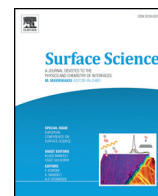




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# Extreme UV induced dissociation of amorphous solid water and crystalline water bilayers on Ru(0001)

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## ABSTRACT

The extreme ultraviolet (EUV,  $\lambda = 13.5$  nm) induced dissociation of water layers on Ru(0001) was investigated. We irradiated amorphous and crystalline water layers on a Ru crystal with EUV light, and measured the surface coverage of remaining water and oxygen as a function of radiation dose by temperature programmed desorption (TPD). The main reaction products are OH and H with a fraction of oxygen from fully dissociated water. TPD spectra from a series of exposures reveal that EUV promotes formation of the partially dissociated water overlayer on Ru. Furthermore, loss of water due to desorption and dissociation is also observed. The water loss cross sections for amorphous and crystalline water are measured at  $9 \pm 2 \times 10^{-19}$  cm<sup>2</sup> and  $5 \pm 1 \times 10^{-19}$  cm<sup>2</sup>, respectively. Comparison between the two cross sections suggests that crystalline water is more stable against EUV induced desorption/dissociation. The dissociation products can oxidize the Ru surface. For this early stage of oxidation, we measured a smaller (compared to water loss) cross section at  $2 \times 10^{-20}$  cm<sup>2</sup>, which is 2 orders of magnitude smaller than the photon absorption cross section (at 92 eV) of gas phase water. The secondary electron (SE) contributions to the cross sections are also estimated. From our estimation, SE only forms a small part (20–25%) of the observed photon cross section.

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## 1. Introduction

Since light with a shorter wavelength can provide better imaging resolution, Extreme ultraviolet (EUV) light, with a wavelength of 13.5 nm, has been chosen for the current generation of high-end photolithography system [1,2]. However, EUV light is strongly absorbed by all materials. Therefore, EUV imaging systems operate in vacuum, and require reflective optics. Photochemical reactions can then occur on the surface of the reflective optics. With a photon energy well above the dissociation energy of water [3], EUV and EUV-induced low energy secondary electrons (SE) readily dissociate water adsorbed at the mirror surface. The dissociation products can cause surfaces of mirrors to oxidize, degrading imaging performance and throughput. To protect EUV optics against oxidation, several metal and metal oxide capping layers have been proposed [4]. The resilience of these capping layers has usually been studied using electron impact (EI) as a proxy for EUV radiation [5–7]. Unfortunately, electrons do not fully emulate the near-surface conditions generated during an EUV light pulse, leaving the relevance of these experiments an open question [4,7,8]. For selecting the right capping material and to predict accurately mirror's long term performance, we need to study the photochemistry at water–metal interfaces under realistic conditions.

Ruthenium is a candidate material for capping EUV optics to protect them from performance degradation due to carbon growth and oxidation [4]. It has been demonstrated that the water/Ru interface is very sensitive to both soft X-rays and low energy electrons. Hydroxyl groups were found on the Ru surface after short exposure to soft X-rays [9] and electrons [6]. Because oxygen up to monolayer coverage desorbs at a relatively high temperature (above 1100 K for Ru) [10], after long exposures, atomic oxygen from dissociated water can accumulate to form an oxide that may penetrate several nanometers under the surface [7]. Electron irradiation studies, on the other hand, found no direct evidence for atomic oxygen on the surface [6]. These differences highlight the need for EUV irradiation studies in preference to electron irradiation studies, and for the early stages of surface oxidation to be more carefully investigated.

Unlike photochemistry in the visible and the UV range [11], SE from EUV excited substrate are highly relevant for the surface reactions. In order to put both photon and SE induced processes into perspective, comparison should be made between their cross sections. However, cross section data for EUV induced dissociation is still lacking. A well defined surface, such as the Ru(0001) surface, is essential for a comparable cross section measurement. Therefore, we revisit the well-known water/Ru interface and explore how it reacts under EUV conditions.

The unique interplay between water–water and water–Ru interactions makes the water/Ru(0001) interface an interesting system to be studied. Depending on adsorption temperature, deposition geometry, and flux, water clusters and aggregates can form [12]. Amorphous

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solid water (ASW) and crystalline water bilayers (CWB) are two intact water structures that can be grown on a Ru surface. Crystalline water wets the Ru surface at 150 K, while ASW has a less ordered structure and remains physisorbed. Most importantly, CWB has a bilayer geometry [13], while ASW consists of three dimensional structures, such as clusters [12]. As water molecules form strong hydrogen bonds, the hydrogen networks inside the two water structures are also intrinsically different. Theoretically, it has been shown that dissociation barrier of water on Ru depends on structure [14]. However, it is still an open question how the structural difference and wetting influence water dissociation under EUV conditions. We will address this structural dependency by comparing EUV induced dissociation of ASW and CWB.

Apart from the intactly adsorbed layers, water can form the partially dissociated overlayer ( $\text{H}_2\text{O} + \text{OH}$ ) on Ru(0001) surface, which is also the most stable adsorption state on Ru(0001) [6,9,14,15]. Both intact and dissociative adsorption layers are well distinguishable in temperature programmed desorption (TPD). Their coverages are also given by the corresponding TPD peak area. On the other hand, reduction in the integrated TPD area indicates dissociation/desorption of water. The atomic oxygen created by the complete dissociation of water will adsorb on Ru crystal surfaces [16]. The adsorbed oxygen can be removed by heating to 1550 K. The desorbed oxygen can be detected by a mass spectrometer to provide surface oxygen coverage [16,17].

In this paper, the results of studies on the EUV-induced dissociation of ASW and CWB on a Ru(0001) surface, along with the subsequent oxidation of the Ru(0001) surface are presented. We use TPD spectroscopy to determine water dissociation and oxidation cross sections for the Ru(0001) surface, which is a necessary first step for predicting degradation rates over longer terms and in an environment with more chemically active species present [10,16,17].

## 2. Methods

The experiments were performed in an ultra-high vacuum (UHV) chamber with base pressure of  $3 \times 10^{-10}$  mbar. The vacuum is achieved using a turbo molecular pump and a Titanium sublimation pump [18]. The chamber is equipped with a quadrupole mass spectrometer (QMS, Hiden HAL 301) for TPD measurements, and an ion gun for sample cleaning. A retractable quartz tube doser is used to dose the ruthenium sample with water, while minimizing the increase in background pressure.

The sample consisted of a circular ruthenium (0001) single crystal (Surface Preparation Laboratories, The Netherlands), mounted on a manipulator. The diameter of the crystal is 11 mm. The sample temperature is controlled via a combination of active heating to 1580 K, and liquid nitrogen cooling to 80 K. The temperature is monitored using a K-type thermocouple, spot-welded to the side of the crystal. The temperature of the crystal is controlled by a Eurotherm temperature controller, which is also used to provide a constant heating rate for the TPD measurements.

Water is very sensitive to surface impurities [15]. Therefore, special care is taken to limit the amount of surface carbon and oxygen. The crystal surface is prepared by first removing surface carbon through annealing in  $2 \times 10^{-8}$  mbar of  $\text{O}_2$  at 1300 K, followed by repeated temperature cycling between 100 K and 1550 K to adsorb and desorb oxygen. The surface is then subjected to repeated cycles of Ar ion sputtering at 1 keV or 2 keV, followed by flash annealing to 1550 K [15,19]. This cleaning process is repeated until reference water TPD spectra [15,19] are consistently reproduced and no CO peak is observed above 800 K in the TPD spectra [4]. Between each subsequent measurement, the sample is flash annealed to 1550 K to remove remaining oxygen on the surface.

The sample is dosed with deionized water that has been further purified by freeze–pump–thaw cycles. During dosing, the doser tube is placed 1 cm away from the crystal surface to keep the chamber pressure as low as possible. The water coverage is computed from the integrated

TPD signals, and calibrated against the saturation coverage dosed at a sample temperature of 160 K [19].

The EUV light is produced by a Xe discharge plasma light source (Philips), operating at a repetition rate of 500 Hz. The broad band light from the plasma is first focused by a ruthenium coated grazing incidence collector, then reflected by a Mo/Si multilayer mirror (Phystex, central wavelength 13.5 nm), and finally passes through a 200 nm thick Zr/Si multilayer spectral purity filter (SPF). Both Mo/Si multilayer mirror and SPF have spectral bandwidths centred at 13.5 nm EUV with full width half maxima of 0.5 nm and 2 nm, respectively. The EUV pulses reaching the sample have a duration of 120 ns, and an energy flux of  $32 \mu\text{J}/\text{cm}^2$ . The beam diameter at the sample surface is 5 mm full width half maximum, resulting in an average intensity of  $16 \text{ mW}/\text{cm}^2$ .

During operation, the pressure in the EUV light source chamber reaches  $2 \times 10^{-3}$  mbar. However, the SPF can prevent the gas from the source chamber entering the main chamber. As a result of this isolation, the pressure in the main chamber can be maintained at  $1 \times 10^{-9}$  mbar during EUV exposure.

TPD spectra were measured by heating the sample at a constant rate, and recording the amount of desorption for several masses. To improve the signal-to-background ratio, the QMS is placed in a differentially pumped housing with a cone-shaped aperture (entrance diameter of 4 mm diameter), which is placed approximately 1 mm from the sample surface. This geometry ensures that the QMS signal is dominated by surface desorption products and not background residual gases. Water TPD spectra were obtained using a heating rate of 1 K/s over a temperature range of 80–500 K. The oxygen TPD spectra were measured at a heating rate of 5 K/s over a temperature range of 500–1570 K. The absolute value of the oxygen surface coverage is calibrated to the saturation value (0.5 ML) for  $p(2 \times 1)$  oxygen overlayer obtained at 400 K with  $2 \times 10^{-8}$  mbar  $\times$  300 s back dosed oxygen [16,20,21].

## 3. Results

ASW and CWB were grown on Ru crystal by dosing water at 83 and 160 K respectively [9,15,22], and exposed to EUV. The resulting photochemical reactions are reconstructed through the changes in the post-irradiation TPD spectra.

In the TPD spectra, the desorption temperature of each desorption peak is related to the strength of the adsorbate–substrate binding, or the energy barrier for recombinative desorption in the case of partially dissociated water. Peaks at relatively higher temperature originate from the molecules which bind stronger with the surface [23]. Since the QMS intensity is proportional to the desorption rate, the integrated peak area is proportional to the surface coverage [23]. The TPD results are divided into two separate subsections for ASW and CWB.

### 3.1. TPD of ASW

As shown by the bottom trace in Fig. 1(a), before exposure to EUV, the ASW TPD shows three desorption peaks, which are the multilayer water peak, C, the molecular water peak, A2, and the partially dissociated water peak, A1 [6,15,19]. Fig. 1(a) also shows the changes to the water TPD spectra for different EUV doses. The most noticeable changes are the peak height variations in A1 and A2, which are more clearly seen in Fig. 2(a). In Fig. 2(a), the A2 and C peak are plotted as a sum of the two, since the sum gives the total amount of molecular water on the surface. As the EUV exposure dose increases, the A2 peak decreases, and the A1 peak starts to increase, which is similar to the electron radiated case [6]. By a dose of  $7 \times 10^{16}$  photons/ $\text{cm}^2$ , the A2 peak has almost vanished, while the A1 peak has grown substantially. This indicates that water, adsorbed directly to the Ru(0001) surface, is partially dissociated ( $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ ) due to EUV exposure.

Furthermore, increases in EUV dose result in lower integrated TPD spectra (Fig. 2(a)), indicating that the total amount of remaining water is reduced. From Fig. 2(a), we see that the peaks change in two

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