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 possess 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.
- Low etch selectivity between PR and low-k dielectrics.
- Low chemical and mechanical strength of the low-k film.

- Increase of k value and leakage current.
- Profile distortion and surface damage.
- Difficult cleaning of etch residues produced in low-k and barrier layer etching.
Low-k Damage during PR Stripping in Dual-Damascene Process Flow

- **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 (O₂, H₂, N₂, H₂/N₂, NH₃)
- Understanding of low-k damage mechanism.
- Optimization of PR strip process.
Effect of Ion Bombardment on Low-k Damage

On blanket porous MSQ films
Initial $k$ value = 2.2

Two most important factors to control low-k damage:
- Ion bombardment. Higher ion energy causes more damage.
- Type of chemistry used for PR strip.
**Effect of PR Strip Chemistry on Low-k Damage**

On blanket porous MSQ films

Initial k value = 2.2

- $O_2$ 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.
PR Strip Rate with Different Chemistries

On blanket porous MSQ films
Initial k value = 2.2

- O₂ plasma strips PR very fast.
- H₂ and N₂ plasmas generate the slowest PR strip rate while NH₃ 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.
$\Delta k$/PR-Strip-Rate Ratio with Different Chemistries

On blanket porous MSQ films
Initial $k$ value = 2.2

- $\Delta k$/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.
Low-k Damage in PR Strip Using $O_2$-free Chemistries

- **Major reactions to cause low-k damage**
  - **H-containing chemistries**
    \[
    \text{Si-CH}_3 + 2\text{H} \rightarrow \text{Si-H} + \text{CH}_4 \quad \Delta H(298K) = -411 \text{ KJ/mol}
    \]
    \[
    \text{Si-O-Si} + 2\text{H} \rightarrow \text{Si-H} + \text{Si-OH} \quad \Delta H(298K) = -325 \text{ KJ/mol}
    \]
    \[
    \text{Si-OH} + 2\text{H} \rightarrow \text{Si-H} + \text{H}_2\text{O} \quad \Delta H(298K) = -325 \text{ KJ/mol}
    \]
  - **N-containing chemistries**
    \[
    \text{Si-CH}_3 + 3\text{N} \rightarrow \text{C-N} + \text{NH}_3
    \]

- **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.
- **k** value change decreases almost linearly with increasing **N₂%** - simple dilution effect.
- Low-k damage in pure **N₂** plasma is the lowest - Less favorable reaction of nitrogen with the Si-CH₃ group.
- Dependence of PR strip rate on **N₂%** is nonlinear.
- Over the entire **N₂%** range of the **H₂/N₂** plasma, the **k** value change is larger and the PR strip rate is lower than those of the **NH₃** plasma.
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.
Sidewall Damage on Porous MSQ after PR Strip
Chemistry Effect

10%O₂/He  H₂/N₂  NH₃

Oxide cap  ULK

Lower row of SEM pictures taken after 20" dip in 1% HF.
Capacitance and RC constant decrease in the following order: diluted O₂ > H₂ > H₂/N₂ > NH₃ > NH₃/N₂
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.
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, O₂ chemistry generates very severe film degradation. H₂ plasma also causes the same or more low-k damage under strong ion bombardment. N₂ and H₂/N₂ mixtures show less damage. NH₃ 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. O₂ plasma results in the highest line capacitance and RC constant, and NH₃ plasma has some of the best values for these parameters. Results for H₂/N₂ and pure H₂ chemistries are between the two extreme cases.

- Based on the results, NH₃ is a good chemistry for PR stripping over ultra low-k films in conjunction with optimized process conditions.