Ru Etching by ICP with O₂and Cl₂- Containing Plasma

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Talk Outline

- Why Ru: Model for ESH/Etch Issue
- Experimental Apparatus
- Experimental Approaches
- Studies of Ru etching and the Effect of Cl₂ Addition
- Conclusions
- Acknowledgement

2

General Ru Etch as Model for ESH/Process Interactions

- Why Ru?
 - Ru and RuO₂ are both conductors and have been proposed as new metal gate electrode materials
 - Proposed metal gate materials include: Ta, Ti, Zr, Ni, Mo, Ru, Pt, Ir, Ni, W; MoN, WN, TiN; In₂O₃, SnO₂, RuO₂;CrSi, WSi_x
 - Many new materials: need to develop <u>systematic procedures</u> to assess process and ESH impacts of etching.
- Ru Etching
 - Ru can be etched readily by O₂ based plasma and forms volatile etching by-product RuO₃, and RuO₄. What about etch by-product interactions with walls? Where do etch products go? How does this depend on chemistry/operating conditions?
- ESH
 - By-product RuO_4 may be toxic; Chose Ru etch as model etch by-product study.

Experimental Apparatus (side view)



* pumps and FTIR not to scale

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4

Experimental Apparatus (Top View)

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Experimental Approach

- Apparatus
 - ICP with *in-situ* diagnostic tools: ion MS, neutral MS, QCM, OES downstream FTIR
- Conditions
 - Ar/O_2 containing plasmas with or without Cl_2 addition
- Etching Rate Measurement
 - Film Etching Rate
 - 150mm wafer with Ru film prepared by sputtering
 - Film thickness measurement before and after etching with 4-point probe
 - Substrate can be biased up to 150V
 - Etching Rate on QCM
 - Ru coated QCM crystal, *In-situ* E/R measurement
 - Etching by floating potential plasma (not biased)

Experimental Approach, cont.



- Case 1 (Film Etching Rate)
 - Substrate: Ru film, QCM: Bare Crystal
 - Measure ER (film etching rate), and Wall
 Deposition Rate (R_{QCM}=R_{depo}-R_{re-etch})
 - Generate significant etch by-products, hence possible be detected by FTIR, ion MS, or Neutral MS.
- Case 2 (Etching Rate on QCM)
 - Substrate: Copper Plate, QCM: Ru Coated Crystal
 - Measure ER_{QCM} (*in situ*)
 - Very small exposed Ru coated area, ~0
 R_{depo}, hence ~0 R_{re-etch}
 - Only small amount of etch gas was consumed, hence inlet gas chemistry was

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studied

Cl₂ addition effect: wall deposition rate, film etching rate and effluent species



RuO₄ was found at the down-stream
 FTIR in other systems.

UCB Results without Cl₂ addition

- Etching Rate ~ 60 A/min
- Most of the etching by-product deposits on the wall.
- No RuO_4 was found at the downstream FTIR

UCB Results with Cl₂ Addition

- Etching Rate ~ 300 A/min
- Zero Wall Deposition Rate, i.e. all etching by-products leave the chamber.
- RuO₄ was detected at the downstream FTIR
- Literature suggests that by Cl₂ addition, RuO₂ etching rate increases due to increasing of O radical density.

Cal **Wall Deposition and Re-etching Processes**

Ar sputtering



-In Ar sputtering, Ru neutrals dominate the wall deposition process

-In Ar and Ar/O_2 plasma, ion flux only contribute partially to wall deposition

- In Ar/O_2 plasma, at zero bias: Ru-containing ion flux to the wall > wall deposition rate. Comparable re-etching process.

- Cl₂ addition: zero wall deposition rate, i.e. high R_{re-etch} or low R_{depo}. (volatile etch byproduct)....Which implies different mechanism dominates etching with Cl₂ addition. NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing



Effect of Cl₂ Addition

- Condition: Power 150W, Pressure 10mT, Ar 15 sccm, O₂+Cl₂ 39 sccm,
- Copper plate on the chuck, Ru coated QCM crystal
- Constant Ion Current (1.3 mA/cm²)



- Small Cl₂ addition
 increases E/R significantly
 - <u>Not</u> due to O density increases
- As increasing Cl₂ addition, E/R reaches maximum at O₂/(O₂+Cl₂) ~ 0.8
- But, reliability of OES?

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Neutral Density: OES vs. Neutral MS

Identical Condition as Previous Page



- Atomic O and Cl densities measured by neutral MS match actinometry by OES.
- Oxygen radical density and ER_{QCM} do not show the same trend, which implies that the reason that causes ER increases is contrary to what was thought in the literature.

Plasma Composition: ions



- Cl₂ Addition
 - Densities for Ru-containing species increase significantly.
 - Ru-containing oxychloride ions were detected.



Conclusion

- In Ru etching:
 - In Ar sputtering, neutral species dominate the wall deposition process.
 - Ru can be etched readily by O_2 containing plasma.
 - With Cl₂ addition,
 - E/R increases significantly
 - Zero wall deposition, i.e. all etching by-products leave the chamber.
 - RuO₄ can be found at the effluent
 - Ru-containing oxychloride possibly plays important role in Cl₂-containing O₂-base etching.
- Etch by-product composition and wall deposition/etch rate are sensitive functions of plasma conditions.
- Wall deposition characteristics affect feature profile critical dimension control: etch by-products used to engineer <u>CD control</u> and <u>selectivity</u>.
- Process control and ESH issues are **coupled** and must be **optimized simultaneously**

13



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