Plasma-induced low-k modification and its impact on reliability

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ABSTRACT

Porous low-k materials are required as interlayer dielectrics in future technology nodes in order to compensate for the RC-delay and power consumption increase associated with continuing device shrinkage. Porous low-k films are typically composed of silica and silsesquioxanes containing organic hydrophobic groups. The exposure of such films to a plasma ambient leads to an unwanted increase of the leakage current and of the dielectric constant of the film. The fundamentals of plasma damage, including low-k material modification and moisture adsorption, are explained and potential ways of reducing plasma damage are discussed. Moisture adsorption also degrades the dielectric reliability margin. This phenomenon is becoming a major challenge but so far has not been adequately addressed nor systematically investigated. Desorbing moisture by thermal anneal improves the electrical properties including reliability performance, but the resulting low-k reliability is still far below that of an optimized integration scheme. Several electrical characterization methods (time-dependent dielectric breakdown (TDDB), triangular voltage sweep (TVS) and thermal desorption spectroscopy (TDS)) were combined to measure the reliability margin, to identify the physical mechanism(s) and to find ways of restoring the margin degradation.

Introduction

Nowadays, porous low-k films based on silica and silsesquioxanes with 10-15% of organic hydrophobic groups are the most favored class of materials for advanced interconnect technology nodes. The hydrophobic groups are bonded to an Si atom in the $SiO_{4/2}$ matrix and can be represented as $O_3\equiv Si\text{-}CH_x$. To reach a k-value below 3.0, introduction of artificial porosity is needed [1]. Advanced low-k materials have a porosity of 30-50%, a typical pore size being close to 2-2.5nm. Although the matrix of these materials has properties similar to traditional SiO_2, their chemical stability and reactivity strongly depend on porosity. Materials with interconnected pores are chemically active because of the high diffusion rate of active chemicals and special efforts are needed to protect the internal surface. The exposure of these films to a plasma ambient leads to the loss of hydrophobic groups and to the densification of their silica backbone. This causes an unwanted increase of the dielectric constant of the film as well as an increase of the leakage current. The extent of this damage strongly depends on the type of plasma conditions such as chemistry and power (energy and intensity of ion bombardment and UV radiation) and on the porosity of the film.

Plasma damage of porous low-k films: fundamentals

During device fabrication, the low-k films are exposed to various plasmas. For instance, a reactive ion etch (RIE) plasma is used for pattern fabrication, a strip and cleaning plasma is needed for resist ash and post dry etch polymer removal, downstream plasma cleaning is used before the metal barrier deposition on the feature sidewalls and post-CMP Cu oxide reduction is applied before fabrication of the next level of metallization [2]. All of these plasmas have different properties and generate different types of damage. For instance, ion sputter cleaning, which is used before barrier deposition, densifies the low-k surface; high pressure NH_3 plasma, which is used for Cu oxide reduction, strongly reduces the CH_3 group's concentration. Damage of low-k materials during RIE can be significantly reduced when an O_2-free fluorocarbon plasma is used [3]. Both the lack of oxygen radicals and the CF_x polymer deposited in the top part of the pores reduce penetration of active radicals and damage of the internal pore surface. The surface densification due to ion bombardment can play a positive role in certain cases. Low-k films with small pore size and/or pores with high degree of tortuousity can be sealed during the densification. As a result, the internal surface of the low-k film becomes inaccessible to active molecules during further processing. The most challenging plasma treatment is related to strip and cleaning plasmas based on oxygen- or hydrogen-containing chemistries. Modification of low-k materials in an oxygen plasma (1) results in the formation of Si-OH groups that are potential centers for further moisture adsorption (Figure 1).

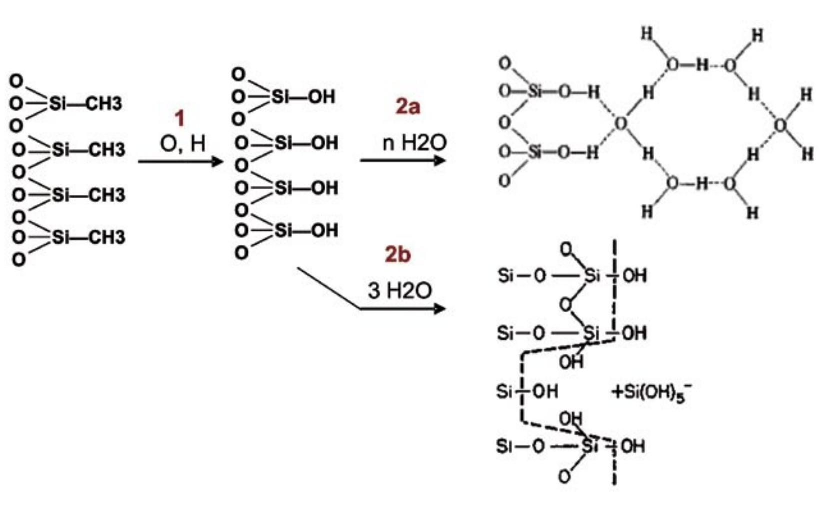

Figure 1. Removal of hydrophobic groups in reaction (1) leads to the formation of silanol SiOH groups. The followed exposure on air leads to multimolecular adsorption of water molecules (2a) and/or irreversible degradation (2b), which is an initial stage of stress corrosion cracking.

If the temperature is sufficiently high, some of the surface silanol groups can condense with partial restoration of hydrophobic properties (2) (see Figure 2).

(1) $\equiv$Si-CH$_3$ +4O $\rightarrow$ $\equiv$Si-OH + CO$_2$ + H$_2$O

(2) $\equiv$Si-OH $\rightarrow$ $\equiv$Si-O-Si$\equiv$ + H$_2$O

Reaction (1) is thermodynamically favorable and the degree of damage in an oxygen plasma is always expected to be high. For the hydrogen plasma, the following 'damaging' reactions have been proposed [4]:

(3) $\equiv$Si-CH$_3$ + 2H $\rightarrow$ $\equiv$Si –H + CH$_4$

(4) $\equiv$Si-O-Si$\equiv$ + 2H $\rightarrow$ $\equiv$Si –H + $\equiv$Si-OH

(5) $\equiv$Si-OH + 2H $\rightarrow$ $\equiv$Si –H + H$_2$O

This modification involves multiple reaction pathways. Unlike O-radicals, the hydrogen species can react at any of the four silicon bonds, including Si-O. Reactions of hydrophobic groups with O and H radicals easily occur without any additional activation. The only way to reduce the plasma damage is to prevent penetration of O and H radicals into pores of the low-k film. Low-k materials of present interest (k<2.5) have an open-pore structure and the diffusion length of volatile species is significantly larger than the film thickness. Therefore, the only factor that still allows a limited depth of plasma damage is related to the recombination rate of active radicals. The recombination rate strongly depends on surface properties and therefore, the damage behavior of different low-k materials can be very different despite having a similar chemical composition. Figures 3 and 4 illustrate these particular mechanisms. The depth of damage of the studied low-k materials is much less in an O$_2$/CF$_4$ plasma than in an N$_2$/H$_2$ plasma (Figures 3 and 4), although the reactivity of the O$_2$/CF$_4$ plasma with organic materials (for instance, with photoresist) is about 3-5 times higher. Another example is the huge difference of plasma damage between O$_2$/CF$_4$ and O$_2$/SF$_6$ plasmas (Figure 3). A comprehensive understanding of the phenomena related to surface reactions allows the development of special surface treatments initiating surface recombination to reduce the depth of plasma damage [5].

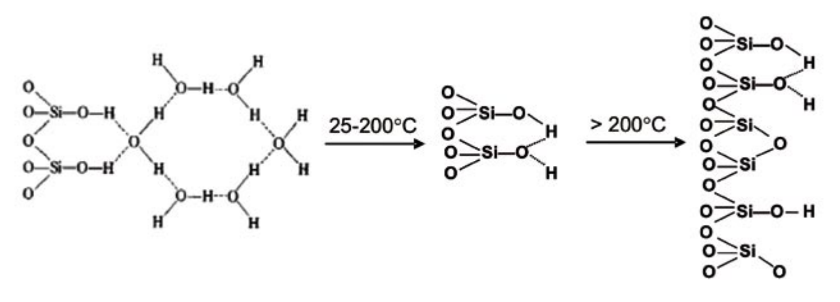

Figure 2. Physically adsorbed water can be removed at temperatures below 200°C. However, the complete removal of silanol groups requires a much higher temperature.

Impact on the dielectric reliability

As mentioned, the adsorbed moisture drastically increases the dielectric constant of the film because of the huge dielectric constant of water molecules (k=55.6 at 100°C and k=78.4 at 25°C). However, much less attention was paid to the impact of adsorbed moisture and of the films' hydrophilicity on the dielectric reliability. Many people believe that the internal pore surface can be restored by thermal annealing that desorbs the water molecules, followed by capping of the barrier layer to avoid further moisture adsorption. However, this optimistic view does not take into account the following important features:

- The temperature range acceptable for back-end-of-line (BEOL) technology (<400-450°C) allows the removal of physically adsorbed and part of chemisorbed water [6,7]. Nevertheless, some isolated hydroxyl groups (especially embedded into the matrix as a result of plasma treatment) still remain in the film, as will be further demonstrated.
- Barrier layers like SiC(N), SiCO and TiN, TaN, etc. deposited on top of low-k materials must be as thin as possible because of their high dielectric constant and higher resistivity in comparison with Cu. Therefore, it is difficult to avoid slow diffusion of small water molecules (some measuring only 3Å). Water molecules that have penetrated through the barriers react with remaining hydroxyl groups and can create critical clusters. This reduces the reliability of the BEOL structure from both an electrical and mechanical point of view.

The evaluation of long-term damage evolution is a special issue that has yet to attract the necessary attention. The analysis of plasma damage using metrology – so-called 'reliability testing' – is extremely important.

Systematic investigation of reliability margin degradation

In order to properly assess and eventually improve the dielectric reliability of Cu low-k interconnects, IMEC has combined several complementary investigation methods including time-dependent dielectric breakdown (TDDB), triangular voltage sweep (TVS) and thermal desorption spectroscopy (TDS).

Characterization techniques

TDDB is systematically used for characterizing the integrated dielectric quality, as it is affected by design, material choice, damascene process steps and integration method. Earlier experiments demonstrated the degradation of the apparent reliability margin when the porosity of the SiOC:H-based dielectrics is increased [8, and references therein]. Recently, the influence of moisture uptake and dielectric modification on breakdown strength was recognized, but complementary techniques are needed to better characterize and understand their contribution. TVS is well suited because it can be used to detect Cu ions and moisture in intermetal dielectrics. A triangular-shape voltage sweep is applied to the capacitor and the current-voltage trace is measured. For metal-insulator-semiconductor planar capacitors, copper ions and moisture are revealed as two distinct peaks (Figure 6). For interconnects, Cu ions and moisture are revealed as a peak and a hump, respectively [9]. The moisture-related peaks and humps are due to protons generated during the measurement itself. The most significant advantage of the TVS technique is that it can be directly applied on damascene lines without special sample preparation.

Complementarily, TDS experiments have been performed to measure the quantity of thermally desorbed moisture. TDS experiments were carried out

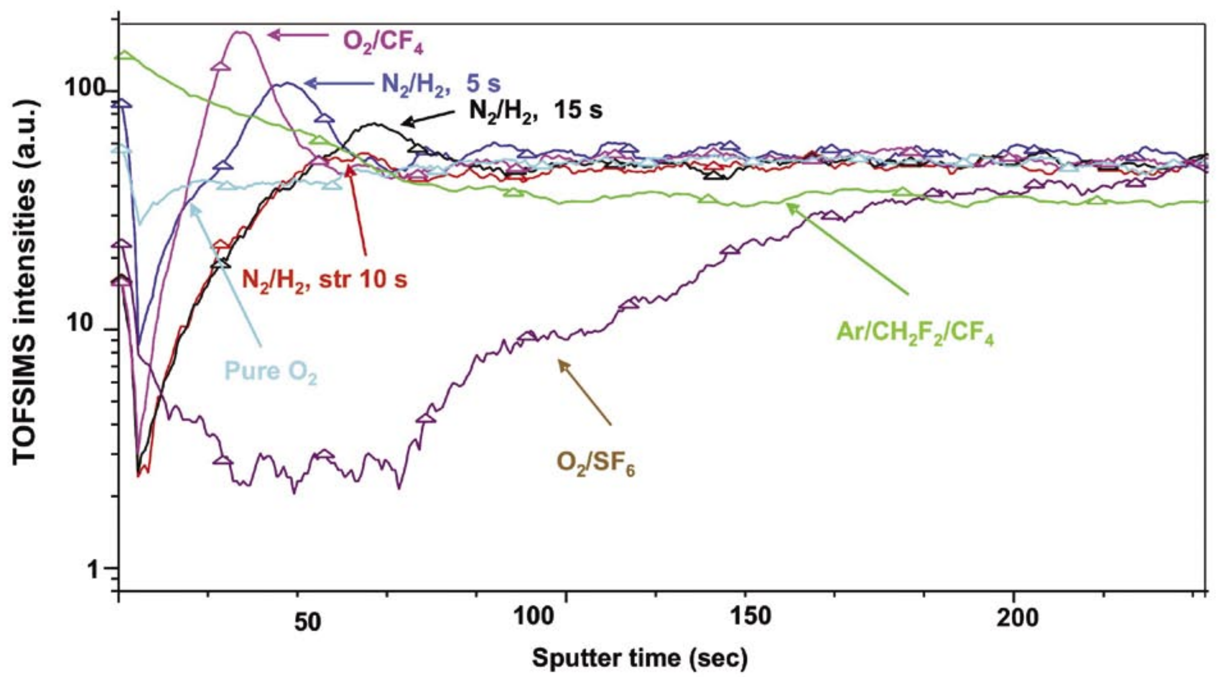

Figure 3. Change of carbon concentration after treatment by different plasmas (time-of-flight (TOF) secondary ion mass spectrometry (SIMS) data).

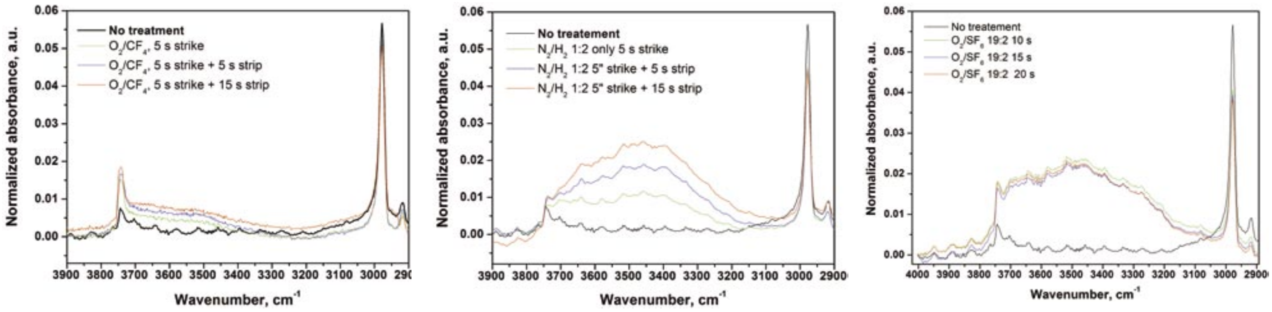

Figure 4. Fourier-transform infra-red (FTIR) spectra of low-k films after exposure in O_2/CF_4 plasma, N_2/H_2 plasma and O_2/SF_6 plasma. The results demonstrate a good agreement with TOF SIMS data.

on bulk low-k SiOC:H films (k=3, porosity=7%, pore size<2nm) that were subjected to different plasma treatments (He, O_2/CF_4, N_2/H_2). Identification of the desorbing species specific to the plasma modified layers is achieved by systematic comparisons of the TDS spectra of modified samples with those monitored for an 'as deposited' reference sample.

Results

Figure 7 shows water-related TDS results for an as-deposited SiOC:H film and for films with different plasma treatments. No significant moisture absorption was found for the as-deposited films and for the O_2/CF_4 and He plasma treated films. For the N_2/H_2 plasma treated films, two water peaks can be seen around 70°C and 350°C respectively. The peaks at the lower temperature are attributed to the 'physically adsorbed (physisorbed) moisture' correlated with weak-bonded water molecules to the SiOC:H skeleton structure. The originally hydrophobic SiOC:H film becomes hydrophilic after an N_2/H_2 plasma treatment. The peaks at higher temperature originate from the 'chemically adsorbed moisture,' which is in connection with a stronger inter-molecule bond. This already clearly illustrates that there are different kinds of moisture within the SiOC:H low-k dielectric film that can be partly removed by high-temperature annealing.

Moisture uptake was confirmed by TVS measurements in damascene samples and presented an apparent hump revealing the presence of water in the low-k film (Figure 8). After annealing at 190°C, the water-related TVS traces become flat, which demonstrates that the annealing could at least remove part of the adsorbed moisture.

A systematic TDDB study was conducted after different thermal anneals. After an anneal treatment at 190ºC, physisorbed water is expected to desorb. Upon an anneal at 400ºC, chemisorbed moisture can be desorbed. The measured I-t curves after the various anneals are shown in Figure 9.

Humps in the I-t curves during the TDDB tests indicate the existence of moisture in the SiOC:H low-k dielectric (samples without anneal). After annealing, the humps are not present, the leakage current is decreased by about one order of magnitude and the average TDDB lifetime increased by about one order of magnitude. After an anneal at 400°C the dielectric reliability is significantly improved and much higher electric fields are required for initiating dielectric failures (Figure 9). Based on these observations, the following mechanism is proposed [10]. Moisture removal induced by thermal annealing at 190°C is likely to correspond to α-bond breakage (desorption of physisorbed moisture; see also Figure 2).

$\alpha\text{: } \equiv\text{Si-OH} \ldots \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{H}_2\text{O}$

This bond breakage through annealing improves the leakage current and TDDB lifetime with one order of magnitude. However, the moisture-related TDDB failure mechanism is not determined by physisorbed moisture, but by another more tightly bound OH-group that corresponds to β–type tightly hydrogen-bonded water:

$\beta\text{: } \equiv\text{Si-OH} \ldots \text{H}_2\text{O} \ldots \text{OH-Si}\equiv \rightarrow 2\equiv\text{Si-OH} + \text{H}_2\text{O}$

Though some water is desorbed in this reaction, OH^- groups remain bonded to Si after annealing. A solid evidence of this correlation is that the TDDB thermal activation energy before and after thermal annealing is very close to the β bond energy [10].

The predicted lifetimes, using a maximum likelihood fit and the E-model for voltage acceleration, are summarized in Table 1. In order to be able to compare at a glance the impact on user conditions, the predicted distributions are depicted in Figure 10.

Although moisture removal by annealing apparently reduces the leakage current and improves the TDDB lifetime of the SiOC:H low-k, due to the residual OH groups characterized by stronger bond energies the SiOC:H low-k dielectric is not restored to the initial state. Therefore, the TDDB reliability remains below that of an optimized scheme where moisture uptake is minimized.

From these findings, it is recommended to mitigate moisture uptake of inter-metal dielectrics from the beginning of the integration flow, rather than relying on thermal annealing to restore the low-k characteristics. As explained, this can potentially be done via special surface treatments that allow the reduction of the depth of plasma damage.

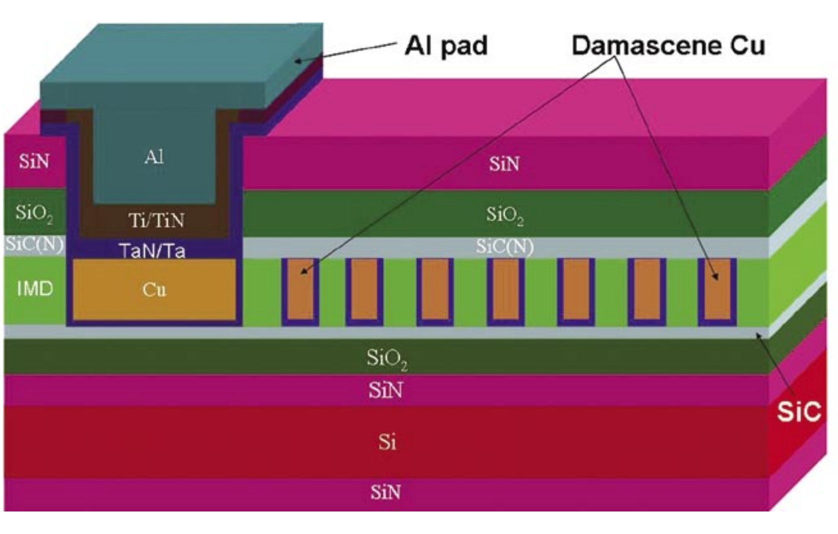

Figure 5. A typical schematic cross-section of the tested SiOC:H damascene copper low-k architecture.

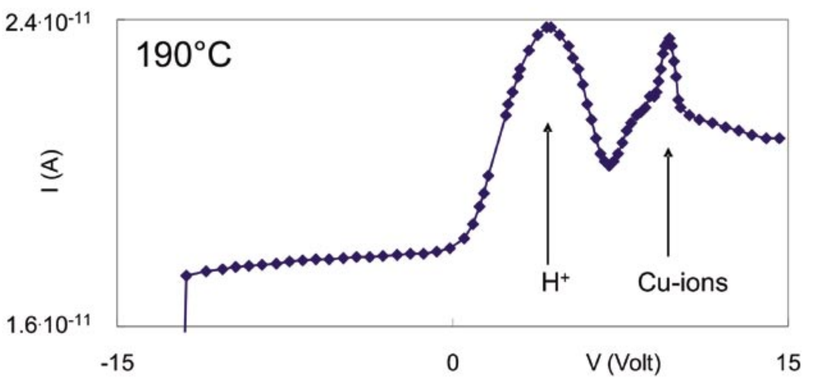

Figure 6. TVS trace showing water-related H^+ and Cu-ion peaks in an N_2/H_2 plasma treated SiOC:H dielectric in combination with a copper electrode.

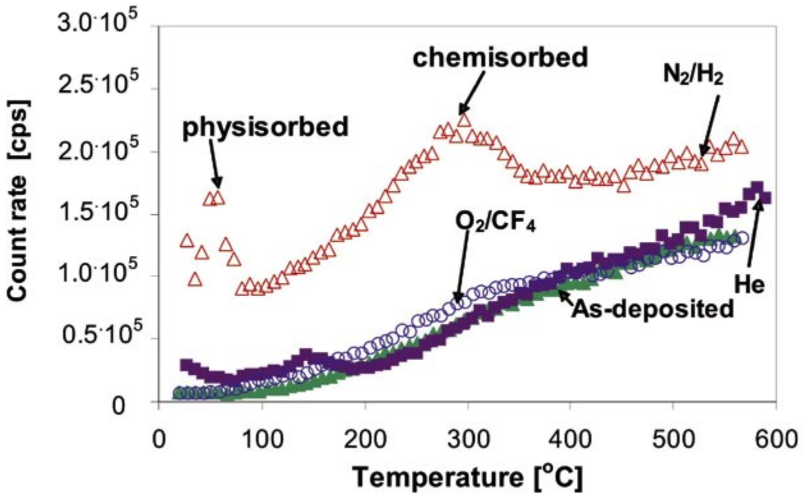

Figure 7. Water-related (H_3O^+) TDS spectra of a SiOC:H low-k film with and without plasma treatments.

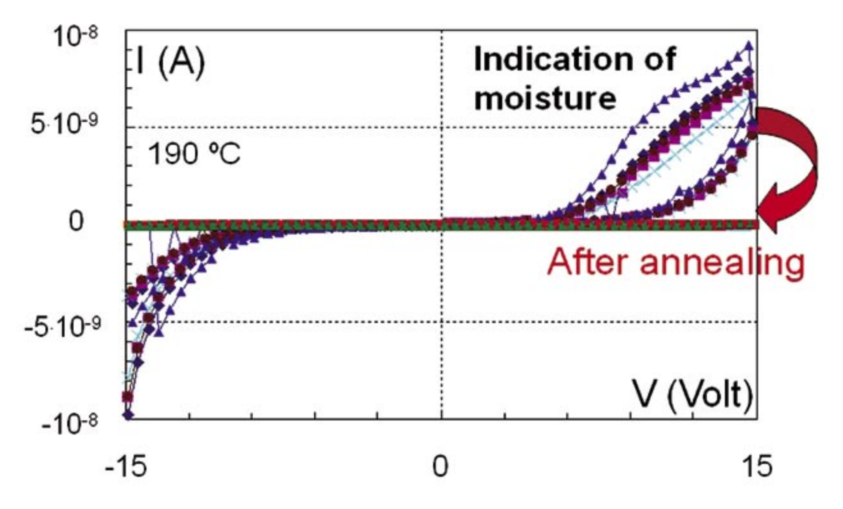

Figure 8. TVS trace showing water-related H+ humps in an N_2/H_2 plasma treated SiOC:H damascene dielectric.

Conclusion

One of the most critical issues in the integration of porous low-k dielectrics is their degradation during plasma treatments. The most challenging plasma treatment is related to strip and cleaning plasmas that contain oxygen or hydrogen. Modification of low-k materials in these plasmas results in the adsorption of moisture which drastically increases the dielectric constant of the film and the leakage current. Moisture adsorption is also known to impact the dielectric reliability of the low-k film. In this study, IMEC has combined various complementary methods (TVS, TDS and TDDB) to systematically analyze the impact of plasma damage on the low-k reliability and to investigate whether thermal annealing can restore

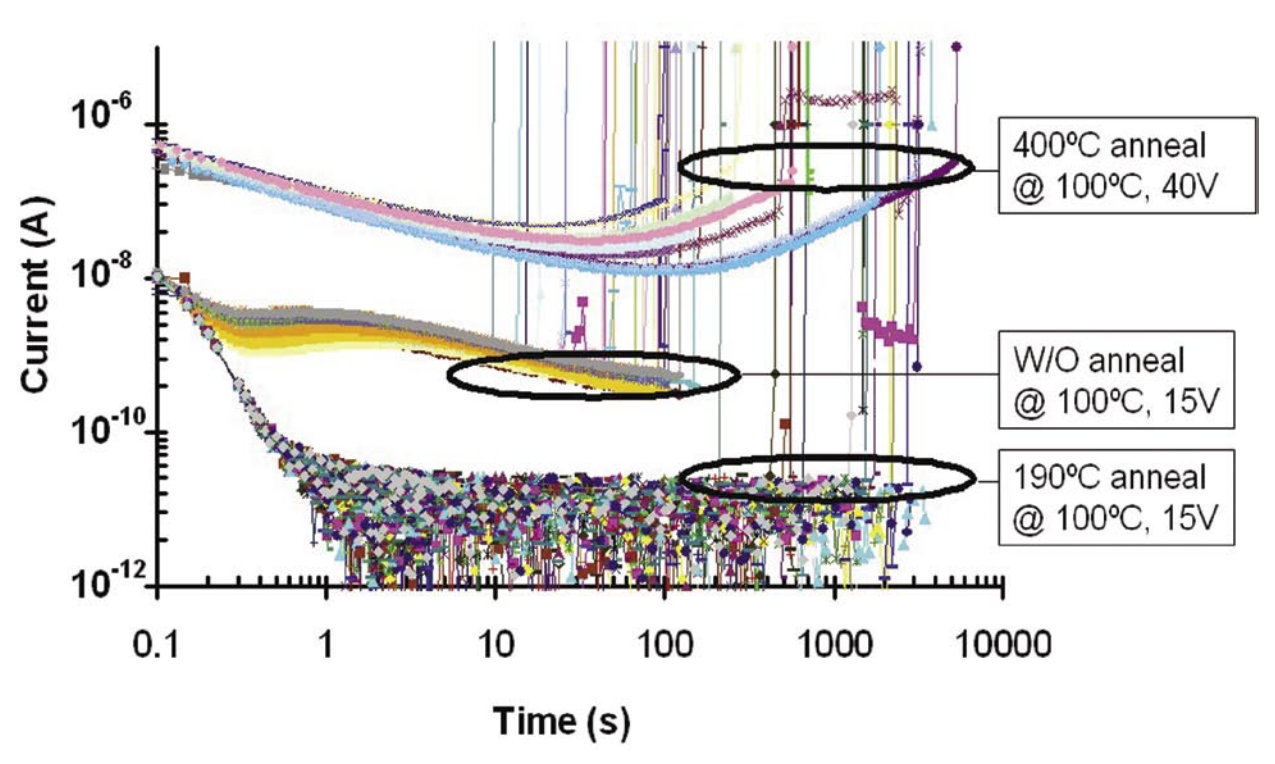

Figure 9. TDDB I-t curves recorded from a SiOC:H damascene copper low-k interconnect before and after thermal treatment.

TABLE 1: PREDICTED LIFETIME OF INTERCONNECTS BEFORE AND AFTER THERMAL TREATMENT

Plasma ash	Predicted median lifetime at 1.2 V 100°C [s]	Distribution width	Predicted 100 ppm lifetime [s]
O_2/CF_4	$2.8^{+1.2}_{-0.9} \cdot 10^{14}$	$1.5^{-0.33}_{-0.33}$	$1.09 \cdot 10^{12}$
Optimized scheme	$2.5^{+0.35}_{-0.31} \cdot 10^{14}$	$0.67^{0.12}_{-0.09}$	$2.1 \cdot 10^{13}$
N_2/H_2 w/o anneal	$1.1^{+0.29}_{-0.23} \cdot 10^{5}$	$0.49^{+0.27}_{-0.13}$	108
N_2/H_2 + 190°C	$1.1^{+0.21}_{-0.18} \cdot 10^{5}$	$0.73^{-0.15}_{0.11}$	7400
N_2/H_2 + 400°C	$1.3^{+0.46}_{-0.34} \cdot 10^{10}$	$1.3^{0.25}_{-0.18}$	$1.06 \cdot 10^{8}$

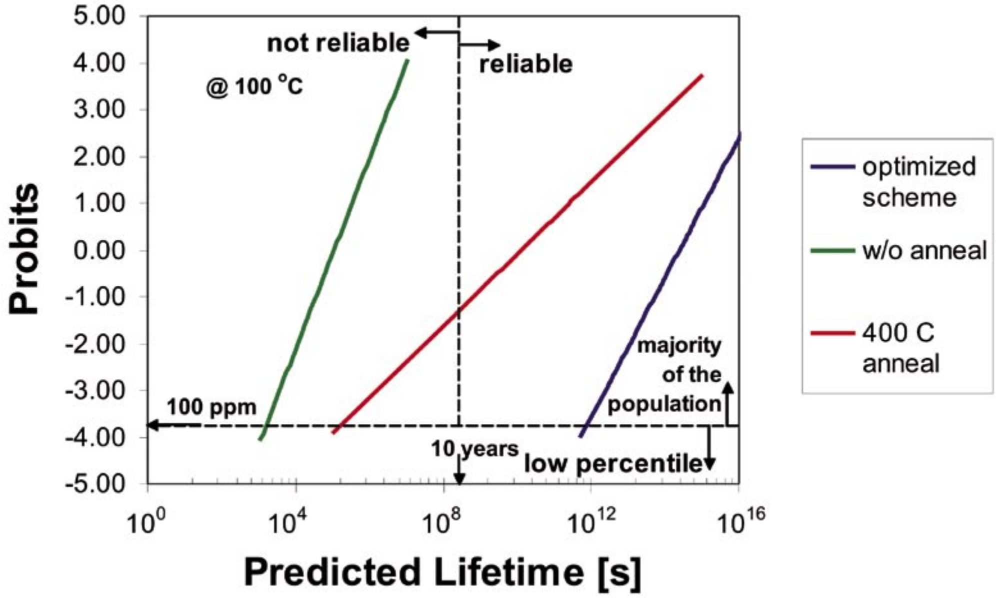

Figure 10. Predicted lifetime distributions at 1.2V and 100°C before and after thermal anneal as compared to an optimized scheme.

the reliability margin. It was found that annealing allows the removal of physically adsorbed (α-bonded) and part of chemisorbed (β-bonded) water. This reduces the leakage current and improves the TDDB lifetime. Due to more tightly bound OH-groups in the dielectric that cannot be removed by thermal annealing compatible with BEOL technology, the SiOC:H reliability is still far below that of an optimized integration scheme. Therefore, moisture uptake should be minimized at the very beginning of the integration flow by developing special surface treatments that initiate surface recombination to reduce the depth of the plasma damage.

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