Full Length Article

Aromatic structure degradation of single layer graphene on an amorphous silicon substrate in the presence of water, hydrogen and Extreme Ultraviolet light

B.K. Mund^{a,*}, J.M. Sturm^a, C.J. Lee^{a,b}, F. Bijkerk^a^a Industrial Focus Group XUV Optics, MESA+ Institute of Nanotechnology, University of Twente, Enschede, The Netherlands^b Quantum Transport in Matter Group, MESA+ Institute of Nanotechnology, University of Twente, Enschede, The Netherlands

ARTICLE INFO

Article history:

Received 28 July 2017

Received in revised form 8 September 2017

Accepted 12 September 2017

Available online 14 September 2017

Keywords:

Single layer graphene

Reflection absorption infrared spectroscopy

Water

Temperature programmed desorption

Extreme Ultraviolet light

Hydrogen

ABSTRACT

In this paper we study the reaction of water and graphene under Extreme Ultraviolet (EUV) irradiation and in the presence of hydrogen. In this work, single layer graphene (SLG) on amorphous Si as an underlying substrate was dosed with water (0.75 mL) and exposed to EUV ($\lambda = 13.5$ nm, 92 eV) with partial pressures of H_2 in the background. The results show that the aromatic structure of graphene, when exposed to EUV and H_2 , breaks down into aryl ketones and enols of 1,3 di-ketone. Infrared (IR) spectroscopy shows that SLG oxidizes, with increasing H_2 pressure leading to the grain boundary edges of graphene forming ketones and carboxylic acids. In situ and post exposure analyses also reveal that EUV exposure reduces the sp^2 content of the graphene layer, with the sp^3 content increasing, resulting in a more defective graphene layer.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Graphene, a two dimensional hexagonally packed network of covalently bound carbon atoms, has a number of unique physical, thermal and chemical properties [1–8]. It is known to be impermeable to gases [9], and has been theoretically shown to act as a diffusion barrier even against molecular hydrogen [10]. Graphene can be grown on an industrial scale via chemical vapor deposition and transferred onto both flat [11] and arbitrary profile substrates [12], broadening its scope for potential applications.

In the optical regime, single layer graphene combines the highly desirable properties of being simultaneously conductive and transparent in the visible [13], and EUV [14] wavelengths. These properties make it a promising candidate for transparent conducting electrodes, required for touch screens, and, potentially EUV adaptive optics. Furthermore, the high transparency in the EUV range is attractive because most optics require a protective top layer to protect them from the highly reactive environment, induced by radiation [15].

Perfect single layer graphene (SLG) is known for its low chemical reactivity due to the densely packed nature of sp^2 hybridized carbon atoms [16]. Unfortunately, during chemical vapor deposition and graphene transfer, defects are generated [17], which can behave as initiation points for graphene to react with its environment [18]. Nevertheless, graphene has been proposed as a useful material in chemically harsh environments, such as Deep Ultraviolet, X-ray systems and Extreme Ultraviolet (EUV) Lithography systems. EUV lithography (EUVL) systems represent a particular challenge: EUVL systems operate at a wavelength of 13.5 nm, in vacuum, and the main optical components are expected to last for the lifetime of the system (>10 years). The optics and background gases, however, are exposed to ionizing radiation, creating a rich environment for surface chemistry that may modify the surface of the optics [19–21]. To reduce the influence of residual gases – mainly water and hydrocarbons – the pressure is increased to a few Pa, by adding hydrogen [22]. The balance between hydrogen as a reducing agent and water as an oxidizing agent allows a dynamic equilibrium between competing processes to be managed [23]. However, the conditions under which such a balance can be achieved varies from material to material. Before graphene can be used in such a system, it is critical to understand its physical and chemical stability, and to determine the reaction pathways that are most favorable under various partial pressures of H_2 and H_2O .

* Corresponding author.

E-mail address: b.k.mund@utwente.nl (B.K. Mund).

Since graphene is a one atom thick layer of carbon atoms, chemical reactivity is highly dependent on the underlying substrate. Current techniques, such as in-situ Raman spectroscopy, can be used to study the generation of defects in graphene. Due to the zero-band gap nature of graphene, the Raman scattering cross section is large, making it the preferred manner to characterize graphene. However, for most other materials, the Raman scattering cross section is much smaller, making it difficult to identify detailed modifications to the structure and molecular composition of the graphene. Furthermore, even though the normal modes of water are both Raman and IR active, Raman spectroscopy is less sensitive to changes in hydrogen bonded water networks [24]. Finally, Raman spectroscopy is susceptible to fluorescence from (in our case) the amorphous Si substrate, which is stronger than the Raman signal by a factor of 10^6 – 10^8 . Therefore, infrared spectroscopy is the preferable method to study surface chemistry of water and its interaction with graphene.

Previous research has shown that defects are generated in single layer graphene during EUV exposure [25,26]. Here, we present an investigation into the reactions of graphene on an amorphous Si layer in an EUV environment. For these experiments, the surface is characterized in-situ using Reflection Absorption Infrared Spectroscopy (RAIRS) during EUV exposure, and temperature programmed desorption (TPD) spectroscopy before and after EUV exposure. RAIRS is used to observe changes in molecular orientation of water and chemical structure of graphene and revealing the pathway by which graphene oxidizes in the presence of water and hydrogen. On the other hand, TPD provides a quantitative measure of the number of molecules that desorb from the surface at a given temperature, providing an accurate measure of the different adsorbed molecules and their binding energies.

X-ray photoelectron spectroscopy (XPS) measurements were carried out ex-situ, before and after EUV exposure, to quantitatively estimate the elemental composition and the chemical state of the surface. This was used to confirm the end result of graphene oxidation.

2. Experimental

Single layer graphene was grown by chemical vapor deposition on a polycrystalline copper foil (purity 99.9%, Alfa Aesar). The copper foil was introduced into a furnace at 1100 °C with a gas flow of 100 sccm of CH₄, 500 sccm of Ar and 6 sccm of H₂ leading to single layer graphene being grown on both sides of the Cu foil. The single layer graphene [10 mm × 10 mm] was then transferred using the wet transfer method [27] on to an amorphous Si surface. The graphene layer was transferred using a PMMA support layer, which was removed by annealing at 350 °C with Ar and H₂ for ~3 h.

The substrate onto which the graphene was transferred was based on a Si wafer, which had a Mo layer (9 nm thick) deposited on it, followed by 22 nm of amorphous silicon. Both layers were deposited by sputter deposition, and the thicknesses were known via deposition calibration based on X-ray reflectivity measurements. The amorphous silicon was not protected from atmosphere after removal from the deposition chamber, thus, the top ~1–2 nm is oxidized. The molybdenum layer is necessary to reflect infrared radiation, allowing reflection absorption infrared spectroscopy (RAIRS) to be performed in situ.

All surface chemistry experiments were performed in the same experimental setup [28,29] sequentially without breaking vacuum. The chamber's base pressure is maintained at 5×10^{-9} mbar. During experiments, hydrogen is introduced to the chamber, increasing the background pressure up to 1×10^{-5} mbar. The chamber is equipped with RAIRS, TPD spectroscopy, surface cleaning facilities, surface dosing, and attached to an EUV source.

Table 1

Experimental conditions of the surface and chamber with initial water dose, partial pressure of H₂ and the final water coverage after exposure.

Experiment	Initial Water Dose (mL)	Partial pressure (H ₂)	Final Water coverage (mL)
No EUV	0.75 mL	2×10^{-9} mbar	0.75
EUV	0.75 mL	3×10^{-9} mbar	0.75
EUV	2.25 mL	1×10^{-7} mbar	3.00
EUV + H ₂	0.75 mL	1×10^{-7} mbar	0.98
EUV + H ₂	0.75 mL	1×10^{-6} mbar	1.42
EUV + H ₂	0.75 mL	1×10^{-5} mbar	3.56

RAIRS spectra are measured at grazing incidence using an FTIR spectrometer (Bruker Vertex 70V), equipped with a liquid N₂ cooled detector. Each spectrum is summed over 256 scans with a resolution of 4 cm⁻¹, with background scans being recorded at the lowest possible stable sample temperature of 80 K. To obtain TPD spectra, the sample temperature is ramped from 80 K to 450 K at a rate of 1 K/sec. The sample is placed normal to the entrance of a cone that is attached to a differentially pumped quadrupole mass spectrometer (QMS – Hiden Analytical). The cone has an entrance aperture of 4 mm, located ~2 mm away from the sample. The temperature is measured using a thermocouple attached to the sample with a Mo clamp. To prevent damage to graphene, the sample temperature was limited to 450 K, which is sufficient to remove water, CO, and hydrogen. Based on experiments on a ruthenium (0001) surface using the same chamber, we show that the background deposition rate of all chamber contaminants is very low (<0.005 monolayers (ML) per hour) [19].

Deionized water, cleaned using the freeze-pump-thaw process, is dosed on the sample through a retractable quartz tube connected to a pinhole. Surface coverage is calibrated against TPD spectra obtained from a clean Ru surface [28].

The chamber is attached to a Xe plasma discharge EUV source (Philips EUV Alpha Source 2) with a repetition rate of 500 Hz. The source is filtered by reflection from a Mo/Si multilayer mirror (55% reflectivity at 13.5 nm) and transmission through a Si/Mo/Zr membrane (35% transmission at 13.5 nm) [30]. This results in a peak reflectivity of 19% at 13.5 nm with a FWHM of 0.2 nm and a broad reflectivity peak of 9% at 21.5 nm with a FWHM of 3.1 nm [14,21,31]. The EUV beam has an average intensity of 35–55 mW/cm², and a profile that is approximately Gaussian with a full width half maximum (FWHM) of 3 mm. Over the course of the experiments, the EUV pulse fluence varied from 90 to 110 μJ/cm².

The general experimental procedure consisted of: the graphene was first cooled to 80 K, and a reference RAIRS spectrum was obtained. The sample surface was dosed with water, and the chamber was filled to a chosen background pressure of hydrogen. The sample was then exposed to EUV and RAIRS spectra were obtained before EUV exposure, and every 10 min during the exposure. After EUV exposure, a TPD spectrum was obtained. The range of exposure conditions are summarized in Table 1.

After TPD/RAIRS experiments had been completed, ex situ X-ray photoelectron spectra (XPS) were measured using monochromatic Al-Kα radiation, employing a Thermo Fisher Theta probe instrument with a beam spot size of 1 mm in diameter. Parallel angle resolved XPS spectra were measured in an angle range from 26° to 80°, the displayed spectra correspond to a take-off angle of 34°.

3. Results and discussion

The graphene on Si sample was exposed to EUV with additional H₂ partial pressures of 0 mbar, at 10^{-7} mbar, 10^{-6} mbar, 10^{-5} mbar (seen in Table 1). All the exposures were 1 h long. The cumulative EUV dose for this experiment was calculated to be 0.32–0.39 J/cm², which is not enough for significant heating (we do not observe

Fig. 1. RAIRS spectra of the C=O stretch peak of CO₂, enols and aryl ketone as seen on the surface of the single layer graphene. Water dose is 0.75 mL unless otherwise specified. A new background spectrum is taken before each exposure, directly before dosing H₂O to the surface.

an increase in temperature during EUV irradiation), eliminating thermodynamically driven processes from consideration. Thus, photon and photoelectron-driven processes are responsible for the observed changes in surface structure and composition.

For these experiments, RAIRS OH peaks, such as the libration modes (750–950 cm⁻¹) and bending modes (1500–1700 cm⁻¹) are too weak for the water coverage used. OH stretching modes from water (3000–3700 cm⁻¹) were visible, but did not provide any significant information about the structure and interaction of water on the surface and are therefore not shown [32].

3.1. Formation of ketones and adsorbed CO₂ on the surface of single layer graphene

As detailed in Gerakines et al. [33], the formation of CO₂ is evidenced by vibrational modes in the 2200–2400 cm⁻¹ region. In Fig. 1, an asymmetric (ν_{as}) C=O stretch peak is present at 2343 cm⁻¹ and 2373 cm⁻¹ (peak I₁, I₂), indicating the presence of CO₂. When only water is present on the surface, in the absence of EUV, an inverse peak is seen for I₂, indicating removal of CO₂ from the surface. Subsequently, at higher partial pressures (10⁻⁶, 10⁻⁵ mbar) of H₂ in the presence of EUV, the peak reappears, indicating CO₂ as a possible end product of carbon oxidation.

With an increase in H₂ concentration, a broad peak starts to form at 2454 cm⁻¹ (peak J₁). This corresponds to literature reports for a C=O stretch for keto-enol formation, specifically the C=O stretches for aryl ketones and the enol forms of a 1,3-diketone (as shown in Fig. 2) [34]. Enol of 1,3-diketones are more favorable due to their increased stability when forming a six membered ring – hydro-

gen bonded in this case. As H₂ pressure increases, this C=O stretch forms a broad peak at 2477 cm⁻¹ (peak J₂), which confirms the formation of ketones on the surface [32]. In addition, a blue-shift is seen for peak J as the hydrogen pressure is increased, indicating more keto-enol vibrations detected on the surface [34]. These ketones are formed due to graphene oxidizing and breaking down into aryl and keto-enol structures, due to EUV induced H₂ and H₂O dissociation on the surface. H radicals, formed by EUV-induced dissociation of H₂, create defect sites in the graphene layer, which are subsequently oxidized by OH groups or O formed by EUV-induced H₂O dissociation. As indicated in Table 1, exposure to a higher pressure of H₂ results in additional water being deposited on the sample, due to contamination of the gas line. In order to check whether the formation of keto-enol species is indeed related to EUV induced reactions in the presence of H₂ and H₂O and not to EUV exposure with larger H₂O coverages, a control experiment with initially higher dosed water coverage (2.25 mL) and low H₂ pressure (1 × 10⁻⁷ mbar) was carried out. Under these conditions (Fig. 1, 3rd line from top) no keto-enol formation is observed, proving that presence of H₂ pressures > 1 × 10⁻⁶ mbar and adsorbed water are both needed for EUV-induced keto-enol formation. Assuming that, for the low exposures in this study, the majority of ketone formation occurs along grain boundaries (see Fig. 2), the most likely forms are enols of 1,3-diketone and hydroxyl aryl ketones.

Keto-enol formation is only seen at a high hydrogen pressure (10⁻⁵–10⁻⁶ mbar), due to higher defect creation by EUV-induced radicals, which is compared in Fig. 3. At a H₂ pressure of 10⁻⁶ mbar and 10⁻⁵ mbar, the height of peak J increases at a rate of 0.0015%/min and 0.0132%/min respectively. This increase in peak

Fig. 2. Graphene breaking down into hydroxyl aryl groups and subsequently forming ketones. Aryl ketones and keto-enol tautomerism have the same stretch vibration absorbed at 2400–2500 cm⁻¹ [34].

Fig. 3. Growth of keto-enol C=O stretch (peak J) as compared to EUV exposure time at different H₂ pressures. The vertical axis indicates the negative peak intensity in the RAIRS transmission plot, so a higher value indicates larger surface coverage.

height is 8.8 times the rate at 10⁻⁶ mbar, indicating that graphene begins oxidizing rapidly with a higher partial pressure of H₂.

Two locations are most likely for oxidation, and the formation of enols and ketones: point defects and grain boundaries. Point defects can be effectively determined using Raman spectroscopy. Results from Cancado et al. [35] state that I_D/I_G ratios of graphene can be used to specify the inter defect distance. A graphene reference layer produced with the same growth process, but transferred onto a Ni surface instead of a Si surface has an I_D/I_G of 0.75, which translates to an inter-defect distance of 14 nm. Since the typical grain size of our graphene is ~100 nm, corresponding to a typical grain area of ~8000 nm², this inter-defect distance would correspond to ~100 point defects per grain, one order lower than the oxidation sites available through grain boundaries [36]. Therefore, it is likely that the RAIRS spectral changes are dominated by ketone formation along the grain boundaries which leads to grain boundaries

unzipping at higher H₂ pressures, to form more sites for oxidation [36].

3.2. Saturation of enol formation on the surface

As discussed earlier, enols of 1–3 di-ketone are most likely formed due to the preferential oxidation of graphene along grain boundaries. Further sequential experiments were conducted to test if oxidation saturates: e.g., that the grain boundaries become fully oxidized and oxidation then slows. This can be seen in Fig. 4 where the growth of the C=O stretch from enols and aryl ketone (peak J) for different exposures is shown. As noted earlier, peak J first appears when the H₂O covered surface is exposed to EUV and molecular H₂ at 10⁻⁶ mbar (trace I), indicating that graphene is starting to oxidize. As mentioned previously, this peak increases with increasing mol. H₂ pressure (trace II). Following these exposures, the surface

Fig. 4. Change in keto-enol formation (peak J) after subsequent exposures of EUV and H₂ to the graphene layer at 10⁻⁶ and 10⁻⁵ mbar. A new background spectrum is taken after each exposure.

Fig. 5. Change in keto-enol formation (peak J) over time after subsequent exposures of EUV and H₂ to the graphene layer at 10^{−6} and 10^{−5} mbar. A new background spectrum is taken after each exposure.

Table 2

Rate of growth of keto-enol formation (peak J) as seen in Fig. 5.

Traces	Transmission % minute
I: EUV + H ₂ , 10 ^{−6} mbar	0.0015
II: EUV + H ₂ , 10 ^{−5} mbar	0.0132
III: EUV + H ₂ , 10 ^{−6} mbar	0.0008
IV: EUV + H ₂ , 10 ^{−5} mbar	0.0023

was again exposed to EUV and H₂ at 10^{−6} mbar (trace III). As seen in curve III in Fig. 4, there is no indication of further (out of plane) enol or aryl ketone formation on the surface for this partial pressure. This is because oxidation of the graphene layer at H₂ pressure of 10^{−6} mbar has saturated, and for further oxidation to happen, the H₂ pressure needs to be increased to create additional defect sites where water can react. Furthermore, at a subsequent exposure at an H₂ partial pressure of 10^{−5} mbar (trace IV) enol and aryl ketone growth is much slower than in the previous experiment at the same pressure (trace II), indicating that the oxidation process is saturating.

This growth for peak J can be quantified in Fig. 5 where the change in keto-enol formation is measured over the course of one hour at different EUV exposures and H₂ pressures. As seen in Table 2, the rate of growth of peak J is shown to reduce with increasing molecular H₂ pressure in the presence of EUV, indicating that keto-enol formation saturates as exposure time to EUV and H₂ increases.

3.3. Temperature programmed desorption of water from graphene surface

In Fig. 6, the temperature programmed desorption of water from the graphene/Si surface is shown. When the surface is exposed to EUV, the coverage of water does not change significantly. An increase in water coverage is observed for higher hydrogen pressures; 0.23 mL for 10^{−7} mbar of H₂, 0.67 mL for 10^{−6} mbar of H₂ and 2.81 mL for 10^{−5} mbar of H₂. The amount of water desorbed for increasing H₂ partial pressures is high due to water contamination from the H₂ line.

Also, two distinct peaks can be seen for the TPD spectra in Fig. 6, indicating that water has two binding modes on the substrate. When water is first dosed on the cold surface, it forms an H-bonded 2D ice network on the graphene layer [37]. As more water is

deposited on top of the surface, a 3D ice network forms. The desorption peak seen at ~139 K in Fig. 6 is due to H₂O molecules desorbing from 3D ice networks. Following this, the graphene bound H₂O molecules in 2D ice networks are the next to desorb at ~160 K.

For very low coverage of water, when the surface is left for 120 min in the chamber with no water dosed on the surface, Fig. 7(a) shows that water coverage on the surface increases with time due to residual gases. This is also clearly noted for low coverages in Fig. 7(b) as well, when a small amount of water (0.01 mL) is dosed on the surface. Compared to the case with no initial coverage, the amount of water in Fig. 7(b) increases by a factor of 3.4 and 7.3 for 60 and 120 min, relative to 30 min exposure to residual gas, respectively. In comparison, in Fig. 7(a), the water on the surface increases by a factor of 0.1 and 0.6 for the same periods of 60 and 120 min, indicating that water is more likely to attach to water molecules than it is to the graphene layer. Additionally, the two peaks seen for low coverages in Fig. 7(a) illustrate that a 2D water network is the first to form, with water molecules attaching to the defects and grain boundaries of graphene, and then water attaching to the defect bound water. Similarly in Fig. 7(b), a common leading edge is seen, such that the desorption peak shifts to a higher temperature for increasing coverage, indicating peaks the two peaks in Fig. 7(a) converging to form a singular peak. Consequently, this becomes the first desorption peak in Fig. 6. This 0th order desorption behavior is characteristic for desorption of water adsorbed to other water molecules as shown in Clay et al. [38]. Since graphene is known to be hydrophobic in nature [39], water clusters are more likely to form, such that 0th order desorption of water can be observed, even for sub monolayer coverages.

3.4. X-ray photoelectron spectroscopy

Fig. 8 shows the XPS spectra and fit for the C 1s peak of graphene before and after it is exposed to multiple doses of H₂O, EUV and H₂ seen in Figs. 1–7. Table 3 lists the atomic concentration of sp², sp³ and C–O bonds along with the full width half maximum of the fitted sp² peak for the unexposed graphene sample and the sample exposed to EUV. Notably, the sp² bond concentration decreases from 13 ± 1% to 6 ± 4% after exposure, while, in contrast, the sp³ concentration increases from 5 ± 1% to 12 ± 4%. The increase in sp³ bonding is a consequence of combination of oxidation and hydrogenation, as expected. It should be noted that the separation of the sp² and sp³ peaks is not sufficient to make a unique peak fit for the

Fig. 6. TPD spectra of H_2O after deposition of water and exposure to EUV and H_2 . The numbers refer to additional water seen on the surface as compared to the surface without EUV and H_2 . The spectra have been smoothed over 4 values.

Fig. 7. Control experiments for residual gas in chamber with (a) low coverage and (b) coverage (0.01 mL) with water on the surface.

Table 3
Atomic concentration of C 1s spectral components, carbon thickness, native SiO_2 concentration of the substrate of graphene samples before and after exposure to multiple doses of EUV and H_2 . The C thickness is measured using angle resolved XPS.

Sample	C sp^2 (atomic %)	C sp^3 (atomic %)	C—O (atomic %)	Si—O (atomic %)	O 1s (atomic %)	sp^2 FWHM (eV)	Carbon thickness (nm)
Unexposed graphene on Si	13 ± 1	5 ± 1	1.0 ± 0.3	16 ± 1	26 ± 1	0.90 ± 0.1	0.34
Exposed graphene on Si	6 ± 4	12 ± 4	7 ± 2	15 ± 1	26 ± 1	0.9 ± 0.2	0.40

exposed sample, which has been reflected in the error margins of the quantification.

The concentration of C—O groups increases from 1% to 7%, confirming that graphene oxidizes in the presence of adsorbed water, and exposure to EUV and H_2 . It should be noted that the high sp^2 content of pristine graphene results in a tail of the sp^2 peak extending up to the binding energy range where C—O bonds are detected for exposed graphene [40]. Therefore, the quantified amount of C—O species may be overestimated for the unexposed sample.

Finally, a slight increase in carbon thickness was observed, due to the deposition of amorphous hydrocarbons from residual hydrocarbons in the EUV source, or due to sample handling [41,42].

4. Conclusions

Single layer graphene on an amorphous silicon substrate exposed to EUV radiation in the presence of water and hydrogen, is shown to break down from its signature aromatic structure

Fig. 8. XPS spectra of graphene covered Si sample before (top) and after (bottom) exposure to EUV and H_2 . The C1s spectra is raw data, while sp^2 , sp^3 and C—O curves are fitted.

through the formation of ketone and enol groups, such as the enol forms of 1,3- diketone, most likely at the grain boundaries and/or point defects. This formation is noted via RAIRS, which indicates that ring structure degradation occurs through graphene oxidation, due to the water present on the surface. Additionally, this can be confirmed by XPS which shows an increase in the bond percentage of oxygen bound to carbon on the surface after EUV exposure. Meanwhile, sp^2 bonds in graphene cleave to form sp^3 bonds, also confirmed via XPS, due to EUV photons and/or hydrogen radicals breaking sp^2 bonds, leading to graphene becoming more defective. Furthermore, the rate of the oxidation process at given water coverage and hydrogen pressure slows down and nearly saturates over time, while still sp^2 carbon is left after the exposure. This behavior could be attributed to saturation of the reaction occurring at grain boundaries and point defects. Finally, this work shows that the balance of EUV-induced photochemistry of graphene in the presence of water and hydrogen is very different from ruthenium, an important reference capping material for EUV optics [43]. While for ruthenium an increased pressure of H_2 leads to (complete) reduction of the oxidation of the Ru resulting from EUV induced reactions of water, in case of graphene the oxidation reaction is enhanced by a higher hydrogen pressure. This shows that a balance between oxidation and reduction of a graphene cap can most likely not be obtained, such that the use of graphene with a low defect density is of utmost importance.

Acknowledgements

The authors would like to thank Dr. Robbert van de Kruijs and Mr. Theo van Oijen for preparation of substrate, Mr. Eldad Grady for help with synthesis of graphene and, Mr. Luc Stevens and Mr. Goran Milinkovic for help with experimental measurements. This research is supported by the Dutch Technology Foundation STW (project number 140930), which is part of the Netherlands Orga-

nization for Scientific Research (NWO), and which is partly funded by the Ministry of Economic Affairs as well as ASML and ZEISS. We also acknowledge the financial and facilitary contributions by ASML, ZEISS, PANalytical, and the Province of Overijssel through the Industrial Focus Group XUV Optics at the MESA+ Institute.

References

- [1] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nat. Mater.* 6 (3) (2007) 183–191.
- [2] A.K. Geim, Graphene: status and prospects, *Science* 324 (5934) (2009) 1530–1534.
- [3] S. Hu, M. Lozada-Hidalgo, F.C. Wang, A. Mishchenko, F. Schedin, R.R. Nair, E.W. Hill, D.W. Boukhvalov, M.I. Katsnelson, R.A.W. Dryfe, et al., Proton transport through one-atom-thick crystals, *Nature* 516 (7530) (2016) 227–230.
- [4] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A.K. Geim, Two-dimensional atomic crystals, *Proc. Natl. Acad. Sci. U. S. A.* 102 (30) (2005) 10451–10453.
- [5] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, *Science* 321 (5887) (2008) 385–388.
- [6] M. Han, B. Özyilmaz, Y. Zhang, P. Kim, Energy band-gap engineering of graphene nanoribbons, *Phys. Rev. Lett.* 98 (20) (2007).
- [7] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H.L. Stormer, Ultrahigh electron mobility in suspended graphene, *Solid State Commun.* 146 (9–10) (2008) 351–355.
- [8] Y. Zhang, Y.W. Tan, H.L. Stormer, P. Kim, Experimental observation of the quantum Hall effect and Berry's phase in graphene, *Nature* 438 (7065) (2005) 201–204.
- [9] J.S. Bunch, S.S. Verbridge, J.S. Alden, A.M. van der Zande, J.M. Parpia, H.G. Craighead, P.L. McEuen, Impermeable atomic membranes from graphene sheets, *Nano Lett.* 8 (8) (2008) 2458–2462.
- [10] V. Berry, Impermeability of graphene and its applications, *Carbon* 62 (0) (2013) 1–10.
- [11] A.M.V.D. Zande, R.A. Barton, J.S. Alden, C.S. Ruiz-Vargas, W.S. Whitney, P.H.Q. Pham, J. Park, J.M. Parpia, H.G. Craighead, P.L. McEuen, Large-scale arrays of single-layer graphene resonators, *Nano Lett.* 10 (12) (2010) 4869–4873.
- [12] J.W. Suk, A. Kitt, C.W. Magnuson, Y. Hao, S. Ahmed, J. An, A.K. Swan, B.B. Goldberg, R.S. Ruoff, Transfer of CVD-grown monolayer graphene onto arbitrary substrates, *ACS Nano* 5 (9) (2011) 6916–6924.
- [13] R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, A.K. Geim, Fine structure constant defines visual transparency of graphene, *Science* 320 (5881) (2008) 1308.
- [14] B.L. Henke, E.M. Gullikson, J.C. Davis, X-ray interactions: photoabsorption, scattering, transmission, and reflection at $E = 50$ –30,000 eV, $Z = 1$ –92, *At. Data Nucl. Data Tables* 54 (2) (1993) 181–342.
- [15] M. Bayraktar, W.A. Wessels, C.J. Lee, F.A. van Goor, G. Koster, G. Rijnders, F. Bijkerk, Active multilayer mirrors for reflectance tuning at extreme ultraviolet (EUV) wavelengths, *J. Phys. D: Appl. Phys.* 45 (49) (2012) 494001.
- [16] D.-E. Jiang, B.G. Sumpter, S. Dai, Unique chemical reactivity of a graphene nanoribbon's zigzag edge, *J. Chem. Phys.* 126 (13) (2007) 134701.
- [17] L. Liu, M. Qing, Y. Wang, S. Chen, Defects in graphene: generation, healing, and their effects on the properties of graphene: a review, *J. Mater. Sci. Technol.* 31 (6) (2015) 599–606.
- [18] P.A. Denis, F. Iribarne, Comparative study of defect reactivity in graphene, *J. Phys. Chem. C* 117 (37) (2013) 19048–19055.
- [19] M. Pachecka, J.M. Sturm, C.J. Lee, F. Bijkerk, Adsorption and Dissociation of CO_2 on Ru(0001), *J. Phys. Chem. C* 121 (12) (2017) 6729–6735.
- [20] T.E. Madey, N.S. Faradzhev, B.V. Yakshinskiy, N.V. Edwards, Surface phenomena related to mirror degradation in extreme ultraviolet (EUV) lithography, *Appl. Surf. Sci.* 253 (4) (2006) 1691–1708.
- [21] D.I. Astakhov, W.J. Goedheer, C.J. Lee, V.V. Ivanov, V.M. Krivtsov, K.N. Koshelev, D.V. Lopaev, R.M. van der Horst, J. Beckers, E.A. Osorio, et al., Exploring the electron density in plasma induced by EUV radiation: II. Numerical studies in argon and hydrogen, *J. Phys. D: Appl. Phys.* 49 (29) (2016) 295204.
- [22] B.M. Mertens, B. van der Zwan, P.W.H. de Jager, M. Leenders, H.G.C. Werij, J.P.H. Benschop, A.J.J. van Dijkveld, Mitigation of surface contamination from resist outgassing in EUV lithography, *Microelectron. Eng.* 53 (1–4) (2017) 659–662.
- [23] L.E. Klebanoff, M.E. Malinowski, W.M. Clift, C. Steinhaus, P. Grunow, Use of gas-phase ethanol to mitigate extreme UV/water oxidation of extreme UV optics, *J. Vac. Sci. Technol. A: Vac. Surf. Films* 22 (2) (2004) 425–432.
- [24] Q. Sun, The Raman OH stretching bands of liquid water, *Vib. Spectrosc.* 51 (2) (2016) 213–217.
- [25] A. Gao, E. Zoethout, J.M. Sturm, C.J. Lee, F. Bijkerk, Defect formation in single layer graphene under extreme ultraviolet irradiation, *Appl. Surf. Sci.* 317 (2014) 745–751.
- [26] N. Mitoma, R. Nouchi, K. Tanigaki, Photo-oxidation of graphene in the presence of water, *J. Phys. Chem. C* 117 (3) (2013) 1453–1456.
- [27] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, et al., Large-area synthesis of high-quality and uniform graphene films on copper foils, *Science* 324 (5932) (2009) 1312–1314.

- [28] F. Liu, J.M. Sturm, C.J. Lee, F. Bijkerk, Extreme UV induced dissociation of amorphous solid water and crystalline water bilayers on Ru(0001), *Surf. Sci.* 646 (2016) 101–107.
- [29] J.M. Sturm, C.J. Lee, F. Bijkerk, Reactions of ethanol on Ru(0001), *Surf. Sci.* 612 (2013) 42–47.
- [30] W.A. Soer, M.J.J. Jak, A.M. Yakunin, M.M.J.W. van Herpen, V.Y. Banine, Grid spectral purity filters for suppression of infrared radiation in laser-produced plasma EUV sources, in: F.M. Schellenberg, B.M. La Fontaine (Eds.), *Spie* vol. 7271 (2009), 72712Y–72712Y–9.
- [31] E.R. Kieft, J.J.A.M. van der Mullen, G.M.W. Kroesen, V. Banine, Time-resolved pinhole camera imaging and extreme ultraviolet spectrometry on a hollow cathode discharge in xenon, *Phys. Rev. E* 68 (5) (2003) 056403.
- [32] R.W. Silverstein, G.C. Bassler, Spectrometric identification of organic compounds, *J. Chem. Educ.* 39 (11) (1962) 546–553.
- [33] P.A. Gerakines, Infrared band strengths: laboratory techniques and applications to astronomical observations, *Bull. Am. Astron. Soc.* 34 (2002) 911.
- [34] R.M. Silverstein, F.X. Webster, D.J. Kiemle, D.L. Bryce, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, 2014.
- [35] L.G. Cancado, A. Jorio, E.H. Ferreira, F. Stavale, C.A. Achete, R.B. Capaz, M.V. Moutinho, A. Lombardo, T.S. Kulmala, A.C. Ferrari, Quantifying defects in graphene via Raman spectroscopy at different excitation energies, *Nano Lett.* 11 (8) (2011) 3190–3196.
- [36] C.S. Ruiz-Vargas, H.L. Zhuang, P.Y. Huang, A.M. van der Zande, S. Garg, P.L. McEuen, D.A. Muller, R.G. Hennig, J. Park, Softened elastic response and unzipping in chemical vapor deposition graphene membranes, *Nano Lett.* 11 (6) (2011) 2259–2263.
- [37] A. Clemens, L. Hellberg, H. Gronbeck, D. Chakarov, Water desorption from nanostructured graphite surfaces, *Phys. Chem. Chem. Phys.* 15 (47) (2013) 20456–20462.
- [38] C. Clay, S. Haq, A. Hodgson, Intact and dissociative adsorption of water on Ru(0001), *Chem. Phys. Lett.* 388 (1) (2004) 89–93.
- [39] T. Werder, J.H. Walther, R.L. Jaffe, T. Halicioglu, P. Koumoutsakos, On the water-carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes, *J. Phys. Chem. B* 107 (6) (2003) 1345–1352.
- [40] J. Díaz, G. Paolicelli, S. Ferrer, F. Comin, Separation of the sp³ and sp² components in the C1s photoemission spectra of amorphous carbon films, *Phys. Rev. B* 54 (11) (1996) 8064–8069.
- [41] J. Chen, E. Louis, H. Wormeester, R. Harmsen, R. van de Kruijs, C.J. Lee, W. van Schaik, F. Bijkerk, Carbon-induced extreme ultraviolet reflectance loss characterized using visible-light ellipsometry, *Meas. Sci. Technol.* 22 (10) (2011) 105705.
- [42] J. Chen, E. Louis, C.J. Lee, H. Wormeester, R. Kunze, H. Schmidt, D. Schneider, R. Moors, W. van Schaik, M. Lubomska, et al., Detection and characterization of carbon contamination on EUV multilayer mirrors, *Opt. Express* 17 (19) (2009) 16969–16979.
- [43] I. Nishiyama, H. Oizumi, K. Motai, A. Izumi, T. Ueno, H. Akiyama, A. Namiki, Reduction of oxide layer on Ru surface by atomic-hydrogen treatment, *J. Vac. Sci. Technol. B* 23 (6) (2005) 3129.