Organic removal on EUVL Ru-capped Mo/Si multilayer by ozonated DI water (DIO3) to reduce surface damage

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Abstract

Since the introduction of EUVL technology, it has been achieved a remarkable progress. Because photons of 13.5 nm wavelengths are heavily absorbed by all materials even in the air, imaging system operates in reflection by mirror in vacuum atmosphere and use of pellicle is forbidden. Therefore, EUVL mask surface, Ru capping layer and absorber layer, is *not only exposed to outside and easy to be contaminated during fabrication. And cleaning* process is much more significant in result.

SPM, conventional organic cleaning solution, is ineffective for highly dense carbon contaminant in Ru-capping layer. On the other hand, ozonated water (DIO3) shows high cleaning performance on to both absorber and Ru-capping layer without residue. However, DIO3 causes the damage and increases the roughness of Ru-capping layer and eventually lead to reflectivity downfall. In this study, various experiments and measurements were performed to understand the critical DIO3 cleaning process condition for Ru-capping without surface damage. Available DIO3 process conditions were theoretically calculated and tested on Ru-capping layer.

Keywords: EUVL, mask, lithography, cleaning, DIO3, organic contaminant, ruthenium, roughness

Introduction

❖ EUVL mask cleaning

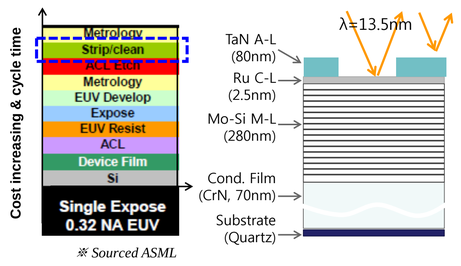
- Quartz, Si, Ruthenium, TaOx
- Particle, Nano-structure, Metal, Roughness, Carbon contamination and Reflectivity
- ~100% cleanness, Repeatability

❖ Carbon contamination

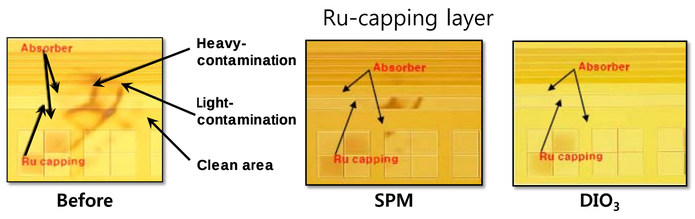
- Disadvantages :
  - Reflectivity loss / CD change / Throughput loss
- Feature : thin and high-densed
- Solutions :
  - Mitigation, Prevention / Cleaning

❖ Carbon cleaning challenge

- SPM :
  - Carbon contaminant on absorber layer was removed but not on Ru-capping layer
- DIO3 :
  - Carbon contaminant was removed not only on absorber layer but also Ru-capping layer



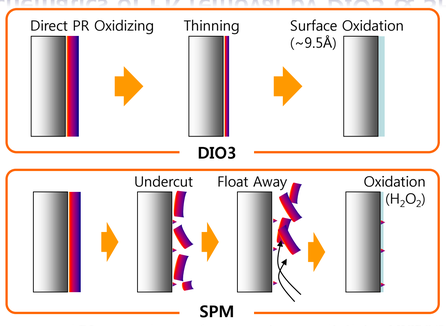
※ Sourced ASML



❖DIO3 cleaning for Organic contaminant removal

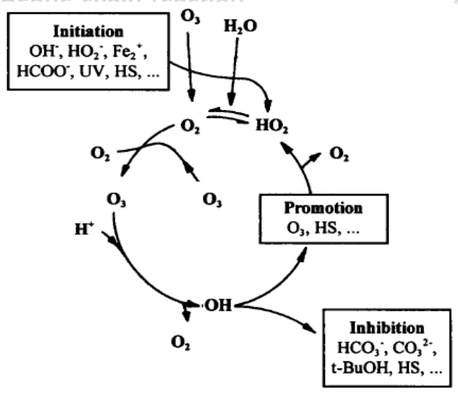
- An environmentally friendly alternative to sulfuric acid-based cleaning chemistries, DIO3 processing can lower operating costs while minimizing defect densities and surface residues.
- PR removal Mechanism
  1) **DIO3 :** $R\text{-}CH_2^- + 3O_3 \rightarrow 3O_2 + CO_2 + H_2O$ (No residue)
  2) **SPM :** $H_2SO_4 + H_2O \rightarrow H_2SO_5 + H_2O$
     $R\text{-}CH_2 + 3H_2SO_5 \rightarrow 3H_2SO_4 + CO_2 + H_2O$ (Toxic)

❖Schematics of PR removal by DIO3 & SPM



※ 'Using an ozonated DI-water technology for photoresist removal', Akrion, MICRO(2001)

❖Ozone chain reaction



❖DIO3 chemical reaction & Ru damage mechanism

Direct Oxidation

$2Ru + O_3 \rightarrow Ru_2O_3 + 6e^-$
$2Ru_2O_3 + O_2 \rightarrow 4RuO_2 + 4e^-$
$2RuO_2 + O_2 \rightarrow RuO_4 + 8e^-$

Indirect Oxidation

$Ru + 8OH^- \rightarrow RuO_4^{2-} + 4H_2O + 6e^-$
$Ru + 8OH^- \rightarrow RuO_4^- + 4H_2O + 7e^-$

Ruthenium Damage Mechanism

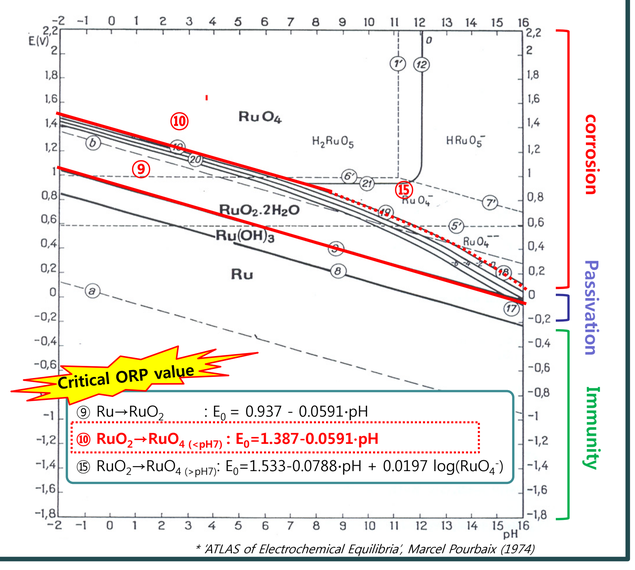
$4RuO_4^- + 2H_2O \rightarrow 4RuO_4^{2-} + O_2 + 4H^+$
$3RuO_4^{2-} + 4H^+ \rightarrow RuO_2{\cdot}2H_2O + 2RuO_4^-$

❖Potential-pH equilibrium Diagram

- Also known as a Pourbaix diagram
- maps out possible equilibrium phases of an aqueous electrochemical system
- guide to the stability of a particular metal in a specific environment
- **Y-axis** : voltage potential (Eh) with respect to the SHE as calculated by Nernst Eq.

$$Eh = E^0 - \frac{0.0592}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- **X-axis** : pH for –log function
  pH = - log [H⁺]
- **Immunity** : metal is not attacked
- **Passivation** : metal forms stable coating of an oxide or other salt on its surface
- **Corrosion** : general attack will occur



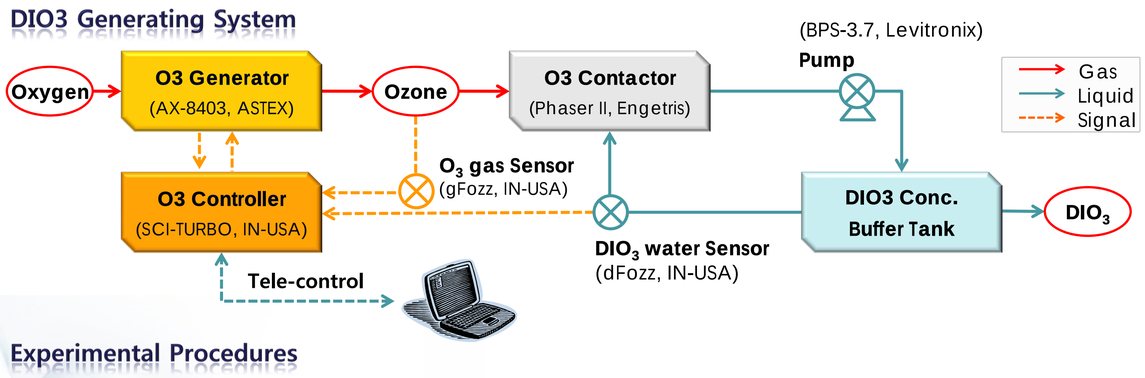
* 'ATLAS of Electrochemical Equilibria', Marcel Pourbaix (1974)

Experimental Procedures

❖ Analysis Tools

Sample Preparation (2.5nm RuM/L - Qz) → Sample Treatment (DIO3, additive gas, pH) → Theoretical approach (Potential-pH analysis) → Experimental Confirm (AFM)

❖ DIO3 Generating System

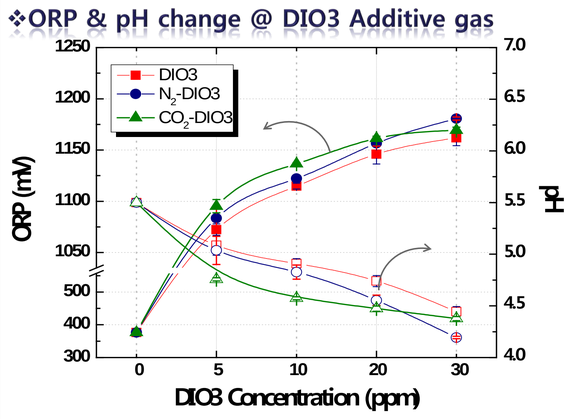


❖ Experimental Procedures

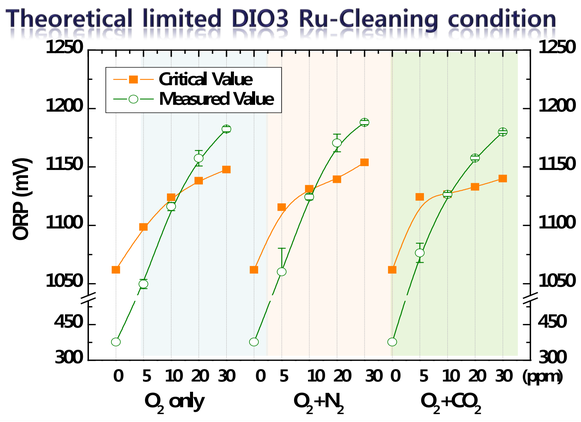
- DIO3 treatment condition
  - Add gas : O_2 only / 10% of N_2 / 3% of CO_2
  - DIO3 : 5ppm / 10ppm / 20ppm / 30ppm
  - pH adjustment (Normal pH / pH3.8 / pH3.2)
- DIO3 generation Condition
  - 5 LPM Flow / O_3 gas as 20psi @ 1 atm / R.T
- Analysis :
  - DIO3/O3 ppm (dFozz, gFozz, IN USA)
  - pH / ORP (PCD-6500, Eutech, USA)
  - Roughness (XE-100, Park systems)

Results & Discussion

❖ORP & pH change @ DIO3 Additive gas



❖ Theoretical limited DIO3 Ru-Cleaning condition

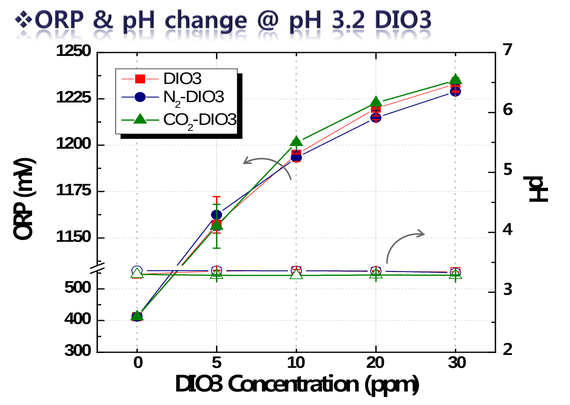


- DIO3 concentration ∝ ORP / pH
  - ORP: 380mV→1200mV /pH 5.5 →pH4
- Additive gas free DIO3 shows lowest ORP value and the highest pH

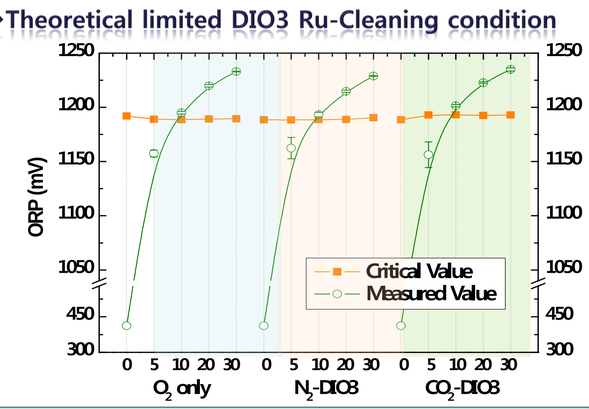
- Critical ORP value (ORP of Ru→ RuO_4)
  $RuO_2 \rightarrow RuO_4$: E_0 = 1.387 - 0.0591·pH

❖ **Available DIO3 concentration :**
O_2-DIO3 (13ppm), N_2-DIO3 (12ppm), CO_2-DIO3 (10ppm)

❖ORP & pH change @ pH 3.2 DIO3



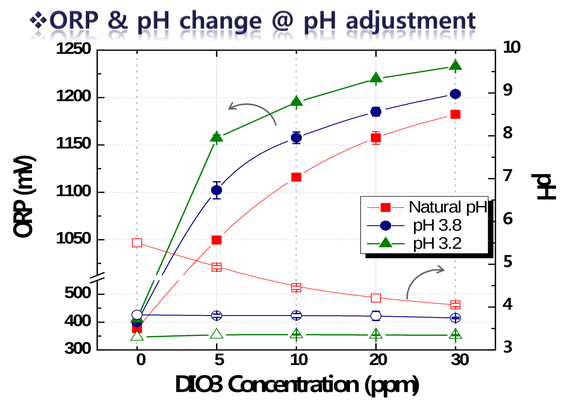
❖Theoretical limited DIO3 Ru-Cleaning condition



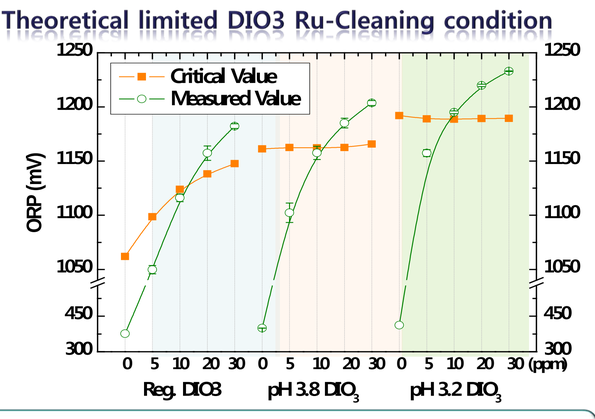
- The effect of DIO3 pH adjustment (pH3.2)
- Overall ORP values were increased, and the effect of additive gases were low in low pH adjusted DIO3

❖ **Available DIO3 concentration :**
O_2-DIO3 (9.4ppm), N_2-DIO3 (9.1ppm), CO_2-DIO3 (9.0ppm)

❖ORP & pH change @ pH adjustment



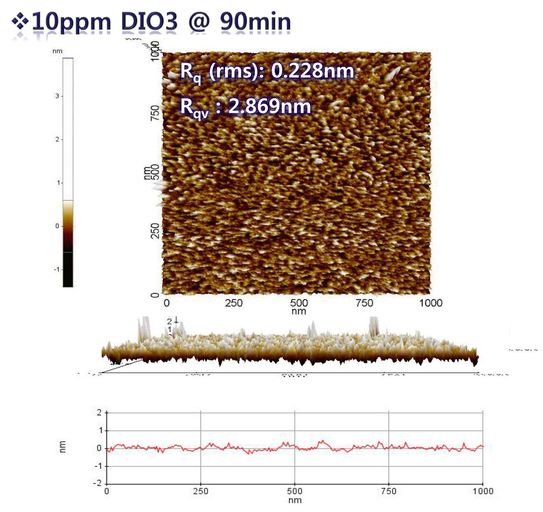
❖Theoretical limited DIO3 Ru-Cleaning condition



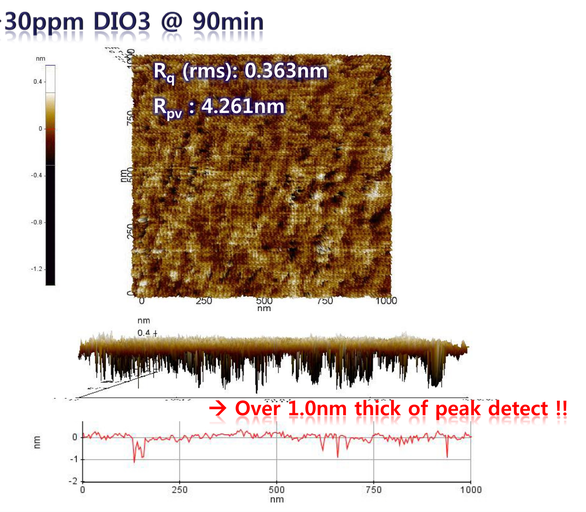
- Natural pH has the lowest ORP values
- The amount of potential increase is bigger than potential margin by pH decrease

❖ Available DIO3 concentration :
Natural pH-DIO3 (13ppm), pH 3.8 DIO3 (11ppm), pH 3.2 DIO3 (9.4ppm) w/o additive gas

❖10ppm DIO3 @ 90min



❖30ppm DIO3 @ 90min



- Hazard test: Ru-capping mask @ 10ppm & 30ppm (90min)
- Line profile shows > ~1.5nm thick. of Pit-type damage
- The R_{pv} is suitable parameter for real surface roughness

❖ High concentration of DIO3 is effective for C-contaminant removal, but it cause serious PIT-type damages on Ru surface

Summary

1. SPM is inefficient for High dense thin c-contamination on Ru-capping layer
2. Alternative DIO3 is effective for Carbon on both Ru-capping & absorber layer, but leave serious Pit damages on Ruthenium
3. The trial of ORP control of DIO3 were performed
   - Additive gas : O_2-DIO3 (13ppm), N_2-DIO3 (12ppm), CO_2-DIO3 (10ppm)
   - pH & add-gas : O_2-DIO3 (9.4ppm), N_2-DIO3 (9.1ppm), CO_2-DIO3 (9.0ppm)
   - pH adjustment : Natural pH (13ppm), pH 3.8 (11ppm), pH 3.2 (9.4ppm)

❖ **Solution of surface damage reduction @ DIO3 cleaning**
- **No Additive gas & pH control**
- **Under 13ppm DIO3**

→ Over 15ppm of DIO3 concentration can develop PIT-type damage on Ruthenium

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