Full Length Article

Formation of H₂O on a CO₂ dosed Ru(0 0 0 1) surface under Extreme Ultraviolet Light and H₂B.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 Institute of Engineering, Fontys Hogescholen, Eindhoven, The Netherlands

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ABSTRACT

In this work, we study the reaction of the dissociation products of carbon dioxide on a Ru(0 0 0 1) surface under Extreme Ultraviolet (EUV) light with a partial pressure of hydrogen. Our results show that both amorphous carbon and H₂O are the end products of the CO₂ dissociation at the Ru surface, and these are produced only in the presence EUV and H₂. Partial dissociation of CO₂ on the Ru surface is an intermediate step in the overall reaction. Using Reflection Absorption Infrared spectroscopy (RAIRS) and Temperature Programmed Desorption (TPD), only water is detected as molecular reaction product. We further show that this reaction deactivates the Ru surface due to the formation of an amorphous carbon layer, thereby confirming the catalytic role of Ru in the total reaction.

1. Introduction

CO₂ has been shown to dissociate when in contact with metal surfaces, such as Fe [1,2], Ni [1,2], W [3], Re [4] and Al [5], into CO and O [6]. In the chemical industry, transition metals are widely studied as catalysts [7], due to their high efficiency to convert carbon dioxide to methane and methanol. Thus, to understand the transition metal driven catalytic conversion of CO₂ to other compounds, the interaction of CO₂ with metal surfaces needs to be studied [8].

Besides its relevance for catalysis, Ru is also employed as a protective cap for optics for Extreme Ultraviolet (EUV) light. EUV optics must operate in a moderate vacuum where there may be a complex balance between, on the one side photochemical reactions of residual hydrocarbons and water on the cap, and on the other side, cleaning by hydrogen radicals. One option to control reaction pathways is to deliberately introduce additional species into the vacuum to consume reactive species. For instance, a balance between ruthenium oxidation and reduction is achieved by controlling the partial pressure of either hydrogen or water [9].

The dissociation products of CO₂ reacting with hydrogen to form hydrocarbons on the optics surfaces to prevent oxidation and consume excess reactive hydrogen is an attractive prospect in highly reactive environments, such as in the case of Extreme Ultraviolet (EUV) Lithography. However, to prevent oxidation and consume hydrogen via this pathway, a reverse water gas shift reaction needs to take place [10]. Ruthenium surfaces have previously been used as catalyzing

agents for reverse water gas shift reactions, but ruthenium's interaction with CO₂ has not been fully investigated [8,11]. Furthermore, this catalyzing behavior is shown in Density Functional Theory (DFT) calculations as well, where CO₂ adsorption and dissociation is seen on a Ru surface, hydrogenating to form CH_x species [12,13].

Prior experiments [14] have shown that CO₂ adsorption on a Ru (0 0 0 1) surface results in partial dissociation, shown by the existence of both CO₂ and CO species on the surface. Furthermore, this dissociation was observed to saturate with increasing CO₂ coverage. Additionally, no evidence was found for oxygen desorption, indicating that the oxygen was consumed by forming additional CO and/or H₂O via reactions with residual carbon and/or hydrogen on the crystal surface.

However, these experiments were not extended to more realistic scenarios, involving the presence of hydrogen and EUV. Thus, it is unknown if the partial dissociation of CO₂ is sufficient to induce further reactions with excess hydrogen. In order to understand the preferred reaction pathways under more realistic conditions for EUV optics, the reactions of CO₂ on the Ru(0 0 0 1) surface, in the presence of EUV light and H₂ are studied in more detail in this work.

For this work, the surface was characterized, *in-situ*, using Reflection Absorption Infrared Spectroscopy (RAIRS) and Temperature Programmed Desorption (TPD) spectroscopy. RAIRS measurements are sensitive to study the changes in adsorbed molecular groups, their orientation, density, and surrounding environment via changes in vibrational modes.

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Fig. 1. RAIRS spectra of the OH peak (3000–3800 cm^{-1}) with (a) 1×10^{-5} mbar H_2 background pressure, (b) adsorbed $\text{CO}_2 + \text{H}_2$ background and (c) adsorbed CO_2 and H_2 background under EUV irradiation. Spectra are shown in 10-min exposure increments from top to bottom.

2. Experimental

For this work, a ruthenium (0001) single crystal, 11 mm in diameter and ~ 3 mm in thickness, prepared by Surface Preparation Laboratories, The Netherlands, was used. The crystal was mounted on a 3-axis positioning manipulator in Ultra-High Vacuum (UHV) conditions and maintained at a base pressure of 10^{-10} mbar. A K-type thermocouple is spot welded to the side of the crystal to measure the surface temperature. A Eurotherm temperature controller was used to control the temperature of the surface.

All surface chemistry experiments were performed in the same experimental setup, sequentially without breaking vacuum. The crystal surface was treated with a cleaning process involving oxidation, annealing and argon ion sputtering. Firstly, oxidation was performed to remove carbon from the surface, by increasing the surface temperature to 1300 K, with a partial pressure of 1×10^{-7} mbar of O_2 in the chamber. Secondly, ion sputtering was conducted. Finally, the surface was annealed at 1300 K for 30 min and flashed to 1580 K. Repeated sputtering and annealing was performed until a reference TPD spectrum from water and CO on clean Ru(0001) could be reproduced [15].

The experimental chamber is also equipped with RAIRS and TPD spectroscopy, and is attached to an EUV source [16,17]. RAIRS spectra are measured at grazing incidence using a Fourier Transform Infrared Spectrometer (Bruker vertex 70 V), equipped with a liquid N_2 cooled mercury-cadmium-telluride (MCT) detector. Each IR spectrum is accumulated over 256 scans with a resolution of 4 cm^{-1} , with background and measurement scans recorded at 85 K. To obtain TPD spectra, the surface is placed ~ 1 mm away from the entrance aperture of a Hiden Analytical 3F/PIC quadrupole mass spectrometer (QMS), housed in a differential pumped system, to ensure the signal is dominated by surface desorption.

Carbon dioxide (99.998% purity; residuals: O_2 2 ppm, N_2 8 ppm, hydrocarbon 3 ppm, H_2O 1 ppm, CO 1 ppm) was dosed on the surface at a temperature of 85 K. This was done using a retractable quartz dosing tube, placed 1 cm away from the surface. CO_2 is delivered via a pinhole mounted between the gas supply and doser, to maintain an effective

pressure in the 10^{-8} mbar range near the crystal surface. Calibration of CO_2 dose was performed by comparing the amount detected via TPD against reference water TPD spectra [14,17].

The chamber is attached to a Xe plasma discharge EUV source (Philips EUV Alpha Source) with a repetition rate of 500 Hz. The light from the source is filtered via reflection from a Mo/Si multilayer mirror (55% reflectivity at 13.5 nm) and via transmission through a Si/Mo/Zr membrane (35% transmission at 13.5 nm) [18], resulting in a peak transmission of 19% at 13.5 nm with a FWHM of 0.2 nm and an additional transmission of 9% at 21.5 nm with a FWHM of 3.1 nm [19,20,21]. The average intensity of the EUV beam, with a Gaussian profile (FWHM = 3 mm) is $35\text{--}55 \text{ mW/cm}^2$, which corresponds to an EUV pulse fluence of $90\text{--}110 \mu\text{J/cm}^2$.

The experimental procedure begins with dosing the cleaned (unless otherwise noted) Ru(0001) surface with 0.2 ML of CO_2 , followed by exposing the surface to EUV with a partial pressure of H_2 . A RAIRS background spectrum is recorded before dosing, and further spectra are recorded after dosing, and for every 5 min of EUV or H_2 exposure. TPD measurements are performed by heating the crystal to 600 K from 80 K at a rate of 2 K/s, followed by further heating to 1580 K at 10 K/s.

3. Results and discussion

To investigate the dissociation of CO_2 and its end product formation, experiments were first performed with an H_2 partial pressure of 1×10^{-7} mbar under EUV illumination. In this case, characterization techniques such as RAIRS and TPD were unable to detect the formation of H_2O and simple hydrocarbons (such as methane, ethylene, formic acid, and methanol). Also, changing the H_2 partial pressure to 1×10^{-6} mbar, while keeping all the other parameters (CO_2 , EUV) the same, did not result in any change in RAIRS OH signals (to detect water) or TPD mass spectra. Therefore, the partial pressure of H_2 was further increased to 1×10^{-5} mbar (keeping the parameters for EUV and CO_2 the same), for which the results are detailed below.

Fig. 2. Comparison of the OH peak area growth over the course of 60 min for a CO₂ dosed Ru(0001) surface exposed to EUV with H₂ at 1×10^{-5} mbar. The Y axis on the left shows the area under the inverse IR peak ($3800\text{--}3000\text{ cm}^{-1}$), while the Y axis on the right shows the corresponding indicative water coverage.

3.1. EUV induced surface water formation

Fig. 1 shows the difference in RAIRS OH vibration peak size, which is sensitive for adsorption of molecular H₂O on the surface, for different exposure conditions. As seen in Fig. 1(a), the peak intensity increases with H₂ exposure time for a clean Ru(0001) surface, indicating increasing water deposition. This water is due to an increased residual H₂O gas pressure from the H₂ gas line [22]. Similarly, an increase in OH peak intensity is seen in Fig. 1(b) for H₂ exposure of a Ru(0001) surface with adsorbed CO₂. However, the OH intensity is lower than it was in the plot shown in Fig. 1(a). This is due to CO₂ (or its partial dissociation products) occupying sites on the surface which prevent H₂O from adsorbing. In contrast, when Ru(0001) is dosed with CO₂ and exposed to H₂ and EUV radiation (Fig. 1(c)), the OH peak intensity is significantly higher than for the other two conditions, with the only difference being the introduction of EUV. This indicates that more water is formed on the CO₂ covered Ru(0001) surface when exposed to EUV in the presence of hydrogen. Fig. 2 shows the rate of OH peak formation.

Fig. 2 compares the growth rate of the OH peak for the three exposure conditions shown in Fig. 1. Water coverage is expressed in terms of both peak area and water coverage. It should be noted that RAIRS is in general not quantitative. However, based on a calibration of RAIRS versus TPD results on Ru(0001) in the same experimental set-up, an indicative water coverage can be provided based on comparison of the peak height in the transmission plots [16]. We see that water coverage increases on the surface over 60 min for all three cases: 0.33 ML for CO₂ + H₂, 0.37 ML for H₂, and 1.36 ML for EUV + CO₂ + H₂. When a clean Ru(0001) surface is dosed with CO₂ and exposed to EUV without introducing H₂, the deposition of water from residual gas amounts to 0.70 ML in 60 min. Furthermore, water deposited in the presence of EUV without CO₂ and H₂ is shown to be less than 0.1 ML. The difference in final water coverage between EUV + CO₂ + H₂ compared to CO₂ + H₂ without EUV is thus 1.03 ML. The individual contributions due to EUV + CO₂ and CO₂ + H₂ added together would amount to 1.03 ML, which is also less compared to exposure to EUV + CO₂ + H₂. The clearly higher water coverage after EUV + H₂ exposure of a CO₂ dosed Ru(0001) surface in comparison with all reference cases indicates that water is produced by an EUV-induced reaction of CO₂ and H₂ or its partial dissociation products.

The formation of water can be attributed to the overall reaction equation (Fischer-Tropsch type reaction):

Although Eq. (1) could be a direct process, previous experiments [14] have shown that CO₂ partially dissociates on Ru(0001) without EUV exposure, therefore a second reaction path is also possible:

In what follows, we show that the formation of water, under reaction conditions investigated here, proceeds only via the second path.

Eqs. (1) and (3) show that molecular hydrogen cracks into atomic hydrogen in the presence of EUV [20]. Both Eqs. (1) and (3) lead to the formation of hydrocarbons (CH_x) and water as products. Since we do not see the formation of volatile hydrocarbons, the value of n can be 0, indicating the formation of amorphous carbon. Also, Eq. (2) can only occur on the surface of Ru(0001) [14], this means Eq. (3) is limited by the formation of CO.

Fig. 3 shows the RAIRS spectra of a clean CO₂ dosed Ru(0001) surface before any EUV and H₂ experiments have taken place. Three distinct peaks are visible, one for CO₂ at 2343 cm^{-1} corresponding to a (ν_3) C=O stretch [23], and two for CO at 2213 cm^{-1} and 1993 cm^{-1} corresponding to a C=O bend and a C=O stretch, respectively [24]. This result shows that for the CO₂ dose used in this study, most of the dosed CO₂ partially dissociates to CO before the RAIRS spectrum is acquired.

In Fig. 4, the C=O stretch for CO is visible when CO₂ is first dosed on the surface, followed by exposure to EUV. Fig. 4(a) shows spectra for a reference experiment where a CO₂ dosed Ru(0001) surface was exposed to EUV without presence of H₂ (other than residual gas) during exposure. In this case the CO peak intensity increases over 30 min of exposure, most likely due to adsorption of CO from residual gas. As H₂ is introduced at pressures of 1×10^{-7} mbar and 1×10^{-5} mbar in Fig. 4(b) and (c), respectively, we see that the CO peak intensity actually decreases over time, indicating dissociation of CO by a reaction that only proceeds under EUV irradiation in H₂ background. Additionally, we observe that there is no corresponding increase in the OH peak from adsorbed water at 1×10^{-7} mbar H₂, while adsorbed water

Fig. 3. RAIRS spectra of a CO₂ dosed Ru(0001) surface before exposure to EUV and H₂. The surface has been dosed with 0.2 ML of CO₂, and maintained at 85 K.

is produced at an H₂ pressure of 1×10^{-5} mbar (see Figs. 1 and 2).

While the sharp CO peak decreases under exposure to EUV and H₂, the formation and increase of a broad peak around 1983 cm^{-1} is observed, which might correspond to the vibrational frequencies of several simple hydrocarbons (methane, ethylene and propadiene) [23].

However, since no other desorbing species than H₂O, H₂, CO₂ and CO are detected by TPD, this indicates that amorphous C and/or C_xH_y species stay bound to the surface. Furthermore, the broad peak may be caused by CO molecules that have a different binding strength to the surface due to a change in coverage and the presence of co-adsorbed molecules or C_xH_y species [25].

This comparison of EUV exposure at different H₂ pressures thus shows that the dissociation of CO is not a pure photochemical reaction. Only in the presence of H₂ and/or H radicals produced by EUV radiation, EUV exposure leads to dissociation of CO into amorphous (hydro) carbon and oxygen adsorbed on the Ru surface. At an H₂ pressure of 1×10^{-7} mbar, no significant formation of H₂O by reactions of adsorbed O with H radicals is observed. Only at a pressure of 1×10^{-5} mbar H₂, water is produced by (EUV induced) reactions of H₂ and adsorbed oxygen originating from (partial) dissociation of CO₂.

More evidence for the formation of water due to the presence of CO₂, EUV and H₂ is presented in Fig. 5. Under EUV, CO₂ and H₂, the amount of water on the surface is measured to increase by a factor of 3.7 and 4.1 when compared to water coverage of a surface only exposed to H₂ and CO₂ + H₂ respectively, while only EUV and CO₂ produce 0.70 ML of water, a factor 0.5 as compared to the surface exposed to EUV, CO₂ and H₂.

Furthermore, TPD spectra showed us that the other products desorbing from the surface were CO₂, CO and H₂. Simple hydrocarbons, such as methane (mass 16), ethylene (mass 28), methanol (mass 31), ethanol and formic acid (both mass 46), and formate (desorption of CO₂ and H₂ at the same temperature) [26], were not detected. Therefore, it is highly likely that non-volatile reaction products, such as (hydrogenated) amorphous carbon are formed on the surface, although it cannot be fully excluded that small molecules undergo EUV induced desorption.

Fig. 4. RAIRS spectra of the CO peak when Ru(0001) is dosed with CO₂ and exposed to EUV in the (a) absence and presence of H₂ at (b) 1×10^{-7} mbar and (c) 1×10^{-5} mbar. The EUV exposure time is indicated on each plot.

Fig. 5. TPD spectra of H₂O (mass 18) for different exposure conditions after 60 min: H₂, CO₂ + H₂, EUV + CO₂ + H₂ at 1×10^{-5} mbar and EUV + CO₂ at 10^{-9} mbar. The plot indicates the peak desorption temperature and water coverage on the surface after 60 min in monolayers (ML), as compared to TPD peak areas on clean Ru(0001) [14,16]. The spectra have been smoothed over 4 values over temperature.

3.2. Coverage of Ru(0001) surface with amorphous carbon/hydrocarbons

If the formation of water requires partial dissociation of CO₂ to CO as a first step, then water formation could be limited by the availability of catalytic sites on the Ru surface. The formation of amorphous carbon implies that Ru sites are gradually covered with amorphous carbon/hydrocarbons. In order to find out whether the EUV-induced reaction of CO₂ and H₂ indeed leads to amorphous carbon formation on Ru surface sites, and to confirm that the Ru surface has a catalytic role in the CO₂ dissociation reaction, the de-activation of the CO₂ dissociation reaction was studied using multiple reaction cycles.

An, initially clean, surface was exposed to 5 consecutive cycles (or iterations) consisting of CO₂ dosing, followed by 60 min exposure to EUV and H₂ without sputtering or high temperature annealing the surface in between the cycles. After each cycle, the surface temperature was only increased to 600 K for a TPD spectrum. This ensures that any amorphous carbon formed on the surface stays adsorbed on the surface. For each cycle, the same amount of CO₂ (0.2 ML) was dosed on the surface at 85 K.

Fig. 6 shows that the intensity of the OH peak reduces with repeated exposures of EUV and H₂ on a CO₂ dosed Ru surface, with the intensity for iteration V being reduced by a factor of 4 compared to the intensity for iteration I. This indicates that water generation on the surface is reduced with each cycle.

Fig. 7 shows the water TPD spectra corresponding to the RAIRS experiment from Fig. 6, with an indication of the water coverage reached after 60 min of EUV exposure time, based on reference experiments of water on clean Ru(0001) [16,17]. The intensity of the OH peak decreases with each iteration EUV and H₂ exposure. These results confirm that the water produced by the EUV-induced reaction of CO₂ and H₂ decreases for an increasing number of iterations. The final water coverage in the fifth reaction cycle is reduced by a factor of 2 compared to the first reaction cycle. We attribute the reduction to a lower availability of Ru surface sites as they are covered with amorphous carbon.

Water on the surface is shown to come from two sources: the H₂ line or exchange reactions on walls [15] and hydrogen reacting with CO. As mentioned before, after 60 min, 0.33 ML was attributed to the water deposited on the surface from the H₂ line for a reference measurement of CO₂ + H₂ without EUV, while CO₂ reacting with EUV produces 0.70 ML. We speculate that the production of water in the latter case is due to reactions of CO₂ with residual hydrogen on surfaces in the

Fig. 6. RAIRS spectra of OH peak for cycles of CO₂ dosed Ru(0001) after exposure to EUV and H₂ for 60 min. After each exposure the sample is heated to 600 K, after which new CO₂ is adsorbed at 85 K. A new background is taken for each iteration, just before CO₂ dosing.

system exposed to EUV. Assuming that water adsorbs on the surface at the same rate for a clean and carbon contaminated surface, we can say that about $1.36 - (0.70 + 0.33) = 0.33$ ML of the water adsorbed at the end of the reaction cycle is from H₂ reacting with CO on the Ru crystal in the presence of EUV. It should be noted that such a quantitative comparison is not straightforward in view the long reaction times that inevitably lead to adsorption of residual water. However, this quantification of the amount of water formed from reactions on the Ru(0001) surface seems reasonably in line with the initial dose of ~ 0.2 ML CO₂ and the stoichiometry from reaction (1)–(3), when taking into account that some CO was left on the surface at the end of the reaction cycle.

Fig. 7. TPD spectra of water (mass 18) for 5 cycle experiment on CO₂ dosed Ru(0001) in the presence of EUV and H₂. The plot indicates the peak desorption temperature and water coverage on the surface after 60 min exposure in monolayers (ML). The spectra has been smoothed over 4 values.

Fig. 8. Peak desorption temperature of CO at the end of each cycle of EUV and H₂ exposure to a CO₂ dosed Ru(0001) surface.

TPD measurements (Fig. 8) further show that the peak desorption temperature of the unreacted CO, remaining after the EUV exposure, is 469 K for the first iteration. This measurement corresponds to the peak desorption temperature from other experiments done at the same and lower partial pressures of hydrogen (10^{-7} mbar), corresponding to CO desorption from a mostly clean surface. For subsequent cycles of EUV + H₂ exposure, we see that the peak desorption temperature of CO drops to 418 K, and remains unchanged thereafter. This indicates that the bonding of CO to the surface weakens due to the formation of amorphous carbon on the surface.

4. Conclusions

This study shows the formation of H₂O and amorphous carbon when a CO₂ dosed Ru(0001) surface is exposed to EUV with a partial H₂ pressure of at least 1×10^{-5} mbar. We have shown that the reaction pathway proceeds via the partial dissociation of CO₂ into CO and O. This dissociation is not driven by photo-induced processes, but is due to catalytic activity at the Ru surface. The overall photo-induced reaction of CO₂ and H₂ forms water and an amorphous carbon layer, which may be partially hydrogenated. For the reaction conditions and initial CO₂

coverages investigated in this study, the catalytic conversion of CO₂ to CO is rapid compared to photo-induced processes, therefore there is practically no intact CO₂ left at the start of the EUV exposure. The possibility of direct EUV-induced CO₂ dissociation therefore could not be investigated. When exposing a CO₂ dosed surface to EUV photons without H₂ present in the background, only catalytic partial dissociation of CO₂ into CO and O was observed. Photo-dissociation of the formed CO was only observed for simultaneous presence of EUV and H₂. For hydrogen pressures below 1×10^{-5} mbar, no photo-induced formation of water was observed, even though CO was dissociated. Only at 1×10^{-5} mbar H₂, formation of water from EUV-induced reactions of hydrogen and oxygen were observed. This indicates that the EUV-induced generation of hydrogen radical species is most likely the rate-limiting step for the overall reaction. Cycles of CO₂ dosing without cleaning show that the carbon layer covers the Ru surface, reducing the partial dissociation of CO₂ and slowing the production of water in later cycles. This confirms that EUV-induced CO₂ dissociation is either negligible, or does not lead to any detectable reaction products.

These results can be understood in view of previously reported research on EUV-induced and thermal reactions of hydrocarbons, CO₂ and hydrogen on Ru surfaces. Experimental and theoretical results on CH₄ adsorption on Ru(0001) showed that dissociative CH₄ adsorption results in CH₂ groups and surface hydrogen, which further dissociate to CH + H after annealing to 273 K [27]. Theoretical results in that work show that hydrogenation of carbon species would require significantly higher pressures (in the bar range) than used in this study, which explains our finding that no hydrocarbons or alcohols are found as reaction products. Instead dissociation and surface carbon formation dominates. Similarly, reported theoretical [28] and experimental [29] results on hydrogenation of CO₂ by H₂ on Ru refer to hydrogen pressures in the range of 1 bar. EUV irradiation in hydrogen background leads to formation of hydrogen radicals, which are able to clean surface oxygen by H₂O formation [30] and surface carbon by formation of volatile CH_x species [15,31,32]. The results of this work show that H₂O formation from surface O is already effective at a hydrogen pressure of 1×10^{-5} mbar and a sample temperature below 90 K, while for removal of surface C requires higher hydrogen pressure and/or sample temperatures, in line with the results mentioned in Chen et al. [33].

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