Study and Reduction of Plasma Damage of Porous Ultra Low-k Dielectrics during Photoresist Stripping

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Introduction

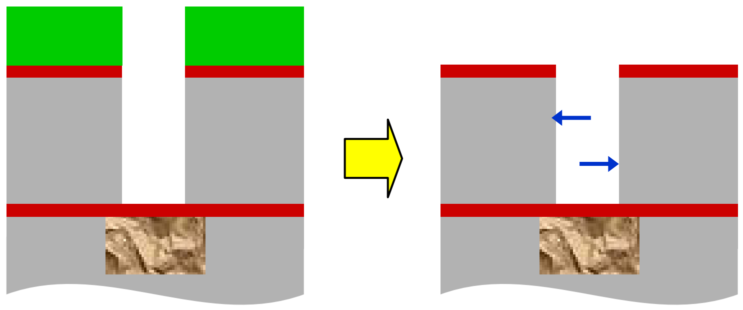
- Copper/low-k technology is being used to reduce the resistance-capacitance (RC) delay of the interconnect to increase the signal processing speed for ULSI devices.
- Low-k dielectric films contain a high content of carbon and posses high porosity, thus are vulnerable to physical and chemical damages during IC chip fabrication.
- In the standard dual-damascene process flow, PR stripping can cause the most severe damage to the low-k film among all plasma etching and cleaning steps.

Challenges in Photoresist (PR) Strip on Low-k Films

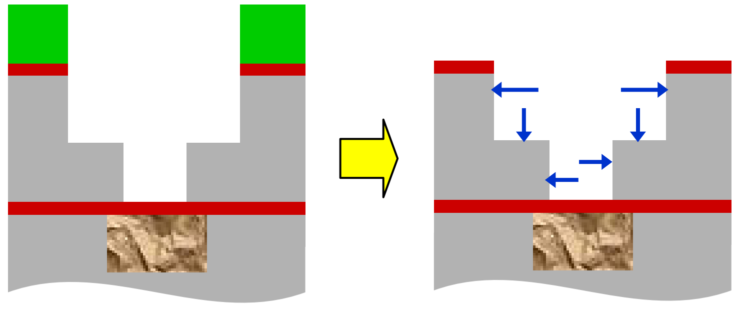
- Dielectric property degradation of low-k material in traditional oxygen-based plasma.
  - → Increase of k value and leakage current.
- Low etch selectivity between PR and low-k dielectrics.
  - → Profile distortion and surface damage.
- Low chemical and mechanical strength of the low-k film.
  - → Difficult cleaning of etch residues produced in low-k and barrier layer etching.

Low-k Damage during PR Stripping in Dual-Damascene Process Flow

post via-etch strip



post trench-etch strip

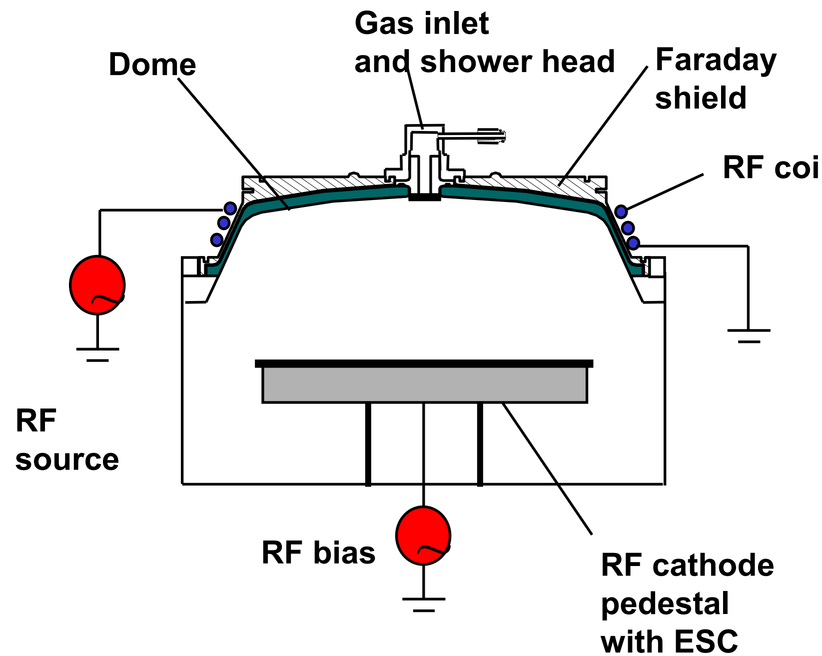


- **Low-k Damage Mechanism**
  - General mechanism understood: PR strip plasma removes carbon and forms strong polar bonds (Si-O, Si-OH) on the surface of low-k materials. The damaged surface also absorbs moisture……
  - Details still under study
- **Low-k Damage Extent**
  - Chemistry, tool and process condition dependent.

Outline of This Work

- **Investigation of low-k damage during PR strip.**
  - High density ICP plasma reactor
  - Porous MSQ film (k~2.2)
  - Blanket and patterned wafers
  - Various process conditions
  - Different chemistries (O_2, H_2, N_2, H_2/N_2, NH_3)
- **Understanding of low-k damage mechanism.**
- **Optimization of PR strip process.**

eHighlands Chamber



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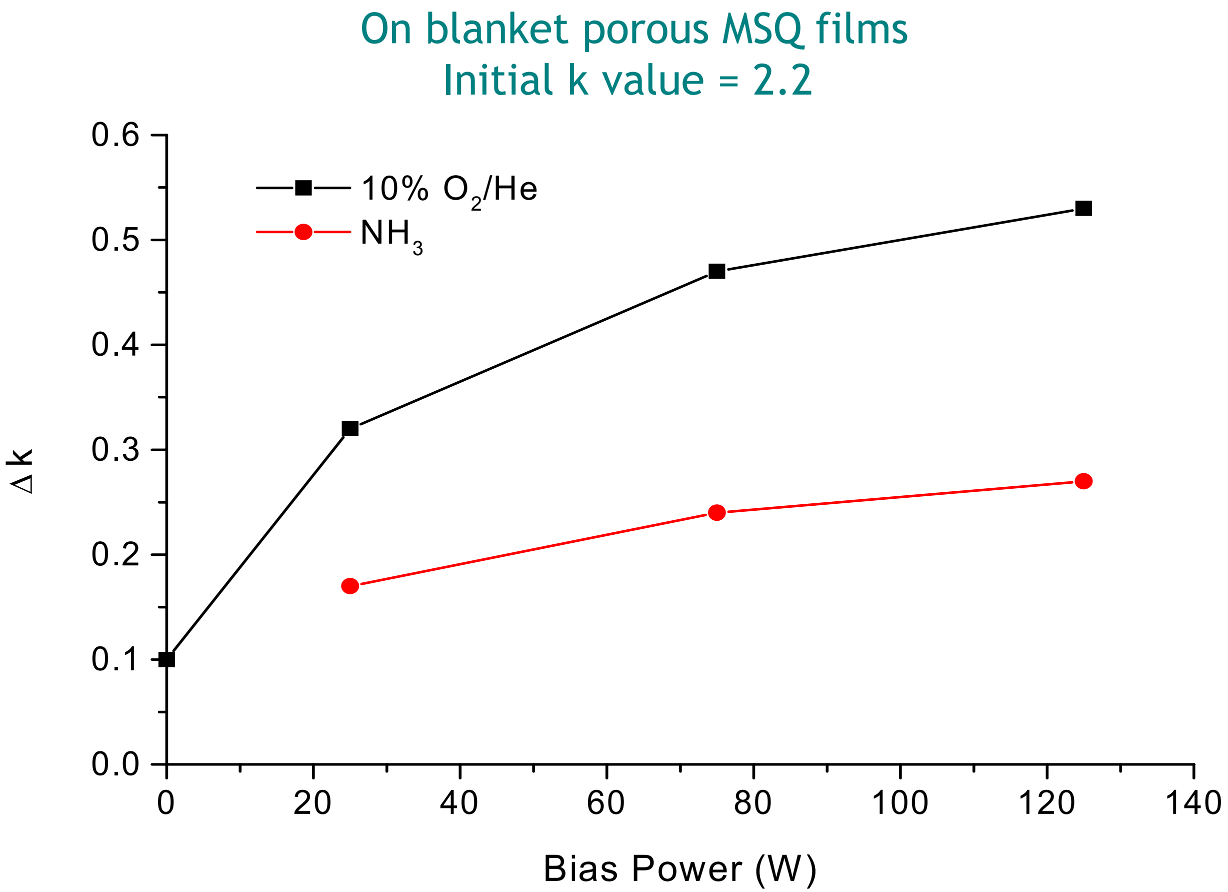
Effect of Ion Bombardment on Low-k Damage



Two most important factors to control low-k damage:

- Ion bombardment. Higher ion energy causes more damage.
- Type of chemistry used for PR strip.

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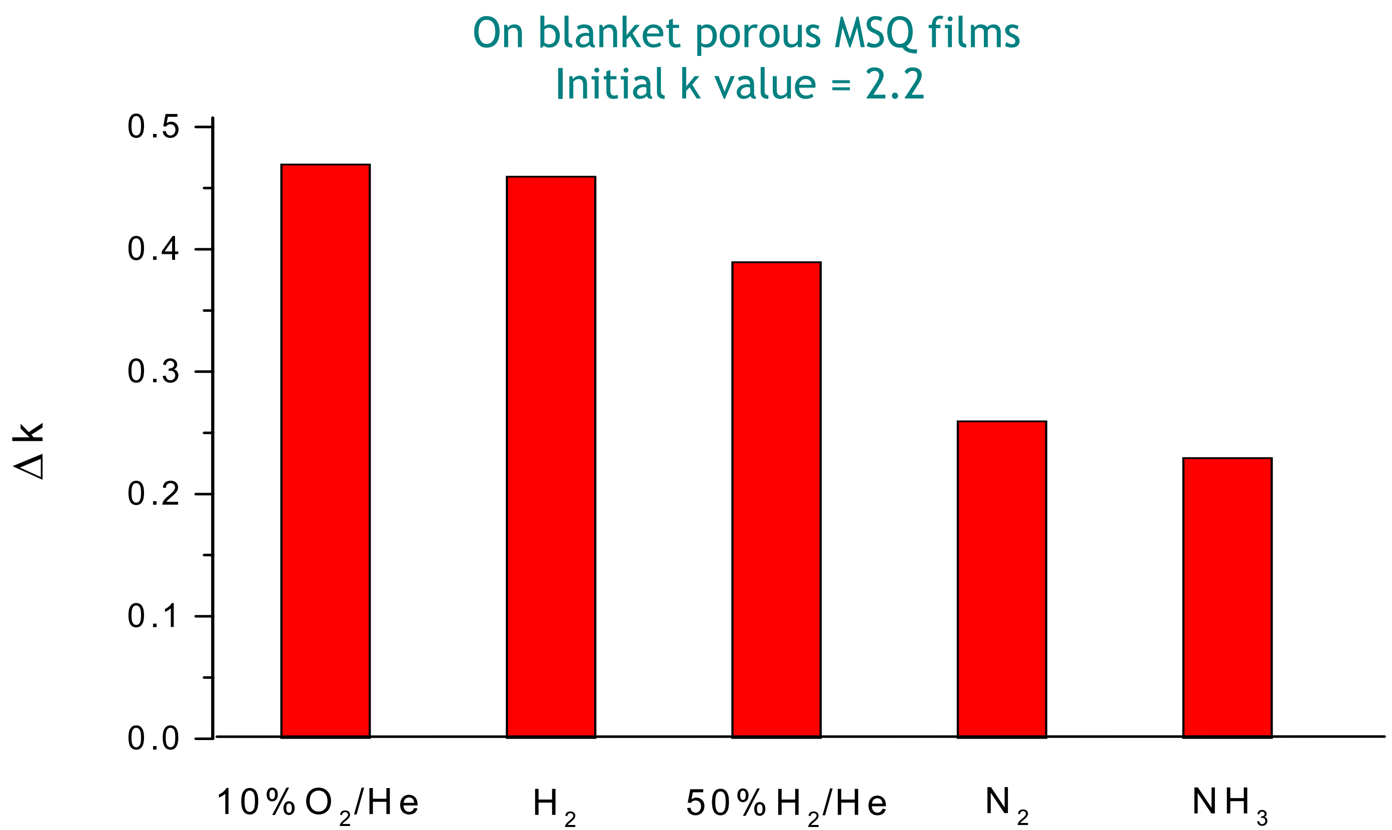
Effect of PR Strip Chemistry on Low-k Damage



- O_2 plasma generates the most severe low-k damage.
- Dielectric constant change in H_2 plasma is also very large with respect to O_2 plasma for the same process time.
- N_2 chemistry shows a much smaller low-k damage, while NH_3 chemistry gives the best performance.

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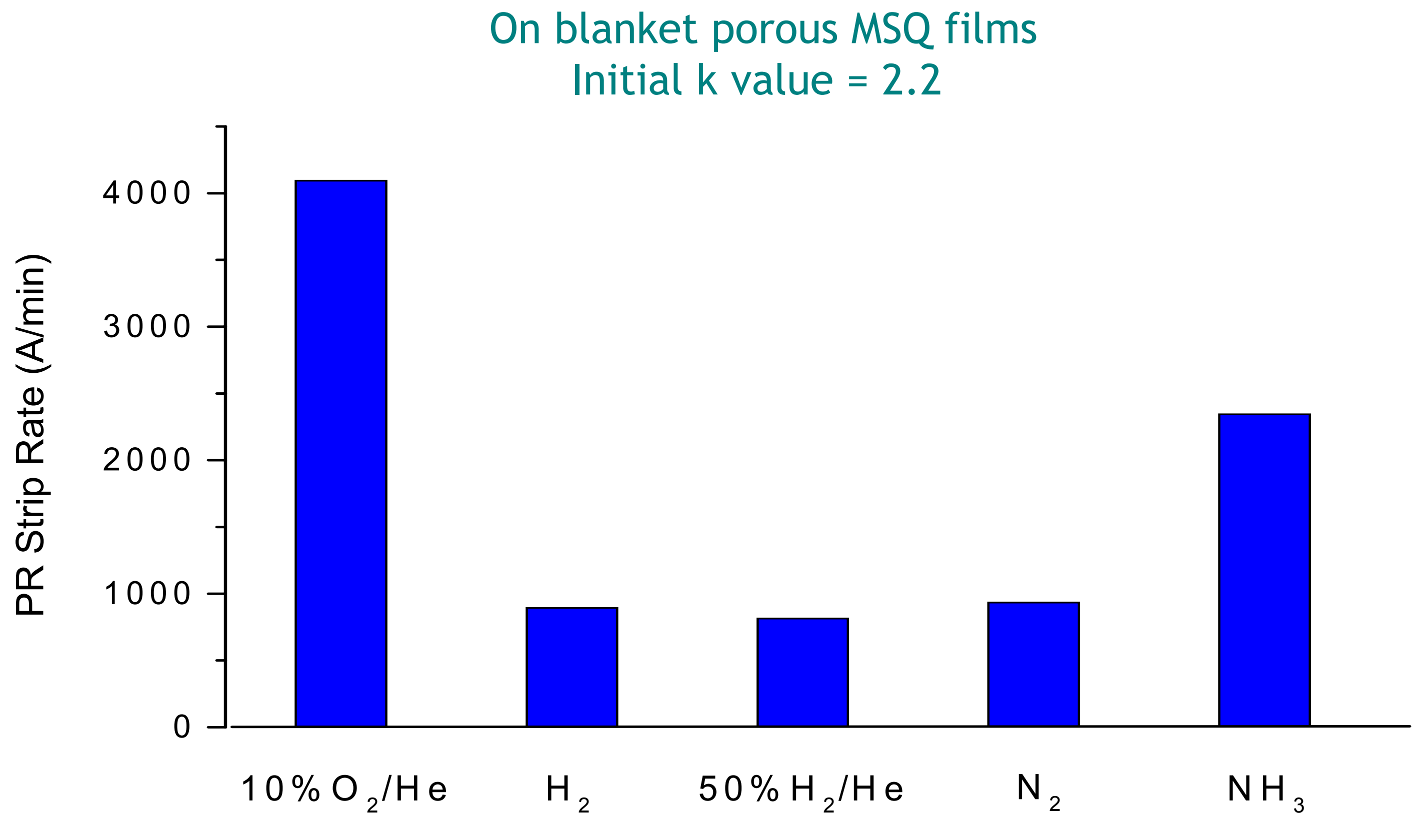
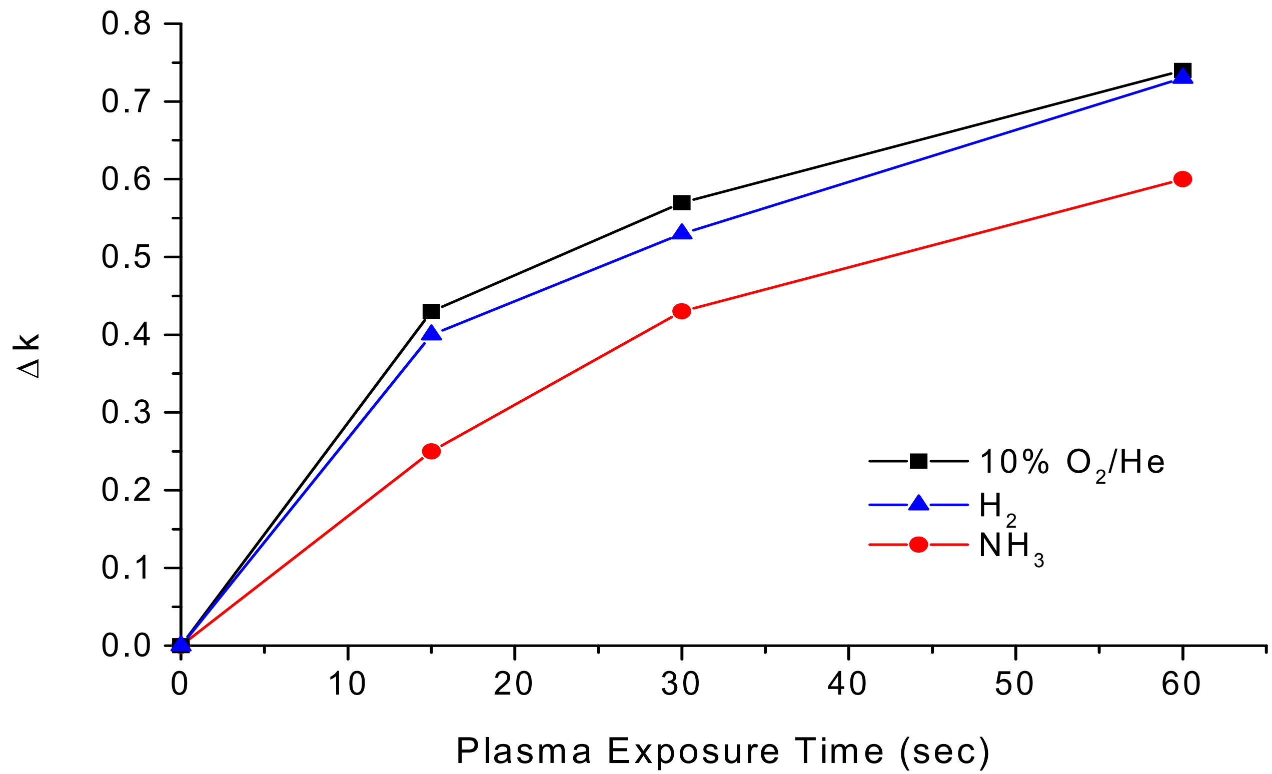
PR Strip Rate with Different Chemistries



- O_2 plasma strips PR very fast.
- H_2 and N_2 plasmas generate the slowest PR strip rate while NH_3 plasma gives the highest one among the reducing type of chemistries.

Effect of Plasma Exposure Time on Low-k Damage

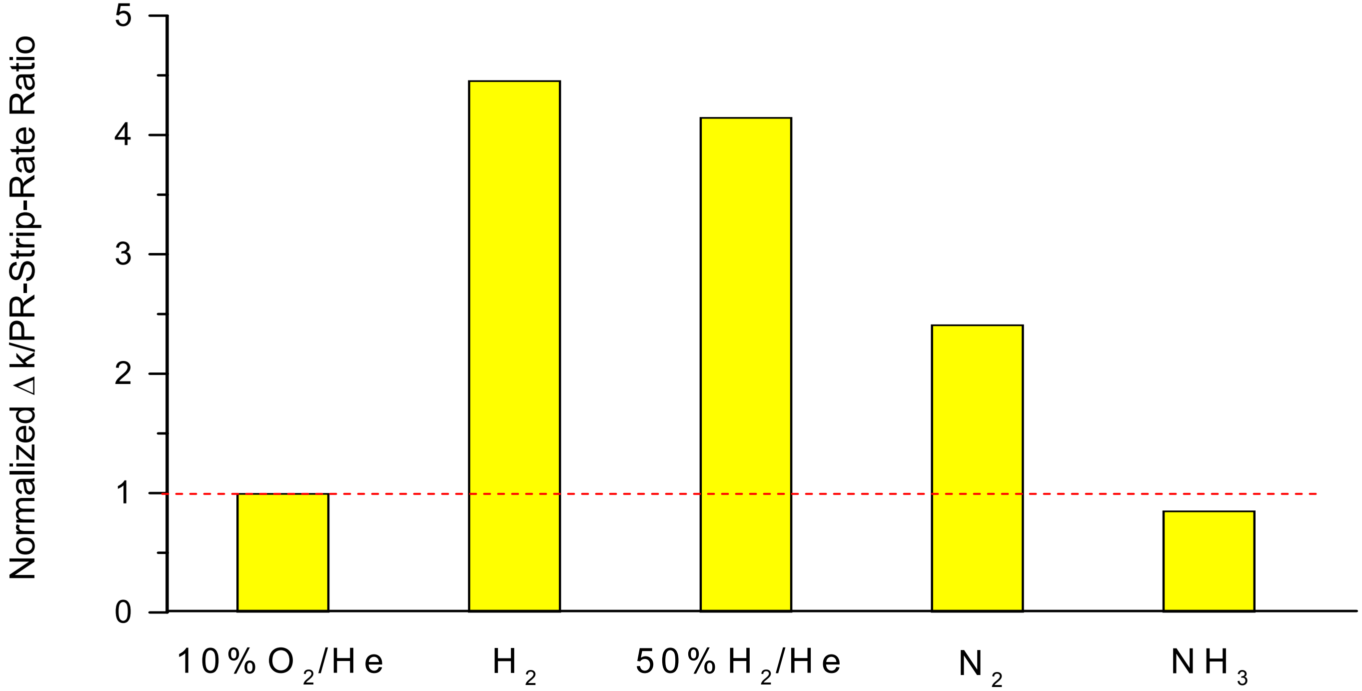
Blanket porous MSQ films exposed to NH_3 plasma
Initial k value = 2.2



Extent of low-k damage increases with plasma exposure time.

Δk/PR-Strip-Rate Ratio with Different Chemistries

On blanket porous MSQ films
Initial k value = 2.2



- Δk/PR-strip-rate ratio evaluates the efficiency of PR strip against the low-k damage to the surface directly exposed to the plasma.
- Both H_2 and N_2 chemistries give much worse results than O_2-based chemistry.
- The performance of NH_3 plasma is better than O_2 plasma.

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Low-k Damage in PR Strip Using O_2-free Chemistries

- **Major reactions to cause low-k damage**
  - H-containing chemistries

$$\text{Si-CH}_3 + 2\text{H} \longrightarrow \text{Si-H} + \text{CH}_4 \qquad \Delta H(298K) = -411\ \text{KJ/mol}$$

$$\text{Si-O-Si} + 2\text{H} \longrightarrow \text{Si-H} + \text{Si-OH} \qquad \Delta H(298K) = -325\ \text{KJ/mol}$$

$$\text{Si-OH} + 2\text{H} \longrightarrow \text{Si-H} + \text{H}_2\text{O} \qquad \Delta H(298K) = -325\ \text{KJ/mol}$$

  - N-containing chemistries

$$\text{Si-CH}_3 + 3\text{N} \longrightarrow \text{C-N} + \text{NH}_3$$

- **Thermodynamically, these reactions are more difficult than those caused by O_2. Therefore, the low-k damage will be less severe without enough ion bombardment intensity. However, under ion bombardment they can cause more severe damage because the time needed to strip a certain thickness of PR is longer for O_2-free chemistries.**

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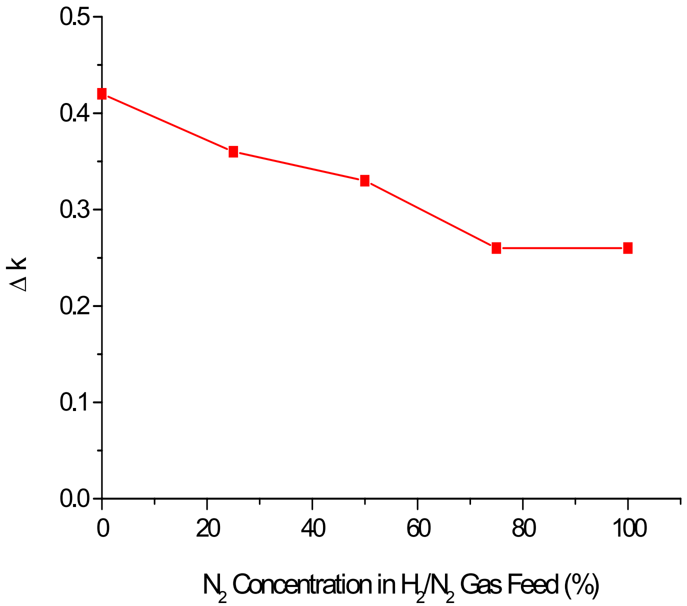
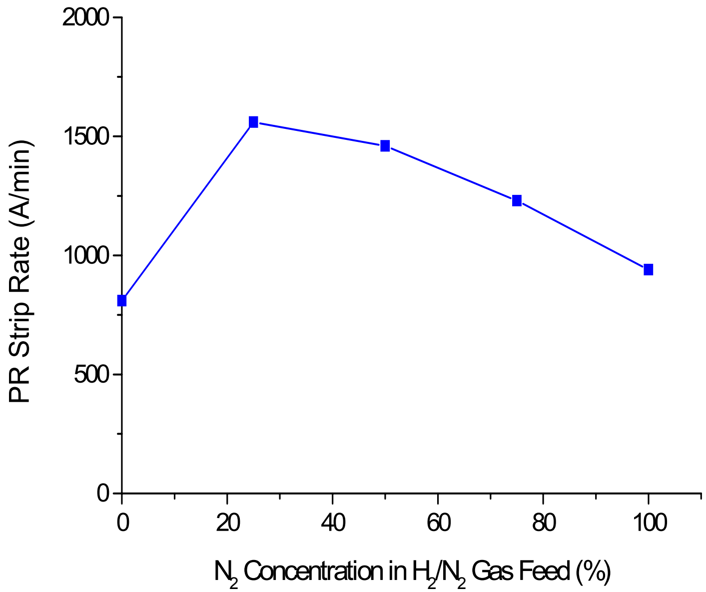
PR Strip Using H_2/N_2 Chemistry – Effect of N_2%

Low-k Damage



PR Strip Rate



- k value change decreases almost linearly with increasing N_2% - simple dilution effect.
- Low-k damage in pure N_2 plasma is the lowest - Less favorable reaction of nitrogen with the Si-CH_3 group.
- Dependence of PR strip rate on N_2% is nonlinear.
- Over the entire N_2% range of the H_2/N_2 plasma, the k value change is larger and the PR strip rate is lower than those of the NH_3 plasma.

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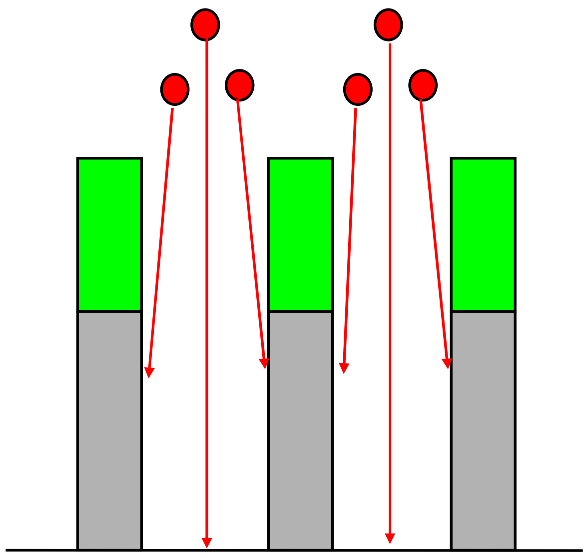
Low-k Damage on Patterned Wafers

- Low-k damage on the dual-damascene structures occurs on the top and bottom surfaces of the via and trench sidewalls. The patterned sidewall is impinged upon by scattered ions and damaged, contributing significantly to RC delay due to large sidewall area.

- Low-k damage on the sidewall can be evaluated through profile distortion after PR stripping, especially after dipping the stripped samples into diluted 1% HF solution, and electrical tests.



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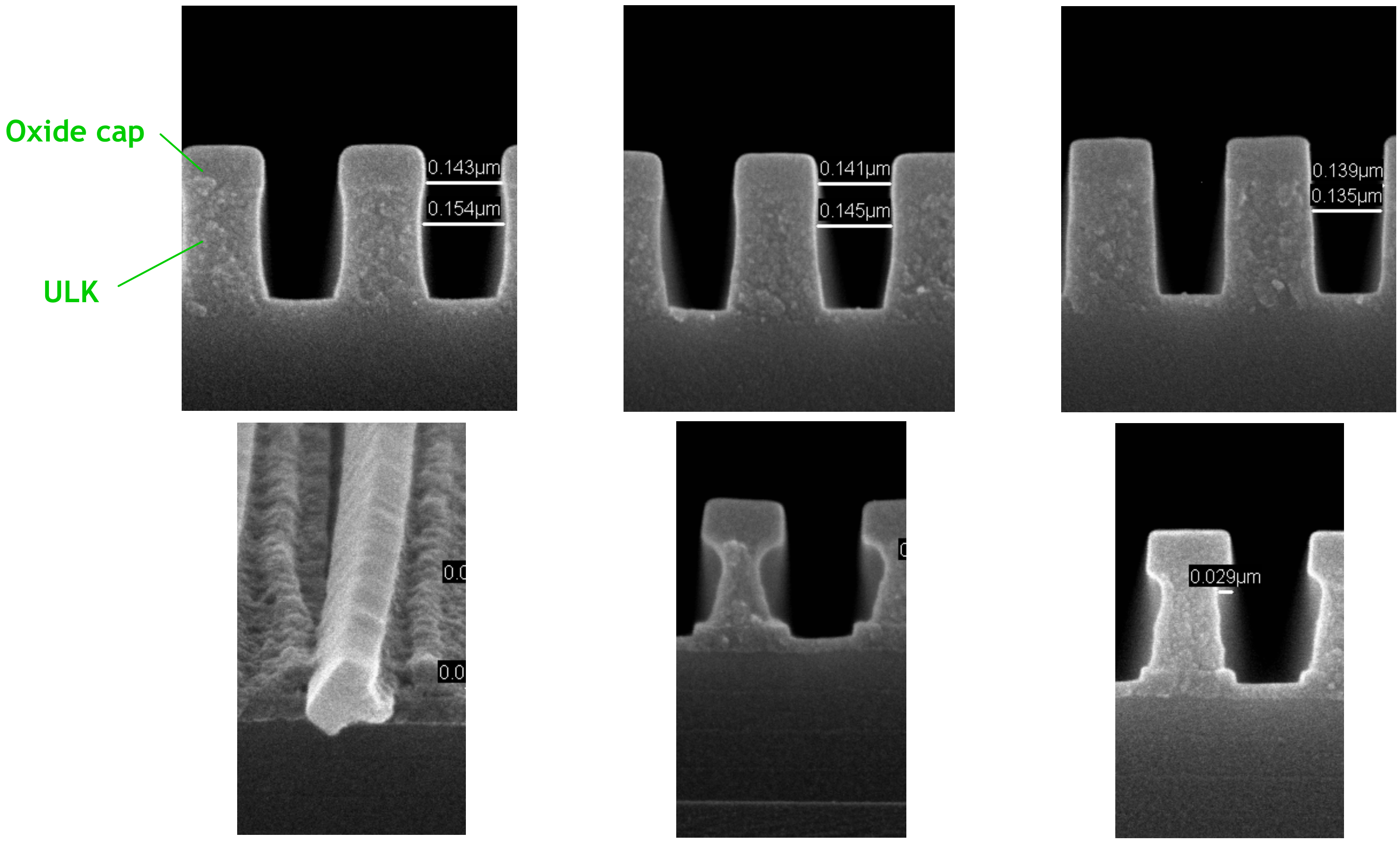
Sidewall Damage on Porous MSQ after PR Strip

Chemistry Effect

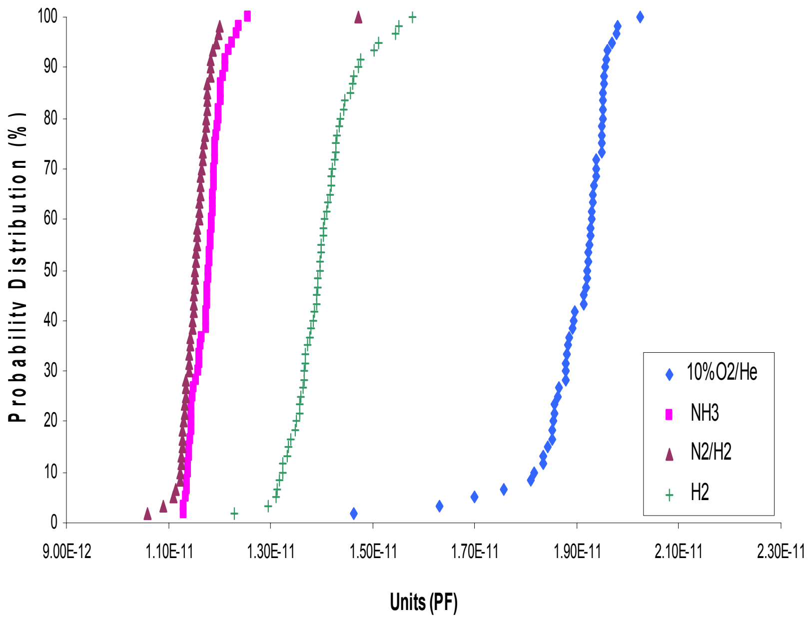
10%O_2/He | **H_2/N_2** | **NH_3**



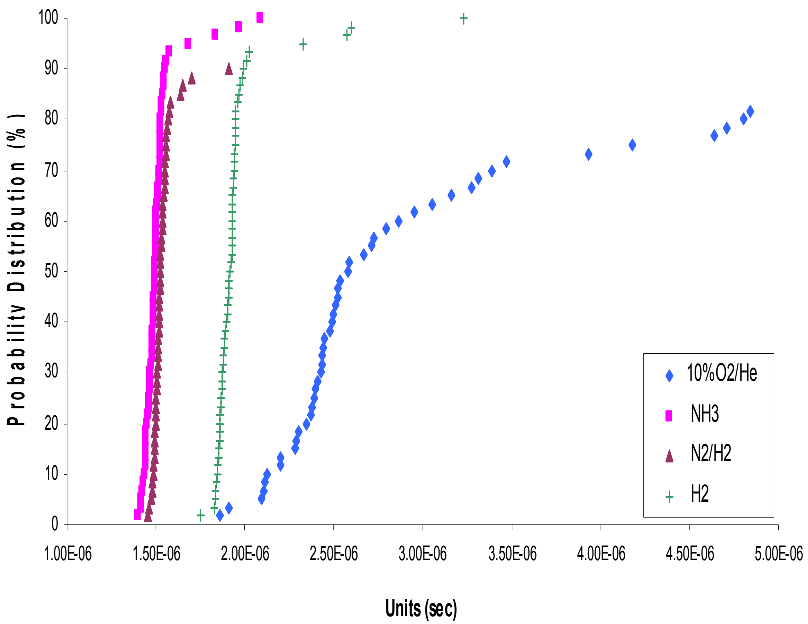
Lower row of SEM pictures taken after 20” dip in 1% HF.

Electrical Performance of PR Strip on Porous MSQ
Chemistry Effect

Capacitance



RC Constant

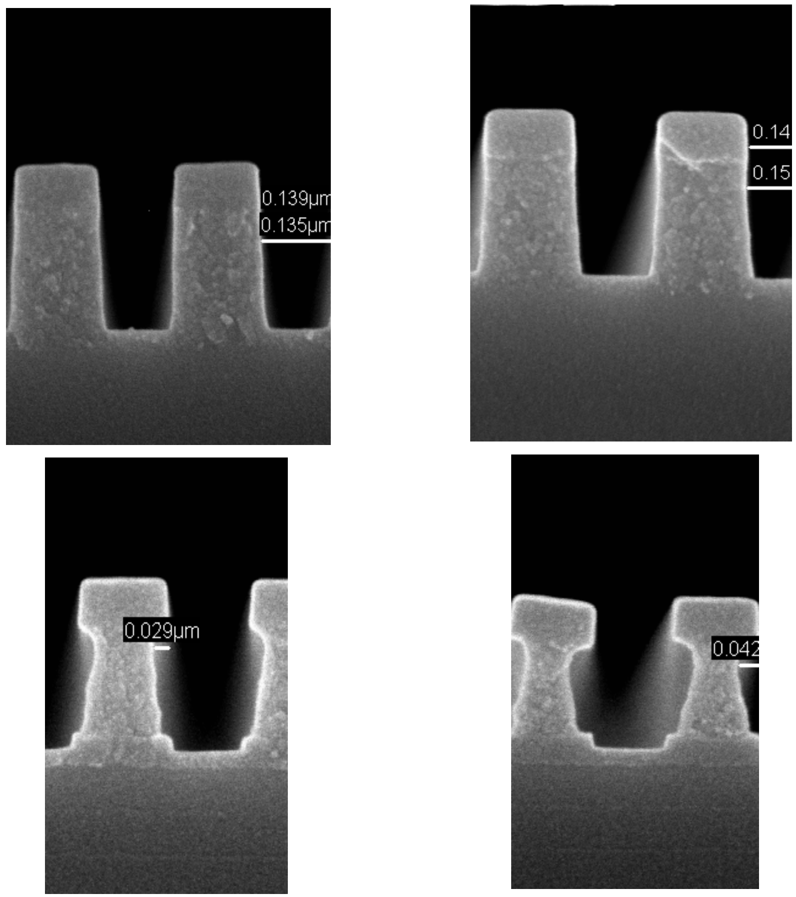


Capacitance and RC constant decrease in the following order:
diluted O_2 > H_2 > H_2/N_2 > NH_3 > NH_3/N_2

Sidewall Damage on Porous MSQ after PR Strip

Source Power Effect

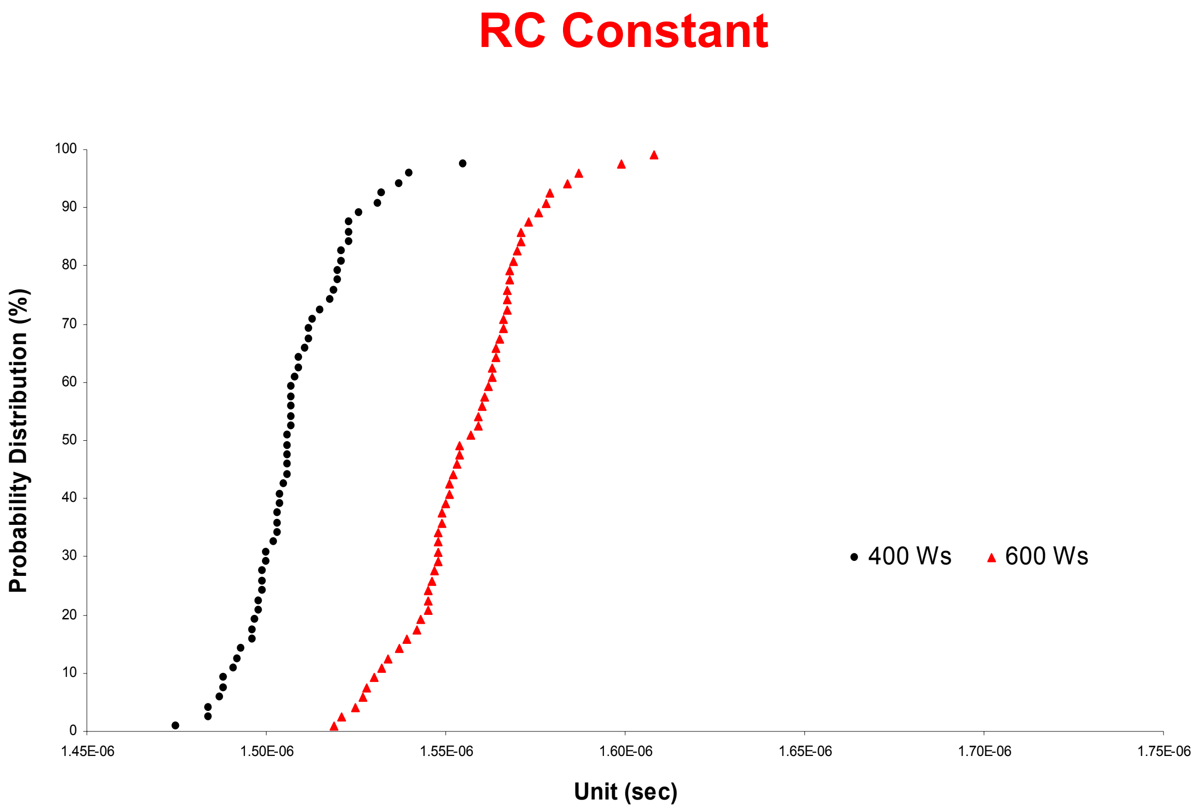
600Ws **1200Ws**



Lower row of SEM pictures taken after 20” dip in 1% HF.

Electrical Performance on Porous MSQ after PR Strip

Source Power Effect



Low-k damage becomes more serious with increasing source power, leading to a larger RC delay.

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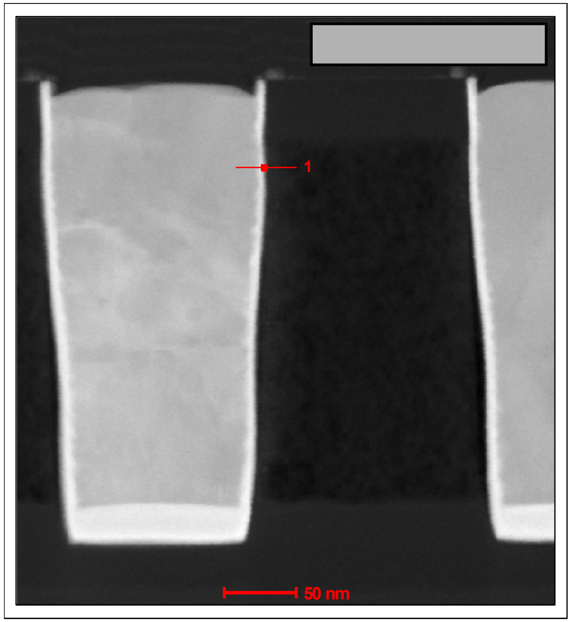
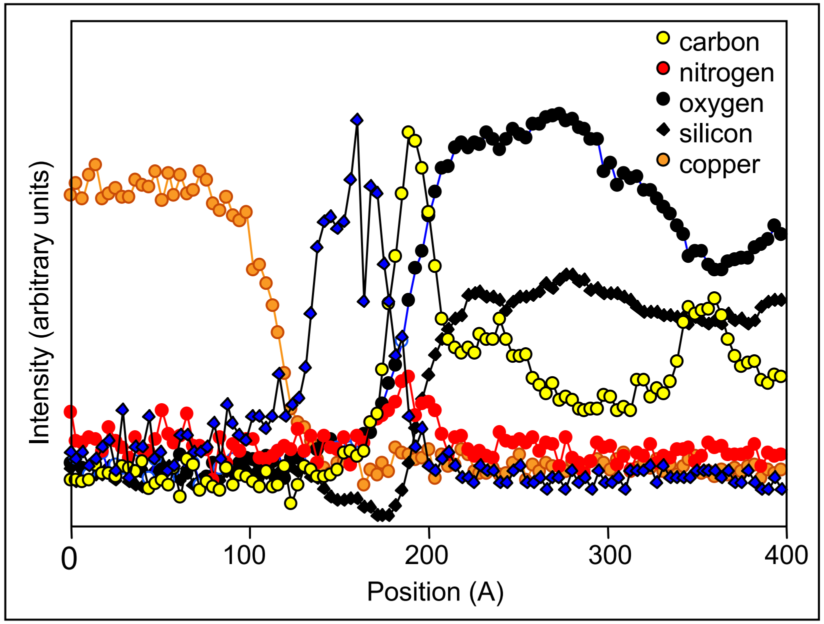
Film Composition Profile – EELS/EDXS Analysis

PR stripped in NH_3 plasma





- A transition layer about 50 Å thick is at the interface between the copper liner and the low-k film.
- Nitrogen content inside the low-k film is very low, eliminating the concern about possible PR poisoning in the trench litho step in the dual-damascene process flow.

Summary

- Low-k film degradation during PR stripping depends on process conditions. Higher ion energy accelerates the carbon depletion and silicon oxide formation, leading to more severe low-k damage.

- On blanket wafers, O_2 chemistry generates very severe film degradation. H_2 plasma also causes the same or more low-k damage under strong ion bombardment. N_2 and H_2/N_2 mixtures show less damage. NH_3 causes the least damage while giving the highest PR strip rate of the reducing chemistries.

- On patterned wafers, low-k damage on the sidewall has a major contribution to the electrical performance. O_2 plasma results in the highest line capacitance and RC constant, and NH_3 plasma has some of the best values for these parameters. Results for H_2/N_2 and pure H_2 chemistries are between the two extreme cases.

- Based on the results, NH_3 is a good chemistry for PR stripping over ultra low-k films in conjunction with optimized process conditions.

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