

# Low energy electron bombardment induced surface contamination of Ru mirrors

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## ABSTRACT

The impact of secondary electrons induced contamination of the Ru surface was investigated. Mirror-like Ru sample was bombarded with low energy (100 eV) electrons and the change in surface chemistry was investigated using X-ray photoelectron spectroscopy (XPS). Along with XPS studies the corresponding effect on *in-situ* EUV reflectivity was examined by exposing the Ru surface to photons at a wavelength of 13.5 nm in an ultrahigh vacuum chamber. Detailed XPS analyses showed a sudden increase in carbon concentrations on the Ru surface in the first 60 min, followed by a slow but linear growth in carbon concentration. In parallel, a noticeable decrease in water content was observed during the time of electrons irradiation along with slight oxidation of pure Ru surface. All chemical changes were discussed in terms of the electrons bombardment mediated dissociation of water and hydrocarbon molecules. A time dependent EUV reflectivity measurements show insignificant change in reflectivity up to 510 min of electrons bombardment. The impact of water molecules on the Ru surface and the accumulation of carbon through dissociation of residual hydrocarbons is discussed in details.

**Keywords:** EUV lithography, multilayer mirror, carbon contamination, Ruthenium capping

## 1. INTRODUCTION

Extreme ultraviolet (EUV) radiation induced surface contamination of Ru capping layer of Mo/Si multilayer mirrors (MLMs) is of great concern regarding mirror performance<sup>1</sup>. In fact, the lifetime of a Mo/Si mirror is severely affected by surface contamination during EUV exposure. This has previously been explained in terms of the interaction of the adsorbed hydrocarbons and water molecules on mirror surface with secondary electrons (SEs) generated by the slowing down cascade of photoelectrons<sup>2</sup>. During such interaction process, water molecules in the test chamber are dissociated on the Ru surface yielding free oxygen atoms and causing further surface oxidation, while carbon is accumulated on the surface following the dissociation of adsorbed hydrocarbons.

Low-energy electron beams can be used to generate surface SEs similar to the SEs created by EUV light during the slowing down cascade of incident electrons<sup>2</sup>. Several studies used this mechanism to simulate the effect of EUV radiation on Ru mirror surface<sup>2-4</sup>. Most of these studies involve injection of different hydrocarbons into the test chamber to amplify the existence of hydrocarbons<sup>4</sup>. In fact, the residual hydrocarbons cannot not be avoided in EUV lithography (EUVL) systems<sup>5</sup>, although these hydrocarbons can be significantly reduced by hard baking an ultrahigh vacuum (UHV) chamber. This is, however, not a choice for EUVL vacuum chamber to avoid heat induced degradation of the EUV optics<sup>6</sup>. Heating of MLM scan initiate a diffusion assisted interlayer mixing, leading to the degradation in mirror reflectivity<sup>7</sup>.

In this investigation we studied the effect of low energy electrons bombardment induced carbon contamination and oxidation of Ru mirror surfaces in vacuum environment similar to EUVL chamber. The real-time contamination caused by native hydrocarbons in the chamber (i.e., without injecting foreign hydrocarbons) is studied using *in-situ* X-ray photoelectron spectroscopy (XPS) and correlated with change in EUV reflectivity (EUVR).

## 2. EXPERIMENTAL DETAILS

A 50 nm thick mirror like Ru film coated on *p*-type Si (100) wafer with  $1 \times 1 \text{ cm}^2$  size was initially sputter cleaned by 2 keV  $\text{Ar}^+$  for 30 min (beam current of  $\sim 0.5 \mu\text{A}$ ) in a mildly baked UHV chamber (pressure  $\sim 2 \times 10^{-8}$  Torr) at our materials characterization laboratory IMPACT at Purdue University<sup>8</sup> (Figure 1). This UHV system is equipped with a suite of *in-situ* diagnostic tools for surface analysis including XPS, Auger electron spectroscopy, ion scattering spectroscopy, and EUVR<sup>8</sup>.

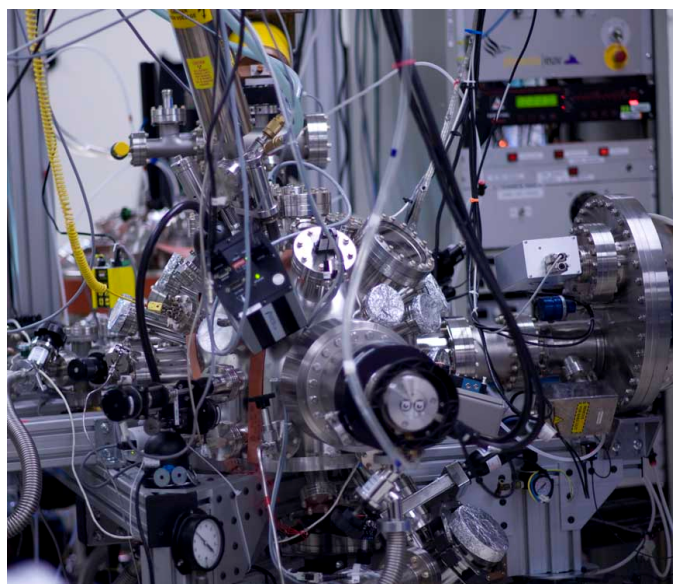


Figure 1: Photo of the IMPACT facility at Purdue University. The system is equipped with a suite of *in-situ* diagnostic tools for surface analysis including XPS, AES, ISS, EUVPS and EUVR.

Low energy electron bombardment of the Ru mirror surface was done using an electron gun. The sample was continuously bombarded for 510 min with a 100 eV electron beam, which is considered to be equivalent to EUV irradiation<sup>4</sup>, giving a current of about 45 nA. During the electrons bombardment high-resolution XPS spectra of the Ru mirrors surface were systematically recorded at different times to follow the changes in surface chemical properties. The XPS measurements were performed using an  $\text{Al-K}_\alpha$  radiation source ( $h\nu = 1486.6 \text{ eV}$ ). Photoelectrons emitted at  $45^\circ$  from the sample surface were analyzed with a PHOIBOS-100 hemispherical electron analyzer. Calibration of binding energy (BE) scale with respect to the measured kinetic energy was made using the  $\text{Au } 4f_{7/2}$  line at 84.00 eV<sup>9</sup>.

Grazing incidence EUVR of the Ru films has been investigated using Phoenix EUV source<sup>10</sup> that emits light in the range of (12.5-15) nm with a peak at 13.5 nm (92 eV), and two calibrated EUV photodiodes (PDs, International Radiation Detectors, Inc.).

## 3. RESULTS AND DISCUSSION

XPS spectra for examining the surface properties of Ru surfaces during continuous low energy (100 eV) electron bombardment have been recorded and analyzed to study the changes in chemical composition of the surface. Such changes are expected due to secondary electrons induced dissociation of water and hydrocarbons molecules adsorbed at Ru mirror surface<sup>6</sup>. Figure 2 shows the XPS spectrum of Ru 3d region of Ru mirror after sputter cleaning and before starting the electron bombardment. As shown in Fig. 2 the two main peaks are representing the Ru  $3d_{3/2}$  and Ru  $3d_{5/2}$  doublet. Pure state of Ru was found to be the major component of the sample surface with two peaks situated at 280.1 eV for  $\text{Ru}^0 3d_{5/2}$  and at 284.2 for  $\text{Ru}^0 3d_{3/2}$ . The oxide state of ruthenium was found at the

higher binding energy side of the pure Ru peaks positioned at 280.8 eV for  $\text{Ru}^{+n}3d_{5/2}$  peak and at 284.9 eV for  $\text{Ru}^{+n}3d_{3/2}$ , these two peaks are most likely representing the  $\text{RuO}_2$  according to their peak positions<sup>4,9</sup>. Analyzing the  $\text{Ru}3d$  region is always a challenging task due to the presence of  $\text{C}1s$  peak interfered with  $\text{Ru}3d_{3/2}$  peak, we address this issue by using the intensity ratio of  $\text{Ru}3d_{5/2}$  to  $\text{Ru}3d_{3/2}$  peaks by a factor of 1.5<sup>9</sup>. After applying signal intensity ratio constraint another peak positioned at 284.6 eV was needed to be added which represent the  $\text{C}1s$ line<sup>4,9</sup>. Asymmetric lines shapes were used for all spectral lines, typical fitting components after subtracting the background are found to well reproduce the experimental data.

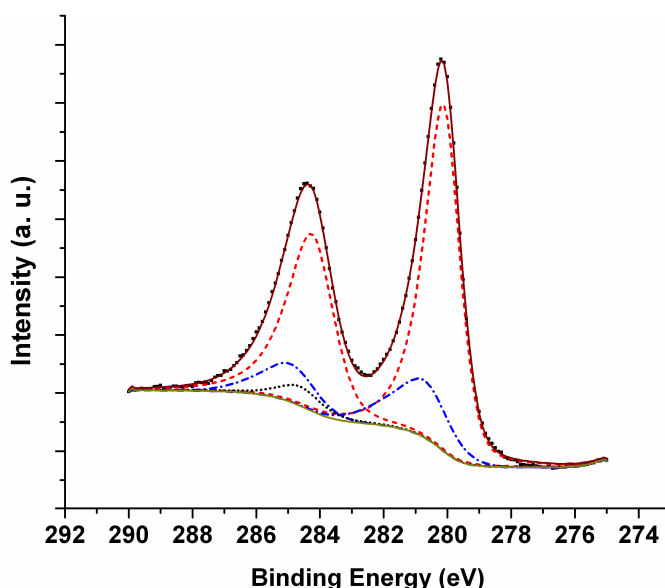


Figure 2: XPS spectra of Ru mirror Ru  $3d/\text{C}1s$  region after sputter cleaning. XPS spectra were fitted with asymmetrical peaks. The fitting components for  $\text{Ru}^0$  peaking at 284.2 eV and 280.1 eV (dashed line), for  $\text{RuO}_2$  peaking at 284.9 eV and 280.8 eV (dash dot line), for  $\text{C}1s$  situated at 284.6 eV (dotted line).

$\text{O}1s$  region was also analyzed to track the presence of water at the ruthenium mirror surface (Fig. 3). In fact, we found the best fitting of the  $\text{O}1s$  region can be obtained using three components as shown in Fig. 3 where the peaks at 533.2 eV, 531.7 eV, and 530.1 eV are representing water ( $\text{H}_2\text{O}$ ), hydroxyl ( $\text{OH}$ ) radicals, and  $\text{RuO}_2$  molecules<sup>9</sup> respectively. In order to follow the chemical reactions dynamics on Ru surface due to adsorption and/or dissociation of gaseous molecules under electron bombardment, we have carried out EUV reflectivity (EUVR) and XPS studies at both  $\text{Ru}3d$  and  $\text{O}1s$  regions with a 15 min interval in the first hour of irradiation and then every 60 min.

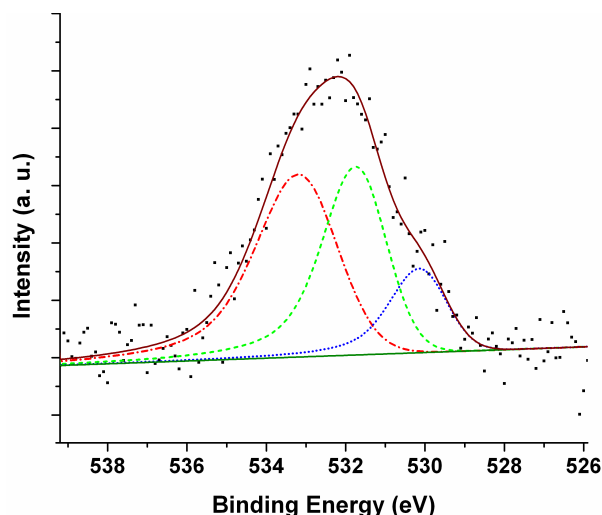


Figure 3: XPS spectrum of Ru mirror O1s region right after sputtering. The fitting component for  $\text{RuO}_2$  peaking at 530.1 eV (dotted line), for OH peaking at 531.7 eV (dashed line), and for  $\text{H}_2\text{O}$  peaking at 533.2 eV (dash-dotted line)

Detailed XPS analyses show continuous decrease in  $\text{H}_2\text{O}$  on the Ru mirror surface after starting the electrons irradiation (see Fig. 4). It is important to note that the sputter cleaning process was stopped 20 min before starting the irradiation process, this period of time was enough for the water molecules to reach saturation in concentration at the Ru mirror surface in high vacuum conditions, the continuous decrease of water is explained by the continuous dissociation process of water molecules due to electrons bombardment<sup>6</sup>. The dissociation of molecules due to electron bombardment can be direct interaction between the incident electrons which is in our case 100 eV with the bonds between atoms (i.e., with the electrons that are shared between two atoms in covalent bond), or due to the interaction between the SE that are generated at the Ru surface during the slowing down cascade of incident electrons<sup>6</sup> with atomic bonds. Here it should be mentioned that these secondary electrons has a higher interaction cross-section (lower kinetic energy) and higher in numbers, but for these SE to be effective in molecules dissociation they have to have sufficient energy greater than the binding energy of the atomic bonds. It is also shown in Fig.4 that the concentration of OH radical is generally decreased with time which also denotes a dissociation process with an exception of some increase noticed between (60-180) min of starting the electrons bombardment, this exceptional increase is most likely due to a reaction between free oxygen and free hydrogen as they accumulate at the surface as a result of a continuous dissociation process of water and hydrocarbons in addition to the OH produced directly by dissociation of water molecules.

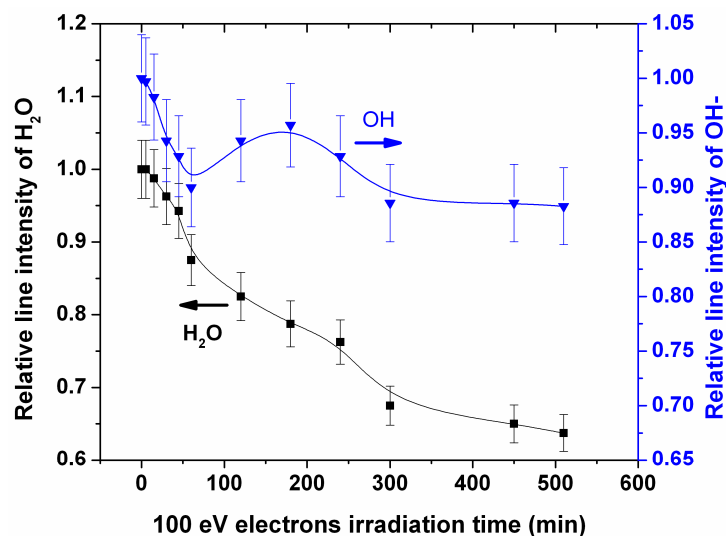


Figure 4: The changes in relative line intensity of H<sub>2</sub>O (left ordinate) and OH (right ordinate) with respect to electrons irradiation time.

It was found also that during the first hour of the experiment the carbon increased dramatically by about 18%. After this initial jump, carbon concentration was found to increase in slower trend at a rate of 1.5 % per hour (Fig.5). The rabid rise in carbon concentration in the first hour is most likely due to the direct adsorption of hydrocarbons on the Ru surface, whereas the slow but linear increase in carbon concentration is associated with the accumulation of free carbon atoms on the Ru surface during electron irradiation due to dissociation of hydrocarbons. On the other hand, it was found that the Ru 3d<sub>5/2</sub> peak intensity is reduced exponentially over the entire period of electron bombardment as shown in Fig. 5. The decrease in intensity of Ru 3d<sub>5/2</sub> represents the reduction in signal due to the surface coverage due to the adsorption of gaseous molecules, such as hydrocarbons and other gaseous contaminants on Ru surface were adsorbed early during the first 60 min, and due to mainly the deposition of free carbon atoms on the Ru surface via decomposition of hydrocarbons during electrons irradiation after 60 min of starting the irradiation process<sup>4</sup>.

To estimate deposited carbon thickness, We use the attenuation equation of Ru 3d<sub>5/2</sub> photoelectron signal (in the time range between 60 to 510 min in Fig. 5):  $I = I_0 \exp(-d/\lambda \cos\theta)$ <sup>4</sup>, where  $I$  is the Ru 3d<sub>5/2</sub> line intensity after carbon contamination,  $I_0$  is the initial Ru 3d<sub>5/2</sub> line intensity,  $d$  is the carbon thickness in nm,  $\lambda$  is the elastic scattering mean free path of electrons when passing through scattering medium, in our case  $\lambda = 2.8 \text{ nm}$ <sup>4</sup>, and  $\theta$  is the emission angle (i.e. 45°). This calculation is based on an assumption of a uniform deposition of carbon in the form of graphite with a density<sup>28</sup> of 2.26 (g/cm<sup>3</sup>). The estimated carbon thickness is summarized in Fig. 6 showing an almost linear increase in thickness to about 2.5 Å with a rate of 0.34 Å/hr.

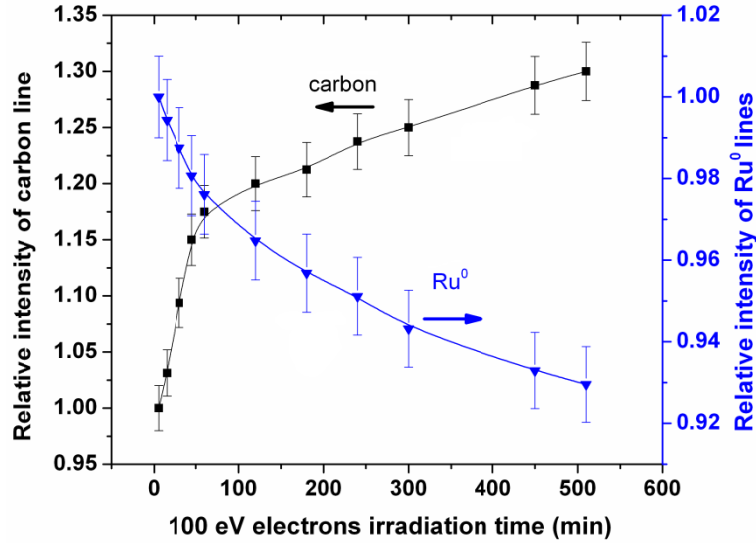


Figure 5: The reduction in pure Ru  $3d_{5/2}$  relative line intensity (right ordinate) and the relative carbon content (left ordinate) with respect to electrons irradiation time

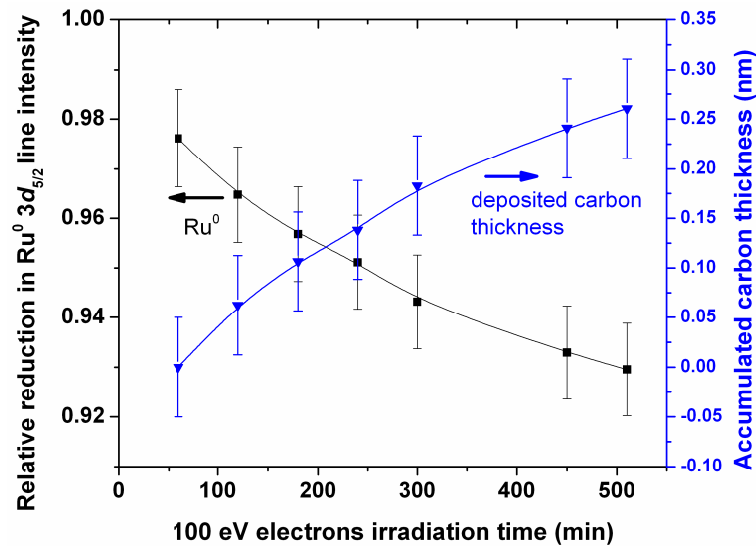


Figure 6: The changes in Ru  $3d_{5/2}$  relative line intensity (left ordinate) and the accumulated carbon thickness (right ordinate) with respect electrons irradiation time

The change in Ru-oxide line intensity with time is shown in Fig. 7. As can be seen,  $\text{RuO}_2$  is decreasing at rate and trend that is approximately similar but not identical to the pure Ru line. This signifies that a slight oxidation or reduction reactions of Ru is taking place during the electron bombardment. Furthermore, we followed the ratio of  $\text{RuO}_2$  to  $\text{Ru}^0$  line intensities during the electron irradiation time (Fig.7) that shows in general an increase in the concentration of  $\text{RuO}_2$  phase over Ru pure phase that indicates little or insignificant oxidation. Such oxidation can be justified by the dissociation of water molecules that yield free oxygen atoms ready to react spontaneously with other atom including  $\text{Ru}^6$ .

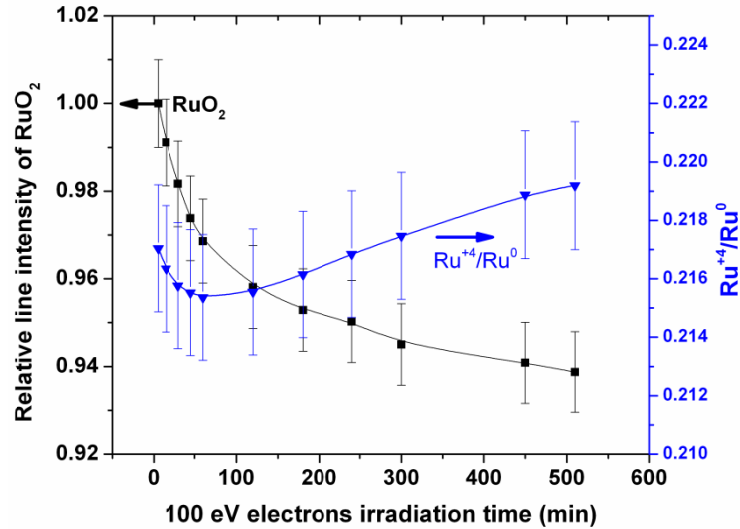


Figure 7: The changes in relative line intensity of  $\text{RuO}_2$  (left ordinate) and the changes in the ratio of  $\text{RuO}_2$  to  $\text{Ru}^0$  line intensities (right ordinate) with respect to electrons irradiation time

Finally, the corresponding EUVR of the Ru surface at a grazing angle of  $\sim 15^\circ$  was not found to be changed significantly during a 510 min of electrons bombardment as shown in Fig.8. Here it should be mentioned that although the thickness of carbon contamination deposited at the Ru mirror surface approach to a single monolayer, the reduction in EUVR was not significant, this finding is in agreement with previous observations and measurements<sup>1</sup>.

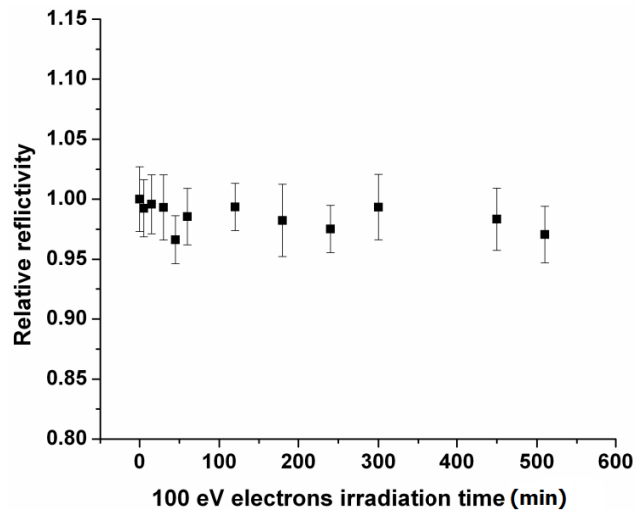


Figure 8: The changes in Ru mirror relative EUV reflectivity with respect to electrons irradiation time

#### 4. CONCLUSIONS

The changes in chemical composition of the Ru mirror surface during 100 eV electron bombardment have been studied using XPS. The contamination at the mirror surface is basically caused by residual impurities, especially hydrocarbons in a mildly baked chamber. Detailed XPS analyses show a decrease in  $\text{H}_2\text{O}$  concentration caused by

electrons assisted dissociation of water molecules. Moreover, a rapid increase in carbon concentration up to 18 % during the first one hour is explained on the ground of adsorption of hydrocarbons at mirror surface, while slow but linear increase in carbon concentration was due to deposition of free carbon atoms via electron-assisted dissociation of residual hydrocarbons. Accumulated carbon layer thickness was calculated to be of about 2.5 Å with a deposition rate of about 0.34 Å/hr. Moreover, the variation in RuO<sub>2</sub> concentration was found to be approximately similar to that for pure Ru, but Ru<sup>+4</sup>/Ru<sup>0</sup> line intensity ratio denotes minor oxidation of the Ru mirror surface during electrons bombardment. However, a change in grazing angle EUVR of the Ru surface was not found to be significant during the 510 min of electrons bombardment.

## ACKNOWLEDGEMENTS

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