Ruthenium and Ruthenium-Dioxide Surface Chemistry

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Challenges to be met by Ru-based Capping Layers

- No degradation of the optical reflectivity
- Blocking H₂/O₂ diffusion
- Chemical Stability
- Thermal Stability
- Suppress Carbon Uptake
Main Reasons for the degradation of optical reflectivity

- Carbon Uptake
- Heterogeneous Surface Composition due to Oxidation of Ru into Ru/RuO$_2$: Optical Roughness

Note: Catalytic Activity of the Ru-based Capping layers may facilitate both carbon uptake and carbon removal.
Physico-chemical Properties of Ru versus RuO$_2$

<table>
<thead>
<tr>
<th>Ru</th>
<th>RuO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hcp crystal structure</td>
<td>Rutile crystal structure (TiO$_2$)</td>
</tr>
<tr>
<td>high</td>
<td></td>
</tr>
<tr>
<td>Good Hydrogenation Catalyst</td>
<td>Poor Hydrogenation Catalyst</td>
</tr>
<tr>
<td>Medium Dehydrogenation Catalyst</td>
<td>Medium Dehydrogenation Catalyst</td>
</tr>
<tr>
<td>Poor Oxidation Catalyst</td>
<td>Good Oxidation Catalyst</td>
</tr>
</tbody>
</table>

→ Two Strategies: Removal of Carbon containing Molecules by REDUCTION or by OXIDATION
Grain Boundaries facilitate H/O diffusion through the capping layer

Polycrystalline 2nm Ru/RuO$_2$ capping layer:
Ru Grain size: about 2nm, mostly oriented along the (0001) direction (S. Bajt: LLNL)

2nm Ru/RuO$_2$ capping layer:

Overcome problem with grain boundaries:
Use an amorphous RuO$_2$ layer (Intel: Dr. M. Fang, Dr. M. Chandhok)
Surface Chemistry:
Model Systems for the Ru Capping Layer

- 2nm thick RuO$_2$(110) single crystalline films supported on Ru(0001): Study the Complex Redox Surface Chemistry under well-defined Conditions.
- Polycrystalline Ru/RuO$_2$ powder: 1000nm particle size
### Chemical Stability of Ru versus RuO₂

<table>
<thead>
<tr>
<th>Ru</th>
<th>RuO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Is not stable under EUVL conditions: Ru oxidizes</td>
<td>- Oxide is stable under EUVL conditions</td>
</tr>
<tr>
<td>- Uptake of Carbon: by Dehydrogenation</td>
<td>- Uptake of Carbon: by Dehydrogenation and Oxidation</td>
</tr>
<tr>
<td>- Formation of a single Graphite Layer possible</td>
<td>- No single Graphite Layer is stabilized</td>
</tr>
<tr>
<td>(e.g. by alkines)</td>
<td>- reducible by CO, MeOH, H₂, ... Exposure (Note EUVL chamber is in oxidizing conditions)</td>
</tr>
</tbody>
</table>

- EUV Environment is **Net-Oxidizing** for Ruthenium
- Heterogeneous Ru/RuO₂ may be even more prone to take up carbon
- RuO₂ is stable under EUVL conditions
Thermal Stability of RuO$_2$(110) under UHV conditions

- Below 800K: RuO$_2$ is thermally stable
- At 1000K also the volatile (and toxic) RuO$_4$ and RuO$_3$ are leaving the Surface.
Understanding the oxidation of Ru on Atomic Scale

- Oxidation of Ru(0001): active RuO$_2$(110)
- Oxidation of supported Ru nano-particles
Autocatalytic oxidation of Ru(0001) metal

**STM image of oxidized Ru(0001)**

- **Heterogeneous Surface → Optical roughness**
- **Use RuO₂ directly as capping layer instead of Ru**

2 x 10^6 L O₂ at 650K (under UHV conditions)
1L = about 10⁻⁶ mbar x 1 second (exposure)

100 nm x 100 nm, 1.21 V, 0.46 nA
*Science 287* (2000) 1474
The Rutile Structure of RuO$_2$(110)

High Resolution XPS

STM, quantitative LEED

**SXRD: Oxidation of Ru(0001) under** \(\text{p(O}_2\text{)} = 10^{-4} \text{ mbar, } T=357^\circ\text{C (630K)}\)

Self-limiting Growth of RuO_2(110) film on Ru(0001):
Thickness = 1.6 nm.
→ Depth control of the oxidation process

Y. B. He, M. Knapp, E. Lundgren, H. Over: JPC in press
Oxidation of Ru by $O_2$ exposure

- Single crystalline Ru(0001): $T > 530 K; p(O_2) = 10^{-5} - 10$ mbar
- Ru Nano-particles (2-3nm): $T >$ room temperature; $P(O_2) = 10^{-5} - 10$ mbar
  DRIFTS: 2073 cm$^{-1}$ of CO characteristic for RuO$_2$

DRIFTS: Infrared Spectroscopy


Supported Ru catalyst: $P(O_2)=2P(CO)=10$ mbar
Understanding the Reduction of RuO$_2$

- Reduction of Ru Nano particles by H$_2$
- Reduction of single-crystalline RuO$_2$(110) by H$_2$
Reduction of Ru/RuO$_2$ Nano Particles by H$_2$

Temperature Programmed Reduction:

RuO$_2$ particles reduce completely to Ru particles beyond 400 K, the desorption temperature of water.

Reduction of 1.6nm thick RuO$_2$ (110) by H$_2$: In-Situ SXRD

P(H$_2$) = 10$^{-5}$ mbar, T=415K

Complete reduction of the RuO$_2$(110) film after 50 minutes
Open problem: Hydrogen may diffuse through the Ru capping layer
Interaction of Methanol and Water with RuO$_2$

- Oxidation of Methanol: over RuO$_2$(110)
- Oxidation of Methanol over polycrystalline RuO$_2$
- Passivation of RuO$_2$(110) by water
Partial Methanol Oxidation: Introduction

- Attention: Formaldehyde may polymerize on the surface.

- On RuO$_2$: Dehydrogenation forms water rather than H$_2$  
  $\Rightarrow$ RuO$_2$ becomes reduced.
Oxidation of Methanol over RuO$_2$

Total Oxidation requires temperatures of 500K even on polycrystalline RuO$_2$ powder.

Formaldehyde CH$_2$O may be bad since it can polymerize on the surface!

Reduction of RuO$_2$(110) by methanol exposure

1) 0.1 L methanol at RT, Annealing to 520K
2) + Annealing to 590K
3) + Annealing to 660K

Exposure of 0.1L corresponds to P(MeOH)=10$^{-7}$mbar for 10s

**Alcohols interact strongly with RuO$_2$: Without oxygen: Methanol reduces the RuO$_2$(110) surface**
**Interaction of water with RuO$_2$(110)**

<table>
<thead>
<tr>
<th>Interaction with Ru</th>
<th>Interaction with RuO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Water: weak (250K)</td>
<td>- Water: strong (420K)</td>
</tr>
<tr>
<td>- Hydrogen: medium (300K)</td>
<td>- Hydrogen: strong (600K)</td>
</tr>
<tr>
<td>$\rightarrow$ Ted Madey</td>
<td>- H$_2$O: able to passivate RuO$_2$(110)</td>
</tr>
</tbody>
</table>

- Dissociative adsorption of Water on RuO$_2$(110).
- Passivation: The bridging O atoms from O$_{br}$-H and the cus-Ru atom are capped by O$_{ot}$-H.
  $\rightarrow$ control chemical activity

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## Carbon Uptake: Ru versus RuO$_2$

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<tr>
<th>Interaction with Ru</th>
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<tbody>
<tr>
<td>- Alkanes: weak (100K)</td>
<td>- Alkanes: weak (100K)</td>
</tr>
<tr>
<td>- Alkenes, Alkines: strong (400K)</td>
<td>- Alkenes (320K, desorbs intact), Alkines: medium</td>
</tr>
<tr>
<td>- Alcohols: medium</td>
<td>- Alcohols: strong (400K)</td>
</tr>
<tr>
<td>- Conjugated double bonds: medium (Benzene: 300K)</td>
<td>- Conjugated double bonds: weak</td>
</tr>
<tr>
<td>- Carboxyl Groups: medium</td>
<td>- Carboxyl groups: medium</td>
</tr>
<tr>
<td>- Carbonyl groups: medium</td>
<td>- Carbonyl groups: (300K)</td>
</tr>
</tbody>
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# Carbon Removal: Ru versus RuO₂

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<th>RuO₂</th>
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<td>Hydrogenation of hydrocarbons, in particular alkenes and alkines</td>
<td>Oxidation of hydrocarbons</td>
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</table>

- Complete Oxidation of hydrocarbons is quite universal, producing CO₂ and water.
- Hydrogenation is mild way but might have a limitation.
- Oxidation of hydrocarbons can form reactive intermediates which are even more difficult to remove than the original hydrocarbons.
Summary

- Ru is not stable under EUVL conditions
- RuO₂ is stable under EUVL conditions
- Ru: up-take/removal of hydrocarbon by dehydrogenation/hydrogenation → make EUVL environment reducing by adding H₂.
- RuO₂: up-take/removal of hydrocarbons by dehydrogenation/total oxidation → make EUVL environment even more oxidizing by adding O₂.
- Water adsorption passivates RuO₂: good for preventing carbon uptake but bad for removal of hydrocarbons.
- Worst situation: heterogeneous Ru/RuO₂ surface → optical roughness and enhanced carbon uptake.
Acknowledgements

- Intel Coop.: Dr. M. Fang, Dr. M. Chandhok
- EU: NanO2: 'Oxidation of Nano Materials'
- DFG: Priority program 'Bridging Pressure and Materials gap'

Dr. G. Mellau, A. Farkas, M. Knapp,
D. Crihan, Dr. Y.B. He: JLU Giessen

'...we expect that insights gained from selected surface science studies will allow engineers to find suitable solutions to minimize mirror degradation in working EUVL systems.'

Ted Madey
Oxidation of 100nm thick Ru films and Ru particles $p(O_2) = 10^{-4}$ mbar, $T = 645$ K

Scanning Electron Microscopy:
- Preparation Pulse Laser Deposition
- Ru-film on MgO(100): 100nm thick
- Grain size in film: 20-40nm
- Ru particles: 500nm – 3000nm
- Grains in Ru particles: 200-500nm
Oxidation of 100nm Ru film and Ru particles
\[ p(O_2) = 10^{-4} \text{ mbar}, \ T= 645 \text{ K} \]

- Scanning PhotoElectron Microscopy (Synchrotron Trieste):
  Ru film more oxidized than Ru particle due to grain boundaries
Reduction of RuO$_2$(110) by CO exposure

- The surface roughens considerably
- Below the metallic Ru film there is still RuO$_2$