Tuning Hydroxylamine Slurries for Copper Barrier Polishing for SiLK^{tm} Low-k Integration Processes.

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Abstract

The CMP performance and characterization of Copper/Low-k (SiLK^{tm}, Dow Chemical) dielectric films (dense and porous versions) using hydroxylamine-based slurries was investigated with silica abrasives. In this continuing study, new slurry formulations with and without silica abrasives were examined. The testing showed good results including sheet and pattern film removal rates, Cu/TaN/SiLK selectivity, Cu and SiLK surface roughness and SiLK film chemical compatibly (FTIR) with electrical and film adhesion data. The SiLK sheet film CMP performance was quite compatible to TEOS film. This paper will also discuss data from stacked film and pattern wafers with SiLK films using a copper phase 1 and a barrier phase 2 slurries. These nitrogen-based slurry processes have the potential of broadening the applications for Cu/SiLK integration.

Introduction

The scaling of ULSI devices to critical dimensions under 0.13 micron has been a major challenge for thin film interconnections. The use of Al(Cu) and SiO_2/SiN dielectrics results in a significant portion of circuit delay caused by the wiring, and the majority of that circuit delay due to capacitive loading (RC delay). [1] The integration of copper and barrier metals and new low-k's (k=2.5 to 2.7) into these devices should translate into reducing the RC delay by ~30%[2,3]. The industry has been for several years developing and evaluating both spin-on and CVD low-k films.

The new low-k dielectric materials can have a number of integration and reliability issues, which include thermal or mechanical induced cracking, adhesion loss, moisture absorption and poor mechanical and chemical compatibility during CMP processes[4]. Other issues include REI control during etch and liner coverage during barrier deposition.

The copper CMP process must not destroy the metal/dielectric structure. The low-k material must also resist chemical attack from the CMP oxidizers, and the final low-k film surface should have a low roughness (rms) value. These requirements have been further complicated by a recent trend to reduce the down force pressure to between 1 to 0.25 psi for these integrated structures. There is concern about reliable control of such low down force pressures. In the near future it may also be necessary to remove the cap and hard mask layer as another means to reduce the effective k value of the final structure.

SiLK^{tm} film (a polyaromatic spin-on resin made by Dow Chemical) can be either as the dense film (k values 2.6) or the porous version, p-SiLK which has a k= 2.1. All new low-k and ultra low-k films have lower hardness values (GPa) than the traditional TEOS ILD i.e.; 8 (k=4) versus 0.16 (k<2.4) for the porous SiLK^{tm} film.

Copper barrier CMP processes needs to remove the remaining copper and the barrier material (Ta/TaN) to insure isolation between the metal lines. This second step maybe designed for barrier removal with either a high selectivity or (in certain cases) non-selective of Cu/TaN/TEOS and the process is stopped at the ILD layer. When considering SiLK^{tm} film low-k structures (both standard and porous), the process must be accomplished without destroying the SiLK^{tm} film dielectric layer.

EKC's copper slurries are composed of hydroxylamine (hydroxylamine free base) and various chemical modifiers and can be adjusted for the desired end effect during copper polishing [5-7]. Though the exact mechanism for polishing copper and tantalum films with hydroxylamine chemistries are still being elucidated, it appears not to be solely depended on the mechanical removal of surface copper oxide species via the oxygen atoms of the copper oxide film as proposed by Wang [9]. Such copper oxide films are formed with hydrogen peroxide slurries. The hydroxylamine-based slurries appear to depend on forming soluble copper complexes and the ability to cycle copper ions through different oxidation states. HDA is a mild reducing/oxidizer agent depending on the solution's pH. At pH's < 6, the HDA is a mild oxidizer (less than hydrogen peroxide), at pH > 6 HDA is a reducing agent [8]. EKC's two-step copper process is separated into phases (Phase I and II) since one step (chemistry) can be followed by the next step with no necessary pad conditioning or rinsing. The Cu Phase-I slurry is a hydroxylamine-based oxidizer with a newly developed alumina abrasive (~ pH 3 to 4.5). Cu Phase-II (barrier-film slurry) is also a hydroxylamine-based chemistry with silica abrasives (pH ~3 to 9).

The current study is focused on Cu Phase II applications for polishing copper when SiLK layers are present instead of TEOS. This study was farther subdivided into two sub applications, one attempting to achieve a high TaN/Ta barrier removal rate and a lower Cu and ILD (TEOS and SiLK^{TM}) rate with Cu:TaN:ILD = 1: 3-10 : ~1. The other application was to study a non-selective process for Cu/TaN/ILD (TEOS) and efficiently stop at the SiLK^{TM} film layers, other schemes include hard masks (SiC deposition on Silk film and SiO_2 on SiCN).

Chemical and abrasive compositions with certain Cu, TaN, and ILD selectivity's were tested for sheet film removal rates. These results were compared with pattern Cu/TaN/TEOS structures. Both silica and non-abrasive systems were included in this selectivity study. The CMP performance was comparable to typical TEOS films. Surface effects, including surface roughness (rms) were similar or better after the CMP polishing process. FT-IR data will also be presented. Electrical data (leakage current and breakdown voltage), adhesion and SEM data will also be presented for p-SiLK^{TM} films.

Experimental

Two hydroxylamine-based slurry processes were investigated. Phase-I used hydroxylamine-alumina based slurries and Phase-II used hydroxylamine-silica based slurries.

The polishing work was done on an IPEC 472 polisher. The polishing with the silica-based slurries were done with a Rodel Politex regular pad and the alumina-based slurries were done with a Rodel IC1000 (k-grove)/Suba IV pad. The silica particles ranged between 65 to 85 nm and the alumna particles where 90 to 130 nm size.

Typical Phase-I polishing down forces were between 2 to 5 psi., other process conditions (back pressure, psi/platen speed, rpm/carrier speed, rpm/slurry flow, and ml) varied between 0/50-90/35-95/150-200/min. The barrier polishing process conditions were 2/0/35-90/35-795/150-200. All experiments used 200 mm blanket wafers and included electroplate copper, TaN, TEOS, dense SiLK^{TM} (low-k film, k = 2.5 to 2.7), porous SiLK (p-SiLK LC/HC low-k film, k=~2.1 with high and low conductivity). Copper pattern wafers including Sematech 931 and 854 as well as copper pattern wafers with dense SiLK films were also used.

A CDE ResMap 176 was used for Cu film thickness measurement; a KLA-Tencor 650 was used for TEOS and SiLK film thickness measurement. A Gaertner ellipsometer was also used for SiLK film measurements. A BioRad FT-IR spectrometer (FTS175C) was used for measuring chemical changes on SiLK surfaces. A Digital Instrument Atomic Force Profile (AFP 200) was used for checking Cu surface roughness (rms). KLA-Tencor P2 long scan profiler was used for copper dishing and oxide erosion determination. SEMs were done with a Hitachi S-4500 SEM. Hydroxylamine was obtained from BASF and the pH was adjusted with sulfuric acid.

Results and Discussions

1. Silica Based Slurry for Cu Phase-II Application

A. High Selectivity Slurry (Blanket Wafers)

The current hydroxylamine-silica based copper Phase-II slurry is designed for a high barrier film (TaN) RR and lower copper and oxide RR, Cu: TaN = 1: >3. The RR for a low-k film was expected to be equal or less than the traditional oxide ILD layer.

Table 1 and Figure 1 summarize four slurry formulations (A to D), using the same oxidizer and two different silica abrasives. The results show that the selectivity values for Cu/TaN/SiLK were similar to or better than the Cu/TaN/TEOS values. It is interesting that formulation C, were the abrasive was 80% less than the formulation A, yet the TaN RR is similar to A. This indicates the chemical activity of the oxidizer toward the barrier film.

Figure 2 shows that as the barrier chemistry C concentration is varied between 25 to 75% (of a set total oxidizer value) the TaN and TEOS removal rates remain nearly constant. However the Cu removal rate was reduced as the chemistry concentration was increased. This indicates that HDA chemistries are altering the chemical composition of the barrier film, yet not increasing the copper rate.

Table 1. Sheet Film Removal Rate and Selectivity Using Silica Based Slurry

Slurry Formulation				Blanket Wafer Polishing MRR (A/min)				Blanket Wafer Selectivity			
Formu	Oxidizer	Silica Solids	Abrasive Type	Cu	TaN	TEOS	SiLK	Cu	TaN	TEOS	SiLK
A	50%	5%	Abra-I	262	1364	118	174	1	5.2	0.5	0.7
B	20%	5%	Abra-I	336	1052	58	22	1	3.1	0.2	0.1
C	50%	1%	Abra-I	118	1330	24	2	1	11.3	0.2	0.0
D	50%	5%	Abra-II	286	1192	168	116	1	4.2	0.6	0.4

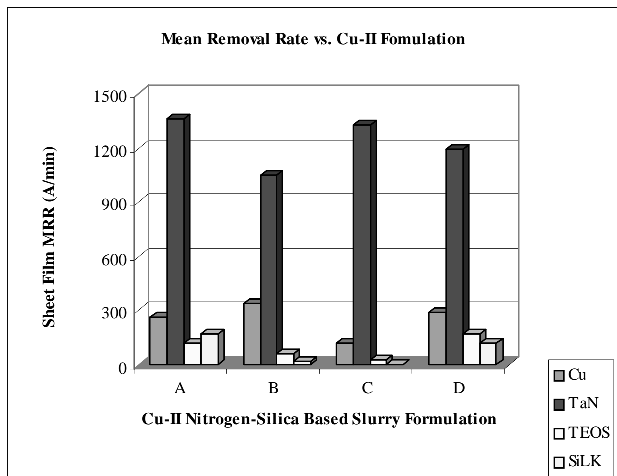

Figure 1. High Selectivity Slurry (A to D) Performance

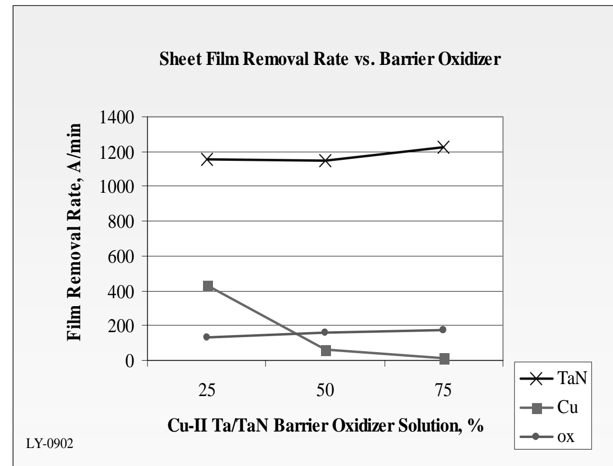

Figure 2. Sheet Film CMP Performance with Slurry C

The CMP performance of p-SiLK (porous SiLK) films is different from dense SiLK. It can be seen from Figure 3 that the removal rates for p-SiLK (porous-LC/HC) are higher than the dense SiLK with slurry A at pH 4.2. This higher removal rate is related to the lower film density, which offers less chemical and mechanical resistance to the hydroxylamine chemistries. Other chemical effects of slurry A will be discussed later. When slurry A was modified by adjusting the pH to 8 (now slurry E), the slurry's activity toward p-SiLK removal rate is significantly reduced ~20X (Figure 4). The other films were only slightly effected. There was no corresponding data for the SiCN film.

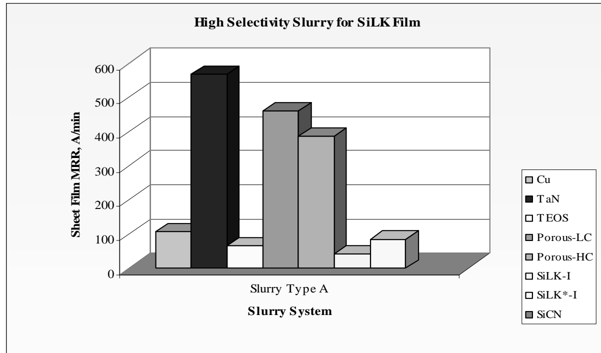

Figure 3. p-SiLK Removal Rate vs. Dense SiLK Film

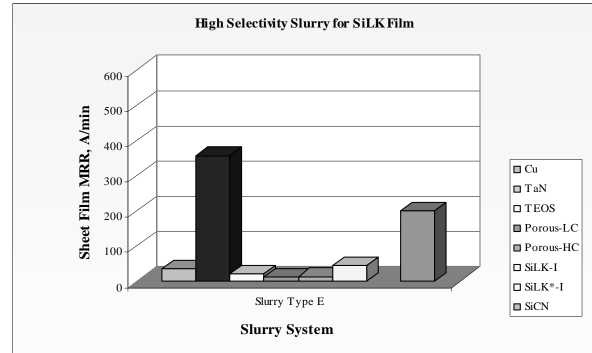

Figure 4. p-SiLK Removal Rate Using Slurry E

B. Non-Selectivity Slurry (Blanket Wafers)

In certain copper CMP processes, the desired surface planarity could be achieved after the Cu Phase-I process. The Phase-II slurry would then be used for removing the barrier (Ta/TaN) film without effecting the final planarity. Hence the Cu/TaN/ILD selectivity is targeted to a 1:1:1 ratio.
Figure 5 shows two formulations (F & G) for this non-selective application. Both of them give similar Cu and TaN removal rates with slurry F having a lower TEOS rate. Both porous and dense SiLK film removal rates are low enough to be considered for a stop layer. Slurry G has a better non-selective performance. A SiCN cap film was also tested with slurry G, which gave almost the same RR as TEOS. The SiCN film will be good for applications in the future when it becomes necessary to remove the cap layer and stop on a SiLK film.

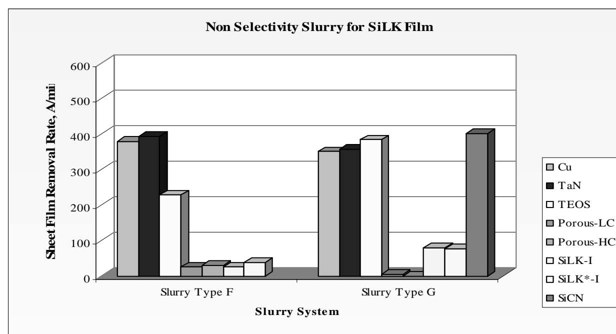

Figure 5. SiLK Film CMP Performance with
Non-Selectivity Slurry

C. High Selectivity Slurry (Pattern Wafers)

A high selectivity copper Phase II slurry (slurry C) was selected for a Cu/SiLK patterned wafer study. Figures (6 and 7) show the Cu patterned wafer dishing and erosion before and after Cu-II (slurry C) polishing. The pattern wafers were previously polished at another facility using a hydrogen peroxide slurry.

Dishing of the line structures was reduced an average 300 A. Except for the center portion of wafer (Figure 7), the erosion values showed increases of only 50 to 100 A after the Cu-II polishing. The increased center value may have been caused by either a center fast reaction or unoptimized process conditions.

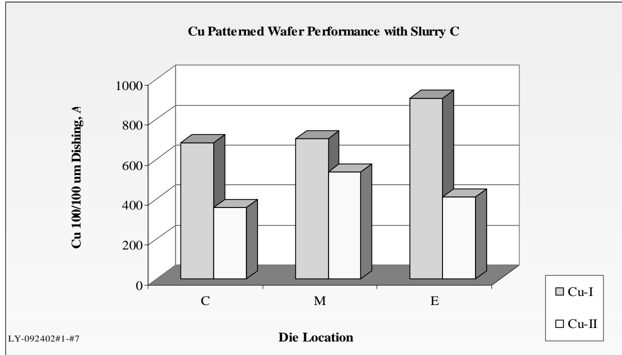

Figure 6. Cu Pattern with 100/100 um Feature Dishing after Cu Phase I and II

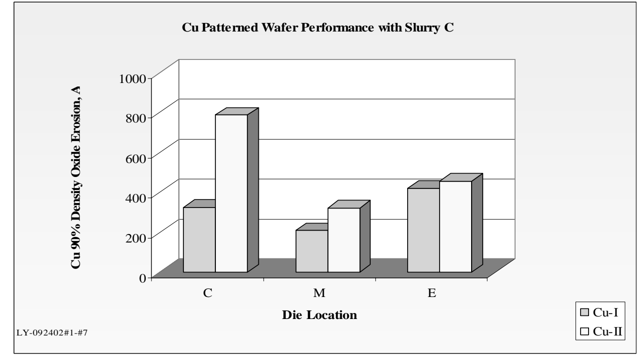

Figure 7. Cu Pattern with 90% Density Oxide Erosion after Cu Phase I and II

D. SiLK Film Chemical and Mechanical Effects

Figure 8 shows dense SiLK sheet film removal rate vs. process-down force. Below 3 psi the removal rates is less than 200 A/min. but at 5 psi the polishing rate is over 3000 A/min. There was no film delamination within these pressure ranges. FTIR spectra showed that both dense and p-SiLK film structures did not have significant chemical changes after the CMP process with any of the chemistries. The surface roughness of both the Cu and SiLK were < 10 A. The SiLK film rms after polishing was nearly identical to the pre-CMP value.

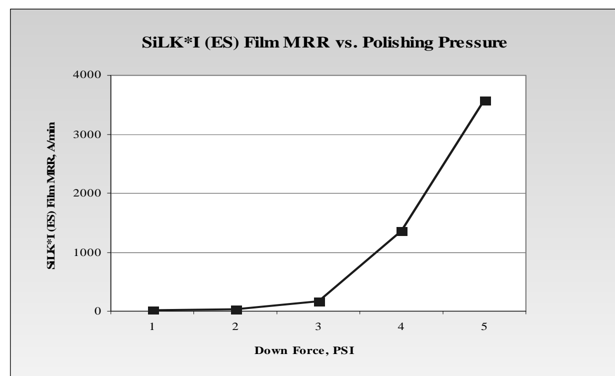

Figure 8. Dense SiLK Film
Removal Rate vs. Polishing Down Force

Blanket p-SiLK films were examined after being polished with slurries A, E, F, G and then tested for various electrical and adhesion parameters. The breakdown voltage (Jouls=1E-5 A/cm^2) after slurries A and E showed that E had 3.63E-5 A/cm^2, while slurry A was only 3.28E-5 A/cm^2. The leakage current was 3X higher for A than E (1.1E-9 @0.5 MV/cm).

Adhesion data (fracture toughness, K_{1C} for the porous SiLK films with A, E, F, and G ranged from 0.42 to 0.45. All of these adhesion values are within an acceptible range.

Cross-section SEM pictures for SiLK^{tm} pattern wafers polished with slurry C showed no dishing of a 100/100 micron line and no Ta/(TaN) barrier attack with the slurry. TEM pictures of p-SiLK films with slurry A and E showed no significant structural effects on the porous film.

2. Conclusion

Two types of SiLK^{TM} low-k dielectric films were investigated with hydroxylamine-based slurries and silica-based abrasives. Seven slurry formulations showed encouraging results for polishing SiLK films. The silica-based slurries could be designed for either a high selectivity process or a non-selective process of Cu/TaN/SiLK structures. The hydroxylamine-based slurries with silica-based slurries produced Cu and SiLK surfaces with low rms values. Though the slurry compositions studied in this paper showed excellent CMP performance for copper and barrier films they can be modified to be either aggressive or non-aggressive with the SiLK film. Copper pattern wafers using slurry C showed dishing values reduced ~300 A after the Cu Phase II polish. Oxide erosion values had been modestly increases with slurry C. The FTIR transmission spectra show no significant chemical structural changes after the CMP process. The breakdown voltage, leakage current did show that slurry A could be more aggressive to the porous films, though the adhesion data showed little or no effect with any of the hydroxylamine-based slurries.

Acknowledgments

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