four different types of DLC coatings have been identified: tetrahedral carbon (α-C), hydrogenated amorphous carbon (α-C:H) hard, α-C:H soft, and hydrogenated tetrahedral carbon (ta-C:H) [20,23,24]. Tetrahedral carbon films contain 80% to 88% sp3 carbon and no appreciable hydrogen. They exhibit hardness values approaching 80 GPa. By contrast, α-C:H soft contains ~60% sp3 carbon, a hydrogen mole fraction between 30 and 50%, and its hardness is less than 10 GPa.

Methods used to deposit diamond-like carbon include ion beam deposition, cathodic arc spray, pulsed laser ablation, argon ion sputtering, and plasma-enhanced chemical vapor deposition [25–35]. Researchers contend that several advantages exist when depositioning DLC coatings in a low-pressure environment. For example, ion bombardment in vacuum is thought to promote denser sp3 carbon networks. Moreover, argon ion sputtering is well suited for coating large parts [13,36,37]. On the other hand, the deposition of DLC in vacuum has several disadvantages, including high equipment cost and restrictions on the size and shape of material that may be treated.

The deposition of diamond-like carbon at ambient pressure has been demonstrated by several researchers. Izake et al. [38] and Novikov and Dymont [39] demonstrated that DLC can be made by an electrochemical process using organic compounds, such as methanol and acetylene dissolved in ammonia. This process requires that the substrate be immersed in liquid. The atmospheric pressure deposition of DLC with a plasma torch has been demonstrated by Kulik et al. [40]. However, this process subjects the substrate to gas temperatures in excess of 800 °C.

In this report, we show that diamond-like carbon films may be deposited using an atmospheric pressure plasma-enhanced chemical vapor deposition (PECVD) process at temperatures between 100 and 350 °C. The films were characterized by solid-state carbon-13 nuclear magnetic resonance, and found to have quantities of sp2 and sp3 carbon consistent with α-C:H soft. These films were tested for adhesion and coefficient of friction.

2. Experimental methods

A schematic of the atmospheric pressure plasma deposition system is shown in Fig. 1. The complete system, with modifications, was purchased from SurfX Technologies, LLC. It contained the following components: an RF VII, Inc. 1000 W RF power generator at 27.12 MHz, an RF VII, Inc. auto-tuning matching network, 3 mass flow controllers, a chamber that could be evacuated, a substrate tray with a resistive
coil heater, a SurfX plasma source, and an LED display and user interface to control the system operation. The chamber featured a removable lid, which the plasma source was housed in, and a glass viewport. Ultra-high purity helium and acetylene (Scott Specialty, purity 99.6%) were fed to the plasma source using nylon tubing. Stainless steel tubing was utilized for the hydrogen gas line as well as for feeding the gas mixture from the control unit to the plasma source.

The coatings were deposited onto two types of substrates: p-type Si (100) wafers and 304 L stainless steel disks, 1.12 in. in diameter. The substrate was placed in the chamber with the plasma source mounted directly above it. The glass viewport was sealed onto the chamber, and the chamber evacuated to approximately 50 Torr. Then, the acetylene flow rate were simultaneously increased to a flow rate of 0.05 L/min. Then the RF power and hydrogen flow rate were simultaneously increased to a final value of 160 W and 0.50 L/min. After the plasma stabilized, acetylene was introduced at 0.01 L/min and slowly increased to 0.05 or 0.10 L/min. The deposition time was varied between 5 and 25 min. After this period, the acetylene flow, hydrogen flow, RF power and heater were turned off, and the chamber was evacuated to 50 Torr and backfilled with helium to 760 Torr. Then, the glass viewport was removed, the helium flow was turned off, and the substrate retrieved from the chamber.

The carbon films were analyzed by nuclear magnetic resonance with a Bruker DXX 300 solid-state NMR spectrometer with operating frequencies of 300.13 MHz and 75.14 MHz for 1H and 13C, respectively. Chemical shift anisotropy was minimized using magic-angle spinning. The 13C cross-polarization/magic-angle spinning (CP/MAS) spectra were obtained at 300.13 MHz and 75.14 MHz for 1H and 13C, respectively. The 13C cross-polarization/magic-angle spinning (CP/MAS) spectra were obtained with a standard Bruker MAS probe using 4 mm (outside diameter) zirconium oxide rotors with Kel-F caps [41]. For maximum sensitivity, the ten-milligram samples scrapped from Si wafers were confined to the middle of the rotor by placing sodium chloride above and below the sample. Potassium bromide (KBr) was used to adjust the magic angle with the upfield methine resonance of adamantane at 29.46 ppm, serving as the external chemical shift reference.

To reduce experimental time as well as enhance the sensitivity, cross-polarization from the abundant 1H nuclei to the dilute 13C nuclei was utilized. The recycle delay between scans in the cross-polarization experiment depends on the spin-lattice relaxation time of the protons. As 1H nuclei possess significantly faster relaxation times than 13C nuclei, data acquisition time is reduced in comparison to direct observation of the 13C signal. All experiments were performed at ambient temperature. A 3.8 μs π/2 pulse length was used with a contact time of 1.5 ms. The recycle delay was 1.0 s with 75,000 as the average number of scans acquired. By using a magic-angle spinning frequency of 10 kHz, it was possible to identify and reduce the intensities of spinning side bands [42–44].

The percentage of carbon hybridization was calculated by deconvoluting the sp2 and sp3 resonance, found in the NMR spectrum at approximately 140 and 40 ppm, respectively [45–49]. The method fitted the observed resonances with 50% Gaussian and 50% Lorentzian lineshapes. As a reference check, a solid-state 13C NMR spectrum was acquired from diamond powder. A sharp resonance with a chemical shift at 34.9 ppm was observed in agreement with the literature value of 36.0 ppm [45].

Thickness measurements of the diamond-like carbon films on the silicon wafers were obtained using a Dektak 7 profilometer. To obtain a step height measurement, the samples were masked and then mechanically scratched. This data also leads to the determination of the deposition rate. These measurements could not be made with sufficient accuracy on the stainless steel coupons due to their higher surface roughness.

The adhesion of the DLC coatings to the stainless steel and Si wafer was determined using a stud pull test [49]. In an effort to remove surface contaminants, samples were briefly treated with an oxygen plasma for 5 min at 250 W RF power, 30 L/min helium flow, and 0.3 L/min O2 flow. The test device was a Romulus III from Quad Group Inc. A metal stud, 0.1” in diameter, was affixed to the coating surface using epoxy glue. The stud was then pulled perpendicular to the substrate at a rate of 6 lb/s. Adhesive strength is defined as the amount of pressure required to remove the stud from the substrate. After the pull test, the fractured surface was examined by scanning electron microscopy (SEM) using a Leo 1455VP. No conducting coating was applied. All images were obtained at 25× with an accelerating voltage of 25 kV and a working distance of 8 mm. Quad-backscattering detection was employed.

Pin on disk testing, per ASTM G99, was performed to obtain the coefficient of friction. A 3.75 mm radius wear track was created at a speed of 2.8 cm/s. Coefficient of friction values were calculated by dividing the normal load (1.0 N) by the force obtained after 100 cycles.

### 3. Results

#### 3.1. Carbon bonding

A solid-state 13C NMR spectrum of the carbon film obtained from several samples is displayed in **Fig. 2**. The process conditions were

![Fig. 1. Flow schematic of DLC deposition process.](image1)

![Fig. 2. Solid-state 13C NMR spectrum of an atmospheric pressure plasma deposited DLC coating.](image2)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Position and area of sp² and sp³ carbon peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon type</td>
<td>Peak no.</td>
</tr>
<tr>
<td>sp²</td>
<td>1</td>
</tr>
<tr>
<td>sp³</td>
<td>2</td>
</tr>
<tr>
<td>sp³</td>
<td>3</td>
</tr>
<tr>
<td>sp³</td>
<td>4</td>
</tr>
<tr>
<td>sp³</td>
<td>5</td>
</tr>
</tbody>
</table>

Please cite this article as: A.M. Ladwig, et al., Diamond Relat. Mater. (2009), doi:10.1016/j.diamond.2009.02.026
160 W RF power, 155 °C substrate temperature, source-to-sample distance of 8 mm, 0.10 L/min acetylene flow, 0.50 L/min hydrogen flow, and 30.0 L/min helium flow. As seen in the figure, two main resonance bands are observed, centered at approximately 128 and 38 ppm. These bands are due to sp² and sp³ carbon bonding, respectively, and demonstrate the successful deposition of a diamond-like carbon film at atmospheric pressures. The sp² band was deconvoluted into two peaks, while the sp³ band was deconvoluted into three peaks. Table 1 lists the position of each deconvoluted peak as a fraction of the total band area. The sp³ peaks centered at about 80 and 15 ppm are due to spinning side bands and were not included in the area calculation. Based on the area under the bands, the fraction of sp² and sp³ carbon was 43 and 57%, respectively. In summary, diamond-like carbon coatings have been deposited using the atmospheric pressure plasma fed with acetylene, hydrogen and helium at a substrate temperature of only 155 °C.

3.2. Effects of process conditions

Shown in Fig. 3 is the effect of temperature on the DLC coating thickness for two different source-to-sample distances. Deposition was carried out for 25 min at 160 W RF power, flow rates of 0.10 L/min C₂H₂, 0.5 L/min H₂, and 30.0 L/min He, and source-to-sample distances of 5 and 8 mm. A loosely bound amorphous carbon by-product is observed at temperatures below approximately 200 °C and 155 °C for 5 and 8 mm source-to-sample distances, respectively. At temperatures above, the coating thickness drops rapidly as the substrate temperature increases to 350 °C. The maximum thickness achieved was 3.16 µm and 3.54 µm for the 5 and 8 mm source-to-sample distances, respectively.

The dependence of the coating thickness on deposition time at the different acetylene flow rates is shown in Fig. 4. The process conditions are the same as reported earlier, except that the substrate temperature is 200 °C and the source-to-sample distance is 10 mm. The thickness varies linearly with time with the lines extrapolating back to the origin. This indicates that there is no induction period for the onset of DLC deposition. The film growth rate is obtained from the slope of the lines, which equals 0.13 ± 0.04 mm/min for 0.10 L/min acetylene flow and 0.22 ± 0.07 mm/min for 0.15 L/min acetylene flow. These results indicate that the deposition rate is positive order in acetylene concentration.

3.3. Adhesion, wear and dielectric strength

The adhesive strength of the DLC coatings, measured by a stud pull test, is shown in Table 2. Samples A and B were generated on stainless
Similar results were observed for DLC deposition on silicon. Remaining around the edges of the circular test region and very thin deposited in vacuum processes [45] report chemical shifts of 120.0 and 34.5 ppm for sp2 and sp3 state 13C NMR peaks are observed at 138.4 and 127.9 ppm for sp2 carbon and at 38.2 ppm for sp3 carbon. These chemical shifts are in good agreement with the values reported for diamond-like carbon deposited in vacuum processes [45–49]. For example, Merwin et al. [45] report chemical shifts of 120.0 and 34.5 ppm for sp2 and sp3 carbon, respectively, whereas Bustillo et al. [47] report chemical shifts of 140.0 and 40.0 ppm for sp2 and sp3 carbon. The broadness of the NMR resonance bands reflects the effect of dispersion in the observed chemical shifts, i.e. different types of sp2 and sp3 carbon bonding in the films [48,51]. The peak at 138.4 ppm may be assigned to unsaturated CH groups, while the peak at 127.9 ppm is due to CH2 groups. On the other hand, the broad band at 38.2 ppm may be assigned to saturated carbon atoms with 1, 2 or 3 hydrogen atoms attached. The fraction of sp2 and sp3 carbon bonding was determined to be 43 and 57%. Based on the four classifications of DLC coatings, the material produced in this study may be designated as α-C:H soft [23]. This seems reasonable given that the films were deposited by a downstream, low-temperature plasma process with the substrate held at 155 °C.

The results shown in Figs. 3 and 4 reveal that the rate of DLC deposition decreased rapidly with increasing substrate temperature up to 350 °C, but increased with the partial pressure of acetylene. The optimal temperature for growth is around 200 °C, since this yields a high rate while at the same time avoiding the formation of a loosely bound carbon deposit. At the higher acetylene flow of 0.15 L/min, a deposition rate of 0.22 µm/min is achieved. This may be compared to vacuum processes where rates have been reported as low as 10–3 µm/min to as high as 0.6 µm/min, depending on the method utilized [52,53].

The coefficient of friction for the DLC obtained in this study was 0.24 ± 0.02. Previous studies report coefficient of friction values for vacuum deposited coatings to be within the range of 0.05–1.00 [1,49,54–57]. For uncoated stainless steel, the coefficient of friction is 0.55 [50].

The work presented above is the first successful demonstration of diamond-like carbon deposition using a downstream, low-temperature atmospheric pressure plasma source. Additional work is needed to improve the process and enhance the properties of the DLC coatings.

4. Discussion

It has been found that diamond-like carbon can be deposited at low-temperature and atmospheric pressure using a downstream acetylene, hydrogen and helium plasma. As shown in Fig. 2, solid-state 13C NMR peaks are observed at 138.4 and 127.9 ppm for sp2 carbon and at 38.2 ppm for sp3 carbon. These chemical shifts are in good agreement with the values reported for diamond-like carbon deposited in vacuum processes [45–49]. For example, Merwin et al. [45] report chemical shifts of 120.0 and 34.5 ppm for sp2 and sp3 carbon, respectively, whereas Bustillo et al. [47] report chemical shifts of 140.0 and 40.0 ppm for sp2 and sp3 carbon. The broadness of the NMR resonance bands reflects the effect of dispersion in the observed chemical shifts, i.e. different types of sp2 and sp3 carbon bonding in the films [48,51]. The peak at 138.4 ppm may be assigned to unsaturated CH groups, while the peak at 127.9 ppm is due to CH2 groups. On the other hand, the broad band at 38.2 ppm may be assigned to saturated carbon atoms with 1, 2 or 3 hydrogen atoms attached. The fraction of sp2 and sp3 carbon bonding was determined to be 43 and 57%. Based on the four classifications of DLC coatings, the material produced in this study may be designated as α-C:H soft [23]. This seems reasonable given that the films were deposited by a downstream, low-temperature plasma process with the substrate held at 155 °C.

The results shown in Figs. 3 and 4 reveal that the rate of DLC deposition decreased rapidly with increasing substrate temperature up to 350 °C, but increased with the partial pressure of acetylene. The optimal temperature for growth is around 200 °C, since this yields a high rate while at the same time avoiding the formation of a loosely bound carbon deposit. At the higher acetylene flow of 0.15 L/min, a deposition rate of 0.22 µm/min is achieved. This may be compared to vacuum processes where rates have been reported as low as 10–3 µm/min to as high as 0.6 µm/min, depending on the method utilized [52,53].

The coefficient of friction for the DLC obtained in this study was 0.24 ± 0.02. Previous studies report coefficient of friction values for vacuum deposited coatings to be within the range of 0.05–1.00 [1,49,54–57]. For uncoated stainless steel, the coefficient of friction is 0.55 [50].

The work presented above is the first successful demonstration of diamond-like carbon deposition using a downstream, low-temperature atmospheric pressure plasma source. Additional work is needed to improve the process and enhance the properties of the DLC coatings.

5. Conclusions

The deposition of diamond-like carbon using a low-temperature, atmospheric pressure plasma process is reported for the first time.
(1998) 1741.