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Use of X-ray photoelectron spectroscopy and spectroscopic ellipsometry to characterize carbonaceous films modified by electrons and hydrogen atoms

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ABSTRACT

X-ray Photoelectron Spectroscopy (XPS) and Spectroscopic Ellipsometry (SE) have been used to interrogate and spatially map changes that occur to ultra-thin (< 10 nm) carbonaceous films as a result of exposure to electrons and hydrogen atoms. Due to post-deposition electron irradiation, as-deposited sp³-like carbon was converted into a more graphitized sp²-like carbon species. This process resulted in measurable changes to the C 1s peak profiles (XPS) of the carbon atoms. Changes to dielectric functions (SE), made possible through XPS's identification of pure as-deposited and graphitic carbon regions were also observed. These transformations could be characterized as a function of electron dose and spatially mapped using: (i) a linear combination of the individual as-deposited and graphitized C 1s components obtained in XPS and, (ii) a Bruggeman effective medium approximation of the SE film response for both types of carbon species. SE and XPS were found to produce very similar results in terms of both film composition (sp² vs sp³ carbon) and film thickness. XPS and SE analysis also revealed that exposure of carbonaceous films to hydrogen atoms resulted in the conversion of graphitized sp²like carbon back into sp³-like carbon species, a process ascribed to the lower atomic hydrogen (AH) etching rates observed for sp²-like vs sp³-like carbon. In summary, this paper highlights the ability and complementary nature of XPS/SE analysis to study and spatially map the chemical and structural transformations that can occur to ultra-thin carbonaceous films.

1. Introduction

Carbonaceous thin films can serve as useful coatings but are also often an unwanted source of surface contamination. As ultrathin films, they have proven effective in reducing friction/wear in tribology, and also as coatings to prevent substrate corrosion [1]. In addition, carbonaceous thin films have been shown to be effective in the assembly of super capacitors, lithium ion batteries, catalytic systems, and in lithography [2-5]. As contaminants, carbonaceous ultrathin films are ubiquitous and can be formed in numerous ways such as atmospheric exposure and as remnants of surface treatments. In extreme UV light lithography, projection optics reflectivity losses caused by nanometerthick carbonaceous films degrades performance below production reauirements [6].

One of the more important mechanisms of carbonaceous film growth is through deposition of adsorbed molecules in the presence of energetic species (ions, electrons and ionizing radiation) [7-10]. This phenomenon occurs predominantly in low pressure vacuum

environments, when surfaces are exposed to hydrocarbons and ionizing radiation simultaneously. In these situations interactions between the energetic species and transiently adsorbed hydrocarbons on the surface of a material or substrate causes deposits to form [7]. This type of deposition is often unwanted such as: the co-deposition and accumulation of radioactive fuel on the walls of tokamak fusion reactors; diminishing response in various electron multipliers; and reduction in beam quality/ stability in UV synchrotrons [11,12]. In electron imaging these deposits can obscure images, convolute spectra, and create problems for techniques such as: energy dispersive spectroscopy (EDAX); secondary electron microscopy (SEM); and transmission electron microscopy (TEM) [13].

The detailed effects of electrons on condensed matter have been well studied [7,14-17]. Interactions between high-energy radiation and matter produce numerous, non-thermal, low-energy, secondary electrons. Inelastic collisions of these electrons with molecules and atoms are considered the primary driving force behind electron stimulated decomposition and deposition. In the case of organic molecules, low

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energy electron induced dissociation preferentially breaks C–H bonds compared to C–C bonds resulting in the formation of strong carbon bonds with the surface and additional C–C bonds within the film [18,19]. For example, electron induced modification of alkanethiol SAMs results in pronounced desorption of hydrogen and carbon containing fragments as well as the appearance of C-C/C=C crosslinks [20]. Generally, electron exposure results in the dehydrogenation and reordering of the network structure into an amorphous and increasingly graphitic carbonaceous film [18,19,21].

Several techniques have been developed to mitigate or remove contaminative carbonaceous films. Hydrogen atoms (AH) have been used with great effect in cleaning surfaces that would otherwise be damaged or destroyed by other contamination removal methods like ion sputtering or chemical etching [22,23]. The erosion of carbonaceous films by AH begins with hydrogenation of the film. Studies using high-resolution electron energy loss spectroscopy show that AH converts sp- and sp²-hybridized CH groups to sp³-hybridized CH_x (x = 2, 3) groups [24]. Further AH exposure eventually leads to the erosion of the adsorbed film through the desorption of volatile C_xH_y molecules, such as methane and ethane [24].

Consequently, it is important to be able to identify the content and spatial distribution of different types of carbon in carbonaceous films. For example, the ratio of sp² to sp³ hybridization has been shown to correlate with many physical properties [17,25,26]. Hydrogenated carbon films rich in sp³ hybridized carbon have been shown to exhibit large band gaps, while graphitic films (sp²) have been shown to be more conductive [25,26]. In addition, sp²/sp³ hybridization ratios have been strongly linked to hardness, and even optical properties [16,17,25,26]. A wide assortment of analytical techniques have been used to differentiate between different forms of carbon including EELS, Auger, X-ray photoelectron spectroscopy (XPS), Raman, and spectroscopic ellipsometry (SE) [17,25,27-32]. XPS is particularly well suited to probe nanometer thick carbonaceous films due to its ability to determine film thickness and the chemical composition of the film (except for hydrogen). Additionally, changes in the core level binding energies as well as the shape of the spectral envelope can sometimes be used to distinguish between different chemical states. In the case of carbon, an XPS instrument with sufficient precision and energy resolution can distinguish between the subtle differences in the C 1s photoelectron peak for sp² and sp³ hybridized carbon in graphite, low-density polyethylene, and diamond [33-35]. Moreover, using internal reference spectra, the ratio of sp³/sp² carbon atoms can be determined by appropriate peakfitting of the corresponding C 1s peakshapes [28].

In addition to composition, speciation, and thickness, advancements in modern XPS instrumentation have given this technique the capacity to laterally map differences in surface composition and bonding. One approach is chemical mapping where signal is collected from a single tightly analyzed spot (~55 μ m in diameter), then repeated at various locations [33]. With a precision stage and analyzer chemical mapping can provide lateral resolutions on the order of 50–100 μ m, and a spectral resolution that can, in principle, map lateral changes in sp² vs sp³-hybridization. It is worth noting that depending on the material and scan window, scans times for this type of XPS imaging can be prohibitively long. A high-resolution chemical map can take upwards of several minutes per pixel resulting in a total scan time of several hours or days depending on the region of interest.

Optical spectroscopies, which rely on the absorption, transmission, or reflection of photons, can be viewed as somewhat complementary analysis tools to XPS in carbon film characterization. Optical methods also offer the potential for rapid, nondestructive film characterization [36–38]. An especially useful optical technique for thin film analysis is spectroscopic ellipsometry (SE), which measures the change in polarization of light upon reflection, recording the complex reflectance ratio, p, of the material. SE is sensitive to many thin film properties including film thickness, surface roughness, and optical properties (measured as a function of wavelength) [39,40]. Due to the numerous factors

influencing the physical parameters obtained by SE measurements, an appropriate model must be used to extract useful information from SE data. Consequently, the physical parameters of a thin film that can be obtained from SE, such as the index of refraction and/or thickness are only as accurate as the model used to parameterize the results [25,39,40].

Modeling SE data starts by selecting an appropriate number of layers or phases. For most carbonaceous thin film analysis, a standard three-phase (air, substrate, and film) model is sufficient. Each phase consists of a set of optical (n,k) or dielectric (ε_1 , ε_2) functions that must be determined [26.41.42]. In the case of ambient air and (most) substrates these optical functions are well known and have tabulated data associated with them. For materials with unknown dielectric functions (i.e. the carbonaceous film), a parameterizable model must be used. Two useful models, regarding amorphous carbon thin films, are the Bspline and Tauc-Lorentz models. The B-spline model uses a series of basis-splines to describe the total spline curve representing the dielectric function of the associated layer [39,43]. The B-spline model is, however, a purely mathematical construct. It can, if improperly utilized, produce unrealistic results. However, as illustrated by Weber et al., a physical result for the parameterized complex dielectric function can be obtained by forcing ε_2 to be positive and using a Kramers-Kronig transform (of the B-Spline approximated ε_2) to predict ε_1 [39,43]. Under these constraints, use of the B-Spline method can be accurate in modeling the dielectric function of films (or substrates) where little to no information is known [39]. In contrast, the Tauc-Lorentz model is physics-based and has been developed and proven to parameterize the dielectric function of amorphous materials with a degree of accuracy limited by the instrument itself [26,39,42,44,45]. Studies by Jellison et al. have shown that many of the fitted parameters of the Tauc-Lorentz model can be correlated with other measured quantities of the material, such as band gap and the ratio of sp^3 to sp^2 hybridized carbon [26,46]. Although the Tauc-Lorentz and B-spline models can parameterize a wide array of substances, they are less useful when describing heterogeneous anisotropic films where the optical properties of a film vary across the surface. In the context of carbonaceous films, this includes films containing various mixtures of different carbon species. In situations like these, the Bruggeman effective medium approximation (BEMA) can be employed [47]. The Bruggeman approximation is designed to give a symmetric description of the effective dielectric constant of multi-component materials. BEMA assumes that each constituent material retains its original dielectric response [48,49]. If the optical properties for the individual constituents are known, the overall material can be parameterized using a combination of the components. The Bruggeman effective medium approximation has been extensively used to approximate the dielectric response of inhomogeneous films for the microelectronics industry [50].

In this paper we employ XPS and SE to characterize nanometer thick carbon films created by electron beam induced deposition of tetradecane. Selected areas of these films were exposed to additional electron irradiation, altering their chemical and structural properties and creating deposits with different forms of carbon. These deposits were examined using the chemical mapping function of XPS and an imaging spectroscopic ellipsometer. XPS peakfitting techniques used to measure sp^2/sp^3 hybridization, normally applied to isotropic films, were applied to anisotropic films. These results were compared to SE data obtained from the same films. Both techniques were also used to monitor AH modification and etching of amorphous carbon films with different sp^2/sp^3 ratios.

2. Experimental

2.1. Sample preparation

2.1.1. Film deposition

Film deposition was accomplished by dosing tetradecane into a customized UHV chamber while a gold coated silicon wafer was exposed to 2 keV electrons generated by an electron gun. A description of the customized UHV system's design, operation, and calibration can be found in the supporting information. Tetradecane was chosen due to its volatility and because it (along with other hydrocarbons) is a common contaminant found in vacuum chambers [13,22,51]. Tetradecane was attached to a gas manifold and introduced into the chamber through a UHV leak valve. During deposition, the partial pressure of Tetradecane was measured using the most intense fragment (57 *m/z*) and was held at a constant pressure (3.0×10^{-6} Torr).¹ The partial pressures of residual gasses such as O₂ and H₂O were also monitored during deposition and remained $\leq 10^{-8}$ Torr.

Carbonaceous deposits were created on the gold coated silicon wafers that were mounted onto a custom sample stage shown in Fig. 1 that also contained an Al coated, Ce: YAG scintillator used to calibrate the electron beam (see Beam Calibration section in SI) and a Faraday cup to determine beam intensity/flux. A primary electron energy of 2 keV was chosen as this value was sufficient to, (a) overcome the energy threshold of the scintillator and, (b) generate numerous low energy (< 100 eV) secondary electrons responsible for the deposition process.

During film deposition and post-deposition modification the trajectory of the electron beam was orthogonal to the plane of the substrate surface. A series of four deposits were made on each substrate. Each deposit was created by simultaneously exposing the sample to both electrons and tetradecane for about 45 min. For each set of depositions, the beam profile was adjusted to be as flat and uniform as possible across a ~3 mm diameter area, as monitored by the scintillator. Limitations of the electron gun prevented a truly flat profile and often resulted in a ring of higher intensity at the perimeter of the beam area. An example deposition beam profile, as imaged by the scintillator, reticle, and camera, can be found in SI Fig. 2 (left panel). A single beam intensity of 22 µA, as measured by the faraday cup, was utilized for all depositions and post deposition experiments. The substrate temperature remained at 24 °C throughout electron exposure as determined by an attached K type thermocouple. The average thickness of the resulting deposits within a given sample set (four) was the same. However, the thickness between samples prepared on different substrates varied from $\approx\!5.0\,\text{nm}$ to $\,\approx\!7.0\,\text{nm},$ thicknesses suitable for analysis by both SE and XPS.

2.1.2. Post-deposition modification

After the initial deposits were made, the sample stage was retracted into the secondary chamber while the primary chamber was baked for several days to remove any latent tetradecane from the system. After bake-out, the cleanliness of the chamber was checked using an attached RGA. The only detectable gasses in the deposition chamber were that of hydrogen and nitrogen/carbon monoxide ($< 1 \times 10^{-9}$ Torr). The partial pressures of other gasses such as O₂, H₂O and tetradecane were below the detection limit of the RGA ($< 10^{-10}$ Torr). An additional measure of chamber cleanliness was determined by exposing a previously unexposed area of the substrate to the electron beam for 100 h to create a "background" deposit. Calibration experiments indicated carbonaceous growth greater than ~2 nm could be visibly discerned by the attached camera. The absence of any visible evidence of a "background" deposit was therefore used as a qualitative indication that the Applied Surface Science 479 (2019) 557–568



Fig. 1. Custom fabricated sample stage featuring an Al coated, Ce: YAG scintillator and faraday cup used to characterize and monitor the electron beam.

partial pressure of tetradecane had been sufficiently reduced by the bake-out. It is worth noting that in the cases where the "background" deposit was visually identifiable (e.g. the deposit marked by an "x" in SI Figs. 3 and 4), the chamber bake-out was continued and the "background" test repeated until no visual evidence of a "background" deposit was observed.

After a bakeout sufficient to eliminate all residual tetradecane from the chamber, samples were exposed to post-deposition irradiation. In these experiments, the size of the electron beam was reduced to a diameter of \sim 1.5 mm, to comfortably fit inside the \sim 3 mm diameter deposits. In contrast to the flat top beam profile used to deposit films, the smaller beam used for post deposition film modification exhibited a Gaussian-like intensity distribution when examined by the scintillator. An example of the post-deposition beam profile, as imaged by the scintillator, reticle, and camera, can be found in SI Fig. 2 (right panel). An attached optical camera was used to position the post-deposition beam inside the deposits. Three of the four initial deposits were exposed to varying doses of the electron beam.

After deposition and post-deposition electron modification, the Au coated silicon substrate was removed from the UHV chamber and deposits were characterized ex-situ using X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry (SE). Following characterization, each set of carbon deposits were also cleaned using a purposebuilt hydrogen atom cleaning system. In brief, the hydrogen atom cleaning system functioned by passing hydrogen gas across a hot filament positioned perpendicularly to and about 1–2 in. from the substrate. It has been shown that the rate of hydrogen atoms cleaning of carbonaceous films is strongly dependent on substrate temperature [52–53]. Consequently, throughout the AH cleaning process the substrate temperature was monitored closely. In our experiments the substrate temperature remained at 24 °C. Following well defined exposures to the AH source, XPS analysis was performed. At the end of the AH cleaning, samples were also analyzed using SE.

2.2. XPS and SE characterization of deposited carbon

2.2.1. XPS

Deposits were analyzed using a Kratos Axis Ultra scanning X-ray photoelectron spectrometer with a DLD detector and a monochromatized Al K α source (1486.6 eV) operated at 300 W. The detection angle was set to be normal to the substrate. The location of the deposits was determined using an attached camera and confirmed in XPS by the increase in the C 1s signal and the corresponding decrease in Au 4f signal. Each deposit was characterized by two different XPS maps obtained using the chemical mapping method described in the

¹ The partial pressures of all gasses in the chamber were monitored by an attached RGA. See Deposition/Post-deposition Exposure Chamber section in SI for details.

introduction. The first XPS map was a succession of Au 4f region scans taken at a series of lateral positions across the deposit; 400 scans were taken at 200 µm intervals across a 4.0 mm × 4.0 mm area. Each scan was obtained using a probe size ≈ 250 µm in diameter, a pass energy of 160 eV, and a dwell time of about 200 ms per eV/step. The attenuation of the Au 4f peak area provided a measure of carbon thickness, d_c , in the deposits as compared to the trace levels of adventitious carbon located in areas of the sample not exposed to the electron beam. d_c was determined using Eq. (1) where I and I_0 are the Au 4f photoemission signals inside and outside of the deposit respectively; λ is the effective attenuation length (EAL) of Au 4f electrons through tetradecane deposits [54]. An EAL of 2.7 nm was used based on the NIST Standard Reference database 82 [55].

$$d_c = \lambda \cdot \ln \left(\frac{I_0}{I} \right) \tag{1}$$

Au 4f XPS film thickness scans were taken after deposition, again after additional exposure to electrons and also at select intervals after well-defined exposures to AH.

For the second XPS map, a series of C 1s region scans were acquired at a series of lateral positions across each deposit; 1024 scans were taken at 100 µm intervals across a $3.2 \text{ mm} \times 3.2 \text{ mm}$ area. Each scan was obtained using a probe size $\approx 125 \text{ µm}$ in diameter, a pass energy of 20 eV, and a dwell time of about 700 ms per eV/step. Each C 1s region scan required about a minute of acquisition time resulting in maps that required a cumulative scan time of (> 5) hours per map.² As a result, these high-resolution scans were time intensive. Consequently, the number of these high-resolution C 1s map scans were limited and only taken prior to AH exposure and again after completion of the AH cleaning process.

2.2.2. SE

Deposits were analyzed using a fixed angle J.A Woolam M-2000F spectroscopic ellipsometer. Each scan was taken at a fixed angle (65°) with a spot size of about $25 \,\mu\text{m} \times 60 \,\mu\text{m}$. Due to the fast acquisition time (on the order of milliseconds per spot), scans were taken at 100 μm intervals across an 8.0 mm v 8.0 mm area which encompassed all depositions on the surface of the wafer. Data analysis and parameterization was performed using CompleteEase software. While the ellipsometer had a functional range between 1.24 and 5.1 eV (~193 and 1000 nm), deadzones in the spectrometer resulted in aberrant spikes in the ellipsometry data around 1.40 and 1.50 eV (see Fig. 4). To eliminate the effect of these deadzones, data fitting and analysis was limited to a range of 1.51–5.10 eV.

3. Results and discussion

3.1. Characterization of deposited films

3.1.1. XPS

As described in the Experimental section, a series of four identical deposits were created. XPS thickness maps indicated < 10% variation in thickness between the four deposits (\pm 0.6 nm variance in samples averaging \approx 6.0 nm). Moreover, there was no difference in the thickness maps between deposits that received no additional electron dose (as-deposited) and those that received as much as 100 h of additional electron dose, as shown in the XPS thickness maps in the left-hand column of Fig. 6. Thus, no measurable carbon was added or removed from the deposits as a result of the post-deposition electron exposure. The lack of deviation in XPS thickness profiles also demonstrates that

the inelastic mean free path of the Au 4f electrons is insensitive to any structural changes induced by the incident electrons. Most importantly, any differences in film properties observed by SE and C 1s XPS analysis can be attributed solely to the effects of electron induced modification.

To understand the chemical and structural effects of additional electron irradiation, C 1s XPS maps were taken of both as-deposited films and films exposed to additional (post-deposition) electron irradiation. The insert in the left-hand panel of Fig. 2 shows the XPS thickness map of a deposit after the central region (white dashed circle) was exposed to 28 h of post-deposition electron irradiation. Analysis of the C 1s XPS data for this deposit revealed that three different and distinct C 1s spectral envelopes were present, each located within specific regions. Outside the deposit (Region A) a small, somewhat symmetrical, C 1s XPS signal was observed with a binding energy of about 285.2 eV. An averaged C 1s profile acquired in this region is shown in the left panel of Fig. 2 (green). This background carbon species can be attributed to the presence of adventitious carbon as well as residual carbon from the polymer used to protect the Au-coated surface during the dicing process. Within the deposit, in areas not exposed to additional electron irradiation, a different C 1s profile was observed with a peak centered around 285.0 eV (as-deposited, Region B), whose intensity scaled with film thickness. This peak exhibited a narrower but slightly more asymmetric spectral profile as compared to the background carbon and was attributed to the as-deposited carbon created during the deposition of tetradecane. Both the peak position and asymmetric profile are consistent with high resolution XPS scans of hydrogenated, sp³ hybridized, amorphous carbon films observed by Lascovich et al. [33,34,56,57] Spectra from Region B were averaged, and the results are shown in purple (left panel, Fig. 2). Examination of the C 1s XPS spectra within regions of the deposit exposed to additional electron irradiation (Region C) revealed the presence of a third C 1s envelope, characterized by an asymmetric peakshape centered around 284.7 eV. Both the observed peakshape and peak position are consistent with sp² hybridized graphene and/or graphitic carbon species deposited onto metal surfaces [28,33,34,57]. Spectra from Region C were averaged; and the results are shown in Blue (left panel, Fig. 2).

Using CasaXPS©, C 1s spectral envelopes were peakfit by means of a linear combination of the three components (background, as-deposited, and graphitized). While the relative intensities of each component were allowed to vary, both peak position and FWHM were fixed. This effectively determined the relative contribution of each carbon component at any point inside or outside the deposition region. Examples of the resulting spectral peakfitting, in locations where more than one type of carbon species was observed, can be found in the right-hand panel in Fig. 2. For example, at the interface between additionally dosed and asdeposited regions, the C 1s profiles (#1 and #2 in Fig. 2) could be well fit by a linear combination of as-deposited and graphitized carbon.

The spatially resolved contribution that the three different carbon species, identified in Fig. 2, make to the C 1s envelopes of different deposits are shown in Fig. 3. Darker and violet shades correspond to near zero intensities while white corresponds to the highest observed intensities. For a tetradecane deposit not exposed to any additional electron irradiation (top row, Fig. 3), regions outside the deposit exclusively contain background carbon while the deposit itself contains only as-deposited carbon. There is no contribution from the graphitized carbon. In a film exposed to 28 h of electron irradiation following deposition (bottom row, Fig. 3), background carbon, once again, is exclusively detected outside of the deposit. In the areas of the deposit not subject to additional electron irradiation, as-deposited tetradecane was detected. In contrast to the unexposed deposit, however, the center of the deposit (area exposed to additional electron irradiation) has been completely transformed into graphitized carbon. The relative concentration of these three-carbon species across the two deposits is shown more quantitatively by the representative line scans through the deposits which plot the relative percentage of each carbon species (background, as-deposited and graphitized).

 $^{^2}$ XPS spectra taken from an as-deposited and additionally dosed carbon deposit were statistically the same as those measured after several hours (> 48 h) of X-ray exposure. This ensured the deposits were invariant to the X-ray source used to probe the samples.



Fig. 2. (Inset, left panel) XPS thickness map of a deposit where the central region (white dashed circle) has been exposed to 28 h of additional electron irradiation. Three different C 1s XPS profiles were identified in and around the deposit and marked accordingly; carbon contamination, found outside of the deposit (A, green), as-deposited tetradecane, located within the deposit (B, purple) and additionally electron irradiated (graphitized) carbon located within the additionally dosed region of the deposit (C, blue). (Left panel) Averaged C 1s spectra acquired from scans taken within each of the three regions (A, B, and C) identified in the inset as dashed circles. (Right Panel) Four example C 1s spectra (black dots) acquired at the four white numbered locations [1–4] shown in the inset, along with the corresponding fits using the three components shown in the left-hand panel. Each of the four numbered locations represents an interfacial region (e.g. between the deposit and the background region) where there are measurable contributions to the C 1s envelope from two of the components identified in the left-hand panel. The red dotted line represents the fitted linear combination of components A, B, C.



Fig. 3. Two-dimensional maps showing the relative contribution of the three C 1s components (background, as-deposited and graphitized carbon) for an as-deposited film (top row) and a film where the central portion has been exposed to an additional 28 h of electron irradiation (bottom row). (Right column) Representative line profiles showing the relative intensity of background, as-deposited and graphitized carbon across the deposit, demarcated by a dashed white line.

3.1.2. SE

SE analysis of both as-deposited and additionally dosed films began by analyzing the raw values of psi and delta, measured at various wavelengths. When compared to results obtained from XPS, it became apparent that the both psi and delta were influenced by the overall film thickness and electron exposure. In general, it appeared that delta variations mostly correlated with overall film thickness (as determined by XPS), while psi variations tended to correlate closely with regions exposed to large doses of electrons. Examples of these psi and delta maps are found in SI Fig. 3. This comparison demonstrated that spatial maps plotting the raw values of delta could be used as fiduciary markers to unify the XPS and SE coordinate systems. In practical terms, maps of delta values, measured at 1.24 eV (~1000 nm), and the corresponding XPS thickness maps were superimposed on top of one another. Their relative X/Y coordinates were adjusted until the two images overlapped, enabling XPS and SE data acquired from the same deposit to be directly compared.

XPS C 1s analysis revealed that the as-deposited tetradecane film was composed exclusively of sp^3 -like, hydrogenated, carbon while the additionally dosed regions of the deposit exposed to 100 h of additional electron irradiation was composed exclusively of graphitized sp^2 -like carbon. To determine whether these different forms of carbon exhibit different optical/dielectric properties, three locations of identical thickness (as measured by XPS) were characterized by SE and plotted in Fig. 4. Since film thickness is the same for all three locations, differences in psi and delta reflect differences in the optical properties of the deposits. Two of the locations (shown in red and purple) were taken from within as-deposited regions while the third (blue) was taken from



Fig. 4. (Left) psi and delta (right) values measured by SE and plotted as a function of energy for three different locations within a deposit with identical thickness (the latter determined by XPS). The red (circle) and purple (triangle) plots correspond to SE data taken from within as-deposited carbon regions while the blue (diamond) represents data taken from within a graphitized carbon region.

a point that had been exposed to an additional 100 h of electron irradiation. As expected, the two locations corresponding to as-deposited carbon show identical variations in psi and delta as a function of wavelength. However, these functional variations are measurably different in the location exposed to additional electron irradiation. Consequently, it can be inferred that electron irradiation changes the optical/dielectric properties of as-deposited films due to graphitization.

For SE to determine film thickness as well as the distribution of asdeposited and graphitized carbon within a deposit, it is necessary to model the SE data. The three-phase model, described in the introduction, was used to model the carbonaceous films [25,39–40,42]. To predict film thickness, the three-phase model requires accurate optical/ dielectric functions for both the substrate and the film. The optical response of the Au-Si wafer (which included the background/contaminating carbon layer (< 1 nm) to reduce complexity of the model) was obtained using SE measurements taken at 30 different locations outside the area where deposition occurred. In CompleteEase™, this was performed by fitting a common B-spline curve to approximate the average optical response of the substrate from all 30 locations. The "goodness of the fit" was monitored using the "mean squared error" (χ^2) . The mathematical details of this parameter can be found in the CompleteEase[™] manual but, in essence, it sums (over all wavelengths) the differences between the measured and model predicted ellipsometry data (psi and delta) [41]. While an ideal model fit should provide a χ^2 equal to one, the best model fits for experimental datasets are generally higher. A χ^2 < 10 is generally considered acceptable [41]. For the B-Spline fit to the substrate, an χ^2 of about 3.9 was found.

Although accurate optical/dielectric functions can readily be obtained for the substrate, for the ultrathin (< 10 nm) carbonaceous films under investigation in this study, it becomes increasingly difficult to separate the changes in psi and delta due to film thickness and those due to the dielectric functions of the film [48,49]. This can be explained, in part, by the significantly weaker signal from the film compared to the substrate. In chemically homogenous regions of deposits where there is a singular type of carbon (as determined by XPS), the dielectric parameters can, however, still be extracted/parameterized by assuming that the optical/dielectric parameters will remain constant while thickness changes. Under these circumstances, any changes in SE are determined by changes in film thickness. Consequently, the invariant optical/dielectric parameters and variable thickness values that provide the best fit to the SE data can be determined.

To this end, 30 locations were chosen within an as-deposited

tetradecane deposit. Two different models were used to parameterize the dielectric functions of the as-deposited film, the Tauc-Lorentz and B-Spline. The multi-sample analysis feature in CompleteEase, (in conjunction with the experimentally determined dielectric coefficients for the substrate) was used to provide a simultaneous calculation of thickness (at each point) and determine (using either the Tauc-Lorentz or B-spline model) a common set of dielectric functions for the as-deposited carbon [41]. To avoid unrealistic results with the B-spline model, both $\varepsilon_2 > 0$ and Kramers-Kronig consistency was enforced. The resulting χ^2 values were 3.9 and 3.4 for the Tauc-Lorentz and B-spline model, respectively. Using the same approach, 30 locations within the deposit that received 100 h additional electron exposure were utilized to simultaneously determine both thickness (at each location) and dielectric functions for graphitized carbon. The χ^{2} 's for the Tauc-Lorentz and B-Spline parametrization were 4.1 and 3.8, respectively.

3.1.3. Comparison of film thicknesses determined by XPS and SE

Film thicknesses, calculated by the multi-sample SE analysis described earlier, were compared to the corresponding thicknesses determined by XPS. Results from this analysis for both SE models (Tauc-Lorentz and B-Spline) and each type of carbon (as-deposited sp³ and graphitized sp²) are shown in Fig. 5. Regardless of the type of carbon or model used, it is apparent that there is a linear correlation between XPS and SE predicted thicknesses. Moreover, the slopes for all these plots are close to unity, indicating a high degree of linear correlation. Both Bspline and TL models give relatively similar slopes for the same type of carbon, for as-deposited sp3-like carbon (1.25 as compared to 1.21) and for graphitized carbon (0.89 as compared to 0.95). The slight deviations from unity are likely due to an inaccurate approximation of thickness by either technique. In the case of XPS, deviations can be the result of an inaccurate EAL. In the case of SE, deviations can be the result of an inaccurate approximation of the optical constants. The y-intercepts are the result of an offset calibration factor that deals with how thickness is calculated with respect to each technique. In general, Fig. 5 highlights the good linear correlation between XPS and SE derived thickness values, suggesting that either method can be used to determine film thicknesses in nanometer scale carbonaceous films with a high degree of accuracy (error $< \approx 10\%$). It is worth noting that, due to the ultrathin nature of the films examined here, identification of the homogeneous regions, where each distinct form of carbon resides, is required for competent SE analysis. Consequently, XPS analysis provides an essential component that greatly improves the confidence with which SE



Fig. 5. (Left) correlation plot, pairing the film thicknesses determined by XPS (x-axis) and predicted by the Tauc-Lorentz SE model for as-deposited (purple) and graphitized (blue) carbon (SE data plotted on the y-axis). A linear fit gives a slope of 1.25 and 0.89 for as-deposited and graphitic carbon, respectively. (Right) Correlation plot, pairing the film thicknesses determined by XPS (x-axis) and predicted by the B-Spline SE model for as-deposited (blue) and graphitic (purple) carbon (SE data plotted on the y-axis). A linear fit gives a slope of 1.21 and 0.95 for as-deposited and graphitic carbon, respectively.

analysis can be performed.

3.2. Probing the electron induced transformations of carbon in more heterogeneous deposits

Using the dielectric functions for as-deposited and graphitic carbon, an SE model can be constructed to account for more heterogeneous deposits where the extent of additional electron irradiation was insufficient to convert all of the as-deposited carbon to graphitized carbon. Experimentally, this insufficient exposure corresponds to deposits exposed to 1 h and 21 h of electron irradiation. For these more complex, heterogeneous films, the Bruggeman effective medium approximation (BEMA) was utilized to approximate the cumulative optical response of the film layer in the three-phase model. The independently derived dielectric functions for as-deposited and graphitized carbon, as determined by the B-spline model, were utilized to construct a two carbon BEMA model [47]. The optical parameters derived from the B-spline model were used due to the slightly better fit to the experimentally determined SE data (lower χ^2) as compared to the TL model. Using the two carbon BEMA model to approximate the optical coefficients of the film layer, the measured SE data was fit with the three-phase model to determine both thickness and the percent of graphitized carbon for both as-deposited and additionally dosed films. The χ^2 (MSE) values, plotted as a function of position (See SI Fig. 4), were observed to be nearly constant (≈ 3.8) throughout the deposits, indicating a good fit for all variations in film thickness and composition.

A comparison of the thickness maps acquired by XPS and SE for deposits exposed to varying degrees of post-deposition electron irradiation (1 h, 21 h, and 100 h) is shown in Fig. 6. The left-hand column shows the thickness maps obtained from XPS, while the middle column shows the thickness maps obtained from the SE BEMA model. Line profiles comparing the film thicknesses derived from these two experimental methods can be found in the graphs featured in the right column. In general, the two carbon BEMA model results in a good agreement between film thicknesses determined by SE and XPS (compare the blue circles and orange triangles) for all deposits. The modest disagreement observed in the center of the 100-hour line profile (Fig. 6, bottom right) correlates with the additionally electron dosed region of the deposit and is a consequence of the B-Spline model's underestimation (compared to XPS) of graphitic carbon thicknesses. It should be noted that the lateral resolution for the XPS thickness maps was about \pm 0.2 mm, much larger than their SE counterparts (\pm 0.05 mm). To enable direct comparison of SE and XPS thickness maps, the SE thickness maps were averaged across a \pm (0.2 \times 0.2) mm² area to mimic the resolution of the XPS data. (Examples of SE thickness maps before and after spatial averaging can be seen in SI Fig. 5).

The effect that varying the dose of post deposition electron irradiation has on the distribution of as-deposited and graphitized carbon within deposits was also evaluated by SE and compared to XPS, the latter determined using the deconvolution method described in the XPS characterization section (Section 3.1.1). To this end, the sp^2/sp^3 distribution of deposits that were exposed to 1 h, 21 h, and 100 h of additional electron irradiation were compared. Results of this analysis by XPS and SE are shown in Fig. 7. As the additional electron dose increases, the extent of graphitization (conversion of as-deposited tetradecane to graphitic carbon) is seen to increase systematically. In the density plots for graphitic carbon, this manifests itself as an increasing whiteness in the central region where electron exposure occurred. For deposits exposed to only 1h of additional electron irradiation, data from both the XPS and BEMA SE model indicate that only about half the as-deposited carbon was converted to graphitized carbon (top right panel). After 21 h of electron irradiation, the extent of graphitization increases and after 100 h, the entire irradiated region has been converted to graphitized carbon. The lateral distribution of graphitic carbon for deposits where graphitization is not complete (i.e. 1 h) exhibits a near Gaussian profile across the deposit, consistent with the Gaussian-like intensity profile of the electron beam used to induce graphitization (see SI Fig. 2). Fig. 7 also highlights that the lateral distribution of graphitic carbon as measured by XPS and SE (using the BEMA model) agree well. Indeed, the similar sp²/sp³ distributions and thicknesses determined by XPS and BEMA SE model indicate the accuracy with which these techniques can be used to determine both thickness and film composition.

3.3. Characterization of films exposed to hydrogen atoms

After XPS and SE characterization, each set of 4 deposits was exposed to hydrogen atoms (AH) for specific periods of time. After each AH exposure, XPS thickness maps were acquired and superimposed on top of the preceding map by adjusting the X/Y coordinates to maximize the correlation between the two thickness maps; the same technique used to compare the SE and XPS thickness maps. The thickness of



Fig. 6. XPS (left column) and BEMA SE (middle column) 2-dimensional thickness plots for both as-deposited films and films exposed to additional electron irradiation (see text for details). Line profiles across the corresponding deposits are plotted on the right with blue circles corresponding to the XPS thickness and orange triangles corresponding to SE thicknesses obtained using the BEMA model. The location of the line scan taken from each thickness plot is shown by the white dashed line.

carbon removed at any point within the deposit was calculated by measuring the change in the Au 4f XPS signal using Eq. (1). Fig. 8 plots the carbon removed as a function hydrogen atom exposure for an asdeposited film (blue) as well as deposits where the central region had been exposed to 7 h (red), 14 (green) hours, and 21 h (orange) of additional electron irradiation. Examination of these plots shows that the rate of removal for as-deposited tetradecane is higher than for carbon which had been exposed to additional electron irradiation. However, within deposits exposed to 7, 14 and 21 h, there is little to no difference in the AH cleaning rate. A best fit line was applied to all data points (0-60 min) for each of the plots to obtain cleaning rates for each deposit; for the as-deposited tetradecane a value of 0.102 nm/min was determined while the slopes for the deposits exposed to 7, 14 and 21 h were 0.074 nm/min, 0.072 nm/min, and 0.067 nm/min, respectively. The coefficient of determination (R^2) was determined to be ≈ 0.99 for all of the associated fits.

AH exposure studies have shown that amorphous carbon films are etched by an Eley-Rideal reaction [58–60]. Moreover, the rate of carbon removal using AH has been shown to be a first order process

[53,58,61]. However, due to the limited penetration depth of hydrogen atoms within carbonaceous deposits, a pseudo-zeroth order reaction is observed when the film thickness is larger than the depth of AH penetration [52]. When this happens, the concentration of accessible/removable carbon can be considered constant, manifesting as a linear reduction in film thickness and a constant cleaning rate, as we observe experimentally. The etching rates (slopes) observed in Fig. 8 show that hydrogenated (as-deposited, sp³) films clean at a higher rate than graphitic carbon (additionally dosed, sp²) films.

As expected, areas not exposed to additional electron irradiation (at the periphery of the deposit) cleaned at the same rate as the as-deposited tetradecane deposits. This results in contrasting cleaning rates within the central region of the deposits, where they were exposed to additional radiation. The effects of this differential in cleaning rates can be visualized in the 3D maps found in Fig. 8. The top set of 3D Figures correspond to a deposit that did not receive any additional electron dose. As a result, carbon is removed at an equal rate across the deposit giving rise to a nearly flat top distribution of carbon removed after 30 min of AH exposure. This is in stark contrast to deposits exposed to



Fig. 7. (Left two columns) two-dimensional XPS C 1s component concentration maps showing the relative intensity of as-deposited carbon and graphitic carbon for deposits exposed to 1 h (top row), 21 h (middle row) and 100 h (bottom row) of additional electron exposure. (Right two columns) Line profiles (dashed white lines) through the deposits showing the fractional concentration of as-deposited carbon (purple squares) and graphitic carbon (blue circles) determined by XPS and the BEMA SE model.



Fig. 8. Carbon etched as a function of hydrogen atom (AH) exposure, plotted for an as-deposited film (purple circle) as well as films where the central portion of the deposit was exposed to an additional 7 h (green diamond), 14 h (orange triangle) and 21 h (blue square) of electron irradiation. Also shown are 3D XPS thickness maps representing the spatial distribution of carbon removed from as-deposited films and films where the central region was exposed to 21 h of additional electron irradiation, after various AH exposures.

additional electron irradiation which show reduced cleaning rates within the electron exposed regions. This manifests as a volcano-like carbon loss profile after both 30 and 45 min of AH exposure. It is worth noting the carbon loss profiles after 15 min of AH exposure. These profiles are visually dominated by the removal of the small amount of background carbon outside the deposit region, which occurs at a faster rate than either the as-deposited or graphitized carbon. These 3D maps illustrate the variance in cleaning rates that can be seen within the deposits themselves for the three different forms of carbon identified by XPS (background, as-deposited, and graphitized). The different cleaning rates measured at several locations in and around a deposit (corresponding to the different forms of carbon) are plotted in SI Fig. 6.

After 60 min of AH exposure, both XPS and SE analysis was performed on the remaining deposit. At this point, according to XPS



Fig. 9. C 1s XPS spectra taken from films of as-deposited carbon (top), graphitized carbon formed after exposing an as-deposited film to 100 h of additional electron irradiation (middle), and after exposing graphitized carbon to 60 min of hydrogen atoms (bottom). A gray line at 285.0 eV is used as a guide to help illustrate the binding energy shifts.

thickness maps, most of the carbon had been removed. For as-deposited films XPS analysis revealed no difference (other than signal intensity) between the C 1s spectral envelopes before and after 60 min of AH exposure. This contrasts with results from portions of the film exposed to additional electron doses. Fig. 9 shows example C 1s XPS spectra for as-deposited carbon (top spectrum), graphitized carbon generated by exposing as-deposited carbon to 100 h of electron irradiation (middle) and the same graphitized carbon after 60 min exposure to AH (bottom). Analysis of Fig. 9 shows that the largely symmetric C 1s envelope of the graphitized carbon has been transformed by AH exposure to an asymmetric peak centered around 285.1 eV (compare the middle and bottom C 1s spectra in Fig. 9). Other than a slightly higher binding energy (by $\approx 0.1 \text{ eV}$) this new peak shape is identical to the hydrogenated sp³ carbon species observed in the as-deposited film (compare the top and bottom C 1s spectra in Fig. 9).

Previous SE, Raman and ATR-FTIR studies on amorphous carbon

films show that hydrogen atom etching occurs as a direct result of film hydrogenation [27,60]. These studies, performed by Jariwala et al., indicate that hydrogenation primarily occurs at graphitic sp^2 sites converting them to more hydrogenated sp^3 CH_x sites [24,27,60,62]. In Fig. 9, the binding energy shift C 1s peak from 284.7 eV (graphitic, sp^2) to a more hydrogenated (sp^3) species at 285.1 eV supports the idea that AH exposure leads to the conversion of graphitized to hydrogenated sp^3 carbon, the latter analogous to the as-deposited carbon. Further progression results in the production of C_xH_y volatile species and the eventual etching of the carbonaceous film. It can be inferred then, that the reduced etch rated observed for graphitic (sp^2) films compared to hydrogenated (sp^3) is the result of the additional sp^2 to sp^3 hydrogenation step needed before etching [24,27,60,62].

SE data, at least qualitatively, supports the XPS findings. The blue and purple plots in Fig. 10 show raw SE data taken from two locations of identical thickness (according to XPS) but different doses of additional electron exposure. As expected, the variation in the distribution of sp^2/sp^3 species between these different locations results in differences between psi and delta. In contrast, after 60 min of AH exposure (Fig. 10, Orange/Brown) all of the locations with identical thicknesses, determined by XPS, exhibit identical SE signals, indicative of the presence of a single carbon (sp^3) species.

It should be noted that the present study focused on the analysis of relatively large millimeter sized deposits. This was dictated by the limitations of the electron gun. In principle, however, the approach adopted in the present study could also be applied to analyze deposits of significantly smaller size. In this regard lateral resolutions would only be limited by the spot size of ellipsometer, 25 um \times 60 um.

4. Conclusions

Electron beam induced deposition of tetradecane has been used to create \sim 6 nm amorphous carbon films. XPS and SE maps of the C 1s spectral regions revealed that electron irradiation of the deposited films resulted in the conversion of carbon from a hydrogenated, sp³-like species into a graphitized, sp²-like species. Based on corresponding attenuation of the Au 4f intensity, this transformation did not, however, change the overall thickness of the film. Spectroscopic ellipsometry demonstrated that this electron induced dehydrogenation process also produced measurable changes in the dielectric and optical properties of the film. Exposing the graphitized sp²-like carbon atoms to hydrogen atoms (AH) caused them to convert back to a more hydrogenated sp³-



Fig. 10. (Left) psi and delta (right) values measured by SE and plotted as a function of photon energy taken from two locations of identical thickness (as determined by XPS) but exposed to different electron doses (1 h (circles) and 100 h (triangles)). Data is shown for paired locations, before (blue (circles)/purple (triangles)) and after (orange (circles)/brown (triangles)) 60 min of hydrogen atom exposure.

like species. The need to convert sp^2 to sp^3 carbon atoms as a discrete step on the way to forming volatile carbon species is believed to be responsible for the observed decrease in AH etching rate of sp^2 vs sp^3 carbon atoms.

As part of this study, protocols were developed to analyze this conversion of as-deposited sp³-like carbon to graphitic sp²-like carbon, particularly in situations where regions of the deposits contained a mixture of both species. For XPS, this protocol utilized linear combinations of the individual C 1s lineshapes associated with as-deposited sp^3 and graphitized sp^2 carbon atoms. For SE, the first step in this protocol involved obtaining the optical/dielectric functions for each carbon species independently; a step that could not be possible without XPS's identification of the pure (as-deposited and graphitic carbon) regions within the deposits. In conjunction with a Bruggeman effective medium approximation, this information enabled the ratio of sp³/sp² carbon atoms as well as the film's thickness to be mapped. The good agreement between composition and thickness maps obtained by XPS and SE indicates the efficacy of both techniques in terms of their ability to follow the interconversion between as-deposited sp³ and graphitic sp² carbon in ultra-thin carbonaceous deposits exposed to electron irradiation and hydrogen atoms.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2019.02.122.

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