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EUV-induced oxidation of carbon on TiO₂

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ABSTRACT

Previously we reported estimates of the maximum etch rates of C on TiO₂ by oxidizers including NO, O₃ and H₂O₂ when irradiated by a spatially-non-uniform beam of extreme ultraviolet (EUV) radiation at 13.5 nm (Faradzhev et al., 2013 [6]). Here we extend that work by presenting temporally and spatially resolved measurements of the C etching by these oxidizers as a function of EUV intensity in the range (0.3 to 3) mW/mm² [(0.2 to 2) × 10¹⁶ photons s^{−1} cm^{−2}]. We find that the rates for NO scale linearly with intensity and are smaller than those for O₃, which exhibit a weak, sub-linear intensity dependence in this range. We demonstrate that these behaviors are consistent with adsorption of the oxidizing precursor on the C surface followed by a photon-stimulated reaction resulting in volatile C-containing products. The kinetics of photon-induced C etching by hydrogen peroxide, however, appear to be more complex. The spatially resolved measurements reveal that C removal by H₂O₂ begins at the edges of the C spot, where the light intensity is the lowest, and proceeds toward the center of the spot. This localization of the reaction may occur because hydroxyl radicals are produced efficiently on the catalytically active TiO₂ surface.

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1. Introduction

Photo-stimulated oxidative reactions at surfaces are widely used in the modern world. Examples of these reactions include destruction of toxic organic compounds [1], cleaning of synchrotron optics [2] and self-cleaning of consumer glass products [3]. This phenomenon also imposes technological challenges such as degradation of organic solar cells [4]. Normally, a reaction stimulated by photons on a surface starts from electronic excitation of either an adsorbed molecule or the surface itself. Catalytic surfaces such as TiO₂ assist the reaction yield or even change the reaction pathways. The reader is referred to multiple reviews discussing mechanisms of photocatalysis on the TiO₂ surface (e.g. Ref. [5]).

In this paper we focus on the photon-stimulated reaction of three strong oxidizers (O₃, NO, H₂O₂) with a carbonaceous layer that was itself formed by photodecomposition of *n*-tetradecane on a TiO₂ film. Here extreme-ultraviolet (EUV) photons (92 eV, 13.5 nm) were used for both the decomposition and oxidative removal of C. In our earlier work [6] we reported that EUV irradiation converted the linear alkane *n*-tetradecane, which was adsorbed on a TiO₂ surface at 20 °C, into a mixture of linear fragments and polycyclic aromatic hydrocarbons in a complex network of *sp* [2]-rich carbon bonds. In the same set of experiments, we demonstrated that the oxidation power of these

three oxidizers was increased by at least one order of magnitude by EUV irradiation, leading to rapid removal of the carbonaceous layer. Here we report on the intensity dependence of photon-induced oxidation via NO and O₃ and present strong evidence that the EUV-stimulated reaction with H₂O₂ relies on a surface-mediated mechanism not present in the other two oxidizers. Since the reactions may be driven directly by photons or indirectly by the low-energy secondary electrons [7], we describe the processes as “photon-induced” or “photon-stimulated” and avoid using the term “photo-oxidation” which implies a direct photoreaction.

2. Material and methods

The experiments were performed at the synchrotron ultraviolet facility (SURF III) at the National Institute of Standards and Technology (NIST) in a vacuum chamber with a base pressure 7×10^{-9} Pa. Samples consisting of a Si substrate with a thin (<2 nm) amorphous TiO₂ film were first cleaned with atomic hydrogen to remove adventitious C. The samples were then irradiated by EUV (92 eV) photons in the presence of tetradecane admitted through a leak valve to a partial pressure of 1×10^{-5} Pa. Photon-induced decomposition of adsorbed tetradecane produced a C deposit on the sample with a lateral thickness distribution that matches the spatial distribution of the EUV intensity, which is well approximated by an asymmetric Gaussian distribution with a peak intensity of 3 mW/mm² (2×10^{16} photons s^{−1} cm^{−2}) and full-widths at half maximum of (1.1 × 0.7) mm. The thickness distribution of the C deposits was determined by *ex situ* mapping of the spot area with small-probed-size X-ray photoelectron spectroscopy (XPS). The C thickness was determined by the C 1s peak growth method using the

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ratio of the measured peak area at each location to that of a graphite sample. (This method was found to yield similar results as the widely used over-layer method [8] which measures the attenuation of the Ti 2p substrate peak.) The effective attenuation length of the C 1s electrons in carbon was assumed to be 2.4 nm based on the inelastic mean free path measured in graphite [9]. The maximum thicknesses of the deposited C spots used here were in the range (3 to 4) nm.

Once the C spot was deposited, the EUV beam was blocked and the tetradecane supply was shut off. The photon-stimulated oxidative removal of the deposited C by nitric oxide (NO), hydrogen peroxide (H_2O_2) and ozone (O_3) was then studied with active temperature control of the surface at 20 °C. For the data presented here, all three oxidizers were admitted to produce an ion gauge pressure of 1×10^{-3} Pa. (Due to the lack of reliable gauge sensitivity factors for H_2O_2 and O_3 , all pressures reported here are uncorrected.) O_3 and H_2O_2 were admitted as mixtures of $\text{O}_3 + \text{O}_2$ and $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$ with ratios of $\text{O}_3:\text{O}_2 > 15\%$ and $\text{H}_2\text{O}_2:\text{H}_2\text{O} \approx 50\%$ as determined by a quadrupole residual gas analyzer. The EUV-induced oxidative cleaning rates of equal pressures of pure O_2 and H_2O were previously shown to both be $< 20\%$ of the rates for the mixtures used here, so O_3 and H_2O_2 are the primary drivers of the observed C removal [6].

Photon-stimulated oxidation was initiated by irradiating a previously deposited C spot with the same spatial distribution of EUV intensity used to create the deposit. Both the C growth during photon-induced decomposition of tetradecane and the C removal during photon-stimulated oxidation were monitored in real time using an *in situ* null-field ellipsometric imaging system (NEIS) [10]. The intensity of the NEIS signal was determined to be proportional to the C thickness by *ex situ* XPS measurements. The thickness resulting from this correlation of NEIS intensity with XPS thickness is reported here as “NEIS optical thickness” with units of nanometers. Due to variations in the intensity of the NEIS light source, the uncertainty of the NEIS optical thickness is estimated to be $\leq 25\%$. The lateral distances of NEIS images and profiles are reported in units of camera pixels and are not corrected for the skewed viewing angle or magnification; however, the distance scales may be inferred from the inherent full width at half maximum of the deposited C spots.

The reader is referred to Ref. [6] for additional details of measurement methods and oxidizer generation techniques.

3. Results

Fig. 1a shows the NEIS optical thickness profiles of a previously deposited C spot at different times during EUV irradiation in the presence of 1×10^{-3} Pa of NO. Fig. 1b plots the NEIS-thickness as a function of time at specific locations along the profile indicated by the vertical dashed lines in Fig. 1a. Since the EUV intensity varies across the spot with a quasi-Gaussian distribution, the curves in Fig. 1b represent the time evolution of the C thickness at different EUV intensities. The linearity of the curves in Fig. 1b indicates that at each profile location (i.e., intensity) bulk C is removed at a nearly constant rate, suggesting that the rate does not depend significantly on thickness. The rates are given by the slopes of the lines and decrease roughly in proportion to the decreasing intensity away from the spot center with a maximum rate at the center of 0.09 nm/h.

Data for EUV + O_3 at 1×10^{-3} Pa are presented in the same way in Fig. 2. Just as with NO, the linearity of the curves in Fig. 2a indicates that bulk cleaning rates are independent of thickness, but unlike NO, the rates for O_3 do not show a linear dependence on intensity. Although accurate correlation of intensity with profile position is complicated by the imperfect alignment of the EUV beam with the previously deposited spot and the skewed perspective of the NEIS viewing angle, the relative intensity of the Gaussian distribution must vary by at least a factor of 3 over the locations for which the evolution is plotted in Fig. 2b. The fact that the slopes of the lines vary by only 30 % suggests that for EUV intensities much in excess of 1 mW/mm^2 (1×10^{16} photons $\text{s}^{-1} \text{cm}^{-2}$) the rate for O_3 at 1×10^{-3} Pa is largely independent of EUV intensity and approximately equal to 0.7 nm/h.

A very different behavior is observed for cleaning by EUV + H_2O_2 . The evolution of the spatial profiles shown in Fig. 3 indicates that the H_2O_2 cleaning rate varies dramatically as a function of time and location on the C spot. In fact, it appears that the C removal primarily occurs at the edges of the spot, not uniformly over the entire spot as in the case of O_3 and NO; however, once the C removal begins at a particular location, it appears to proceed with a constant rate independent of thickness that is approximately proportional to the EUV intensity at that location.

As described in Ref. [6], when the carbon spot was exposed to each oxidative agent for equal time in the absence of EUV irradiation, the decrease in C thickness was $< 0.2 \text{ nm}$, indicating that the photon-

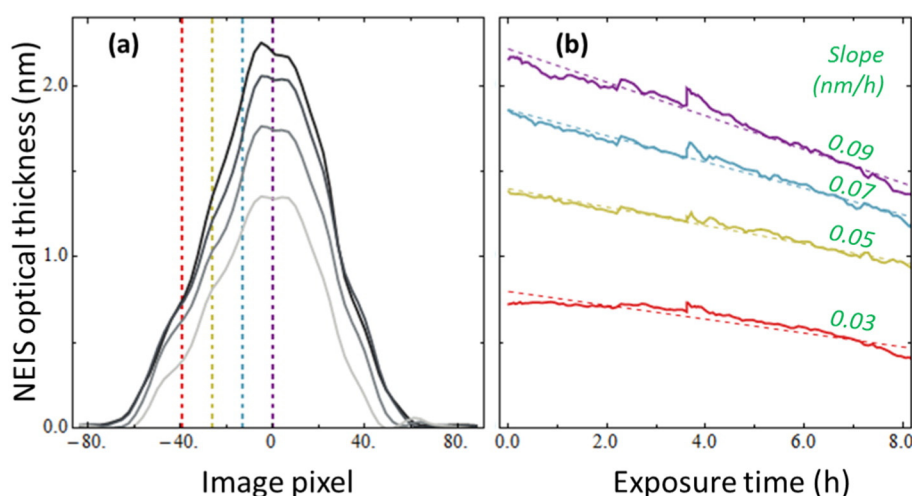


Fig. 1. Time evolution of C thickness on TiO_2 under simultaneous exposure to NO at 1×10^{-3} Pa (uncorrected ionization gauge reading) and 13.5 nm radiation at room temperature. Optical thicknesses determined by *in situ* null-field ellipsometric imaging system (NEIS) were correlated to *ex situ* XPS thickness measurements. (a) Thickness profiles shown as a function of lateral distance through spot center at the start of exposure (black) and at intervals of 2.9 h (gray shades). The full width at half maxima of the original C deposit was approximately 1 mm. (b) Thickness as a function of exposure time for four locations along the lateral profiles indicated by the dashed lines in (a). Due to the Gaussian distribution of EUV intensity, each curve represents the evolution at a different intensity. Imperfect alignment of the EUV beam with the C spot center prevents accurate determination of intensity for each curve, but intensities are in the range (0.3 to 3) mW/mm^2 [$(0.2 \text{ to } 2) \times 10^{16}$ photons $\text{s}^{-1} \text{cm}^{-2}$] and decrease with distance from the center of the spot. The corresponding decrease in the slopes indicates that the C removal rate is approximately proportional to the EUV intensity in this range. [The irregular shape of profiles in (a) and departures from linearity in (b) are attributed to optical interference fringes of the NEIS laser.]

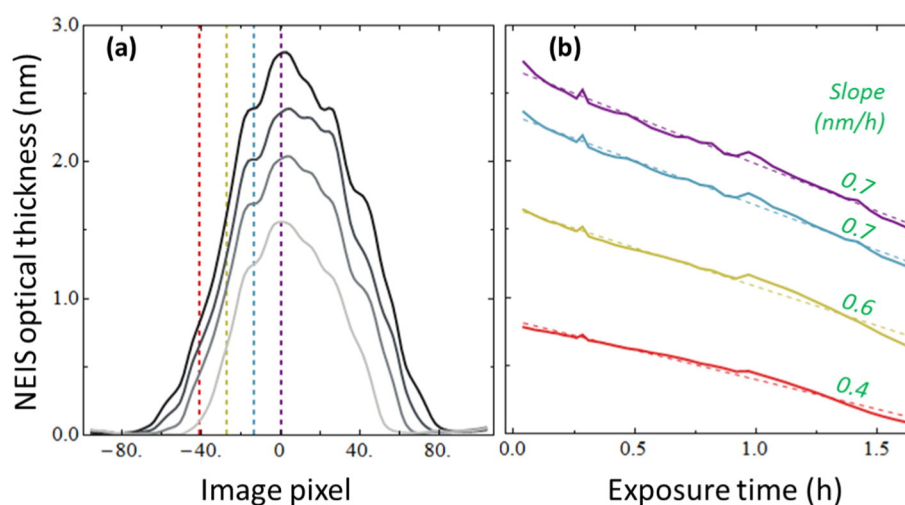


Fig. 2. As in Fig. 1, time evolution of C thickness under simultaneous exposure to O_3 at 1×10^{-3} Pa and 13.5 nm radiation. (a) Thickness profiles shown as a function of lateral distance through spot center for exposure at the start of exposure (black) and at intervals of 33 min (gray shades). (b) Thickness as a function of exposure time for four locations along the lateral profiles indicated by the dashed lines in (a). The very slight decrease in slope with distance from the spot center indicates that the C removal rate saturates at intensities larger than ≈ 1 mW/mm².

stimulated C etching rate is at least an order of magnitude larger than that due to the oxidative precursors alone. Similar null etch rates were obtained for repeated sequential (10 min step) EUV exposures under UHV conditions followed by admission of the oxidizing agent in the absence of EUV. This suggests that the C etching is driven by EUV-induced reactions with the adsorbed oxidative precursors rather than by creation of EUV-induced long-lived excited states in the C layer itself.

4. Discussion

4.1. Kinetics of EUV-induced C removal by NO and O_3

The removal of C by NO and O_3 shown in Figs. 1 and 2 is consistent with the two-step model illustrated in Fig. 4(a,b) in which the oxygen-containing molecule adsorbs on the C surface, then undergoes a photon-stimulated reaction resulting in a radical that reacts with C to produce a volatile species. We assume that the removal rate is proportional to the product of the EUV intensity and the equilibrium coverage of the adsorbed oxide molecules, which is determined by

balancing the adsorption and removal rates. The adsorption rate is proportional to the impingement rate and hence to the partial pressure of the oxidizing precursor molecule. The three most likely processes for removal of an adsorbed molecule are thermal desorption, reaction with an impinging molecule, or photon-stimulated reaction resulting in C removal.

This model has two limiting cases of intensity scaling depending on the size of the photon-stimulated removal rate relative to the rates of thermal desorption and impingement reactions. In the “linear regime” the photoreaction rate is much smaller than either the impingement or desorption rates and the equilibrium coverage of oxidative adsorbates is unaffected by the photon-stimulated process. The resulting C etching rate is therefore simply proportional to the EUV intensity. The cleaning by NO at 1×10^{-3} Pa appears to be in this regime since the rates given by the slopes in Fig. 1b decrease in approximate proportion to the decreasing intensity away from the center of spot. In the “saturated” regime the photon-stimulated reaction rate is much greater than the desorption and impingement rates, and the equilibrium coverage is determined primarily by the balance between the

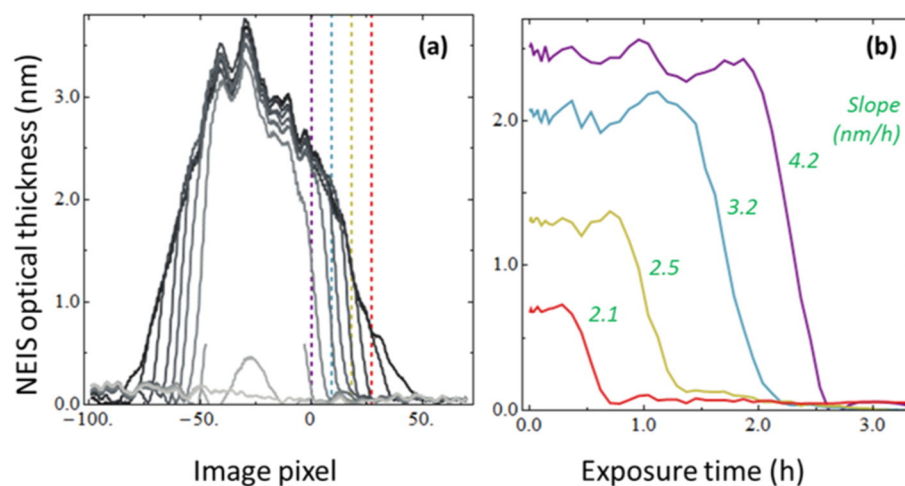


Fig. 3. As in Fig. 1, time evolution of C thickness under simultaneous exposure to H_2O_2 at 1×10^{-3} Pa and 13.5 nm radiation. (a) Thickness profiles shown as a function of lateral distance through spot center at the start of exposure (black) and at intervals of 22 min (gray shades). (b) Thickness as a function of exposure time for four locations along the lateral profiles indicated by the dashed lines in (a). C-etching occurs primarily at the edges of the C spot and proceeds towards the center where the EUV intensity is highest. Once cleaning begins at each location, the slopes suggest that the rate is approximately proportional to the EUV intensity. [The truncated profile in (a) was due to temporary saturation of the detector in the central region of the profile away from the locations used to generate the curves in (b).]

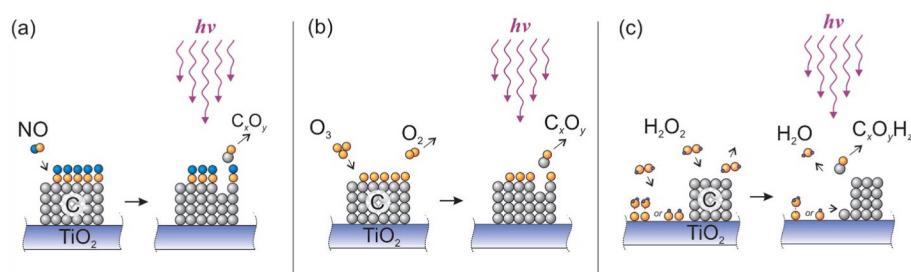


Fig. 4. Schematic illustrations of possible mechanisms for C removal by 13.5 nm irradiation in the presence of oxidizing precursor gases. (a) Intact adsorption of NO or (b) dissociative adsorption of O₃ on the C surface followed by a photon-induced reaction yielding volatile C-containing products. (c) Preferential adsorption (intact or dissociative) and photon-stimulated reaction of H₂O₂ on the TiO₂ substrate rather than on the C surface resulting in C removal at the boundary of C the deposit.

rates of impingement and photon-stimulated reactions. In this case the equilibrium coverage will depend inversely on EUV intensity resulting in a C etching rate that is largely independent of intensity. This is because every adsorbed oxide molecule will volatilize deposited C via a photon-stimulated reaction before it can desorb by thermal or impingement reactions which do not remove C; therefore, in the “saturated” regime the etching rate should simply be proportional to the pressure (impingement rate) and independent of EUV intensity. The sub-linear decrease in the slopes of Fig. 2b suggests that cleaning by O₃ at 1×10^{-3} Pa is nearly saturated at the highest intensities in the EUV beam.

The different scaling for O₃ and NO could be due to a larger photon-stimulated-oxidation cross section for O₃. This is consistent with the very limited literature on the photochemistry of nitric oxide and ozone in the EUV. Gas phase photoabsorption cross sections at 13.5 nm have been reported to be of order 1×10^{-17} cm² for O₃ [11] and below 3×10^{-19} cm² for NO [12]. Similarly, if the oxidative reactions are driven by secondary electrons rather than photons, studies of gas-phase dissociative electron attachment at energies characteristic of secondary electrons (<10 eV) report cross sections 6 times larger for O₃ than for NO [13]. Even though the cross sections for surface reactions are likely significantly smaller than their gas phase analogues due to de-excitation processes, these data are qualitatively consistent with the interpretation that the different behaviors observed in Figs. 1 and 2 are due to a larger cross section for EUV-induced cleaning by O₃ than NO.

The different behavior observed for O₃ and NO would also be expected if the latter had a larger thermal desorption rate (smaller binding energy) than the former. Based on experimental studies of ozone-reacted carbon-nanotubes (CNTs) [14], it is likely that O₃ adsorbs dissociatively on the carbon layer in our experiments, resulting in tightly bound surface functional groups such as C=O, and C–O and a volatile O₂ molecule. In contrast, NO is reported in multiple studies (e.g. Ref. [15]) to adsorb intact on carbonaceous and graphite-like surfaces with a smaller binding energy than the O functional groups from O₃. Here we have assumed that for our C thicknesses (>0.5 nm), the adsorption/desorption processes occur on a C surface rather than on the underlying substrate; however, the substrate may still play a role in the reaction dynamics by influencing the effective secondary electron yield experienced by molecules on the surface.

Although the data presented here, cannot conclusively distinguish between photon and electron mediated processes, the thickness-independent rates indicated by the linearity of Figs. 1b and 2b are more consistent with the former than the latter. The cross section for the electron-driven process will be proportional to the effective quantum yield defined as the number of electrons emitted from the surface per incident photon. Given that the attenuation length of low-energy electrons in C is of order (1 to 2) nm, as the thickness decreases from (≈ 2.5 to ≈ 1.5) nm in Fig. 2b, the effective yield would likely shift from a value closer to that for bulk C towards that the value for bare TiO₂. Since previous measurements have shown that the yield for TiO₂ is nearly 3 times larger than that for C at 13.5 nm [16], one might

reasonably expect a larger departure from linearity if the C-removal by NO were driven by secondary electrons. The same logic applies to the removal by O₃ in Fig. 1; however, it is less convincing due to the smaller change in thickness.

4.2. Kinetics of EUV-induced C removal by H₂O₂ on TiO₂

The simple two-step model of adsorption on the C surface followed by photon-stimulated removal of oxidized C does not describe the kinetics observed for H₂O₂. The data in Fig. 3 could indicate that the reactivity of the peroxide is suppressed by EUV photons since the C etch rate is initially essentially zero at the intense center of the EUV beam; however, this contradicts the previous observation that no (or a very slow) reaction occurs between the C layer and H₂O₂ in the absence of EUV light [6]. Furthermore, according to the increasing slopes of Fig. 3b, once the C removal does begin at the center of the spot, the rate is higher than in the lower-intensity wings of the beam.

Another process consistent with the observed behavior would be the embedment of H₂O₂ fragments (atomic oxygen or hydroxyl radicals) into the carbon matrix which would increase the apparent thickness reported by NEIS. If the rate of increase of the NEIS optical thickness from such incorporation was coincidentally similar to the rate of photon-induced oxidative removal of C, the detected NEIS signal would reveal no C layer thickness change until the layer was fully saturated with radicals and no further embedment was possible. Although unlikely, we tested this hypothesis by analyzing the C spots after exposure to EUV + H₂O₂ using XPS with lateral resolution smaller than the deposited spot and with energy resolution sufficient to detect chemical shifts caused by C–O bonds. The measured spectra in the C 1 s and O 1 s regions were not significantly different before and after exposure to EUV + H₂O₂; hence, we concluded that oxidation from H₂O₂ affects only the top-most C layer and does not diffuse into the bulk.

The results appear most consistent with an active involvement of the TiO₂ surface in the H₂O₂ photon-induced removal of C. This might be explained by preferential adsorption of hydrogen peroxide on TiO₂ and its subsequent reaction with C at the edges of the spot (Fig. 4c). In recent first-principles studies of TiO₂ reactivity [17,18], the adsorption energies of gas phase hydrogen peroxide were calculated, and it was found that H₂O₂ preferentially adsorbs on Ti_{5c} sites [18]. It was further predicted that on rutile (110), the peroxide adsorbs dissociatively with energy 17.3 kcal/mol (0.75 eV) while on anatase (101) the adsorption is molecular with lower energy 16.5 kcal/mol (0.72 eV) [17]. The adsorption energy of H₂O₂ on a pristine graphene sheet [19] was calculated to be just 0.05 eV, but this increases to 0.53 eV for a graphene sheet functionalized with carboxyl groups. Although neither of these carbon forms is a direct analog to the EUV-induced C deposits used here, these calculations are consistent with a much higher adsorption energy for H₂O₂ on TiO₂ than on the C deposit. As a result, the equilibrium coverage of H₂O₂ or its dissociation product OH is likely much higher on the TiO₂ surface than on the C layer, which would lead to a significantly higher rate of photon-induced C etching around the perimeter than on the surface of the C spot.

The uniqueness of the complex interaction between hydrogen peroxide and TiO₂ under photon exposure has been observed for both UV and visible light. Pulido Melián et al. [20] studied the decomposition of 2,4-dichlorophenol in the presence of TiO₂ suspensions illuminated by a broadband UV source with a peak intensity at 365 nm. Of the three oxidants tested – hydrogen peroxide, ozone and sodium peroxodisulphate – only H₂O₂ resulted in enhancement of the photocatalytic process. This enhancement was attributed to the direct photolysis of H₂O₂ ($\text{H}_2\text{O}_2 + h\nu \rightarrow 2\cdot\text{OH}$) resulting in formation of OH radicals reacting with organics or carbonaceous layers. On the TiO₂ surface, formation of OH radicals can also occur under UV irradiation via dissociation of adsorbed H₂O₂ by a hot electron from the conduction band of the semiconductor into peroxide yielding both an OH anion and a radical [21]. With the preferential adsorption of H₂O₂ on TiO₂ versus C, all of these mechanisms are consistent with the localization of the C etching in our H₂O₂ experiments due to efficient photon-induced production of hydroxyl radicals on the catalytically active TiO₂ surface.

4.3. Comparison of estimated maximum and spatially resolved etch rates

The previously reported estimates of the maximum etch rates [6] were defined as the rate of decrease of the peak thickness at the spot center which was determined by correlating the total NEIS signal integrated over the entire C spot with the thickness in the center of the spot as measured by XPS. As long as the etch rate at a particular location is constant in time and proportional to the beam intensity, this measurement procedure yields the maximum rate at the center of the beam even if it is not perfectly centered on the C spot. The spatially-resolved analysis presented here can be used to assess the validity of these previously reported maximal rates determined by the total-NEIS-signal method.

Figs. 1 and 2 indicate that the bulk etch rates for NO and O₃ are constant in time and that the former is proportional to intensity while the latter saturates at the highest intensities. The non-linearity of the O₃ rate will artificially reduce the maximal rate predicted by the total-NEIS-signal method; however, the effect will be small since this non-linearity only occurs over a small fraction of the total spot footprint. Hence the previously reported maximum etch rates of 0.25 nm/h for NO and 1.5 nm/h for O₃ at 3 mW/mm² (the intensity at the center of our beam) should be reasonably accurate. The fact that the spatially-resolved rates at the spot center for NO and O₃ are, respectively, 2.8 and 2.1 times smaller than their corresponding estimated maxima suggests that the EUV beam was off center by a substantial fraction of the beam radius (half-width at half maxima) in each direction. This corresponds to an alignment error of approximately 0.3 mm, which is reasonable given the thermal and mechanical stability of the beamline over the multi-day period between spot deposition and cleaning. Hence the actual intensities at the location of each profile in Figs. 1–3 were likely at the lower end of the expected range spanning (0.3 to 3) mW/mm².

One would expect the total-NEIS-signal method to dramatically underestimate the maximum etch rates for EUV + H₂O₂ due to the strong non-linearity demonstrated by the spatially resolved analysis in Fig. 3. Indeed, the previously reported estimate of 2.1 nm/h is a factor of two lower than the spatially resolved etch rate of 4.2 nm/h at the high-intensities center of the EUV beam. This is because the total NEIS signal decreased quite slowly during the first two thirds of the cleaning cycle as the etching began in the low-intensity wings of the EUV beam. The larger rates only contributed during the last third of the exposure cycle as the reactive perimeter shrank into the higher intensity central regions of the EUV beam.

5. Conclusions

The EUV-stimulated oxidative etching of a carbonaceous layer was studied for three strong oxidizers: O₃, NO and H₂O₂. The intensity dependence of C removal rates for each oxidizer are reported for

13.5 nm radiation in the range (0.3 to 3) mW/mm² [(0.2 to 2) $\times 10^{16}$ photons s^{−1} cm^{−2}]. The original C deposits were formed by photon-induced decomposition during exposure of the clean TiO₂ surface to 13.5 nm radiation in the presence of admitted n-tetradecane. EUV-induced oxidative etching of the deposited C spot was spatially resolved and monitored in real time using a single-wavelength null-field imaging ellipsometer correlated with *ex situ* thickness measurements by XPS. The partial pressure for each oxidizer was 1×10^{-3} Pa as determined by an uncorrected ionization gauge.

- The C removal rate of NO was found to scale approximately linearly with EUV intensity over the range (0.3 to 3) mW/mm². The rates for O₃ were nearly independent of intensity above ≈ 1 mW/mm² and scaled sub-linearly down to the lowest resolvable intensity used here (0.1 mW/mm²). The maximum C etching rates measured for NO and O₃ were 0.09 nm/h and 0.7 nm/h, respectively.
- The different intensity scaling and relative magnitudes of the EUV-induced etching rates for NO and O₃ were consistent with a two-step process of adsorption followed by a photon-induced reaction yielding a volatile carbon-containing product. NO is known to adsorb intact onto C surfaces with a binding energy much lower than the C–O groups formed by the dissociative adsorption of O₃. Furthermore the published cross sections for gas-phase reactions with both EUV photons and low-energy electrons are larger for O₃ than for NO. Both of these factors are consistent with the following observed behavior:
 - Linear intensity scaling of NO resulting from a thermal desorption rate that is larger than its photon-stimulated reaction rate.
 - Larger C etch rates and saturation behavior for O₃ due to the long-lived C–O groups with a thermal desorption rate much lower than the photon-induced reaction rate at the highest intensities used here.
- EUV-stimulated oxidation of the C-layer by H₂O₂ appeared to occur through a different mechanism. The removal of carbon started at the edges of the C spot, where the layer interfaces with the TiO₂ film, and proceeded towards the spot center. Such localization of the reaction at the perimeter is evidence of a catalytic role of the thin (<2 nm) amorphous TiO₂ substrate in the production of hydroxyl radicals, which then reacted with the C around the ever-shrinking perimeter. The rate of this perimeter reaction appears to scale roughly linearly with EUV intensity with a maximum measured value of 4.2 nm/h once the reaction reached the spot center.
- The total C removal rate of all three oxidizers in the absence of EUV was at least one order of magnitude smaller than the rates measured under EUV irradiation. For H₂O₂, however, the presence of EUV caused no detectable increase in the rate for bulk C away from the perimeter of the deposit. Hence, the EUV-induced C etch rate of H₂O₂ could be much smaller than the value reported here on a substrate that lacked the catalytic properties of TiO₂ or for bulk C.

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