



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

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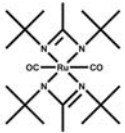


Introduction

- Ruthenium (Ru) and ruthenium dioxide (RuO₂) 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 RuO₂ are good catalysts for many chemical reactions.

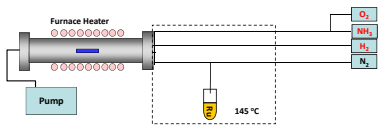
Experimental

Ruthenium Amidinate 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

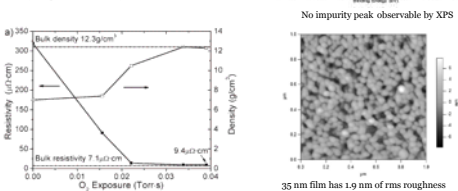
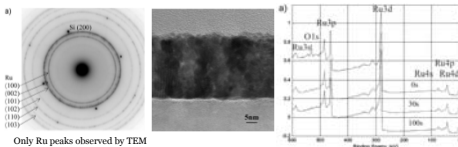
ALD with O₂ → Ru metal film

Narrow window of O₂ 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 O₂
- Film peels off, if over-exposed of O₂

Optimized O₂ exposure (i.e. within the window)

- High purity (Oxygen free)
- Dense (Equal to bulk density, 12.3 g/cm³)
- High electrical conductivity
- Smooth



- Ru thin film can be deposited in an oxidizing ambient
- Compatible with TiO₂ and SrTiO₃ preparation process

Pulsed CVD with NH₃+H₂ → Ru metal film

Pulsed CVD with NH₃, with alternately *in situ* annealing in H₂

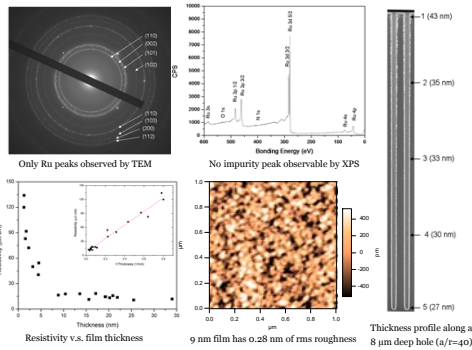
- Each cycle consists of two steps:
 - 1) Pulse precursor while keeping NH₃ flowing
 - 2) Stop flowing NH₃ and flow H₂

Proposed Mechanism

- NH₃ reacts with the precursor and helps it stick on surface
- H₂ helps remove the ligand and lower impurity level in film

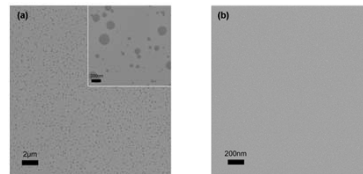
High quality Ru metal film obtained

- High purity (Nitrogen free)
- Dense (Equal to bulk density)
- High electrical conductivity
- Smooth
- High conformality



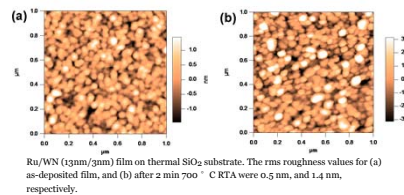
Pin-hole free, good surface coverage

- Only ~ 2 nm Ru can fully cover a WN substrate



After 10-minute etching in H₂O₂/NH₃, 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

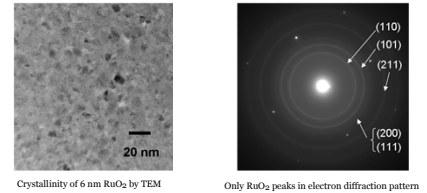


- Ru thin film can be deposited in a reducing ambient
- Compatible with non-noble metal preparation process

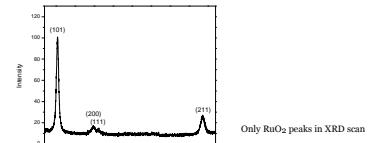
Pulsed CVD with O₂ → RuO₂ film

High quality RuO₂ film obtained

- Good crystallinity
- Dense (Equal to bulk density, 7.02 g/cm³)
- Smooth
- Resistivity (130 μΩ-cm for a 35 nm RuO₂ film)



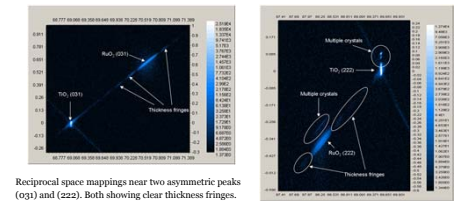
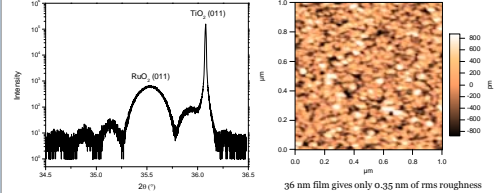
Crystallinity of 6 nm RuO₂ by TEM Only RuO₂ peaks in electron diffraction pattern



High Quality Epitaxy of RuO₂ on Rutile TiO₂ (011)

- RuO₂ has a same structure as rutile TiO₂, with small lattice mismatch (-2.0% in *a* direction, and 0.07% in *c* direction)

Clear fringes show high quality epitaxy



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

Conclusions

- Both Ru and RuO₂ 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 RuO₂ thin film can be prepared with Pulsed CVD with O₂ as the carrier gas.
- High quality epitaxy of RuO₂ on TiO₂ (011) can be obtained.

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