Electrical and structural properties of ultrathin polycrystalline and epitaxial TiN films grown by reactive dc magnetron sputtering

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Outline

- Ultrathin conducting films are an essential part of modern microelectronics
- Titanium nitride (TiN) thin films are widely used in microelectronics
  - as adhesion layers
  - as diffusion barriers in device interconnects
  - as a direct-metal-gate material for metal-oxide-semiconductor devices
- With device dimensions constantly shrinking, the required film thickness is approaching a few nanometers
- For such thicknesses the continuity of a metallic film becomes an important issue
Ultrathin TiN films were grown by reactive dc magnetron sputtering on amorphous SiO$_2$ substrates and single-crystalline MgO substrates at various growth temperatures.

The resistance of the films was monitored in-situ during growth to determine the coalescence and continuity thicknesses.

- Growth of ultra-thin TiN films on SiO$_2$
  - Coalescence thickness and continuity thickness
  - Structural properties
  - Exposure to oxygen

- Growth of ultra-thin TiN films on MgO
  - Structural properties

Summary
Growth of ultra-thin TiN films on SiO$_2$
Ultrathin TiN films were grown by reactive dc magnetron sputtering on thermally oxidized Si (100) substrates. The film electrical resistance was monitored \textit{in-situ} during growth in order to determine the minimum thickness of a continuous film. The film texture was examined \textit{ex-situ} by grazing incidence X-ray diffraction (GI-XRD) measurements and the film composition was determined by X-ray photoelectron spectroscopy (XPS).
The TiN thin films were grown in a custom built magnetron sputtering chamber.

The differential resistance of the TiN film was measured in a standard fourpoint probe configuration during growth using dual lock-in amplifier setup.

The nominal coalescence thickness was determined by finding the maximum of $Rd^2$ vs. the film nominal thickness $d$.

The nominal film thickness which completely covers the substrate was determined by the minimum of $Rd^2$ vs. $d$.

$R$ is the in-situ measured film resistance.


Growth of ultra-thin TiN films on SiO$_2$

- The deposition time at which the film coalesces (circles) and the film completely covers the substrate (squares), as a function of growth temperature.

- The decrease in continuity thickness can be attributed to the increased mobility of the Ti(N) on the surface of the TiN islands with temperature, which causes the voids in the film to be filled more efficiently.

GI-XRD measurements of the 40 nm thick TiN films demonstrate that the films are polycrystalline and that the [111], [200] and [220] crystal orientations are all present in samples grown at 600 °C.

The cross-over of crystal orientation from [200] to [111] is only expected to start occurring at a thickness of 20–50 nm.

The room temperature resistivity $\rho$ of 40 nm thick films versus growth temperature, before and after exposure to oxygen.

Exposure to oxygen does not influence the resistivity of films grown at 500 °C and above.

Growth of ultra-thin TiN films on SiO₂

- The ratio of N and Ti atoms \([N]/[Ti]\) for the TiN grains
- The ratio of Ti bound in the TiN grains to the total amount of Ti
- XPS measurements indicate presence of oxygen in all the samples, highest for films grown at room temperature but up to 10% in films grown at 600 °C

Growth of ultra-thin TiN films on MgO
MgO has a NaCl-type crystal structure with a lattice constant of 4.2112 Å

TiN which has the same crystal structure and a lattice constant of 4.2417 Å

It is well known that TiN grows epitaxially on single-crystalline MgO(001) at a substrate temperature above 600 °C


Magnus et al., MRS Proc. 1156 D03-05 (2009)
The films grown at room temperature and 100 °C give peaks corresponding to the [111], [200] and [220] crystal orientations and are therefore clearly polycrystalline.

The scans have been optimized to give the maximum [200] peak intensity and therefore the [111] peak is barely visible in the scan of the 100 °C grown film.
As the growth temperature is increased to 200 °C there is a clear transition from polycrystallinity to a more ordered crystal structure.

There are no peaks visible in the GIXRD scan and a significantly reduced background - the lattice planes of this film are parallel with the substrate surface.
High angle $\theta - 2\theta$ scans were carried out in order to examine the morphology.

Scans of the room temperature grown films did not reveal a TiN [200] peak indicating that these films are highly polycrystalline.

Even for films grown at 100 °C the TiN [200] peak is visible, although it is quite broad.
**Growth of ultra-thin TiN films on MgO**

- For growth temperatures of 200 °C and above we see well resolved Laue oscillations on both sides of a distinct TiN Bragg peak.
- The period of the Laue oscillations is related to the size of the crystallite in the [200] direction (the crystal coherence length or the film thickness).
Growth of ultra-thin TiN films on MgO

- The crystal coherence length calculated from the Laue oscillations \( \langle D_{\text{Laue}} \rangle \)
- We also determine the grain size from the broadening of the Bragg peak using the Scherrer formula \( \langle D_{\text{Scherrer}} \rangle \)
- The film thickness was also determined by X-ray reflectometry (XRR)
Growth of ultra-thin TiN films on MgO

- The thickness of the films decreases with increasing growth temperature.
- The growth time was 30 min in all cases.
- The total thickness of the room temperature grown film is 116.4 nm, or approximately three times that of the 600 °C grown film which is 38.6 nm.
- The density is very low for the room temperature grown film, or 2.4 g/cm³, less than half of the bulk TiN density of 5.4 g/cm³.

![Graph showing film thickness, growth temperature, and density variations.](image-url)
The surface and interface roughness was determined by X-ray reflectometry (XRR). The TiN/MgO interface roughness is roughly 1 nm in all cases. The TiN surface roughness is significantly higher for the films grown at low temperature (below 200 °C).
Comparison – growth on SiO$_2$ and MgO at 600$^\circ$C
Comparison – growth on SiO$_2$ and MgO at 600°C

- XRR analysis was carried out to determine the film thickness, density and roughness by curve fitting
- The TiN/SiO$_2$ is best fitted by a two-layer model including a 5.6 nm thick surface oxynitride layer
- The TiN/MgO sample can be fitted with a single TiN layer

Magnus et al., MRS Proc. 1156 D03-05 (2009)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Density (g/cm$^3$)</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
<th>Resistivity ($\mu\Omega$ cm)</th>
<th>Coalescence thickness (Å)</th>
<th>Continuity thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>4.9</td>
<td>41.7</td>
<td>2.7</td>
<td>54 ± 4</td>
<td>8 ± 1</td>
<td>19 ± 2</td>
</tr>
<tr>
<td>MgO</td>
<td>5.1</td>
<td>38.7 ($37.5^*$)</td>
<td>1.0</td>
<td>24 ± 4</td>
<td>2 ± 1</td>
<td>–</td>
</tr>
</tbody>
</table>

* From Laue oscillations
Summary
Summary – Growth on SiO₂

- Ultrathin TiN films grown by DC magnetron sputtering on SiO₂ substrate temperature ranging from room temperature to 650 °C are polycrystalline.
- We find that the coalescence thickness of the TiN films has a minimum of 1 nm at a growth temperature of 400–500 °C.
- The thickness where the film becomes continuous decreases with increasing growth temperature and is 2.2 nm at 650 °C.
- Films grown at 500 °C and above are resistant to oxidation, indicating a high density, and have a low resistivity of 54 µΩ cm.
Summary – Growth on MgO

- A minimum substrate temperature of 200 °C is required for good epitaxy.
- Films with a density approaching the bulk value and with a crystal coherence length of up to 97% of the total TiN film thickness can be obtained by raising the temperature to 600 °C.
- Substrate temperatures of 100 °C and below yield low density, textured polycrystalline films but with strong in-plane texture.
The slides can be downloaded at
http://www.raunvis.hi.is/~tumi/nanocircuits.html


