Growth and Properties of Ultrathin Metal Films for ULSI Interconnects

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Cu-Diffusion Barriers for ULSI Interconnect

**ULSI Interconnect**
A barrier layer (generally refractory metals and metal nitrides) must be employed to separate Cu from physical contact with other interconnect materials.

**Metal Via Barrier Requirements**
- Diffusion and electromigration resistance
- Good adhesion
- Low electrical resistivity (~100 $\mu$Ω•cm)
- Good step coverage

<table>
<thead>
<tr>
<th>Production year</th>
<th>2010</th>
<th>2013</th>
<th>2016</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPU 1/2 pitch (nm)</td>
<td>45</td>
<td>35</td>
<td>22</td>
</tr>
<tr>
<td>Barrier thickness (nm)</td>
<td>5</td>
<td>3.5</td>
<td>2.5</td>
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Manufacturable Solutions:
- Known
- NOT Known

Motivation for Ru Barriers

- Challenges on future diffusion barriers
  - Prevent Cu diffusion at a thickness of only 3~5 nm
  - Adhere well to ILD layer and to Cu
  - Seedless Cu plating in high aspect ratio of via holes
- A composite barrier structure is under study.
  - A Ta film serving as the primary diffusion barrier
  - A Ru film in contact with Cu
- Ru is a noble metal and Cu is insoluble in it
- Ru oxide is also conductive and has a favorable reduction potential
- Ru is expected to improve wetting and adhesion properties between Ta and Cu
- Ru could enable direct copper plating on barrier surface without first coating a Cu seed layer.
In-situ Film Deposition and Characterization System

- Ultra-thin film deposition systems
  - Physical vapor deposition (PVD)
  - Chemical vapor deposition (CVD)
  - Atomic layer deposition (ALD)

- Barrier characterization systems
  - Real time XPS and ISS analysis with CO₂ laser annealing
  - Electrical measurement

- Annealing facilities
  - CO₂ infrared laser
  - Halogen lamp

- In-situ sample transfer system
Chemical Vapor Deposition of Ruthenium Using Ruthenium Carbonyl

- Ruthenium carbonyl $[\text{Ru}_3(\text{CO})_{12}]$ is a solid precursor.
- It is stable in air and moisture at room temperature.
- It begins to evaporate at $\sim 80 \degree \text{C}$.
- It decomposes at $150 \degree \text{C}$.

**Why ruthenium carbonyl?**
- A pure Ru film with minimal carbon and oxygen residues can be deposited!
- The compound can be decomposed as low as $150 \degree \text{C}$.
- No reactive gas is needed! (Substrate can be protected!)

**But wait** – the carbonyl gives poor step coverage so it is not feasible for manufacturing. It does show Ru’s potential.

A 150 nm Ta film was deposited on the Si substrate using PVD.
A 6 nm Ru film was deposited on Ta surface without any reactive gas at the temperature as low as 150 °C.
XP spectra indicated a pure Ru film with low C and O contents (<1 %) was deposited at this low temperature.

A 3 nm Ru film was deposited on the SiO$_2$ substrate. The Ru film roughness was ~1.4 nm, measured by AFM. The SiO$_2$ substrate roughness was 0.2 nm.
Ru Film Properties – Microstructure of 30 min film

- Polycrystalline and columnar structure
- Average grain size was ~ 20nm.
- Grains are granular → Reveals limitations of Ru-carbonyl precursor; need a different precursor to increase the nucleation density.
- XRD shows crystalline & hexagonal structure of the film.
Ru Film Properties – ISS/XPS

- LEISS → Surface coverage
- Substrate Si peak is attenuated by overlaying Ru film. The Si peak intensity is function of film thickness and mean free path. $I/I_0 = \exp\left(-d/\lambda \cos\theta\right)$
- Calculated minimum thickness of continuous Ru film → ~ 3nm
Film thickness measurement

- Min. thickness of continuous Ru film was ~ 3nm.
- However, SEM/TEM shows a much thicker film; ~25nm for the 30-min sample.
- The error seems to be caused by film roughness or film discontinuity. ISS overestimates surface coverage due to a shadowing effect, and XPS can detect the substrate Si peak due to surface roughness or film discontinuity.
Cu/Ru/Ta MOS capacitor was built, and the flat band voltage shift of a C-V curve ($\Delta V_{FB}$) was used to characterize barrier effectiveness against Cu diffusion.

- Samples need to be prepared carefully to obtain reproducible C-V curves.
  - Annealing for 90 min at 350 °C in high vacuum to neutralize interface trapped charges.
  - *In situ* deposition of Cu dots on the top of Ru dots with shadow mask.
  - To minimize device damages caused by sputter deposition, two-step Cu deposition was applied.
    - A 20 nm Cu film was first deposited using 10 W DC power.
    - A 200 nm Cu film was then deposited using 50 W DC power.
  - Subsequent anneal for 60 min at 350 °C in 110 mTorr H$_2$/N$_2$ forming gas (after ambient exposure) and test *ex situ*
Challenges of Characterizing Ultra-thin Films

Immediate Challenges:

- Description of the thin films and the true barrier
- Ion and electron spectroscopies best suited for flat surfaces

$E_1/E_0 = f(m_1/m_0)$

Shadowing effect of ISS
- Effect of ion gun & analyzer angles
Shadowing Effect - ISS

\[ \theta: \text{Ion gun angle} \]
\[ \delta: \text{Detector angle} \]
\[ d: \text{Pitch} \]
\[ t: \text{Grain height} \]
\[ g: \text{Grain size} \]
\[ \alpha: \text{Surface coverage} \]

- **Assumption:** Ru grains are equally sized and spaced.
- Fraction of sub. peak: \( \frac{I_{\text{sub}}}{I_{\text{tot}}} = \frac{b}{(a+b+c)} \)
- \( I_{\text{sub}} \propto b \), since \( \frac{I_{\text{tot}}}{(a+b+c)} = \text{const.} \)
- \( b = \{ (1-\alpha) \cdot d - (1/\tan \theta + 1/\tan \delta) \cdot t \} \cdot \sin \theta \)
- **Minimum \( \alpha \) that sub. peak disappears:** \( \frac{1}{\alpha_{\text{min}}} = 1 + (1/\tan \theta + 1/\tan \delta) \cdot (t/g) \)
Shadowing Effect - ISS

- Grain height & size ratio was assumed to be one, \( d=g \).
- As angles decrease, \( \alpha_{\text{min}} \) decrease.
  - Sub. peak disappears with lower surface coverage.
- Shadowing effect will be gone with \( \theta=\delta=90^\circ \).
- With \( \theta=\delta=60^\circ \) and \( d=g \), substrate peak disappears with only 47% of surface coverage.
Shadowing in XPS

- Assumption: X-rays can penetrate Ru and reach the substrate. Ru film is discontinuous and thick enough to completely attenuate Si peak under Ru.
- \( d_{\text{min}} = \ell \): Minimum space that detector can see Si peak.
- With 60º of takeoff angle and 20 nm of Ru film, \( d_{\text{min}} = 11.5 \) nm.
Why is there a Si XPS Signal for the 30-min film?

$d_{min} = 11.5 \text{nm}$

TEM

SEM

Avg grain size \( \sim 20 \text{ nm} \)

Si 2p predicts \( \sim 3 \text{ nm for 30 min} \)
CVD Film Continuity versus Thickness

ISS

XPS

(a) 0 min
(b) 10 min
(c) 20 min
(d) 30 min
Comparison of PVD and CVD Film Structures

~3.5 nm PVD (quartz balance and XPS) Ru

0.105 nm rms
Δ0.53 nm (line scan)

~3.5 nm CVD - XPS

1.443 nm rms
Δ5.3 and 7.9 nm (line scan)

SEM Images of Ru
XPS and ISS measurements for PVD Ru film

The thickness for fully covering Si substrate is between 1.2 to 2.2 nm
Determining Film Growth Mechanism by Combined Use of ISS and XPS

\[
\Theta_i = \frac{ARu,i}{ARu,o} + \frac{ASi,i}{ASi,o}
\]


Energy Dispersive Spectroscopy (EDS) Approach

The detection depth of EDS is much larger than XPS, so it is not sensitive to the surface morphology.
## EDS Measurement for PVD and CVD Ru Films

<table>
<thead>
<tr>
<th>Ru Film</th>
<th>EDS counts</th>
</tr>
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<tbody>
<tr>
<td>3.5 nm PVD Film</td>
<td>81.6</td>
</tr>
<tr>
<td>12 nm PVD Film</td>
<td>284.4</td>
</tr>
<tr>
<td>3.5 nm CVD Film</td>
<td>201.6</td>
</tr>
</tbody>
</table>

CVD Film thickness = 7.8 to 8.6 nm
XPS Depth Profile for CVD Ru film (~ 4 nm thick)
XPS Depth Profile for 3.5 nm PVD Ru Film
If we assume after the line is the interface, then the thickness of CVD film is 7.8 nm, calculated from the sputtering time.
Comparison of PVD and CVD Film Structures
Equivalent Thickness is ~\((2-3 \times)\) or ~ \((8 \times)\)

~3.5 nm PVD (quartz balance and XPS) Ru

0.105 nm rms
\(\Delta 0.53\) nm (line scan)

~3.5 nm CVD - XPS

443 nm rms
\(\Delta 5.3\) and 7.9 nm (line scan)

EDS of 3.5 and 11 nm PVD films and the “3.5” nm CVD film suggests a 7.8 to 8.6 nm CVD film

XPS depth profiling suggests the “3.5” nm CVD film is 7.8 nm
Understanding the True Barrier

• Barrier likely to be much thinner than the physical thickness of the metal film and just when this continuous layer is formed remains an experimental challenge.
• More extensive studies with 2D (PVD) films needed to establish the barrier properties and interfaces that form with the substrate layer.
• New precursors and growth processes (ALD) under study are leading to smoother films than the Ru$_3$(CO)$_{12}$ system presented.
• Island nucleation is the key to thinner films.
• As film roughness increases we need a way to relate in situ measures to film thickness – the equivalent film thickness.