Electrochemically Enhanced Wet Cleaning of Ru Capping Thin Film for EUV Lithography Reflector

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We report the effective wet cleaning of a Ru thin-film surface for an extreme ultraviolet (EUV) lithography reflector by combining the passivation of the Ru layer with a surfactant [tetramethylammonium hydroxide (TMAH)] and by tuning the electrochemical interaction of the Ru surface in a propylene carbonate (PC) solution. Adding 1% TMAH to PC showed effective cleaning performance, which reduced the accumulation of carbon amounts and surface chemisorbed O species, while it does not etch or roughen Ru surfaces. It was observed that the PC + 1% TMAH solution effectively removes the residual photoresist on Ru thin films. The cleaning mechanism of PC + 1% TMAH is regarded to be a combined effect between the chemical Ru surface passivation of 1% TMAH and the electrostatic interaction between Ru surfaces and ions in the PC solution. This cleaning scheme may be extended to facilitate the elimination of carbonaceous species on the thin film or nanoparticle surfaces.

Extreme ultraviolet (EUV, \( \lambda = 13.5 \text{ nm} \)) lithography is a leading technology for future semiconductor device manufacturing. At an EUV wavelength, the projection of a beam is designed by the reflective rather than refractive optics because significant light absorption occurs at the optical lens. Therefore, reflection mirrors play a crucial role in an EUV lithography system, and achievement of optimized EUV mask mirrors is the most critical task in implanting EUV-radiation-induced oxidation of Si surfaces significantly reduces the lifetime of mirrors.

Another critical issue of top surface layers in EUV mask mirrors is the carbon deposit on the surfaces under EUV radiation as well as in air. The previous report has shown the serious adverse effects of contamination on a Ru surface with a surfactant [tetramethylammonium hydroxide (TMAH)] and by tuning the electrochemical interaction of the Ru surface in a propylene carbonate (PC) solution. Adding 1% TMAH to PC showed effective cleaning performance, which reduced the accumulation of carbon amounts and surface chemisorbed O species, while it does not etch or roughen Ru surfaces. It was observed that the PC + 1% TMAH solution effectively removes the residual photoresist on Ru thin films. The cleaning mechanism of PC + 1% TMAH is regarded to be a combined effect between the chemical Ru surface passivation of 1% TMAH and the electrostatic interaction between Ru surfaces and ions in the PC solution. This cleaning scheme may be extended to facilitate the elimination of carbonaceous species on the thin film or nanoparticle surfaces.

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surface in air and to estimate the surface roughness. Surface morphology analysis was performed using an AFM (RHK Technology, molecular imaging) operated in contact mode using a silicon nitride tip. SEM images of the AFM tips revealed a tip radius of 30–40 nm. Because the contact AFM experiment was carried out at a low load (<5 nN), the change in tip radius was ignorable.

The wet solution treatment was performed in a Pyrex container. PC (anhydrous 99.7 wt %, Sigma-Aldrich), TMAH [25 wt % in deionized (DI) water, Sigma-Aldrich] and a mixture of PC and TMAH (1–10% volume fraction of TMAH in the solution) were used for cleaning. Small samples (typically 0.25 in. diameter) were introduced into the fresh mixture for 10 min at room temperature. After that, the samples were rinsed in DI water and flushed out with N₂.

Results and Discussion

XPS analysis of Ru thin films cleaned in wet chemical solutions.— Figure 1a and b respectively represents the Ru 3d and O 1s XPS spectra for the as-deposited and cleaned 50 nm Ru thin-film surfaces on Si substrates with TMAH (25%, diluted with DI water), PC + 1% TMAH, and pure PC. The Ru 3d on the left part in Fig. 1a has two main spin-orbital splitting components of Ru 3d₅/₂ (278–283 eV) and Ru 3d₇/₂ (282–289 eV). In each Ru 3d₅/₂ spectrum, three different Ru bonding states are observed: metallic Ru₀ states at 279.8 eV, full Ru oxidation states (Ru–O₄, i.e., bulk oxides) at 280.8 eV, and Ru partial oxidation states (Ru–Oₓ, x < 4, i.e., surface suboxides) at 281.9 eV. Note the changes in peak states of C at 284.5 eV and of CHₓOᵧ at 285.7 eV.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (Color online) (a) Ru 3d and (b) O 1s XPS spectra for as-deposited and cleaned Ru thin films with TMAH, PC + 1% TMAH, and PC. In each Ru 3d₅/₂ spectrum, three different Ru bonding states are observed: metallic Ru₀ states at 279.8 eV, full Ru oxidation states (Ru–O₄, i.e., bulk oxides) at 280.8 eV, and Ru partial oxidation states (Ru–Oₓ, x < 4, i.e., surface suboxides) at 281.9 eV. Note the changes in peak states of C at 284.5 eV and of CHₓOᵧ at 285.7 eV.

In contrast to Ru surfaces cleaned with all other cleaning solutions, pure-PC-cleaned Ru shows the significant COₓHᵧ (285.6 eV) deposit on the Ru surface. This observation is very interesting when comparing the cleaning results of PC + 1% TMAH. In fact, the addition of 1% TMAH to PC seems to affect the surface reaction dramatically; i.e., significantly COₓHᵧ deposits on the Ru surfaces cleaned in pure PC solution, but effective carbon removal was observed with 1% TMAH addition in PC solution. The possible mechanism of surface reaction about this difference is discussed in detail later.

Figure 1b shows the O 1s XPS spectra for each Ru surface. Two oxidation states are deconvoluted in the spectra: full Ru oxidation states (OₓRu, i.e., bulk oxides) at 529.7 eV, the overlapped peak of Ru partial oxidation states (OₓRu, x < 4, i.e., surface suboxides), and weakly bound oxygen states at 531.5 eV. Therefore, these bonding states in the O 1s spectra are counterparts of each Ru oxidation state in the Ru 3d XPS spectra. In contrast to Ru 3dₓ/₂ XPS states, the relative ratio changes in suboxide and bulk oxide depending on the cleaning solutions are clearly distinguished. This difference is supposedly due to the presence of chemisorbed and subsurface O species. The subsurface O species are first affected by the chemical reactions between the cleaning solution and the Ru surfaces. Therefore, it can be stated that PC + 1% TMAH removed the subsurface O species significantly but removed the Ru oxides very slightly. As known from the O 1s XPS data for the as-deposited Ru samples, the native oxides with the higher subsurface O contents are present on the surface of Ru thin films. The presence of native oxide on Ru surface grown in air was reported in previous studies.

Therefore, the critical aspect of a Ru native oxide is the kinetics of oxidation in air as well as EUV radiation conditions. Although the
cleaning process successfully removes the surface oxide on Ru, it is highly possible that cleaned Ru surfaces quickly reoxidize under air exposure unless atomic level passivation on Ru surfaces is achieved. This fact also raises a very crucial aspect of Ru surface preparation for various applications in addition to EUV capping layer application. For example, the catalytic activity of Ru surfaces is greatly affected by Ru oxide formation.\textsuperscript{20,25} It is obvious that for EUV mask capping layer applications of Ru thin films, native Ru oxides should be regularly controlled by the cleaning procedure to maintain the reasonable reflectivity level of mask optics.

As shown in Fig. 1a, the O 1s XPS spectrum for the pure-PC-treated Ru also reveals a new bonding state of O—C bonds. The stoichiometric ratio of C/Ru calculated from Ru 3d XPS spectra and (right y-axis) stoichiometric ratio of C/Ru calculated from Ru 3d XPS spectra in Fig. 1. The total Ru oxide fraction including Ru—O and Ru—O\textsubscript{2} states over the Ru 3d\textsubscript{5/2} peak area hardly changes with the cleaning solutions from −1 to +8% against that in the as-deposited surface. However, changes in the suboxide fraction (i.e., O—O, O—Ru—, and O—CH\textsubscript{4} bonding states) among different cleaning solutions are apparent from 0.4 to 1. The suboxide fraction for Ru cleaned with PC is mostly ascribed to the O—C—H bonding state of the carbonaceous film deposit. Therefore, the results in Fig. 2a suggest that the suboxide layers at the very top surfaces of Ru consisting of chemisorbed O and Ru—O\textsubscript{2} bonds are removed in TMAH and PC + 1% TMAH cleaning solutions, but the bulk Ru oxide (i.e., Ru—O\textsubscript{2}) and, possibly, the partial Ru—O\textsubscript{2} bonds are retained but apparently not further oxidized in these cleaning solutions.

An important cleaning capability of a cleaning solution is to remove carbon contaminants on Ru surfaces. Figure 2b represents the relative stoichiometric ratio of C/Ru calculated from the C 1s and Ru 3d XPS peak areas considering the sensitivity factors of 0.25 for the C 1s orbital and 3.6 for the Ru 3d orbital.\textsuperscript{26} Both the TMAH and PC + 1% TMAH reveal that the effective removal of carbon contaminants decreases the stoichiometric ratio of C/Ru from 4 to 2 in the as-deposited. Although the amount of C contaminants is reduced, the relative stoichiometric fraction of C is much higher than Ru. The authors believe that these high C and low Ru stoichiometric fractions stem from the relative physical locations of chemical element distribution. In other words, C contaminants are present as the layer at more top surface regions, while Ru chemical elements exist in the films beneath carbonaceous layers, and therefore, the peak intensity of Ru is attenuated. This speculation is supported by the increased C amounts at surface regions with the angle-resolved XPS analysis in the previous study.\textsuperscript{16} The thickness of carbonaceous layers can be estimated from the attenuation of metallic Ru\textsuperscript{0} peak intensity in Ru 3d\textsubscript{5/2} XPS states using the following equation

\begin{equation}
I = I_0 \exp(-\frac{d}{\lambda \cos \theta})
\end{equation}

where \(I_0\) is the peak intensity of Ru 3d\textsubscript{5/2} for each cleaning solution, \(d\) is the thickness of the carbon layer, and \(\lambda\) is an inelastic mean free path (2.8 nm) of carbon deposit assuming a continuous graphic ML of uniform thickness (bulk density 2.26 g/cm\(^3\)).\textsuperscript{7} As a result, PC + 1% TMAH reduced the thickness of the carbonaceous layers by 1.4 nm.

PC without TMAH addition resulted in a thicker (7 nm) carbonaceous contaminant deposit with CH\textsubscript{4}O\textsubscript{2} species than that of PC + 1% TMAH solution. Therefore, it is evident that TMAH addition plays a crucial role in the change of the surface reaction of Ru in PC solution.

**Effect of TMAH addition to PC solution on the carbon removal on Ru thin films.**—To investigate the role of TMAH addition to the surface reaction in PC solution, the effect of TMAH fraction in solution has been studied, and the results are shown in Fig. 3a and b. The volume fraction of TMAH in the PC solution has been varied from 0 to 10%. Because pure TMAH shows the ability to remove surface carbon, as shown in Fig. 2, it was expected that a higher TMAH fraction in the PC solution might remove carbon contaminants more effectively. However, PC solutions with 5 and 10% TMAH addition showed the formation of CH\textsubscript{4}O\textsubscript{2} bonds (285.7 eV in Fig. 3a) on Ru surfaces, and only 1% TMAH added PC solution removed the surface C contaminants without CH\textsubscript{4}O\textsubscript{2} formation. Although the 5 and 10% TMAH + PC solution did not cause the significant carbon deposit as much as a pure PC solution, the cleaning capability of those solutions on as-deposited Ru surfaces is inferior to the PC + 1% TMAH solution.

The electrochemical reaction mechanism on Ru surfaces has been developed in methanol oxidation for fuel cell applications.\textsuperscript{27,28} Some of the studies in this field claimed that methanol oxidation reaction on Ru is dependent on pH; RuO\textsubscript{2} formation in the low pH acid solution is apparently observed but is suppressed in a high pH alkali solution.\textsuperscript{24,28} The corresponding Ru surface electrochemical scheme against pH is found in Ref. 29, where RuO\textsubscript{2} formation dominates at low pH regions through the following reaction

\[
\text{RuO}_2^- + 4\text{H}^+ + 2e^- \rightarrow \text{Ru}_2\text{O}_7^2\text{H}_2\text{O}
\]

However, in high pH solutions, the reverse reaction occurs to dissolve RuO\textsubscript{2} into the solution as RuO\textsubscript{2}\textsuperscript{2-}. Although RuO\textsubscript{2} is dissolved into an alkali solution based on Reaction 2, another main species on RuO\textsubscript{2}, RuOH, is stably present at all pH ranges and easily repeats continuous adsorption and desorption and, therefore, functions as the precursors on RuO\textsubscript{2} to capture other molecules such as CO\textsubscript{2}H\textsubscript{2} at the surfaces.\textsuperscript{27,30,31} Although the reaction that causes RuO\textsubscript{2} formation or dissociation can be controlled by the surface potential change,\textsuperscript{25} the treatments with cleaning solutions in this study resulted in the RuO\textsubscript{2} (bulk Ru oxide) thickness at the very constant level regardless of pH variations across the solutions (13.5 for TMAH, 7.5 for PC + 1% TMAH, and 8.5 for PC + 10% TMAH) except in pure PC solution.
Ru oxide surfaces captures HCO₃⁻ the PC solution.27,29

...been developed as a cleaning scheme in integration circuit manufac-

turing, and this approach has utilized the combined effect of passivation action and electrochemical interaction of solvents to increase the solubility of contaminants particularly at low-κ dielectric surfaces.27 The surface carbon recontamination in air after the proposed cleaning is another crucial consideration for practical application. After the wet cleaning with PC + 1% TMAH solution, the carbon concentration was hardly increased (<1%) even in air after 1–2 weeks based on the XPS analysis. However, it is obvious that the rate of carbon recontamination under the EUV exposure would be much faster in time than just in air.

It is a remarkable finding that 1% TMAH can chemically passi-
vate Ru surfaces without any Ru surface corrosion while removing the surface carbon and oxygen species because Ref. 21 reported that TMAH addition to the organic solvents tends to etch low-κ dielectrics significantly. Thus, this chemical passivation of Ru surfaces enables PC to enhance the carbon removal caused by the electro-

chemical interaction. However, the higher TMAH fraction at 5–10% seems to degrade the chemical passivation of Ru in the solution, which causes the slight CH₂O₃ deposits, as shown in Fig. 3a. Therefore, it is concluded that the 1% TMAH addition optimized the chemical passivation of Ru surfaces in the PC solution. In contrast to a pure PC solution, TMAH residues were not present on Ru surfaces. Although TMAH is immiscible in a PC solution, it is an aqueous solvent that dissolves in water. Therefore, it is suggested that the final cleaning step consisting of DI water rinse and N₂ drying successfully removed the residual TMAH from Ru surfaces.

To confirm the surface morphology and etching effect of each cleaning solution, AFM (Fig. 4) has been performed. Ru surfaces cleaned with pure TMAH and 1% TMAH + PC did not show the noticeable surface morphology changes against that of as-deposited Ru surfaces. The root-mean-square surface roughness levels are constant at 1.4–1.5 Å for the as-deposited, TMAH, and 1% TMAH + PC cleaned Ru. Therefore, these AFM results correspond to the stable Ru oxide surface chemistry, as revealed in the XPS data. However, the AFM image for the PC-cleaned Ru showed the significantly different surface morphology, which is due to the carbonaceous deposit surfaces. As a result, the AFM results confirm the damage-free Ru surface cleaning in PC + 1% TMAH.

The analysis for reflectivity at 13.5 nm of the cleaned Ru capping layer on a Si/Mo ML is important for its practical use as EUV mask mirrors. An as-deposited 3 nm Ru thin film (deposited in a same manner in this study) on a Si/Mo ML with a period of 6.8 nm
yielded 60% of reflectivity at 13.5 nm. The optical calculation considering the transmission at 13.5 nm of continuous carbon layer at the residual thickness estimated from the XPS spectra in Fig. 2b gave the reflectivity increase by −1% for PC + 1% TMAH solution and 0.8% for TMAH solution but the reflectivity decrease by 4% for PC solution against that for the as-deposited Ru surfaces.

Cleaning of residual PR on Ru thin film with PC + 1% TMAH solution.— The important cleaning test for an EUV lithography mask reflector is to evaluate the removal efficiency of residual E-beam lithography PR used to form the pattern on the mask reflector. This residual PR on an EUV mask reflector should be removed because it would be a significant process-induced carbon contamination source on Ru surfaces. Figure 5 represents (a) the Ru 3d XPS spectra and (b) the AFM images for the as-coated and cleaned PR (using PC + 1% TMAH solution) on Ru thin films. The Ru 3d XPS spectra for the as-deposited PR showed the typical CH$_2$O$_x$ (285 and 286 eV) and C–C (284.3 eV) bonding states of E-beam lithography PR. No bonding state associated to Ru was observed because of the uniform PR layer —200 nm thick.

The 200 nm PR layer was effectively removed by cleaning using PC + 1% TMAH solution, and the resultant XPS spectra indicated that CH$_2$O$_x$ bonding states were almost completely removed; all Ru metallic and oxide bonding states were seen again, and C–C bonding states were reduced as in the as-deposited Ru surfaces. This result clearly proved the very promising cleaning efficiency of PC + 1% TMAH solution on heavy organic residues from the PR layer. AFM images in Fig. 5b also showed the morphological difference of the PR and Ru surfaces with a small amount of C after the PR layer was removed.

Regarding the PR residue removal efficiency of other cleaning solutions, only a pure PC solution revealed an effective cleaning of the PR layer that is comparable to that of the PC + 1% TMAH solution. Nevertheless, as discussed earlier, the PC solution has a limitation in removing low concentration C residues on clean Ru surfaces so it should be compensated by another cleaning solution that is effective for Ru surface cleaning.

As a result, the cleaning process based on the PC + 1% TMAH solution provides a promising cleaning approach for both heavy CH$_2$O$_x$ and C residues from the PR and low concentration C residues on Ru surfaces from the air contamination.

Conclusions

In summary, the effective wet cleaning designed for a Ru thin-film surface for EUV mask capping layers was proposed. The surface carbon contaminants were present in the native Ru oxide layer for as-deposited Ru films of 1.7 nm estimated from XPS analysis. The addition of 1% TMAH to PC showed an effective cleaning performance, which significantly reduced (i) the carbon amounts to half of the stoichiometric ratio of C/Ru for the as-deposited and showed that (ii) top surface chemisorbed O species does not attack Ru surfaces. The cleaning mechanism of PC + 1% TMAH is regarded to be a combined effect of the (i) chemical Ru surface passivation of 1% TMAH and (ii) electrochemical interaction assisted cleaning of PR. Except for the optimized solution of PC + 1% TMAH, other PC solutions with more TMAH addition (5–10%) and without TMAH revealed carbonaceous (CH$_2$O$_x$) deposits. Therefore, the important role of 1% TMAH is the aqueous chemical Ru surface passivation in the solution. The proposed cleaning scheme might be extended to the cleaning of thin film and nanoparticle Ru surfaces for other catalytic applications, which requires damage-free, carbonaceous contaminant-free, and process-induced oxidation-free Ru surface treatments.

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