Atomic hydrogen interactions with amorphous carbon thin films

Bhavin N. Jariwala, a Cristian V. Ciobanu, 1, 2,a and Sumit Agarwal1,a
Department of Chemical Engineering, Colorado School of Mines, Golden, Colorado 80401, USA
Division of Engineering, Colorado School of Mines, Golden, Colorado 80401, USA

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The atomic-scale interactions of H atoms with hydrogenated amorphous carbon (a-C:H) films were identified using molecular dynamics (MD) simulations and experiments based on surface characterization tools. Realistic a-C:H films developed using MD simulations were impinged with H atoms with a kinetic energy corresponding to a temperature of 700 K. The specific chemical reactions of the H atoms with the a-C:H surface were identified through a detailed analysis of the MD trajectories. The MD simulations showed that hydrogenation occurs primarily at the sp² sites and converts them to sp³-hybridized C atoms. Depending on the hybridization of the next-nearest neighbor, a dangling bond may or may not be created. The hydrogenation reaction is highly exothermic, >2.5 eV, and proceeds with a negligible activation energy barrier via a mechanism similar to Eley–Rideal. In certain cases hydrogenation may also cleave a C–C bond. The reaction events observed through MD simulations are consistent with the surface characterization of D-exposed a-C:H films using Raman spectroscopy, spectroscopic ellipsometry, and in situ attenuated total reflection Fourier-transform infrared spectroscopy. © 2009 American Institute of Physics. [doi:10.1063/1.3238305]

I. INTRODUCTION

Hydrogenated amorphous carbon (a-C:H) is a versatile material with a vast number of applications, such as a wide band gap semiconductor for high-performance electronic devices, 1 protective coatings for infrared (IR) optical elements and magnetic storage disks, 2–4 inert biocompatible coatings, 5,6 and as cold cathode emitters for flat-panel displays. 7–10 a-C:H films are generally deposited over large areas at relatively low substrate temperatures by plasma-enhanced chemical vapor deposition (PECVD) using hydrocarbon feed gases such as CH₄ or C₂H₂ diluted in H₂ or an inert gas, such as Ar. 11–14 The properties of these films depend on the sp³-to-sp² hybridization ratio and the H content. 15–17 Depending on the composition, these films demonstrate different characteristics, such as hardness, electrical resistivity, optical transparency, and chemical inertness. Films with hardness and resistivity similar to that of diamond, as well as DLC. 20,24 The interaction of H atoms with carbon-cased films has been studied both during the postexposure of the films to H atoms and during film growth from hydrocarbon plasmas with the feed gas heavily diluted with H₂. Briefly, in previous studies, using a combination of Raman spectroscopy, x-ray photoelectron spectroscopy, and atomic force microscopy, Mikami et al. 25 observed that an increase in the H₂ flow rate increased the sp³ fraction and the disorder during the deposition of DLC films by radio-frequency (rf) magnetron sputtering. Vietzke et al. studied the H-induced chemical erosion of C atoms from a-C:H films using mass spectrometry. These authors reported the formation of CH₃ radicals along with a wide range of higher hydrocarbons due to the reaction of thermal H atoms with a-C:H films. 26 Kuppers and co-workers 19,27–29 used high-resolution electron energy loss spectroscopy to study the above interactions occurring on model C:H surfaces. These authors showed that hydrogenation of sp- and sp²-hybridized CH groups led to the formation of sp³-hybridized CHₓ (x=2,3) groups 23 and suggested that hydrogenation eventually leads to erosion of surface C atoms by desorption of volatile CₓHₓ molecules. 22,28 The three primary interactions of H with a-C:H—hydrogenation, H abstraction, and chemical erosion—were proposed to synergistically lead to preferential graphite erosion, which is assumed to be the controlling step in the low-pressure synthesis of diamond or DLC films. 20,21 Biener and co-workers prepared model a-C:H films using ethane ions at 160 eV and impinged these films with H atoms. The authors hypothesized a certain activation energy barrier for the hydrogenation reaction and proposed that it proceeds via an Eley–Rideal mechanism. 19,21 Two different cross sections—1.3 and 4.5 Å²—were reported for the H atom interaction with C:H films deposited in two different

1aAuthors to whom correspondence should be addressed. Electronic addresses: cciobanu@mines.edu and sagarwal@mines.edu.
reactors. The reason for the difference in the cross sections was attributed to the uncertainty in estimating the H flux from the H atom sources.

Interactions of H atoms with graphite and diamond surfaces have also been reported in literature. Dementjev and Petukhov used Auger electron spectroscopy to demonstrate that interaction of H atoms with a graphite surface at 300 K changes the hybridization of the C atoms from $sp^2$ to $sp^3$. Balooch and Olander observed that over a temperature range of 400–2200 K, H atoms etch graphite to form CH and C$_2$H$_2$.

It is well known that hydrocarbon gases heavily diluted in hydrogen are used as a precursor for the growth of microcrystalline and nanocrystalline diamond at relatively high temperatures. However unlike the formation of nanocrystalline Ge (Ref. 35) and Si (Ref. 36) due to H$_2$ dilution of GeH$_4$ and SiH$_4$, respectively, the mechanism for nanodiamond formation due to H$_2$ dilution is not well understood. This is because C can bond in $sp^x$- as well as $sp^y$-hybridized states unlike Ge and Si. Angus and co-workers were the first to propose that during chemical vapor deposition of diamond, atomic H etches the graphic nuclei preferentially over the diamondlike phase. Furthermore, it has been proposed that abstraction of H from a surface CH$_x$ group ($x=1, 2, 3$) by atomic H is a key step that provides a bonding site for the incoming hydrocarbon species and thus, controls diamond growth. However, the detailed mechanisms of the set of reactions that lead to such structural transformations and their energetics have not been identified.

In this article, we focus on the interactions of H atoms with a-C:H surfaces using classical molecular dynamics (MD) simulations and experiments based on surface diagnostic tools such as Raman spectroscopy, spectroscopic ellipsometry (SE), and surface IR spectroscopy. Using MD, we have created realistic a-C:H films, developed a method to characterize the $sp^x$-$to$-$sp^y$ hybridization ratios in the films, and visualized the reaction pathways of H with the a-C:H surface. We further show that the reaction pathways observed in the MD simulations are consistent with our experimental measurements. Specifically, we observe that hydrogenation of the a-C:H surface by thermal H atoms proceeds at the $sp^2$ sites via a highly exothermic mechanism similar to Eley–Rideal in that it has a negligible activation energy barrier. This reaction generally converts the $sp^2$ C atoms to $sp^3$ C atoms.

This article is organized as follows. In Sec. II, we present the computational details for creating realistic a-C:H films and describe the MD simulations to visualize the trajectories of H atoms impinging on these films. In Sec. III, we describe the experimental approach used to deposit hard a-C:H films and the in situ and ex situ surface diagnostic techniques used to identify the hydrogenation/deuteration reaction occurring at the surface of these films. The computational and experimental results are presented and discussed in Sec. IV. Finally, our key conclusions are summarized in the Sec. V.

II. MOLECULAR DYNAMICS SIMULATIONS

A. Interatomic potential

The modified extended Brenner (mXB) potential, developed by Sbraccia et al. was employed for the MD simulations. The mXB potential is an improvement over the extended Brenner (XB) potential, which is a modified version of the Brenner potential for hydrocarbons that includes treatment of the interactions for Si along with C and H. The original Brenner potential for hydrocarbons has certain shortcomings, such as a short cutoff distance for C–C interaction, which results in an underestimation of $sp^3$ fractions in a-C:H (Refs. 40 and 41) and the omission of the torsional potential term for hindered rotation around C–C bonds. The XB potential also has a few limitations, such as the presence of false minima in the potential energy curves of ethane with respect to the C–C distance. The mXB potential eliminates many of the drawbacks of other Brenner-type potentials by modifying the parameters of the XB potential. The mXB potential employs longer C–C interaction cutoff radii to eliminate the underestimation of $sp^3$ C–C bonds during simulations. The range of local interactions is slightly increased by reducing the first neighbor cutoff radii and increasing the second neighbor cutoff radii for C–C, C–H, and H–H interactions. The modification of the cutoff radii as well as changes in several other parameters eliminate the occurrence of overcoordinated C atoms and lead to the correct potential energy curves for ethane. Thus far, the mXB potential has been successfully used to study the chemisorption of hydrocarbon molecules on Si surfaces.

B. Realistic a-C:H films

Using MD, plasma-deposited thin films can be simulated by repeated impingement of radicals onto a substrate, provided the plasma composition is well characterized. Employing this procedure, Maroudas and co-workers created amorphous hydrogenated silicon (a-Si:H) films by repeated impingement of SiH$_3$ radicals onto a Si(001) substrate. SiH$_3$ was previously experimentally identified as the primary radical for the deposition of device-quality a-Si:H films from a SiH$_4$ plasma. Stuart et al. used a Brenner-type empirical potential to simulate the structure of amorphous carbon films and characterized the model films in terms of ring size distributions, concluding that the $sp^2$ content was generally larger than in experiments. Krstic et al., Reinhold et al., and Stuart et al. also studied the interactions of H and D with amorphous carbon films, analyzing in detail the energy and angle spectra of sputtered particles, hydrogen reflection, and methane production at the impact of deuterium and or hydrogen with amorphous carbon. Neyts et al. performed MD simulations of a-C:H films deposited in a C$_2$H$_2$/Ar expanding thermal plasma by impinging the substrate with the hydrocarbon radicals experimentally detected by Benedikt et al. This procedure is, however, not feasible for simulating a-C:H films deposited using other plasma sources due to an insufficient knowledge of the relative flux of the large number of radicals that are generated in these hydrocarbon discharges. Therefore, in this study, we have developed a stepwise procedure for creating realistic...
$a$-C:H films from crystalline diamond. The procedure involves tuning of the bulk film density, randomization of the atomic coordinates, and hydrogenation of the film such that the resulting structure and composition are similar to plasma-deposited $a$-C:H films. The stepwise procedure is as follows.

(a) We begin with a crystalline, unreconstructed diamond (100) slab with periodic boundary conditions in the (100) plane, as shown in Fig. 1(a). This slab initially has 1176 C atoms with in-plane dimensions of 17.6 x 17.6 Å$^2$. The bottom five layers of this slab are fixed to simulate the underlying bulk substrate.

(b) The bulk density of diamond (3.5 g/cm$^3$) is much higher than the experimentally reported range of densities for $a$-C:H films (1.6–2.2 g/cm$^3$). Therefore, a certain number of C atoms, calculated based on the desired density of the $a$-C:H film, are randomly removed from the slab, as shown in Fig. 1(b). The remaining atoms, excluding the bottom five layers, are then given random displacements of at most one-third of a C–C bond length in diamond.

(c) The slab is thermalized at 1000 K for 5 ps to allow the atoms to rearrange and relax. The resulting film is then relaxed to its local minimum energy configuration using a conjugate-gradient algorithm. The film obtained through this procedure is shown in Fig. 1(c).

(d) During this procedure, several carbon atoms change their hybridization from $sp^3$ to $sp^2$, but the film also contains a large number of dangling bonds. To determine the location of these dangling bonds, the neighbors of each C atom are first identified based on a maximum bond length of 1.7 Å, which is ~10% greater than the $sp^3$-$sp^3$ bond length of 1.54 Å. The dangling bonds are then identified based on the number of nearest neighbors; a bond length cutoff of 1.50 Å is used to differentiate between $sp^2$- and $sp^3$-hybridized C atoms, which would have different numbers of neighbors for complete coordination. These dangling bonds are passivated by H atoms and the film structure is again relaxed. The somewhat arbitrary cutoff of 1.50 Å, determined by numerical experimentation, leads to a sufficient number of H atoms in the film that is representative of hard $a$-C:H. This relaxed, hydrogenated, and amorphized film is again thermalized at 700 K for 25 ps. Some overhydrogenation of the film is observed due to the choice made for the bond length cutoff, but the extra H atoms desorb as stable hydrogen molecules during the thermalization process. The total energy of the film becomes almost constant at 700 K after 25 ps. The film obtained using the above procedure is shown in Fig. 1(d).

The $a$-C:H films generated by the procedure above were characterized for the $sp^2$-to-$sp^3$ hybridization ratio and the H content by developing a more accurate set of criteria than the one discussed above. Since C atoms can be $sp^3$, $sp^2$-, or $sp$-hybridized, and can also have some dangling bonds left unpassivated after the procedure described above, it would be incorrect to identify the type of hybridization of a C atom based solely on its number of nearest neighbors. Moreover, the bond lengths [see Fig. 2(a)] and bond angles have a wide distribution in amorphous materials, making it difficult to identify the type of bonding configuration. We have therefore used bond energy cutoffs to differentiate between a C–C double bond and a single bond. Figure 2(b) shows the bond energy distribution for the film shown in Fig. 1(d), which gives two sharp peaks centered at $-4.91$ and $-3.64$ eV with minimal overlap because the difference in the bond energy of a C–C double bond (C=C in ethylene is $-6.37$ eV) and a single bond (C–C in ethane is $-3.56$ eV) is a few eV. The cutoff energy to differentiate a single bond from a double bond was chosen to be $-4.15$ eV, which is the energy that corresponds to the minimum in the bond energy distribution in Fig. 2(b). If the C–C bond energy is below $-4.15$ eV, the bond is characterized as a double bond; otherwise it is a single bond. Since no bond energies below $-8$ eV are obtained for the final relaxed and thermalized film, there are no $sp$-hybridized C atoms in the film (for reference, the C=C bond energy in acetylene is $-8.4$ eV). We also did not observe any C atoms with more than four neighbors, indicating no over coordination in the film. To determine the hybridization state of a given C atom, the number of neighbors and the bond energies of the C–C neighbors are used. If the number of nearest neighbors is 4, the C atom is $sp^3$-hybridized. If the number of neighbors for the central C atom is 3, it may have 1 C and 2 H, or 2 C and 1 H, or 3 C atoms as neighbors. In any case, if one of the carbon neighbors has a double bond...
with the central C atom (indicated by the bond energy), the central C atom is \(sp^2\)-hybridized with no dangling bond. If all C–C neighbors have single bonds, the central atom is \(sp^3\)-hybridized with a dangling bond. Similar logic using bond energies of C–C neighbors is implemented to determine the hybridization of C atom with a different number of neighbors for details, refer to the chart in supplementary information, Fig. 1-SI (Ref. 60). The density of the final film is 2.2 g/cm\(^3\) with 33% atomic H, which is representative of experimentally deposited, hard \(a\)-C:H films.18

The \(sp^3\) fraction in the film is 20%, which is characteristic of a hard graphitic \(a\)-C:H film deposited at high bias voltages using PECVD.18,61

Figure 2(c) shows the total C–C radial distribution function (RDF) calculated for the \(a\)-C:H film created using the above mentioned procedure. The RDF clearly indicates the amorphous nature of the film, as evidenced by the absence of peaks beyond \(\sim 2.65\ \text{Å}\). The first peak at 1.43 Å shows a large number of conjugated \(sp^2\)-hybridized C atoms in the film, indicating that a hard graphitic film was created using this procedure. The shoulder at 1.54 Å shows that there are also \(sp^3\)-hybridized C atoms present in the film, but their fraction is smaller than that of \(sp^2\)-hybridized C atoms.

C. H interactions with \(a\)-C:H

H atoms were repeatedly impinged at random locations on to the computationally generated \(a\)-C:H film from a distance of 2 Å above the topmost atom of the surface with initial velocities directed normal to the surface and corresponding to a temperature of 700 K. The entire system was equilibrated for 4 ps between any two consecutive H atom impingement events. The time step used for the MD simulations was 0.1 fs and the atomic trajectories of the H atoms were visualized by taking snapshots of the atomic configurations at 1 fs intervals. To calculate the energetics of the reactions observed, the MD configurations before and after the reaction were relaxed using a conjugate-gradient algorithm.

III. EXPERIMENTAL

The \(a\)-C:H films used for the experiments were deposited in a PECVD reactor. The reactor consists of a stainless-steel vacuum chamber with a base pressure of \(\sim 10^{-7}\ \text{Torr}\) (see Fig. 3). The plasma is generated between two asymmetric parallel plates: The plate spacing was set at 4 cm using a linear-shift manipulator. Radio frequency power at 13.56 MHz was applied to the upper electrode via an in-house-built L-type matching network. Hard \(a\)-C:H films were deposited at room temperature on a Si substrate on the powered electrode using a 1:1 mixture of CH\(_4\) and Ar [50 SCCM (SCCM

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FIG. 2. (a) Bond length distribution for the \(a\)-C:H film generated using MD simulations. The length distribution was fitted with two Gaussians with a significant overlap. (b) Bond energy distribution for the \(a\)-C:H film in Fig. 1(d) fitted using two Gaussians centered at \(-4.91\) and \(-3.64\) eV, representing the \(sp^2\) and \(sp^3\) fractions, respectively. The dotted line represents the bond energy cutoff at \(-4.15\) eV for the \(sp^2\)- and \(sp^3\)-hybridized states. (c) Total carbon-carbon RDF, \(g(r)\), for the \(a\)-C:H film in Fig. 1(d). The \(g(r)\) was calculated for the amorphous region and all the H atoms along with the bottom five fixed layers were excluded.

FIG. 3. Schematic of the capacitively coupled plasma reactor with the in situ ATR-FTIR spectroscopy setup.
denotes cubic centimeter per minute at STP) each] as the precursor gases, a chamber pressure of 50 mTorr, and 100 W power to the plasma source.

The SE (Woollam M-44) data were analyzed by regression analysis using a three-layer optical model with a surface roughness/a-C:H film/native SiO$_2$ structure on a 1 mm thick c-Si substrate. The a-C:H film layer was fitted with the Tauc–Lorentz (TL) model for amorphous semiconductors, proposed by Jellison and Modine. The surface roughness layer was fitted using the effective medium approximation with 50% void fraction and 50% of the underlying a-C:H film layer. The Tauc band gap, film thickness, surface roughness, and optical constants for the a-C:H films were obtained using this model. Micro-Raman spectroscopy (LabRamHR) was performed using a 532 nm diode laser in a backscattering geometry. To observe the hydrogenation/deuteration reaction, the as-deposited film was placed on the grounded electrode and exposed to D$_2$ plasma for 1 h at a substrate temperature of 150 °C, a pressure of 100 mTorr, and 10 W rf power to the plasma. The plasma was operated at a very low power density to minimize the bombardment of the surface with energetic ions. After the D$_2$ plasma exposure, the a-C:H film was again characterized using ex situ SE and micro-Raman spectroscopy.

For in situ characterization of H(D)-atom interactions with a-C:H, an isotope-exchange experiment was conducted using real-time, in situ attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy, as shown in Fig. 3. Briefly, in this setup, an IR beam from a FTIR spectrometer was directed using a series of mirrors and lenses into the flat face of a 1 × 10 × 50 mm$^3$ trapezoidal internal reflection crystal (IRC) with its short faces beveled at 45°. The IR beam was internally reflected on the bottom and top faces since the angle of incidence was greater than the critical angle for total internal reflection. In this geometry, there were 25 reflections on each flat face. The IR beam exiting from the opposite beveled edge of the IRC was collimated using a KBr lens and was directed by a series of mirrors onto a mercury cadmium telluride A (MCT-A) detector. We used KBr windows on both sides of the beam path, which are transparent in the IR up to 400 cm$^{-1}$. However, the spectral range was limited by the ZnSe IRC, which is transparent in the IR up to 400 cm$^{-1}$. Therefore, the change in absorbance due to the stretching vibrations of CH$_n$ and CD$_x$ (x = 1, 2, 3) groups at ~3000 and ~2000 cm$^{-1}$, respectively, were observed simultaneously. We used ZnSe as the IRC because its refractive index, ~2.2, is closely matched to that of hard a-C:H. For the range of refractive indices typical of dense a-C:H films (1.7–2.3), the reflectivity at the films’ interface with ZnSe is very low and therefore, total internal reflection occurs at the vacuum-film interface and not the crystal-film interface. Thus, the IR beam passes through the film twice for each reflection, greatly enhancing the signal-to-noise ratio. A hard a-C:H film was deposited at room temperature on the powered electrode on a ZnSe IRC as well as on a Si wafer using a CH$_4$ plasma operated at a flow rate of 25 SCCM for CH$_4$, a chamber pressure of 100 mTorr, and 25 W rf power to the plasma source. Compared to the conditions used for the deposition of films for ex situ characterization, a relatively high pressure and low power were used to reduce ion bombardment of the surface. Films deposited at conditions identical to the ones used for the ex situ studies described above led to highly conductive a-C:H films, which rendered the ZnSe IRC opaque in the IR due to free electron absorption. To confirm that the film was indeed hard a-C:H, the one deposited on the Si wafer was characterized using SE (see Sec. IV B). The ZnSe crystal with the as-deposited film was then placed on the grounded electrode and a background IR spectrum was collected. The film was exposed to a D$_2$ plasma at a substrate temperature of 150 °C, a pressure of 100 mTorr, and 10 W rf power to the plasma source. We used D$_2$ instead of H$_2$ to clearly distinguish between H atoms already in the film from the D atoms impinging from the gas phase since the stretching vibrations of CH$_n$ and CD$_x$ are well separated in the IR. After every 20 s of D$_2$ plasma exposure, an IR difference spectrum was collected, which represents changes in the film composition due to interactions with D atoms. It should be pointed out that a small fraction of the D atoms and D$_2$ molecules impinging onto the surface with energies much higher than in the MD simulations as the neutral species undergo elastic and inelastic collisions with high-energy ions in the plasma sheath at the grounded electrode. However, this small fraction of high-energy neutrals and ions should not drastically alter the comparison with the MD simulations where the H atoms are incident at thermal energies.

IV. RESULTS AND DISCUSSION

A. MD simulations

A large fraction of the H atoms that were impinged on the a-C:H film reflected back into the gas phase. Most of the remaining atoms were adsorbed on sp$^2$ sites on the surface, hydrogenating the film. Three such hydrogenation reactions are shown in Fig. 4, where the sp$^3$-hybridized C atoms are shown as dark gray spheres (red, in the online version), the sp$^3$-hybridized C atoms are light gray (blue), and the hydrogen atoms are shown as smaller spheres. The halved small sphere represents the incoming H atom. Reactions (a) and (b) in Fig. 4 resulted in a change in the hybridization state of the adsorption site from sp$^2$ to sp$^3$ with complete passivation of the carbon atom, whereas in reaction (c) such conversion was accompanied by the formation of a dangling bond.

In the reaction shown in Fig. 4(a), the incoming H atom bonded to the sp$^2$-hybridized C atom is labeled 1 (C1). Before the attachment of H to C1, the central, sp$^2$-hybridized atom C2 was bonded with three sp$^3$-hybridized neighbors C1, C3, and C4, similar to a C atom in graphene. The binding of H to C1 changed its hybridization from sp$^2$ to sp$^3$, as reflected by the change in the C1–C2 bond energy from −5.03 to −3.69 eV, and by an increase in the C1–C2 bond length from 1.42 to 1.54 Å. The hybridization state of C2 did not change, and no dangling bond was created on this atom. This was inferred from the energies (−4.94 and −4.92 eV) and the lengths (1.40 and 1.39 Å) of the C2–C3 and C2–C4 bonds, which were consistent with a central sp$^2$-hybridized atom (C2) bonded with two sp$^2$ neighbors, similar to a C
atom in benzene. In other words, the double-bond character of the C2–C3 and C2–C4 bonds increased from 33% to 50% resulting in the elimination of the possible dangling bond.

The exothermicity of the hydrogenation reaction (a) was 2.28 eV.

In the reaction shown in Fig. 4(b), the incoming H atom also attached to the sp²-hybridized atom C1 with two nearest-neighbor sp² atoms, C2 and C3. The next-nearest neighbors of C1 were also sp²-hybridized. After the H atom attached to C1, it changed its hybridization from sp² to sp³.

The bond energy of the C1–C2 and C1–C3 bonds changed from −5.28 to −3.88 eV and from −5.02 to −3.69 eV, respectively; the bond lengths increased from 1.40 to 1.54 Å for C1–C2, and from 1.42 to 1.54 Å for C1–C3. Thus, we concluded that C1–C2 and C2–C3 have become single bonds upon the adsorption of H. However, no dangling bond was created on C3 as the double-bond character of C3–C4 and C3–C6 increased from 33% to 50%. Similarly, the double-bond character for the C2–C5 bond increased, eliminating a possible dangling bond on C2. The exothermic energy of this reaction was 3.06 eV.

In the reaction shown in Fig. 4(c), the incoming H atom attaches to the sp²-hybridized atom C1. After the H atom attaches to C1, the bond between C1 and C2 transforms into a single bond, as shown by the bond energy change from −6.27 to −3.87 eV and the bond length increase from 1.32 to 1.54 Å. Since the C2–C3 bond is also a single bond, a dangling bond is created at C2. After the reaction, C2 becomes sp³-hybridized with three neighbors (2 C and 1 H) and a dangling bond; this was concluded from analyzing the variations in bond energies and bond lengths. The exothermicity of the reaction obtained was 2.49 eV. In all of the above reactions, the H atom attaches to the sp² site instantaneously (within 1 fs) without being thermally equilibrated with the surface before attachment. Hence, the reaction proceeds via an Eley–Rideal type of mechanism. For all reactions in Fig. 4, the activation energy barrier from the MD analysis was negligible. The formation of a dangling bond on a nearest neighbor of the adsorption site depends on the hybridization state of the first- and second-order neighbors of that site. In all the above reactions, the sp² site converts to a sp³ upon hydrogenation which leads to an increase in the sp³ fraction in the film; this is consistent with our experimental observations of increased sp³ fraction after D₂ plasma exposure of an as-deposited a-C:H film.

Another interesting reaction observed is shown in Fig. 5, in which the attachment of a H atom leads to the splitting of a surface cluster. The incoming H atom attaches to C1, which has a (first-order) neighbor sp³-hybridized (C2) and another...
The number of H atoms increases the overall reaction of the film due to H atoms attaching to neighboring C3 are reactions such as those shown in Fig. 5 lead to an increase in and 2.94 eV, respectively; these reactions are highly exothermic with exothermicities of 1.32 and 2.94 eV, respectively; the C1–C3 bond transforms into a pure double bond (bond energy of −6.23 eV) as the remaining two neighbors of C3 (C6 and C7) are sp3-hybridized. The attachment of the H atom and the breaking of C1–C2 occur spontaneously, before the incoming H atom reaches thermal equilibrium with the surface. Hence, the entire reaction proceeds via an Eley–Rideal type of mechanism. The activation barriers for the hydrogenation reaction and for the subsequent breaking of the C1–C2 bond are negligible, and both of these reactions are highly exothermic with exothermicities of 1.32 and 2.94 eV, respectively (Fig. 5). While it appears that reactions such as those shown in Fig. 5 lead to an increase in the number of sp2 sites, further attack by incoming H atoms eventually converts such sites to sp3. Therefore, the overall result of hydrogenation is again an increase in the sp3 fraction of the film due to H atoms attaching to sp2 C atoms and converting them to sp3.

**B. Surface diagnostics**

Figure 6 shows the SE data for the a-C:H film, collected over the spectral range of 300–1300 nm, before and after D2 plasma exposure. A refractive index of 2.01 at 600 nm was obtained for the as-deposited film, typical of hard a-C:H. After D2 plasma exposure, the Tauc band gap of the film increased from 0.72 to 0.81 eV indicating that the sp3 fraction in the a-C:H film increased. This is consistent with our MD simulations, which show hydrogenation of sp2 sites by H atoms increases the overall sp3 content. Further hydrogenation leads to eventual etching of the film through desorption of stable hydrocarbon molecules. Furthermore, the surface roughness of the film increased from 1.2 to 3.5 nm, while the film thickness decreased from 339 to 302 nm indicating H/D-induced etching of a-C:H films, which previously has been reported in literature.

The micro-Raman spectra of the a-C:H film before and after D2 exposure are shown in Fig. 7. The visible Raman spectra of a-C:H films consist of the G band at ~1550 cm−1 and the D band at ~1350 cm−1. The G band corresponds to the bond stretching vibrations of all pairs of sp2 atoms in both rings and chains, and the D band corresponds to the breathing mode of sp2 atoms in rings. Therefore, if the D band is not observed, there are no sp2 ring structures in the film. Ferrari and Robertson proposed a model that discusses in detail the relationship between the a-C:H film’s band gap, the position of the G band, and the ratio of intensities of the D band, I(D), to that of the G band, I(G). Ac-
According to this model, as the band gap decreases, both the $G$ peak position as well as the $I(D)/I(G)$ ratio decrease. The $G$ peak position and the $I(D)/I(G)$ values for the $a$-C:H film before $D_2$ plasma exposure were 1540 cm$^{-1}$ and 1.47, respectively, which decreased to 1535 cm$^{-1}$ and 0.57, respectively, after $D_2$ plasma exposure. Since both values decreased, it was concluded that the band gap of the film and its $sp^3$ content increased. Thus, Raman spectroscopy data complement the band gaps obtained through SE, and are also consistent with the MD simulations.

The film deposited for the in situ ATR-FTIR spectroscopy study was under slightly different deposition conditions, as discussed in Sec. III. This film had a band gap of 1.65 eV and a refractive index of 1.9 (at 600 nm); these values are within the range reported for hard $a$-C:H.18,71 The difference IR spectrum obtained after 30 min of $D_2$ plasma exposure is shown in Fig. 8. The decrease in absorbance in the C–H stretching region around ~2900 cm$^{-1}$ and the corresponding bending region around ~1400 cm$^{-1}$ was clearly identified in the spectrum.72 The peaks at 1620 and 1580 cm$^{-1}$ were assigned to olefinic $sp^2$ C–C and aromatic $sp^2$ C–C stretching vibrations, respectively.72 In the difference spectrum in Fig. 8, the large decrease in absorbance due to the above mentioned peaks indicated chemical erosion of the $a$-C:H film due to $D_2$ plasma exposure: The $D$ atoms from the plasma insert into the C=C bonds, which eventually lead to the formation of stable molecules that desorb into the gas phase. If there was only $D$ insertion with no chemical erosion, only the bands at 1620 and 1580 cm$^{-1}$ would show a decrease in absorbance with a shift in frequency in the CH$_2$ region due to the formation of higher hydrides and a change in hybridization from $sp^2$ to $sp^3$. This is further confirmed by the increase in absorbance in the ~2100 cm$^{-1}$, which was primarily due to $sp^3$ CH$_x$ ($x=1,2,3$) species.22 This increase in absorbance could be interpreted as either due to the deuteration of the $sp^3$ sites, which converts them to $sp^3$ sites (see Sec. IV A), or due to the D-atom passivation of dangling bonds that were created by abstraction of $H$ by $D$ from surface $sp^3$ CH$_x$ ($x=1,2,3$) sites. Since it is known that rate of hydrogenation is an order of magnitude greater than the rate of abstraction,19 the increase in absorbance due to $sp^3$ CH$_x$ ($x=1,2,3$) species, created by hydrogenation of the $a$-C:H film, would be much greater than the increase due to the abstraction-passivation reaction.

V. SUMMARY AND CONCLUSIONS

The specific interactions of $H$ or $D$ atoms with hard $a$-C:H films were investigated using a combination of atomistic simulations and experiments based on surface spectroscopic techniques. To study these interactions, realistic $a$-C:H films were created using MD simulations, which were subsequently impinged with $H$ atoms at thermal energies. We developed a procedure to characterize the $sp^2$ and $sp^3$ hybridization states in the $a$-C:H film, which was based not just on the number of nearest neighbors, as previously reported in literature, but also on the bond energy. This facilitated a more accurate description of the reaction pathways of $H$ atoms with $a$-C:H surfaces due to the ability to identify the creation of dangling bonds and the corresponding change in hybridization. The analyses of the MD trajectories revealed that the hydrogenation of hard $a$-C:H films occurs primarily at the $sp^2$ sites via an Eley–Rideal type of mechanism. The hydrogenation reaction was highly exothermic with a negligible activation energy barrier. This fast mechanism therefore provides a way to transform the unsaturated $sp^3$ sites on the surface into $sp^3$ CH$_3$ sites, which is followed by etching of these sites. Thus, at high fluxes of atomic hydrogen that are used to deposit microcrystalline and nanocrystalline diamond films,32 the Eley–Rideal-based hydrogenation reaction provides an efficient way to eliminate the $sp^3$ carbon in the film. We observed that hydrogenation at the $sp^2$ sites may or may not create a dangling bond: This depended on the first and second neighbors of the C atom to which $H$ atom was attached. The experimental data were consistent with the MD simulations. Both the SE and Raman data indirectly showed that the $sp^3$ content of the $a$-C:H film increased upon exposure to $D$ atoms. The ATR-FTIR data confirmed D addition to the $a$-C:H film and subsequent etching. While the set of reactions discussed herein show that interaction with $H$ or $D$ atoms led to an overall change from $sp^2$ to $sp^3$ hybridization in these films, the films remained amorphous and did not evolve to diamondlike structures. Thus the interaction of $H$ atoms with $a$-C:H films is more complex than with amorphous films of other group IV elements such as Si and Ge, which show increased crystalline order upon $H$ exposure.33,73 We speculate that other reaction pathways must also exist that eventually lead to ordering of these films at temperatures much lower than those required for thermal annealing.

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