RC25652 (WAT1703-002) March 10, 2017

IBM Research Report

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Son Van Nguyen[1], Shobha Hosadugra[1], T. Haigh Jr.[1], Y. Yao[2], L. Tai[2],
S. Cohen[3], T. Shaw[3], C. K. Hu[3], E. Liniger[3], K. Virwani[4],
A. J. Kellock[4], D. Canaperi[1]

[1]IBM Research at Albany Nanotech
257 Fuller Road
Albany, NY 12203 USA

[2]IBM System Technology Group
Hopewell Junction, NY 12533 USA

[3]IBM Research Division
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598 USA

[4]IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, CA 95120-6099 USA

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[a] IBM Semiconductor Technology Research, 257 Fuller Rd., Albany, NY 12203 USA
[b] IBM T.J. Watson Research Center, Yorktown Heights, New York 10598 USA
[c] IBM System Technology Group, Hopewell Junction, New York 12533 USA
[d] IBM Almaden Research Center, San Jose, California 95150 USA

As integrated circuits for high performance CMOS devices scale down to <=10 nm dimension, further reductions in cap thickness to reduce capacitance are required for the Cu barrier while maintaining sufficient mechanical strength, low leakage, high dielectric breakdown, and fabrication integration robustness. This paper presents the development of a second generation robust Low Hydrogen SiCN to enable cap thickness reduction to <=10 nm by simply altering/reducing the hydrogen concentration in the SiCN film. This is achieved by the simple addition of Hydrogen precursor in the plasma deposition chemistry.

INTRODUCTION

The metallization of integrated circuits for high performance CMOS devices involves the use of copper with low-k or ultra-low k dielectrics to reduce RC delay and cross talk in devices. Progressing from the 90nm to the 14 nm CMOS device nodes, conventional silicon nitride was replaced by new dielectric barrier low k materials such as SiCN, C-Rich SiCN and SiNO (1-6). As devices scale down to <=10 nm dimension, further reduction in cap thickness is required for the Cu barrier while maintaining sufficient mechanical strength, low leakage, high dielectric breakdown, and fabrication integration robustness. In a previous report (6), we showed that a single layer $SiCN_x$ film deposited by plasma enhanced CVD with TMS+NH_3 is robust down to around 15-20 nm thickness range. This paper presents the development of a second generation robust Low Hydrogen SiCN to enable cap thickness reduction by simply altering/reducing the hydrogen concentration in the SiCN film composition. The new SiCN cap film is named as Low H SiCN ~~is~~ in comparison to the standard SiCN film deposited at the same condition without the Hydrogen reactant. Optimal process chemistry and deposition conditions are not changed except for addition of the hydrogen reactant. This new PECVD $SiCN_x$ cap film was developed to achieve: 1) Lower hydrogen content in SiCNx while achieving robust mechanical properties, good barrier properties, and an excellent interface with the Cu interconnect. 2) A better Cu diffusion barrier and oxidation barrier even with reduced thickness. This improved barrier exhibits good plasma RIE selectivity and high chemical mechanical polishing stability. The new low hydrogen film was integrated successfully into 7 nm CMOS BEOL test devices and improved reliability electrical performance was demonstrated.

EXPERIMENT

The low hydrogen $SiCN_x$ films were deposited in a commercial high throughput production-worthy 13.6 MHz RF 300 mm Plasma Chemical Vapor Deposition process (PECVD) system at 350 C using a combination of Trimethyl Silane (TMS) + Ammonia (NH_3) + Hydrogen precursors. The standard SiCN dielectric was also deposited at 350 C using a combination of Trimethyl Silane (TMS) + Ammonia (NH_3) for comparison. The plasma deposition conditions (rf power, pressure) and ratio of $TMS/NH_3/H_2$ were optimized to achieve good uniformity of the cap film. The difference between the optimal process condition for standard SiCN and low H SiCN is the addition of Hydrogen as a reactant gas. $SiCN_x$ films were deposited with various Silicon, Carbon and Nitrogen ratios and k values. The as-deposited films have good uniformity (1 sigma < 1 %), repeatable refractive indices and uniform composition across the 300 mm wafer. For reference, the standard SiCN cap film deposited with TMS+NH3 was deposited under the same optimal conditions for comparison in all measurements. As-deposited films were analyzed using aluminum/copper dot Metal-Insulator-Semiconductor (MIS) and Metal-Insulator-Metal (MIM) electrical measurement characterization techniques at elevated (150 ^{0}C) temperature for breakdown voltage, leakage and Cu diffusion (6). The film's mechanical properties such as modulus (H), hardness (E), and stress at 400nm thickness were also measured. Fourier Transform Infrared (FTIR), X-Ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering and Hydrogen Forward Spectrometry (RBS/HFS), and X-Ray Reflection (XRR) measurement techniques were used to study the chemical bonding, density and Si, N, C and H compositions in sample films. Post film deposition UV cure (7) was also done to evaluate it effect on film's properties. An oxidation resistance test (6) was done after the barrier film/copper blanket stack was annealed at 310°C for 24 hours in ambient atmosphere. The level of oxidation was examined by depth profile X-ray photoelectron spectroscopy (*d*-XPS), focusing on oxygen profile in samples. Multi-level 7nm copper interconnect structures were built for Electro-migration (EM) and Time Dependent Dielectric Breakdown (TDDB) measurement at elevated temperature (150-300°C).

RESULTS and DISCUSSION

For both low H SiCN and standard SiCN deposited under the same conditions with and without Hydrogen gas, the introduction of Hydrogen (1000-4500 sccm in the plasma deposition reactants improves the Low H SiCN film's uniformity deposited on 300 mm wafers from 1.70 % to 0.82 % (1 sigma). This uniformity improvement will help the implementation of the film into a manufacturing environment. The low H SiCN deposition rates decrease with the increasing Hydrogen reactants as shown in figure 1. The reduction in deposition rate using the same deposition process with Hydrogen addition suggests that there is an increasing "etching component" occurring with Hydrogen plasma which is removing more weakly bonded or more volatile deposition species in plasma gas phases such as $-SiH_x$, $-NH_y$ and CH_z (x, y, z = integer 1-3). This will reduce the overall film's deposition rate. Furthermore, the film's refractive index is ~~o~~ increased from 1.88 to 1.98 with the increasing amount of Hydrogen flow into the film, figure 2. The increase in film's uniformity refractive index and density is expected to improve the cap film's performance as Cu barrier, figures 1 & 2 and table 1.

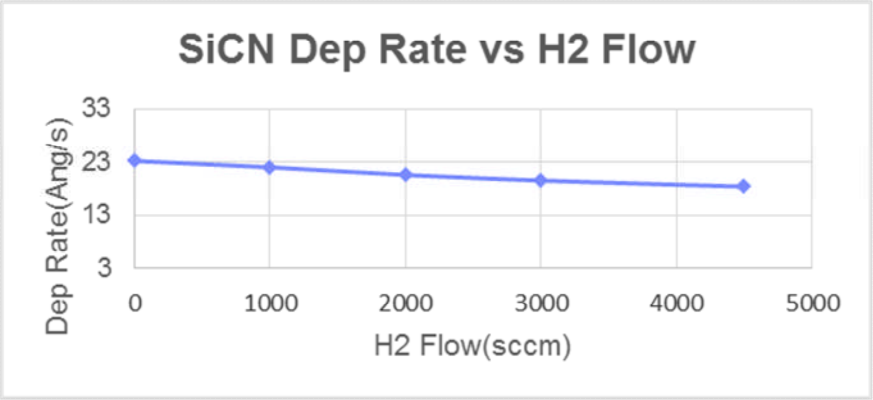

Figure 1. The reduction of low H SiCN film deposition rates with Hydrogen addition.

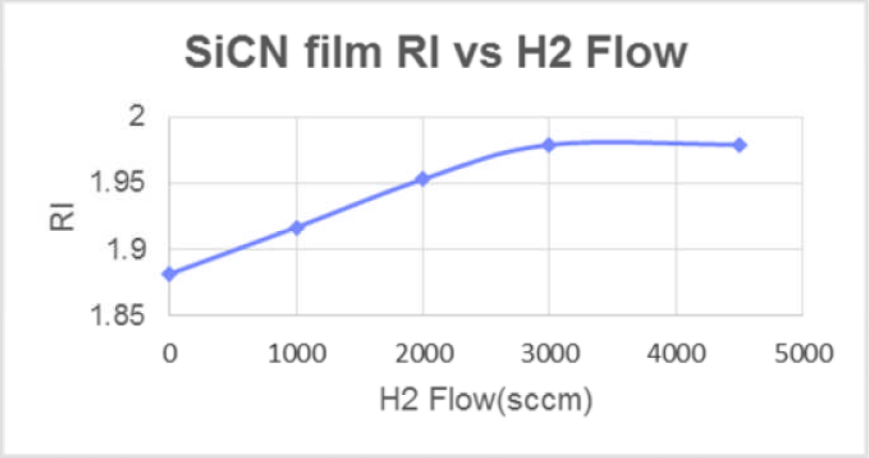

Figure 2. The increase of Low H SiCN refractive index with Hydrogen addition

Table 1 shows the change in film's uniformity and XRR density typical of standard SiCN and Low H SiCN caps deposited at various H_2 flow rate from 0 to 4500 sccm H_2. The overall improvement in film uniformity, density and reduction in deposition rate were observed in a large range of the deposition process parameter space.

TABLE 1. Low H SiCN film's uniformity and density change vs H_2 flow rate.

Hydrogen Flow Rate(sccm)	**Uniformity (1 sigma)**	**XRR Film's Density (gram/cm3)**
0	**1.70**	**2.05**
1000	**1.15**	**2.18**
2000	**1.20**	**2.31**
3000	**1.06**	**2.43**
4500	**0.73**	**2.54**

Table 2 summarizes the standard SiCN and Low H SiCN cap deposited at 4500 sccm H_2 film properties and device performance. Overall, the low H SiCN cap has better electrical, mechanical, and device reliability performance as compared to ~~than~~ the standard SiCN cap deposited with TMS+NH3 only. The low H SiCN film has higher density, modulus, hardness and significantly higher compressive stress, both as-deposited and post 5 minutes direct UV cure, Figure 3. In fact, the film stress of Low H SiCN deposited at 4500 sccm H_2 after 3 minutes UV cure (385 C) is about 500 Mpa (Compressive), which is the same as the as-deposited standard SiCN cap. The characteristic of compressive stress change post UV cure is highly desirable in the Cu-Low k interconnect film's stack where UV cure is normally used (7) in the bulk dielectric SiCOH low k formation. The thin cap's high compressive stress is normally balances out the tensile stress of the thicker but low tensile stress low k film, thus making the overall multilayer Cu-low k stack become more stable

Table 2. Typical film's properties and device's reliability performance of SiCN vs low H SiCN cap (4500 sccm H_2).

Property	**$SiCN_x$ cap ($TMS+NH_3$)**	**Low _ H $SiCN_x$ cap ($TMS + NH_3 + H_2$ =4500 sccm)**
K at 150^{o}C	**5.3**	**5.1**
150^{o}C Intrinsic breakdown (MV/cm)	**4.75**	**4.55**
Modulus, GPa	**~100-110**	**124**
Hardness, GPa	**11-13**	**~ 20**
Stress, Mpa as dep/after 5 min UV cure (385^{o}C)	**-450 (compressive) 500 (tensile)**	**-1316 (compressive) -500 (compressive)**
Density XRR((g /cm3)	**~2.05**	**2.54**
Composition RBS (at %) Si / N/ C/H	**27.3/20.9/17.7/34.1**	**29.3/21.7/20.1/28.9**
RBS/HFS H bonding ratios (H/Si, H/N, H/C ratios)	**1.25/1.63/1.93**	**0.99/1.33/1.44**
Cu Oxidation /TVS test	**Fail at ~ 10 nm thickness**	**Pass at 10 and 6 nm thickness**
Time Dependent Dielectric Breakdown performance comparison to (7 nm BEOL)	**1x at 14 nm thickness**	**~4X better at 10 nm thickness**
Electro Migration performance comparison to (7 nm BEOL)	**1X at 14 nm thickness**	**~10X better at 10 nm thickness**

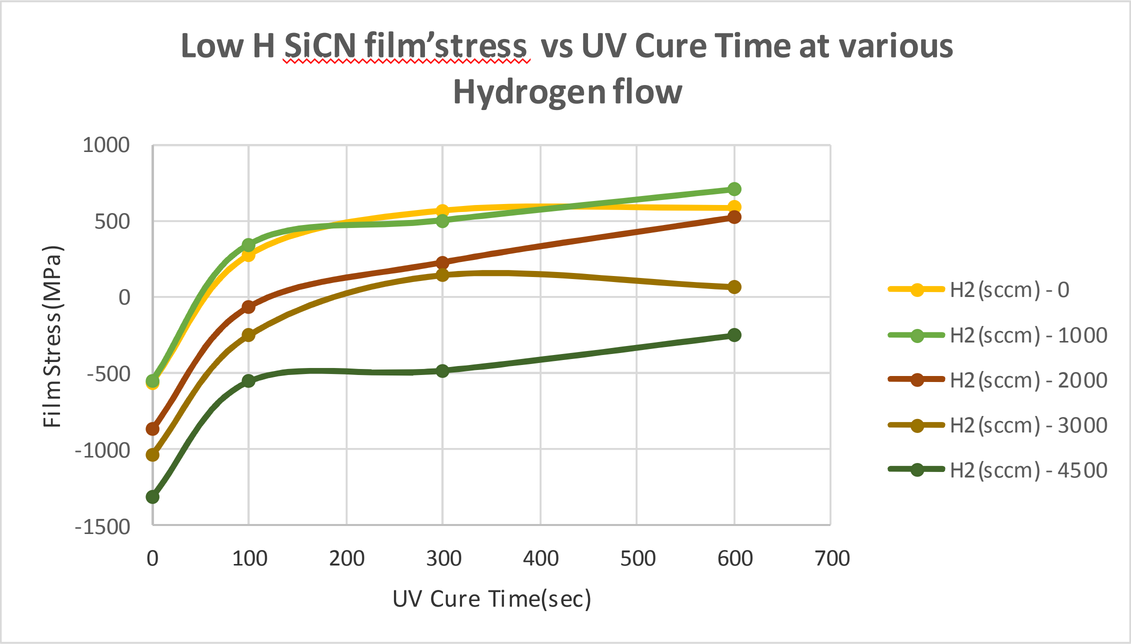

Figure 3- Low H SiCN film Stress vs UV cure time at various H_2 flow rates.

XPS Depth profiles of a typical 9 nm thick Low H SiCN cap show good depth profile uniformity with the small amount of oxygen at the interface, figure 4. It should be noted that the variation in Si, N, C compositions of low H SiCN film with various H_2 flow rates (1000-4500 sccm) are relatively small; in the range of 3 atomic percent. Typical RBS/HFS compositional analysis shows that PECVD SiCNx cap films deposited with the addition of hydrogen precursor actually have less hydrogen than films deposited without hydrogen under the same optimized deposition condition, table 3. Film deposition rates decrease slightly and the hydrogen reduction in the bulk film is attributed to the increase removal (etching) of weakly bonded -Si-H_x and -N-H_y species in the film during the plasma deposition process. Total Hydrogen is consistently reduced with increased H_2 flow.

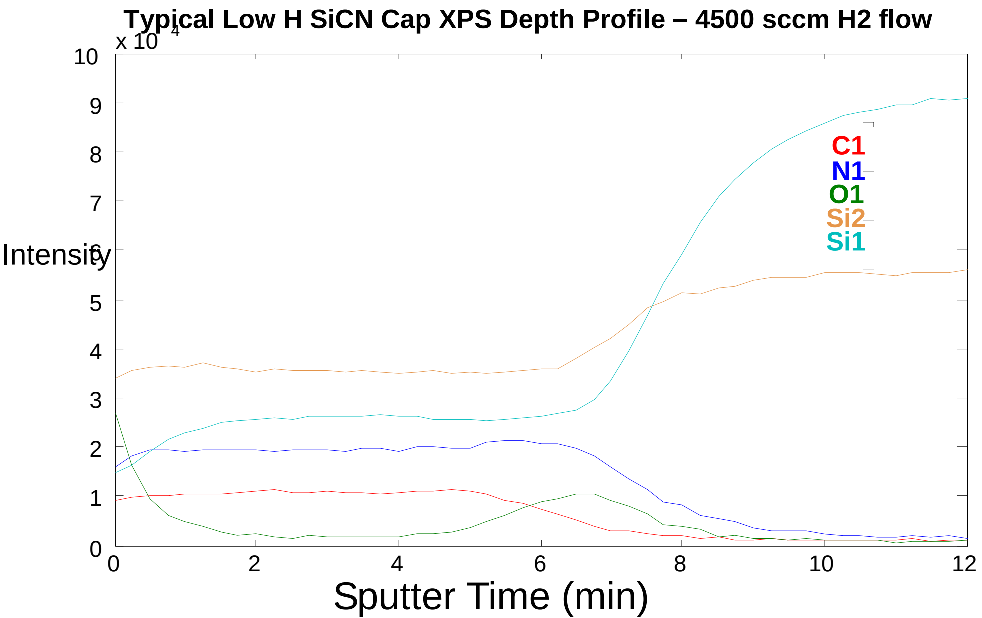

Figure 4- Typical XPS depth profiles of 9 nm thick low H SiCN (4500 sccm H_2)

TABLE 3. Typical RBS/HFS compositional analysis and elemental ratios of Si,N, C, H elements in standard SiCN and low H SiCN (4500 sccm H_2). The total Hydrogen and the ratios of H/Si, H/N and H/C are lower in Low H SiCN dielectric cap.

Film/Composition	Standard SiCN film	Low H SiCN film
Si (atomic %)	**27.3**	**29.3**
N (atomic %)	**17.7**	**20.1**
C (atomic %)	**1.20**	**2.31**
H (atomic %)	**34.1**	**28.9**
N/Si ratio	**0.77**	**0.74**
C/Si ratio	**0.65**	**0.69**
H/Si ratio	**1.25**	**0.99**
H/N ratio	**1.63**	**1.33**
H/C ratio	**1.93**	**1.44**
XRR density (gr/cm^3)	**2.05**	**2.54**
Comment	**Higher H, Lower film's density**	**Lower H Higher film's density**

FTIR analysis shows that the thickness normalized Si-C and Si-N bonding absorbance density increases in the low H SiCN dielectric, which is consistent with the increase in film density, modulus and harness. The N-H, C-H and Si-H bonding is also consistently reduced with increasing H_2 flow. Low Hydrogen SiCN deposited with 3000 and 4500 sccm Hydrogen flow rate consistently have reduced NH_2/NH, CH_3/CH_2, Si-NH_2, -CH_2, Si-CH_3, Si-CH_2-Si and Si-H absorbance bonding density normalized with thickness as shown in figure 5.

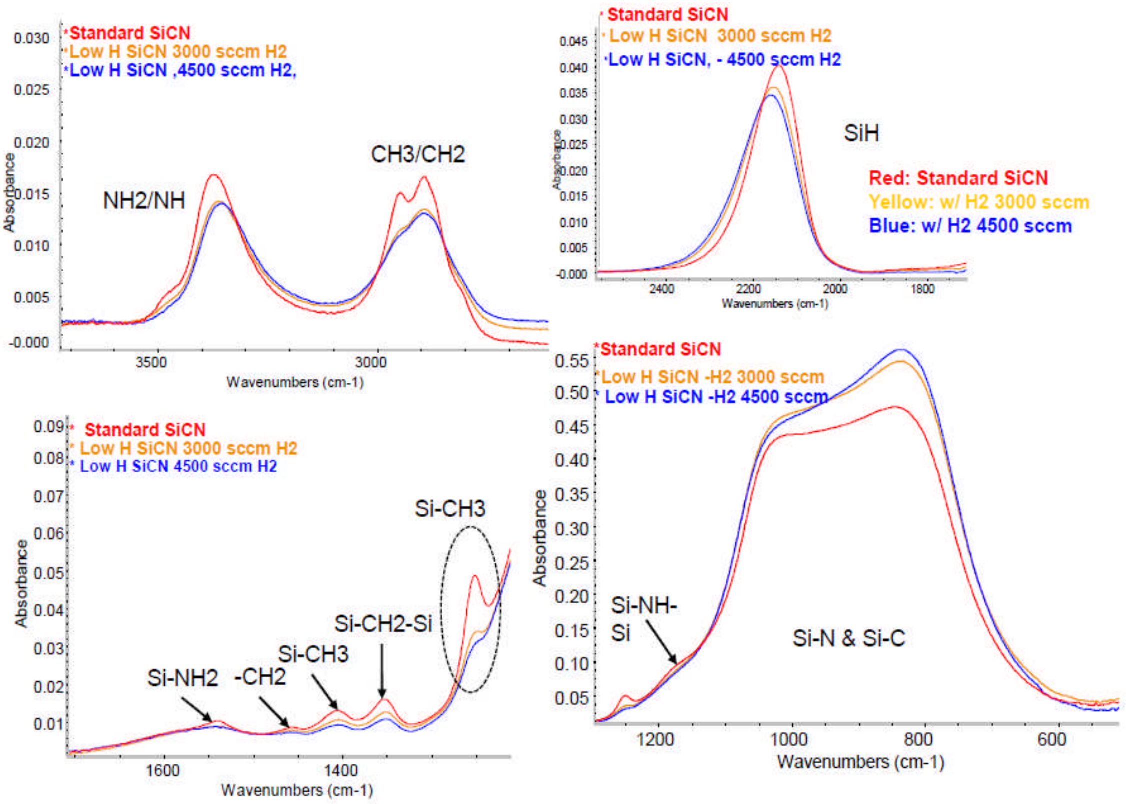

Figure 5 – FTIR Spectra of standard and low H SiCN (3000 and 4500 sccm H_2 flow)
The spectra absorbance values are normalized to the same thickness.

Figure 6 shows a typical Scanning Transmission Electron Micrograph (STEM of a 3nm Co/10 nm Low H SiCN cap on Copper Metal 2 lines in a 7nm interconnect structure. This Cu/Co/Low H $SiCN_x$ cap structure achieves 5-10X better EM/TDDB reliability versus a similar SiCN structure with the previous (non-Low H) $SiCN_x$ cap (Table 1). A Scanning Electron Micrograph (SEM) of the patterned surface after annealing at 310°C for 24 hours in air shows 10 nm Low H SiCN is an excellent oxidation barrier. In fact, the 6 nm thick low H SiCN cap still passes the blanket Cu Oxidation barrier test, figure 7. This shows that the low H SiCN cap is a much more robust dielectric cap than the standard SiCN for Cu-low k. It should be noted that the color change in blanket film is due the light reflection. Dark spot defect density normally occurs and failed samples generally have high dark spots defect density.

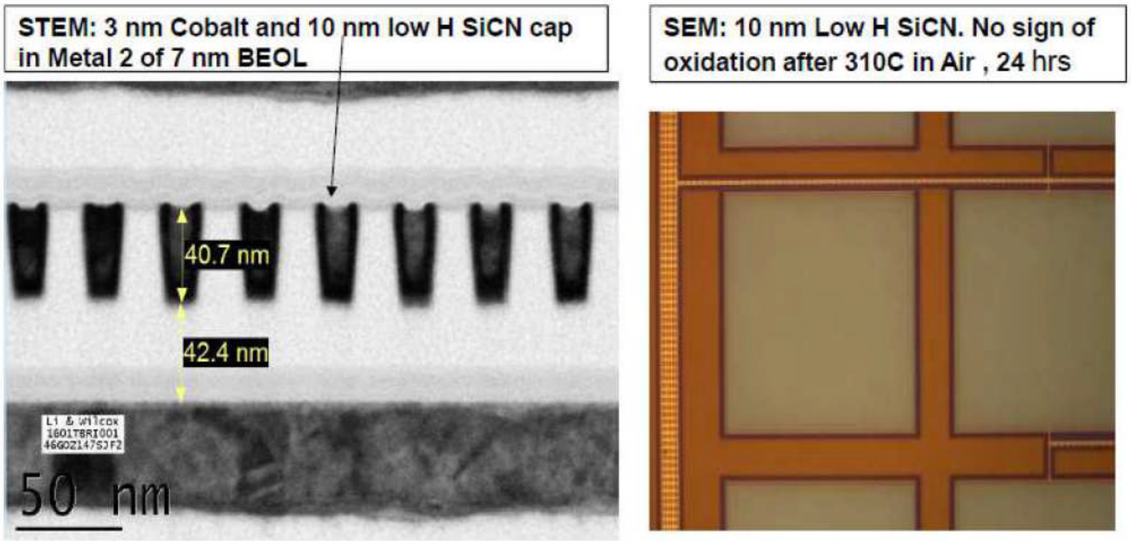

Figure 6 – STEM and SEM of 7 nm patterned Cu interconnected structure fabricated with 10 nm thick low H SiCN cap that has excellent Cu oxidation barrier properties..

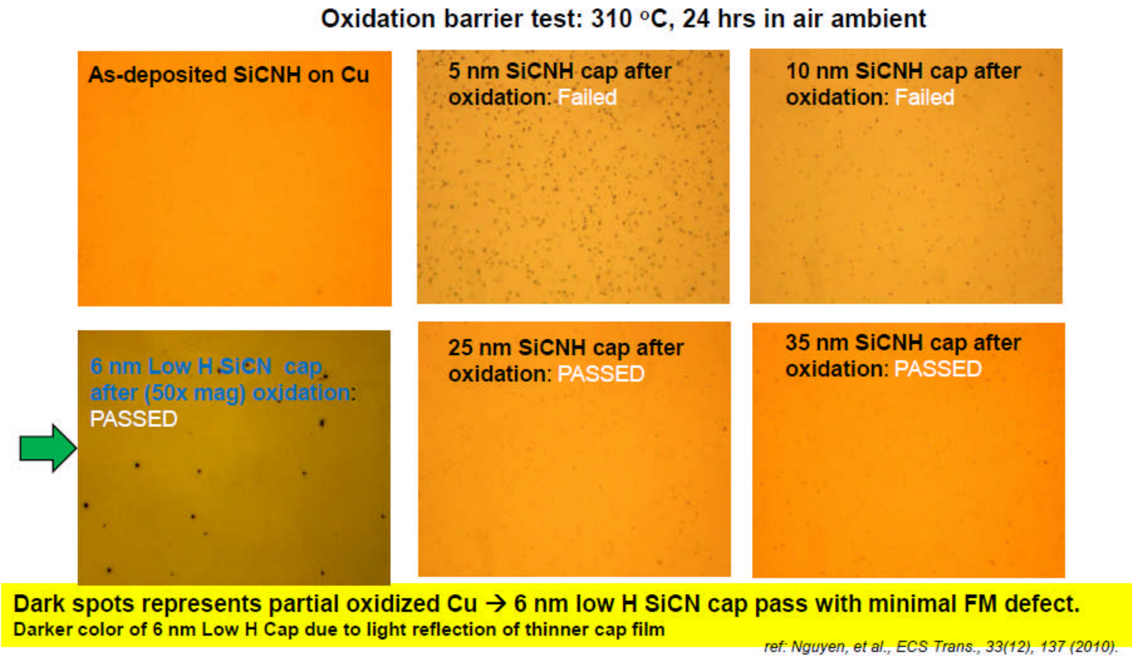

Figure 7- SEM picture of various blanket Cu coated with SiCN and low H SiCN cap. The 6 nm thick low Hydrogen SiCN still passes the 310 C, 24 hours oxidation barrier test.

As the 10 nm thick Low H SiCN is implemented for the Cu cap in the multilayer 7 nm Cu-low k interconnect structure, both TDDB and EM Cu reliability performance improved significantly, figures 8 and 9. It should be noted that both POR and standard SiCN cap are in 14-20 nm thickness range while the Low H SiCN is only 10 nm thick. The thin SiCN cap stills offers better performance due to increases in film density and bonding density, lower hydrogen concentration and better oxidation barrier properties. The low Hydrogen SiCN cap clearly a superior dielectric Cu cap in all tested devices.

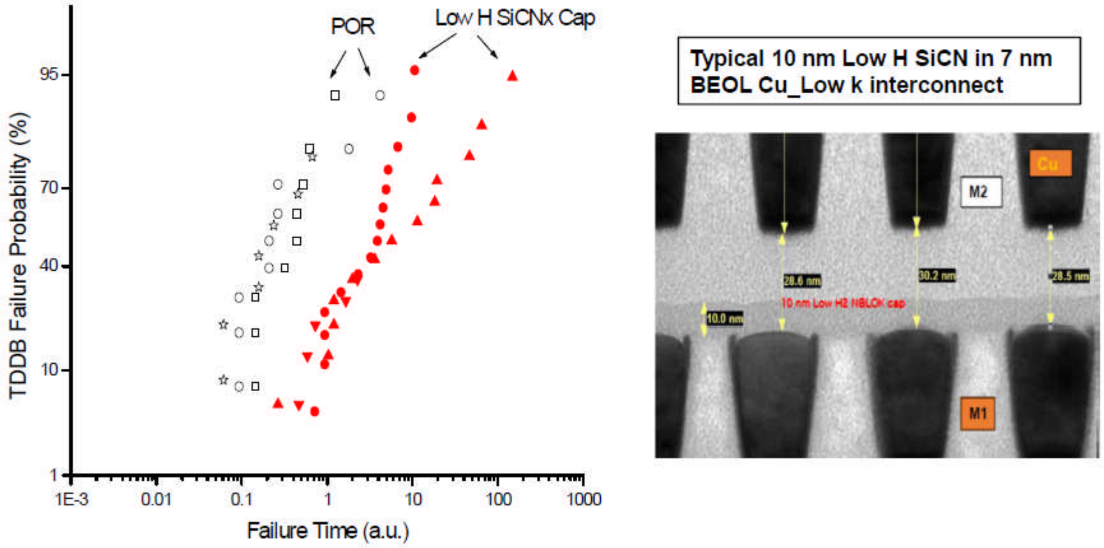

Figure 8- Typical improvement in Cu TDDB failure time between POR SiCN and low H SiCN (10 nm) in a multilayer 7 nm Cu Low k interconnect structures (STEM).

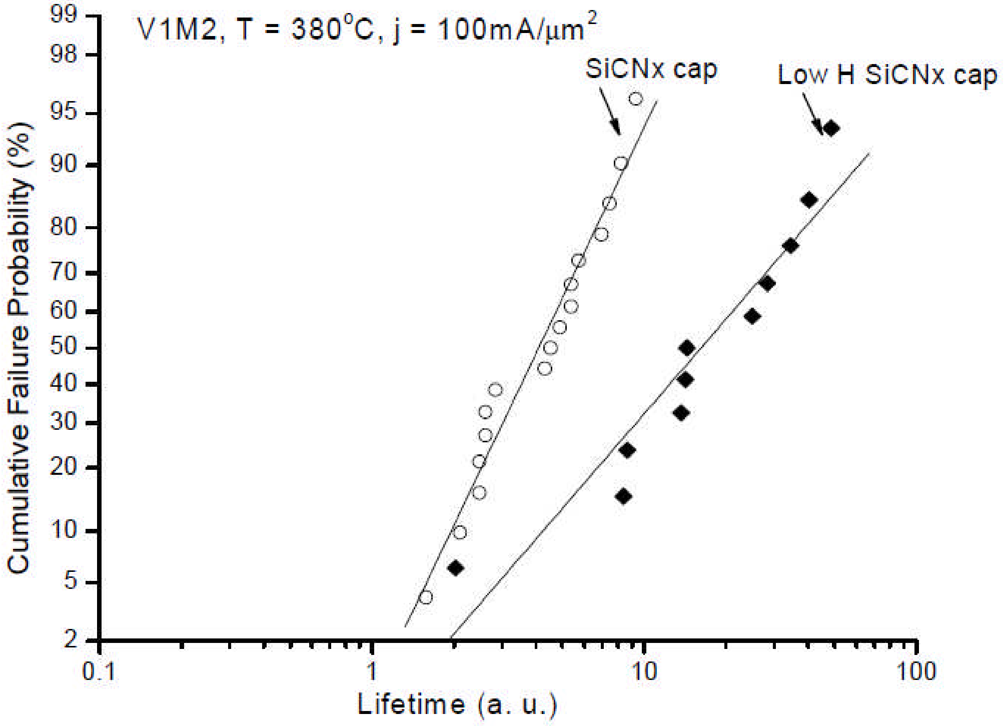

Figure 9- Typical EM reliability improvement with low H SiCN vs SiCN cap

With simple addition of Hydrogen into the reactant gas feed, a thinner low H SiCN robust dielectric cap with higher density, better bonding density, improve mechanical properties and low H content film can be deposited by plasma CVD processing. The ultrathin (<=10 nm) cap implemented in sub-10 nm Cu-Low k interconnect fabrication showed significant reliability performance improvement.

CONCLUSIONS

Low hydrogen SiCN dielectric caps with improved mechanical, oxidation and Cu diffusion barrier properties versus standard SiCN were deposited using TMS, NH_3 and H_2. The new low hydrogen SiCN dielectric cap film showed a significant increase in Si-C and Si-N bonding density and a reliability performance improvement in 7 nm Cu interconnect structures at <=10 nm thickness in comparison to standard dielectric caps of previous device generations. The thinner cap not only has a similar k value with improved device reliability, but also has excellent interfacial characteristics and stable chemical and mechanical properties. This cap will enable an overall capacitance reduction in sub-10 nm Cu-Low k interconnects with no change in process integration.

Acknowledgments

This work was performed by the Research Alliance Teams at various IBM Research Facilities. The author would like to thank B. Peethala for some analysis and A. Grill.for discussion.

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