ALD and Pulsed CVD of Ruthenium and Ruthenium Dioxide Thin Films From an Amidinate Precursor

Xinwei Wang[1)*], Hongtao Wang[2)] and Roy G. Gordon[1)]

1) Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138,

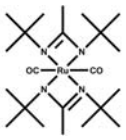
2) Institute of Applied Mechanics, Zhejiang University, Hangzhou 310027, China

Introduction

- Ruthenium (Ru) and ruthenium dioxide (RuO_2) have raised great interest in the semiconductor industry as potential electrodes for transistors and capacitors.
- Ru can also be used as a seed layer for electrodeposition of copper interconnects.
- Ru and RuO_2 are good catalysts for many chemical reactions.

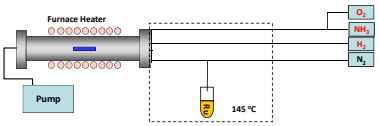
Experimental

- Ruthenium Aminidate Precursor



bis(N,N'-di-*tert*-butylacetamidinato) ruthenium(II) dicarbonyl

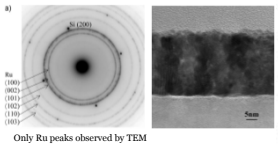
- With this precursor, deposition can be run in either ALD or Pulsed CVD mode.



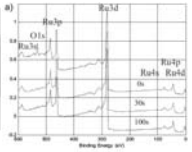
- 1) ALD mode: alternately supply precursor and co-reactant gas
- 2) Pulsed CVD mode: keep carrier gas flowing through while pulsing precursor

ALD with O_2 → Ru metal film

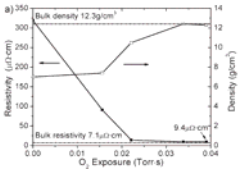
- **Narrow window of O_2 exposure (e.g. 0.02~0.04 Torr·s @ 325°C) to obtain high quality pure Ru film.**
  - Film has low quality, if under-exposed to O_2
  - Film peels off, if over-exposed of O_2
- Optimized O_2 exposure (i.e. within the window)
  - High purity (Oxygen free)
  - Dense (Equal to bulk density, 12.3 g/cm³)
  - High electrical conductivity
  - Smooth

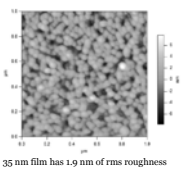


Only Ru peaks observed by TEM



No impurity peak observable by XPS





35 nm film has 1.9 nm of rms roughness

- **Ru thin film can be deposited in an oxidizing ambient**
- **Compatible with TiO_2 and $SrTiO_3$ preparation process**

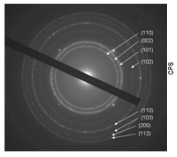
Pulsed CVD with NH_3+H_2 → Ru metal film

- **Pulsed CVD with NH_3, with alternately *in situ* annealing in H_2**
- **Each cycle consists of two steps:**
  - **1) Pulse precursor while keeping NH_3 flowing**
  - **2) Stop flowing NH_3 and flow H_2**

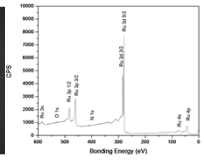
◆ Proposed Mechanism

- ◆ NH_3 reacts with the precursor and helps it stick on surface
- ◆ H_2 helps remove the ligand and lower impurity level in film

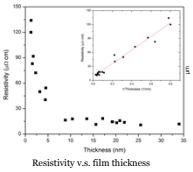
- **High quality Ru metal film obtained**
  - High purity (Nitrogen free)
  - Dense (Equal to bulk density)
  - High electrical conductivity
  - Smooth
  - High conformality



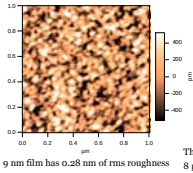
Only Ru peaks observed by TEM



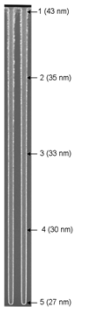
No impurity peak observable by XPS



Resistivity v.s. film thickness

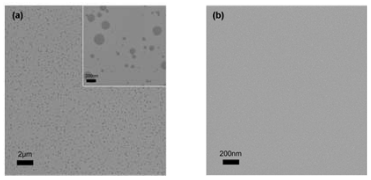


9 nm film has 0.28 nm of rms roughness



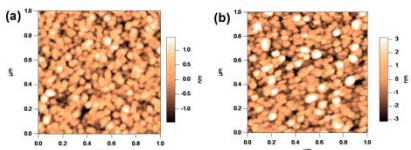
Thickness profile along a 8 μm deep hole (a/r=40)

- **Pin-hole free, good surface coverage**
  - Only ~ 2nm Ru can fully cover a WN substrate



After 10-minute etching in H_2O_2/NH_3 , which dissolves WN but not Ru, (a) 1.3 nm Ru on 10 nm WN film showed many pinholes, but (b) 2.3 nm Ru on 10 nm WN film did not have pinholes.

- **Remain smooth after RTA @ 325°C**

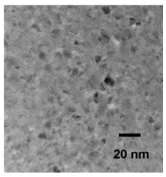


Ru/WN (13nm/3nm) film on thermal SiO_2 substrate. The rms roughness values for (a) as-deposited film, and (b) after 2 min 700 ° C RTA were 0.5 nm, and 1.4 nm, respectively.

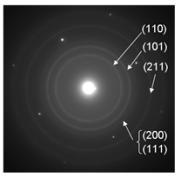
- **Ru thin film can be deposited in a reducing ambient**
- **Compatible with non-noble metal preparation process**

Pulsed CVD with O_2 → RuO_2 film

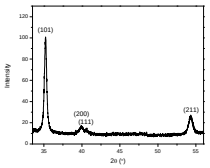
- **High quality RuO_2 film obtained**
  - Good crystallinity
  - Dense (Equal to bulk density, 7.02 g/cm³)
  - Smooth
  - Resistivity (130 μΩ·cm for a 35 nm RuO_2 film)



Crystallinity of 6 nm RuO_2 by TEM



Only RuO_2 peaks in electron diffraction pattern

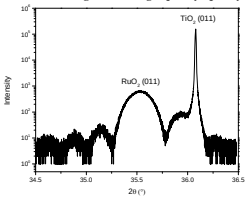


Only RuO_2 peaks in XRD scan

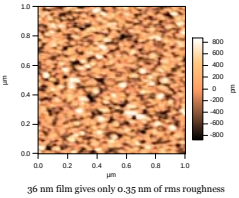
- **High Quality Epitaxy of RuO_2 on Rutile TiO_2 (011)**

● RuO_2 has a same structure as rutile TiO_2, with small lattice mismatch (-2.0% in *a* direction, and 0.07% in *c* direction)

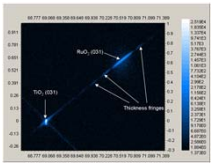
■ Clear fringes show high quality epitaxy

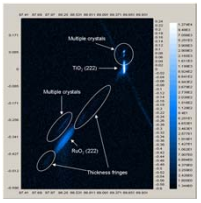


■ Ultra smooth surface



36 nm film gives only 0.35 nm of rms roughness





Reciprocal space mappings near two asymmetric peaks (031) and (222). Both showing clear thickness fringes.

■ Resistivity reduced by 34% (86μΩ·cm), due to grain-boundary free epitaxy structure

Conclusions

- Both Ru and RuO_2 can be made from our amidinate precursor.
- High quality Ru metal thin film can be made in either oxidizing or reducing ambient.
  - Depending on the deposition ambient requirement, either ALD or Pulsed CVD should be chosen accordingly.
- High quality RuO_2 thin film can be prepared with Pulsed CVD with O_2 as the carrier gas.
  - High quality epitaxy of RuO_2 on TiO_2 (011) can be obtained.

Acknowledgements

➢ Center for Nanoscale System (CNS), Harvard University.

*Correspondence: xwang@fas.harvard.edu