EUVL multilayer mirror oxidation modeling

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1. Introduction

Oxidation is one major cause which degrades the reflectivity of the multilayer mirrors used for optics of EUV exposure tools. To estimate the change of reflectivity due to oxidation, modeling of the multilayer mirror oxidation was becoming greater importance.

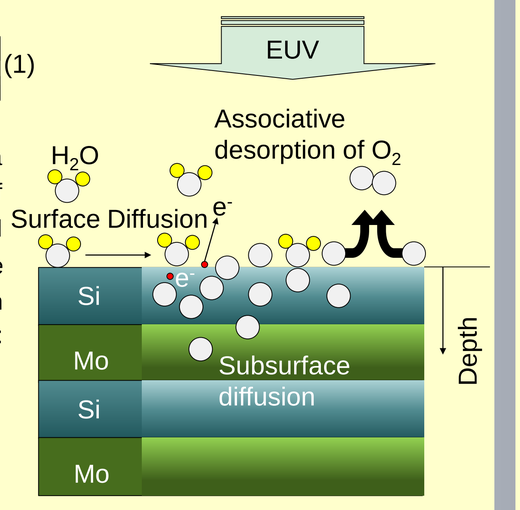
Bajt, et al. experimentally evaluated the oxidation of the EUV multilayer mirrors with Ru cap using ALS at Lawrence Berkeley National Laboratory [1] . They compared the oxidation of EUV multilayer mirror cased by electron beam irradiation and EUV irraditation [2] . Klebanoff, et al. proposed the mitigation of oxidation by use of the ethanol [3] . Hollenshead and Klebanoff modeled EUV/H_2O oxidation of Ru coatings [4] . They detailed the oxidation of Ru coatings causing by H_2O.

We have modeled the oxidation of the EUV multilayer mirror based on these prior studies. We have evaluated EUVL multilayer mirror oxidation model comparing its prediction with experimental data.

2. Multilayer mirror oxidation model

Rate equation for adsorbed H_2O molecules

$$\frac{dN_{ad}^{H_2O}}{dt} = s\Gamma_{mol} - N_{ad}^{H_2O}\left[\frac{s\Gamma_{mol}}{N_{ad}^{\max}} + \frac{1}{\tau} + \sigma_{ph} I_0 (1+R) + \sigma_{SE} N_{SE}(D)\right] + \frac{1}{r}\frac{\partial}{\partial r}\left[D_{SD} r \frac{\partial N_{ad}^{H_2O}}{\partial r}\right] \quad (1)$$



$N_{ad}^{H_2O}$: the number density of adsorbed water molecules per area (molecule/ Å^2), s : condensation coefficient, Γ_{mol} : impingement rate of water molecules from the vapor, $N_{ad}^{\max}$: maximum allowable adsorbed water density, τ: residence time. The central terms in Eq. (1) shows the rate of dissociation of water molecules as shown in Eq. (3). Last term in Eq. (1) shows surface diffusion. r: distance from EUV beam center, D_{SD}: Diffusion coefficient of surface diffusion.

Rate equation for dissociated oxygen atoms

$$\frac{dN_{ad}^{O}}{dt} = \left[1 - \frac{N_{ad}^{O}}{N_{ad}^{O_\max}}\right]\left[\sigma_{ph} I_0 (1+R) + \sigma_{SE} N_{SE}(D)\right] N_{ad}^{H_2O} - D_{bulk(1)} \frac{\partial N_{diff(1)}^{O}}{\partial z}\Big|_{z=0} \quad (2)$$

$$\frac{molecules_dissociated}{time} = \left[\sigma_{ph} I_0 (1+R) + \sigma_{SE} I_{SE}(D)\right] N_{ad}^{H_2O} \quad (3)$$

The central term in Eq. (2) shows the rate of dissociation of water molecules as shown in Eq. (3) .

I_0 : photon flux (photon/Å^{2}s^{-1}), σ_{ph} : relevant cross section for directphoton-induced dissociation (Å^2/molecule)、R : mirror reflectance $N_{ad}^{H_2O}$: number of adsorbed water molecules per area(molecule/Å^2). $I_{SE}(D)$: relevant cross section for electron-induced dissociation (Å^2/molecule). D : depth, N_{ad}^{O} : number density of oxygen atoms, $N_{ad}^{O_\max}$: maximum allowable concentration of oxygen as oxide.

Diffusion into optics

Here we consider the multilayer structure consists of m layers. $M_n (n = 1,2,3\cdots m)$ is the element of of the n'th layer. The diffusion coefficient of each layer is $D_{bulk(n)}$. $N_{diff(n)}^{O}$ is density of oxygen atom diffusing into n'th layer. Eq. (4) shows the diffusion.

$$\left.\begin{aligned}
\frac{dN_{diff(1)}^{O}}{dt} &= \frac{\partial}{\partial z}\left[D_{bulk(1)} \frac{\partial N_{diff(1)}^{O}}{\partial z}\right] && at \quad 0 \le z < z_1 \\
\frac{dN_{diff(2)}^{O}}{dt} &= \frac{\partial}{\partial z}\left[D_{bulk(2)} \frac{\partial N_{diff(2)}^{O}}{\partial z}\right] && at \quad z_1 < z < z_2 \\
\frac{dN_{diff(3)}^{O}}{dt} &= \frac{\partial}{\partial z}\left[D_{bulk(3)} \frac{\partial N_{diff(3)}^{O}}{\partial z}\right] && at \quad z_2 < z < z_3 \\
&\vdots \\
\frac{dN_{diff(m)}^{O}}{dt} &= \frac{\partial}{\partial z}\left[D_{bulk(m)} \frac{\partial N_{diff(m)}^{O}}{\partial z}\right] && at \quad z_{m-1} < z \le z_\infty
\end{aligned}\right\} \quad (4)$$

Initial and boundary conditions

Eq. (5) shows the initial condition.

$$N_{diff(1)}^{O} = N_{diff(2)}^{O} = N_{diff(3)}^{O} = \cdots = N_{diff(m)}^{O} = 0 \quad at \quad t = 0 \quad (5)$$

Eq. (6), (7) and (8) show the boundary condition. Eq. (8) derives from mass conservation of oxygen. l_n is mono layer thickness of the oxide which is determined by Eq. (9) where the oxide of the element M_n is $M_n O_{x_n}$ and the molecular volume of $M_n O_{x_n}$ is v_n. s is solubility.

$$s l_1 N_{diff(1)}^{O} = N_{ad}^{O} \quad at \quad z = 0 \quad (6)$$

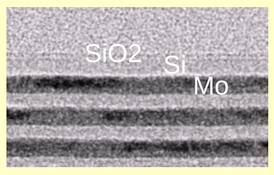
$$N_{diff(m)}^{O} = 0 \quad at \quad z = z_\infty \quad (7)$$

$$\left.\begin{aligned}
l_1 N_{diff(1)}^{O} &= l_2 N_{diff(2)}^{O} && at \quad z \to z_1 \\
l_2 N_{diff(2)}^{O} &= l_3 N_{diff(3)}^{O} && at \quad z \to z_2 \\
l_3 N_{diff(3)}^{O} &= l_4 N_{diff(4)}^{O} && at \quad z \to z_3 \\
&\vdots \\
l_{m-1} N_{diff(m-1)}^{O} &= l_m N_{diff(m)}^{O} && at \quad z \to z_{m-1}
\end{aligned}\right\} \quad (8)$$

$$l_n = \left(v_n / x_n\right)^{1/3} \quad (n = 1,2,3\cdots m) \quad (9)$$

3. Multilayer mirror structure

Si cap sample TEM observation (initial)

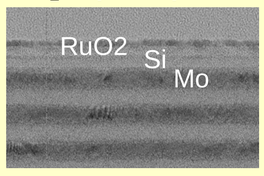


Initial reflectivity= 66.7%

Si cap model (initial)

SiO2, 30.4Å
Si, 23.1Å
MoSi2, 12.5Å
MoO2, 0Å
Mo, 18Å
MoSi2, 12.5Å
Si, 26.8Å
MoSi2, 12.5Å
Mo, 18Å

RuO_2 cap sample TEM observation (initial)



Initial reflectivity= 65.8%

RuO_2 cap model (initial)

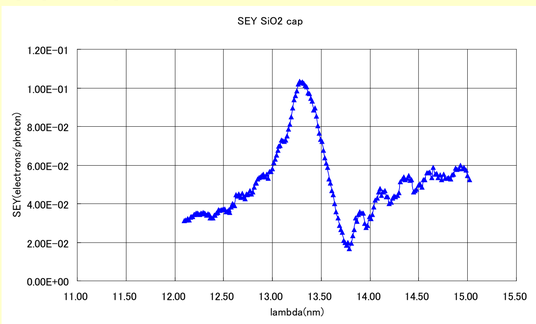
RuO2, 13.7Å
SiO2, 14.0Å
Si, 27.3Å
MoSi2, 12.5Å
MoO2, 0Å
Mo, 18Å
MoSi2, 12.5Å
Si, 26.8Å
MoSi2, 12.5Å
Mo, 18Å

Each multilayer model was constructed by XPS result, measured reflectance and TEM observation. "Initial" means "as-deposited" .

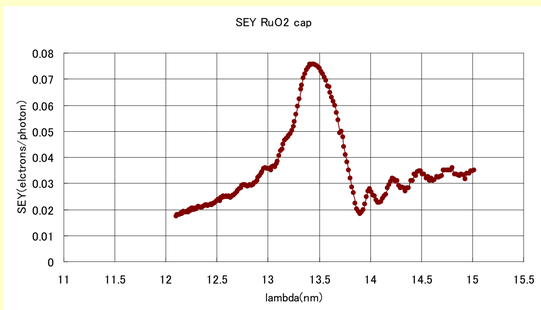
4. SEY (Secondary electron yield)

Spectral SEY was measured for calculation of secondary electron generation. Measurement was done experimentally using beam BL-11D at Photon Factory in KEK (High Energy Accelerator Research Organization).

Si cap (initial)



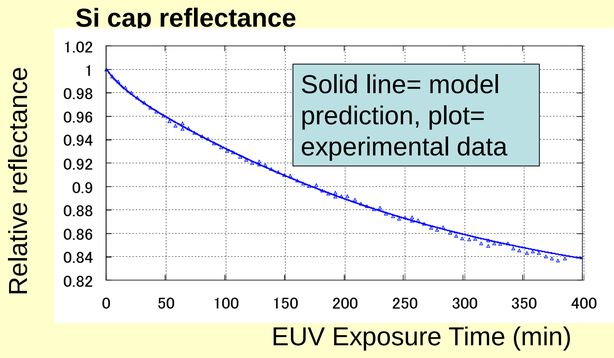
RuO_2 cap (initial)



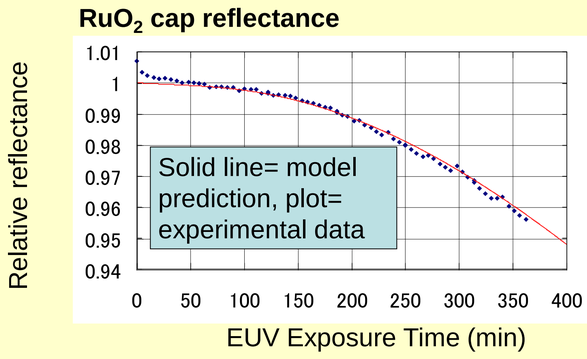
5. Model fit to experimental data and material properties

The exact value of "diffusion coefficient" and "adsorption energy of water" of multi-layers are not available. So we fit the model output (reflectance) to the experimental data (reflectance) by tweaking "diffusion coefficient" and "adsorption energy of water" as parameters. Model fit was done at one experimental condition: EUV irradiance=80mW/mm^2, EUV exposure duration= 6hour, H_2O partial pressure=1mPa and EUV beam diameter=690μm for both Si cap and RuO_2 cap cases. Eventually we obtained estimated "diffusion coefficient" and "adsorption energy of water" as shown in Table 1. In this table, we have also listed literature values [5] , [6] and they are very close to our estimated values. This would reinforce the validity of our multilayer mirror oxidation model.

Si cap reflectance

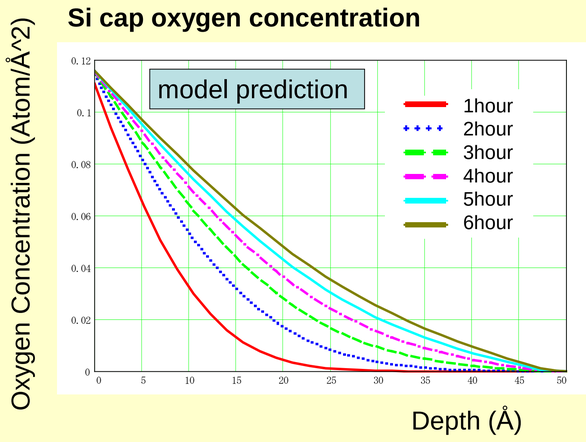


RuO_2 cap reflectance

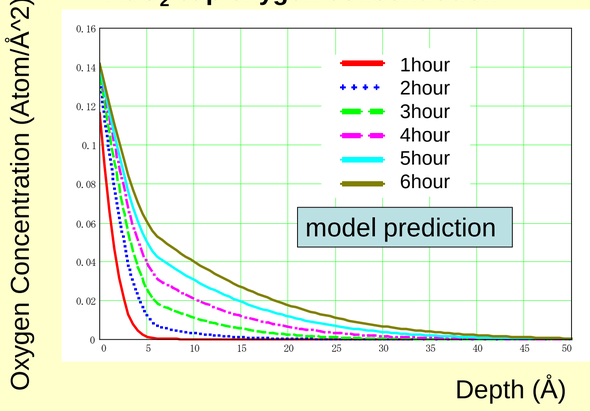


See poster OP-05 "Oxidation durability of the Mo/Si multilayers with an oxide capping layer" by T. Yamaguchi

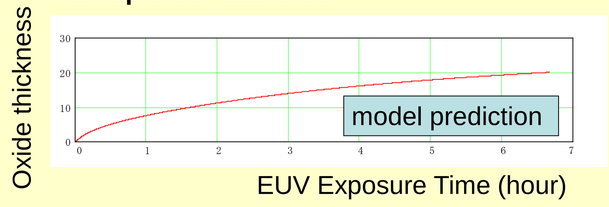
Si cap oxygen concentration



RuO_2 cap oxygen concentration



Si cap oxide thickness



RuO_2 cap oxide thickness

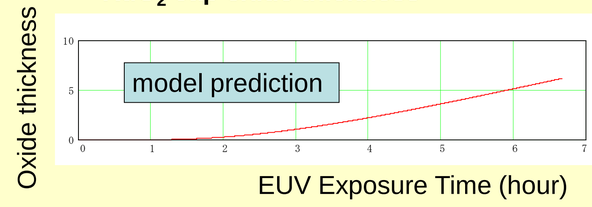


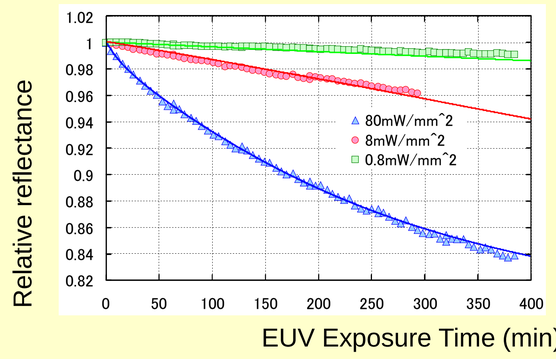
Table 1

Material	Adsorption energy of H_2O molecule (kJ/mol)	Diffusion coefficient of oxygen (m^2/sec)
SiO_2	50.5 (≈50 as quartz [5])	1.48E-22
RuO_2	51 (51.3 as metal Ru [6])	7.3E-24
Mo	To be obtained	3.8E-24

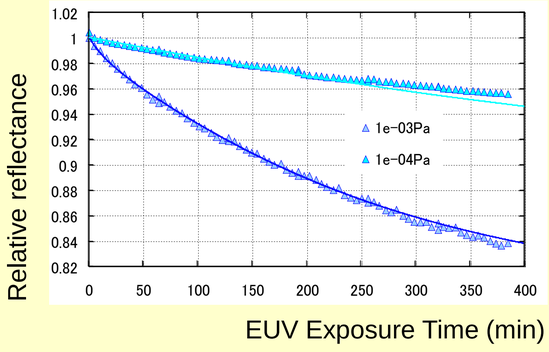
6. Model prediction for various experimental conditions

Using the estimated "Diffusion coefficient" and "adsorption energy", we compared the model prediction with experimental data obtained in other experimental conditions shown below. Good agreement between model predictions and experimental data has been successfully verified.

6.1 EUV irradiance dependence (Si cap, H_2O partial pressure=1mPa)



6.2 H_2O partial pressure dependence (Si cap, EUV irradiance=80mW/mm^2)



Solid lines= model predictions, plot= experimental data

7. Summary

-- Multilayer oxidation model successfully predicts reflection change in various experimental conditions.
-- Life time estimation of EUV optics in various conditions becomes available.

8. Acknowledgement

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9. References

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[6] S. Meng, E. G. Wang, and S. Gao, "Water adsorption on metal surfaces: A general picture from density functional theory studies," Phys. Rev. B **69**, 195404 (2004).