Advanced Metal Nitride Select Etch for 7 nm FEOL and BEOL Applications

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Agenda

- **Metal Nitride (MNx) Select Etch Requirements and Challenges**
- Effect of Nitridation, Temperature and Surface Film Properties on TiN Etch Rates
- Development of Select Etch Chemistries for FEOL and BEOL Applications
- Results
- Conclusion

Metal Nitride (MNx) Select Etch Requirements and Challenges

- Single-wafer processing; milder processing conditions
- Partially remove (“pull back” 10-30 Å removal) or totally remove hard mask (HM, 200-300 Å removal), profile trimming (< 30 Å)
- Wide range of selectivity/compatibility requirements (e.g., high k, low k, TEOS, BARC, metal gate, W, Al, Cu, SiGe, Ge, and III-V)
- Management/compatibility of:
  - Thin ALD films
  - Work function metal/metal alloys
  - BARC in FEOL & BEOL patterning/profiling

Metal Nitride (MNx) Select Etch Challenges

Performance of Standard/Conventional Etch Chemistries

Description	Temp.	TiN	TaN	SiN	TEOS	BARC	W	Al	AlN	CU
100:1 DHF	25° C	3	1	7	> 60	< 0.4	2	> 500	> 35	< 5
SC-1 (5:1:1 H_2O-28%NH4OH-30%H_2O_2)	65° C	> 100	0	1	1	> 100 (lift-off)	> 500	> 800	> 100	> 30

<u>Standard HF-based etchants</u>

- Ineffective MNx etch; TiN etch rates are too low to be useful
- Poor compatibility with TEOS, Al and AlN

<u>Standard alkaline peroxide-based etchants, such as SC-1</u>

- Good TiN etch rates
- Poor compatibility with W, Al, AlN, Cu and BARC (lift-off)

<u>Conventional etch chemistries</u>

- Cannot meet MNx etch needs for 7 nm nodes

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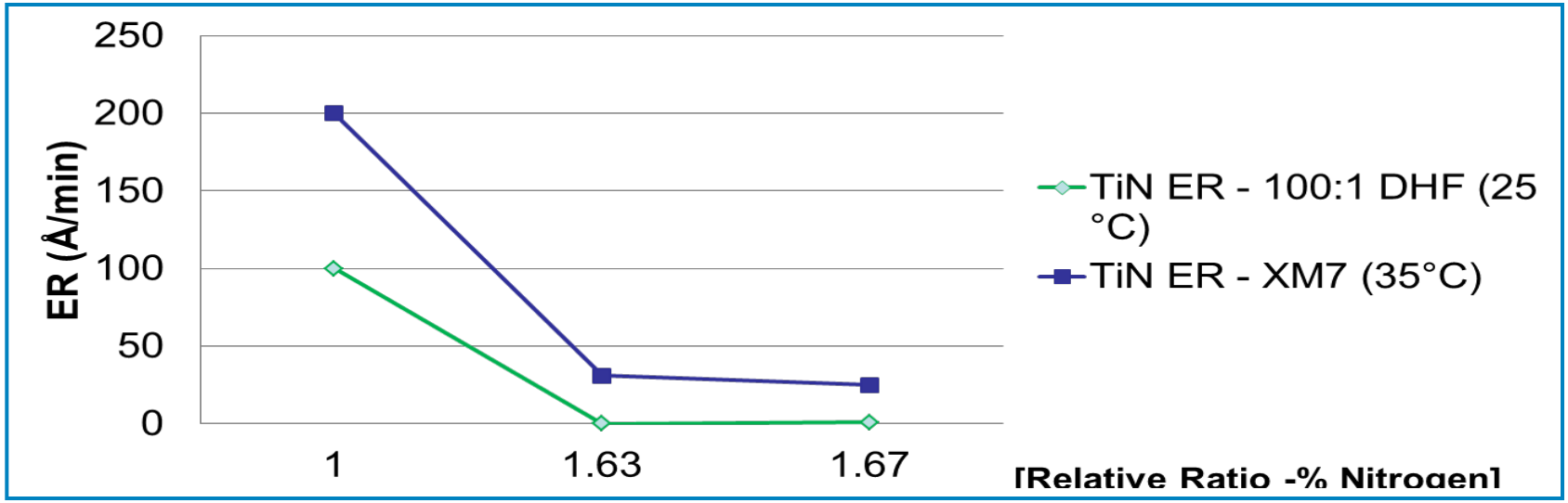
Effect of Nitridation on TiN Etch Rate

Sample Description	Atomic % Nitrogen	Atomic % Titanium	Etch Rate (Å/min) by 100:1 DHF at 25 °C	Etch Rate (Å/min) by XM-7 at 35 °C
PVD TiN #1	1X (standard)	1Y	> 100	200
PVD TiN #2	1.63X	0.31Y	0	31
CVD TiN #3	1.67X	0.27Y	1	25



- Relative % Nitrogen of TiN films increase from 1X to 1.6-1.7X
- TiN etch rates by 100:1 DHF decrease to < 1%
- TiN etch rates by XM-7 decrease to < 16%
- ***For ≤ 14 nodes (including 7 nm), most TiN films are higher % Nitrogen and more etch resistant***

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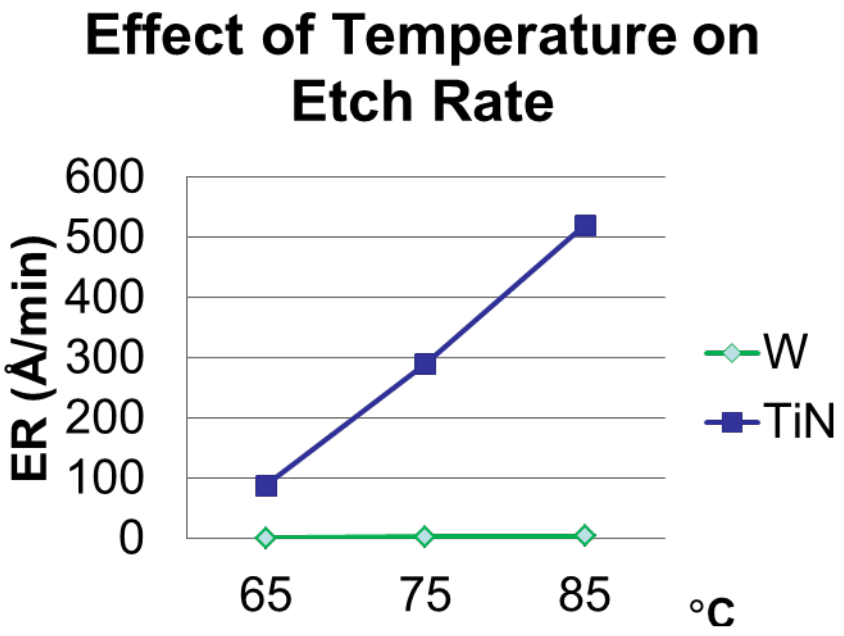
Effect of Temperature on Etch Rate: Example XSE-1

Material Description	Temp.	Etchant XSE-1
TiN	65 °C	88
	75 °C	290
	85 °C	520
W	65 °C	0.4
	75 °C	2.2
	85 °C	3
Low-k	65 °C	0
	75 °C	0.1
	85 °C	0.6



Observations for XSE-1:

- TiN etch rate is impacted significantly by temperature
- XSE-1 has superior W and low-k compatibility

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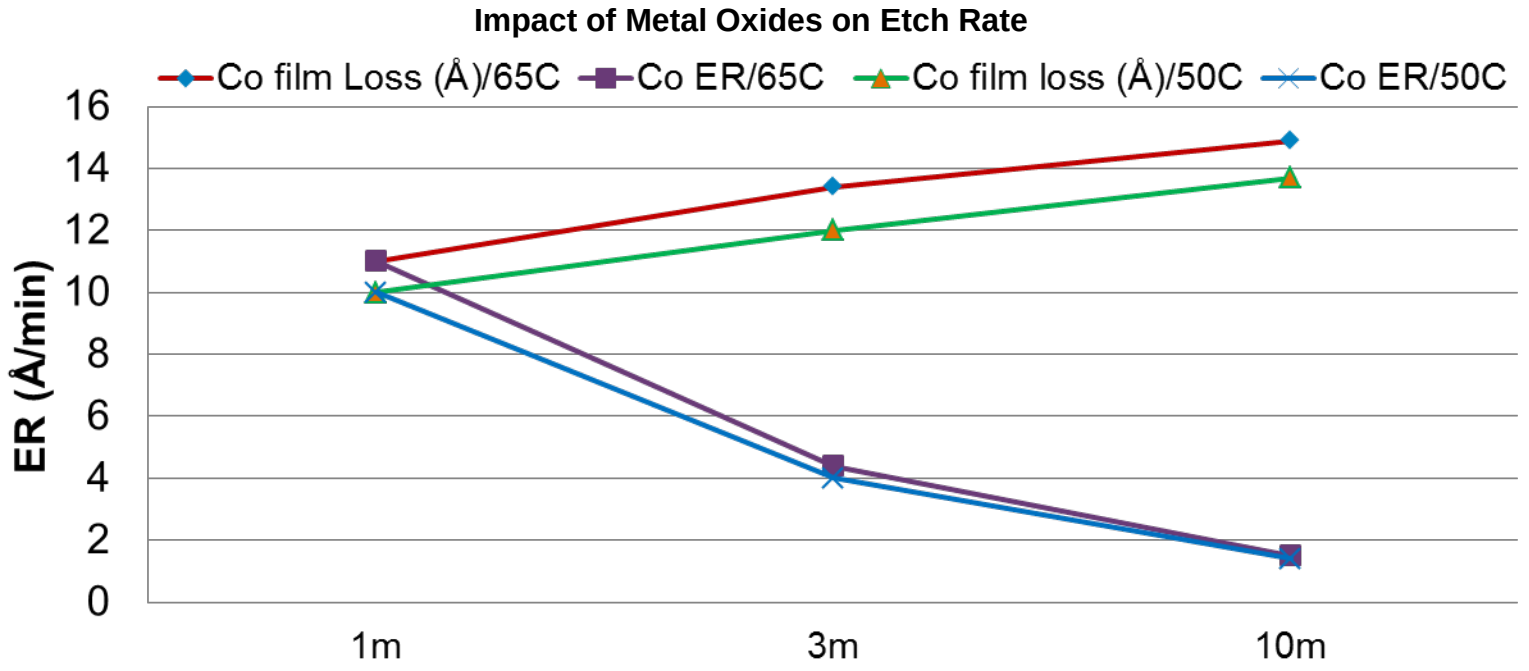
Effect of Surface Film Properties on Etch Rates

Co Etch Rate/Compatibility Study
3:1 XSE-7 with H_2O_2



Results:

- **"Co film" loss: large initial loss within first minute; minimal loss after**
- Likely ~ 10 Å CoO (cobalt oxide) on 15-20 Å Co film readily removed by this chemistry
- Etch rate: 1.5-11Å/min for CoO/Co film at 65 °C (depends on dipping time)
- **Literature: ~ 25 Å CoO for > 50 Å Co film. Metal oxides much less on < 25 Å Co film.** [L. Smardz et. Al. J. Appl. Phys, 5199 (1992)]

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Metal Nitride – A Number of Functional Constituents

Constituent Type	Titanium	Tantalum
Metal-Nitride	TiN	TaN
Metal Oxynitride	TiOxNy	TaOxNy
Metal Oxide	TiO_2, Ti_2O_3	Ta_2O_5
Metal-Metal	Ti-Ti	Ta-Ta

- Multiple types of bonding in metal nitride films (aside from M-N bonds)
- Other bonding types include metal-metal (m-m), metal oxides and metal oxynitrides
- Need to consider all of the bondings referenced above in evaluating metal nitride etch behaviors

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Development of Metal Nitride Select Etch Chemistries

J.T.Baker® chemistries are designed to:

- Include solubility factors at various pH and redox states (i.e., the full dissolution of all components and products/by-products from etches or cleans in solvent matrices)
- Eliminate particle-generating reactions: no self-internal reactions or reactions, especially those with the atmosphere/environment (e.g., air, oxygen, moisture)
- Manage and remove all film constituents: metal nitrides, metal oxynitrides and metal oxides – including pre-existing or generating in-situ surface oxides
- Address broad, expanding substrate/metallization compatibility requirements: ultrathin ALD films, BARC use in FEOL processing, work function alloys, etc.

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Metal Nitride Select Etch Chemistries

Summary Table: FEOL, MOL and BEOL Applications

Description	Temp.	TiN	TaN	SiN	Low-K	BARC	HfOx	W	Al	AlN	Cu
XSE-1	70 °C	180	12	5	< 2	> 100	14	0.4	4	-	> 800
XSE-2	70 °C	125	6	1.5	< 2	> 100	7	0.4	9	< 3	> 800
5:1 (XSE-3) – 30% H_2O_2	65 °C	180	0.7	0.4	< 3	0	0.1	> 800	> 800	-	12
5:1 (XSE-4) – 30% H_2O_2	65 °C	180	0	0.1	< 3	0	0.2	> 800	0	-	11
3:1 (XSE-6) – 30% H_2O_2	65 °C	350	3	0.2	< 3	< 5	0.1	> 400	< 10	1.5	< 3
3:1 (XSE-7) – 30% H_2O_2	50 °C	103	-	-	0	-	-	-	-	1	1
XSE-5	45 °C	20	< 0.9	0.7	< 3	< 0.4	5.4	3	> 800	> 35	> 800
	55 °C	73	< 0.9	2.4	-	< 0.4	>16	15	> 800	-	-
	65 °C	150	0.9	6	-	0.4	>16	40	> 800	> 35	-
100:1 DHF	25 °C	3	1	7	< 3	< 0.4	2	2	> 500	> 35	< 5
SC-1 (5:1:1)	65 °C	> 100	0	1	< 2	> 100 (lift-off)	0.1	> 500	> 800	> 100	> 30

Avantor has developed novel solutions that enable MNx select etch

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TiN Etch/Removal with Broad Capability

Compatible with Cu, Co, Al, AlN, High-k, Low-k, BARC

Description	Temp.	TiN	TaN	SiN	Low-k	HfOx	BARC
3:1 XSE7-30% H_2O_2	50 °C	100	-	-	0	-	-
3:1 XSE6-30% H_2O_2	65 °C	350	3	0.2	< 3	0.1	< 5
5:1 XSE4-30% H_2O_2	65 °C	180	0	0.1	< 3	0.2	0

Description	Temp.	Cu	Co	Al	AlN	W	
3:1 XSE7-30% H_2O_2	50 °C	1	1.5	-	1	-	
3:1 XSE6-30% H_2O_2	65 °C	< 3	< 3	< 10	1.5	> 400	
5:1 XSE4-30% H_2O_2	65 °C	11	1	0	-	> 800	

- **XSE-7 with peroxides**: TiN pull back/removal, Cu/Co/AlN/low-k compatibility
- **XSE-6 with peroxides:** TiN pull back/total HM removal; Cu/Co/AlN/low-k and HfOx/BARC compatibility
- **XSE-4 with peroxides:** TiN pull back/HM removal, ≈ XSE-6, + Al compatibility

Multiple options for various, customized needs

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TiN Etch/Removal with Broad Capability

Compatible with W plus Low-k, BARC, Al, AlN (suitable for M1 and other applications)

Description	Temp.	TiN	TaN	SiN	Low-k	BARC	HfOx	W	Al	AlN
XSE-1	70 °C	180	12	5	< 2	> 100	14	0.4	4	-
XSE-2	70 °C	125	6	1.5	< 2	> 100	7	0.4	9	< 3
XSE-5	45 °C	20	<0.9	0.7	< 3	< 0.4	5.4	3	> 800	> 35
	55 °C	73	< 0.9	2.4	-	< 0.4	> 16	15	> 800	-
	65 °C	150	0.9	6	-	0.4	> 16	40	> 800	> 35

- **XSE-1**: TiN pull back/total removal; W/low-k/Al compatibility
- **XSE-2**: TiN pull back/total removal; ≈ XSE-1, + SiN/AlN compatibility
- **XSE-5**: Select TiN etch vs. TaN, plus BARC compatibility

Multiple options for various, customized needs

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Conclusion

- **Surface film property studies provide a better understanding of metal nitride etch mechanisms**
  - Higher nitridation levels increase etch resistance
  - Certain nitrides show large temperature effects
  - Surface metal oxides and oxynitrides impact MNx etch behaviors
- **J.T.Baker® chemistries enable metal nitride etch**
  - Multiple chemistries for a wide range of compatibility needs: W, TEOS, low-k, high-k, BARC, Cu, Al and Al alloys
  - Excellent etch selectivity: 100x or greater
  - Tunable metal nitride etch rates: 0 to > 600 Å/min
  - Suitable for FEOL, MOL and BEOL applications on single wafer tools

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