Contamination Control in The Projection Optics Environment

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1 Introduction

Mo/Si multilayer mirrors with a ruthenium capping layer have, to date, been shown as the best candidates to meet the lifetime requirement for the projection optics of an EUVL tool. The reflectivity of the multilayer mirrors is degraded by oxidation and carbon growth on the mirror surfaces and is directly related to the level of contamination in the vacuum environment and in particular to the partial pressures and surface chemistry of the various species present. The behaviour of hydrocarbon species on the mirror surface can vary significantly depending on the chemical type and the presence of secondary electrons, induced by the incident radiation.

We have investigated the uptake and cracking of different hydrocarbon species on single crystal Ru(0001) under typical, simulated, EUV incident photon conditions, by the use of low energy electrons. Alkanes, alkenes, aromatics and oxygenates have been studied and shown to have quite different adsorption characteristics. Results suggest that in order to meet the 30,000 hour lifetime requirement a typical partial pressure threshold of approximately 1×10^{-13} mbar is required for 'sticky' or harmful species and 1×10^{-10} mbar for benign or non-sticky species.
We will also update on the previously reported PPT detection level selective hydrocarbon sensor.

2 Experimental Set-Up

- Surface science measurements were carried out in a UHV chamber, see figure 1, operated at a base pressure of $< 5 \times 10^{-10}$ mbar.
- The spectrometer is equipped with:
  - VSW water-cooled x-ray source, with dual Al/Mg anode
  - VSW HA100 concentric hemispherical analyser
  - VG Quartz quadrupole mass spectrometer, allowing the monitoring of both residual and dosed gases within the chamber.
- A Ru(0001) single crystal, polished on both sides, was installed in the chamber and cleaned by cycles of Ar+ sputtering (1 keV, 4 μA) followed by annealing at 1000 K, until no impurities were detectable by XPS.
- Binding energies were calibrated against the Ru $3d_{5/2}$ peak at 280.1 eV.

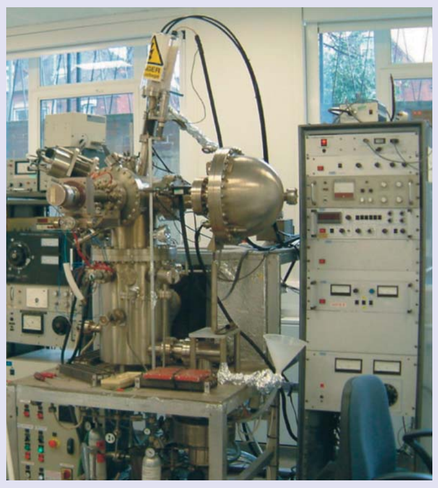

Figure 1. X-ray Photoelectron Spectrometer

3 Contaminant Dosing

- Contaminants were dosed directly onto the sample through a 6mm diameter collimator tube, thus allowing high partial pressures of gases to be dosed locally at the sample surface, without exposing the rest of the equipment to high, and potentially deleterious, gas pressures.
- Each contaminant was dosed at a pressure of 3.5×10^{-7} mbar (corrected for ionisation and collimator tube enhancement factor).
- n-pentane (99+ %), n-hexane (99+ %), n-heptane (99+ %), n-octane (99+ %), toluene (99.8 %), 1-butene (99.9 %), n-butane (99+ %), propane (99.95 %) were used. All liquids were purified using repeated freeze-pump-thaw cycles.

E^- Gun Exposure Conditions

- The incident electron energy was 87.5 eV resulting in a measured sample drain current of -550mA. The power density delivered to the sample was 2.1 mW/mm^2.
- Taking into account the electron yield for ruthenium at 13.5nm (92.5 eV) of 0.021 and the sample size (0.79 cm^2) the equivalent power density under EUV photon irradiation can be calculated as being 174 mW/mm^2.
- Note, the sample temperature during deposition was 343 K

4 Electron Assisted Carbon Growth

- Figure 2 shows electron assisted uptakes of various hydrocarbons on the Ru (0001) surface. Carbon film thickness is plotted as a function of dose time.
- Short-chain alkanes, up to n-heptane (C_7), are observed to have a negligible carbon growth rate, while toluene and n-octane contaminate the surface significantly.
- It is proposed that for short chain alkanes (C_3 to C_7) and 1-butene the availability of physisorbed hydrocarbon on the sample surface is limiting the subsequent dissociation and deposition of carbon.

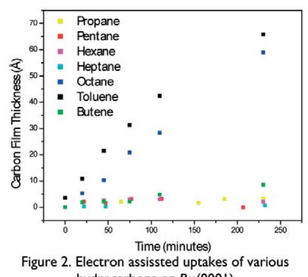

Figure 2. Electron assisted uptakes of various hydrocarbons on Ru(0001)

- Table 1 shows calculated surface residence times as a function of chain length. The surface lifetime of the hydrocarbon is the dominant effect responsible for the increase in carbon growth rate with chain length.

Chain length, N	ΔH°_{ad} (kJ mol^{-1})	Residence time (s)
5	-60.7	1.8×10^{-4}
6	-69.0	3.2×10^{-3}
7	-78.2	8.1×10^{-2}
8	-83.1	4.5×10^{-1}

5 Carbon Removal with Oxygen or NO

- Using toluene graphitic-like carbon films were deposited on Ru(0001) to thicknesses of 3.2 nm for the oxygen experiment and 2.4 nm for the NO based removal.
- In the absence of electron irradiation there was no observed change in carbon film thickness in the presence of either nitrogen monoxide (NO) or oxygen.
- Under e^- stimulation carbon removal was observed as shown in figures 3 and 4.
- O_2 is efficient at removing carbon films but does give rise to oxide growth on the Ru surface.
- Similar carbon removal rates are observed for NO cleaning as for O_2 though.

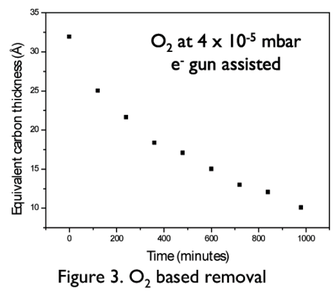

Figure 3. O_2 based removal

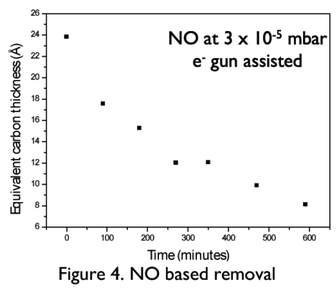

Figure 4. NO based removal

6 Oxidation Growth via H_2O and Subsequent Removal with CO

- Figure 5 shows a series of experiments performed on a cleaned Ru(0001) surface exposed to a water pressure of 4×10^{-5} mbar.
- In the absence of electrons (0 to 540 mins) there is negligible oxide growth, under e^- stimulation (540 to 980 mins) significant oxidation occurs.
- After the formation of the surface oxide layer CO was introduced at 4×10^{-5} mbar with e^- irradiation and a reduction of the surface oxide layer was observed.

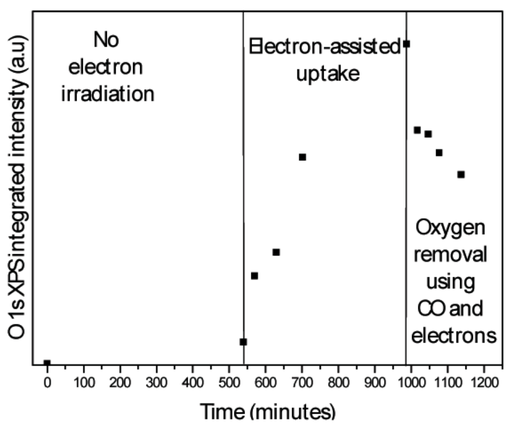

Figure 5. Electron assisted uptake of H_2O and subsequent oxide removal with CO

7 Conclusions

- Single crystal Ru(0001) has been used as a surrogate EUV multi-layer mirror surface for the investigation of carbon and oxygen growth under simulated EUV exposure conditions, achieved by direct low energy electron stimulation.
- Electron assisted deposition of carbon on the ruthenium surface shows that simple alkane chains, up to C_7, are quite benign on the Ru surface, however longer chains and more functionalised molecules such as toluene have higher sticking coefficients and are consequently more detrimental to the mirror.
- The carbon growth characteristics follow a similar trend to that observed during previous experiments on the Pt surface of the previously reported hydrocarbon sensor, see ref 1.
- The partial pressure threshold to meet the 30,000 hr lifetime requirement is calculated to be $< 5 \times 10^{-13}$ mbar for toluene or other similarly harmful species and $< 2 \times 10^{-10}$ mbar for the more benign short chain alkane species.
- Both NO and O_2 under electron irradiation are effective chemicals for oxidative removal of carbon from a Ru(0001) surface.
- The build up of surface oxygen, specifically that produced by H_2O, can be inhibited/reversed by supplying CO in the presence of electron irradiation.

Reference
1. PPT (10^{-9} mbar) Sensor for Trace Detection of Organic Contamination in Vacuum Environments, 3rd EUVL Symposium, Miyazaki, 1- 4 November 2004

5th EUVL Symposium, Barcelona, Spain (15 - 18th October 2006)

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