Mat. Res. Soc. Symp. Proc. Vol. 649 © 2001 Materials Research Society

Adhesion Quantification of Post-CMP Copper to Amorphous SiN Passivation by NanoIndentation

J. B. Vella*, S. M. Smith**, A. A. Volinsky*, I. S. Adhihetty*

* Motorola DigitalDNA™ Labs, Process and Materials Characterization Lab, Mesa, AZ
**Motorola Labs, Physical Sciences and Research Lab, Tempe, AZ

ABSTRACT

In this study, film interfacial fracture is induced by nanoindentation to quantify the practical work of adhesion of a post-CMP copper film to an amorphous silicon nitride passivation film. Poor adhesion of electrodeposited copper to SiN passivation is observed following CMP due to copper oxide growth prior to plasma enhanced silicon nitride deposition. Four point bend testing has shown that failure by brittle fracture of test structures occurs at the Cu/CuO interface. Hydrogen, ammonia, and nitrogen plasma treatments of the post-CMP copper surface can be used to remove the oxide, shown by auger electron spectroscopy, and to increase the surface roughness of copper, shown by atomic force microscopy. Both effects can be used to improve the Cu/SiN adhesion. Nanoindentation with a conical indenter (1.59 μm tip radius) was used to induce SiN film delaminations from Cu, the sizes of which were measured and correlated with the practical work of adhesion.[1,2] In order to more reliably and repeatably produce these delaminations a TiW (10wt% Ti) superlayer was sputter deposited on to the test structures.[2,3] Mechanical properties, including elastic modulus and hardness of SiN, electrodeposited copper, and TiW measured by nanoindentation are also reported here.

INTRODUCTION

IC industry migration from Al to Cu interconnects has raised a number of thin film adhesion issues. One of which concerns the adherence of SiN passivation films that are often used to cap last metal interconnect layers following chemical-mechanical polishing (CMP). The fracture toughness of the porous oxide of copper (CuO and CuO_2) that is formed during CMP is far lower than copper and is a potential site of device failure. Often times the Cu/CuO interface can not withstand the deposition stresses of the plasma enhanced CVD deposition of SiN capping layer. Delamination and blistering of the SiN/CuO bilayer from the copper interconnect can result.

Reduction of the copper oxide can be achieved by several plasma etch treatments using gases such as N_2, H_2, and NH_3. In nearly all cases, oxide reduction has been observed to dramatically improve the Cu/SiN interfacial fracture toughness. These plasma treatments not only reduce the brittle oxide thickness, but also systematically increase the surface roughness of the copper film. This increase in surface roughness, increases the surface area of the copper, therefore the overall surface energy of the Cu/SiN interface, and also retards interfacial crack propagation due to the jagged contours of the interface. However, high film roughness can make for a porous film interface following next film deposition and may hinder device function. A root mean square (rms) roughness of <4nm was required by this application. Therefore, the interfacial chemistry had to be optimized rather than rely on surface roughness.

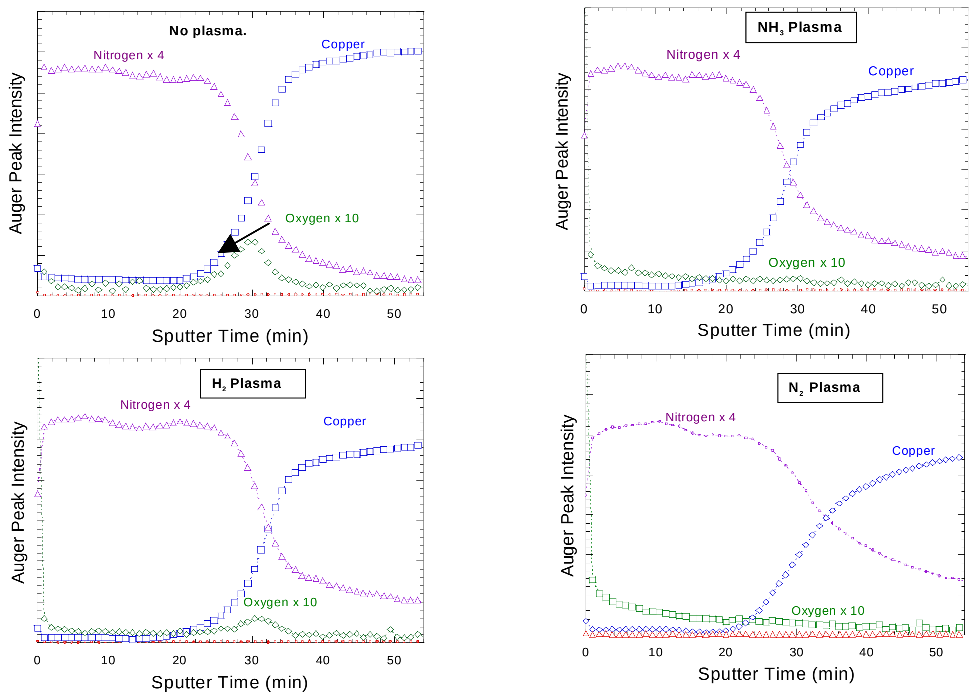


Figure 1. Auger Electron Depth profiles of SiN/Cu interface following various plasma treatments of the post-CMP copper surface

NH_3 treatment

N_2 treatment

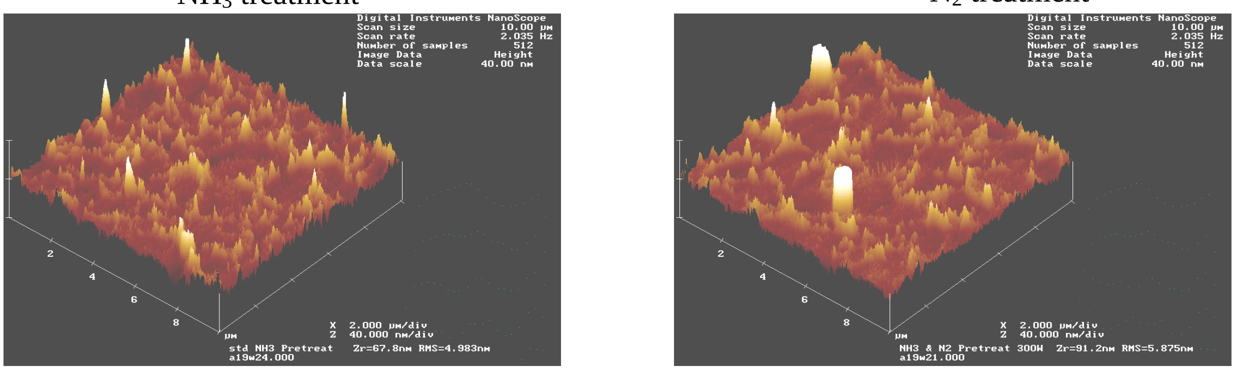


Figure 2. Atomic Force microscopy scans that demonstrate rms roughnesses of 4.98 and 5.88 nm respectively

Initial studies of copper oxide reduction through plasma treatments demonstrated the effect of strong adhesion, despite surface roughness values that exceeded application tolerances. Figure 1 illustrates the oxide reductions of 3 plasma surface treatments, including N_2, NH_3, and H_2 plasmas, in four Auger electron spectroscopy depth profiles that survey the SiN/Cu interface. However the surface roughening incurred by these processes exceeded surface roughness requirements of this application, seen in AFM surface scans in Figure 2.

A novel method of measuring the fracture toughness of this interface utilizes indentation stress as well as film deposition stresses to drive interfacial fracture. Nanoindentation using a conical indenter to loads commonly between 25-700mN can be employed to induce film delamination blisters around the indentation. If the driving forces for the delamination, such as indentation stress, residual film stresses, and film buckling stress can be elucidated, then the area of the delamination blister can be correlated with the practical work of adhesion. The calculation of this adhesion measurement is outlined elsewhere.[1,2] In this calculation, deformation of the buckling films are assumed to be entirely elastic, which requires the delaminating films to be hard and tough enough to store the amount of elastic strain energy necessary to relieve driving force stresses only through an interfacial crack. This is often not the case; for example amorphous SiN is quite brittle and will easily crack under indentation loading rather than elastically buckle. However, if one deposits a hard, yet tougher superlayer on to the film of interest, indentation induced delamination of the bilayer will be much larger due to the superlayer's ability to store elastic energy. Furthermore, the superlayer can act as a capping layer to prevent plastic flow of the underlying film in the vertical direction[3] The superlayer's residual stress can also be tailored to further drive the interfacial fracture. The calculations used for this method are described elsewhere.[2]

EXPERIMENT

All test structures were prepared in a class 100 clean room environment. Silicon <100> wafers were coated with 300nm of plasma enhanced CVD silicon dioxide, followed by 25nm of a Ta barrier layer, then sputter seeded, electroplated copper which was then chemical-mechanically polished to thickness of 400 nm. Each of these wafers, except for non-etched control wafers, were treated by a variety of NH_3, H_2, and N_2 plasma etch treatments to remove the copper oxides that formed during CMP. Without breaking vacuum, the copper films were then capped with 200nm of an amorphous SiN. Each test structure was then capped with a 1μm TiW (10wt% Ti) superlayer.

Film residual stresses were measured for each film by making wafer curvature measurements (using FSM 128 apparatus) before and after each deposition step using separate test wafers. Wafer curvature measurements were then correlated with residual film stresses using Stoney's relation.[8] Elastic moduli necessary for this and other calculations were measured via nanoindentation using a sharp Berkovich tip (<100nm tip radius) on blanket films of each film type deposited on a silicon <100> wafer.

Each test structure was then indented with a sharp conical tip (1.59 μm tip radius) to a load of 300mN to induce SiN/TiW delamination from the copper underlayer. Delamination blister radii were then optically measured using a 50x objective lense with Nomarski contrast. Representative blister radii were then confirmed by SEM imaging of the blister cross section. These cross sections were cut using a focused ion beam (FIB) of elemental gallium.

The composition of the Cu/SiN interface was measured by Auger electron spectroscopy. The surface roughness of post-CMP and plasma treat copper was measured by atomic force microscopy.

RESULTS

Thin film mechanical properties were measured by Berkovich tip nanoindentation, using the continuous stiffness option of the MTS NanoIndenter XP™. Residual stress values were then measured by wafer curvature (Table 1).

Table 1. Mechanical properties and residual stress measurements of constituent films in adhesion test structure stack. A positive sign indicates compressive stress.

	Elastic Modulus,E (GPa)	Hardness (GPa)	Residual Stress (MPa)
Cu	133 ± 10	1.59 ± .24	-100
SiN	170.6 ± 4.4	16.64 ± .54	-150 to 200
TiW	268 ± 11	14.22 ± .66	240 to 980

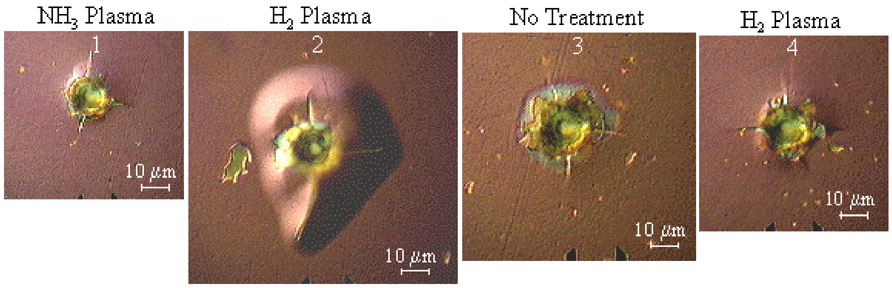


Figure 3. Delamination blisters formed without the use of TiW superlayer

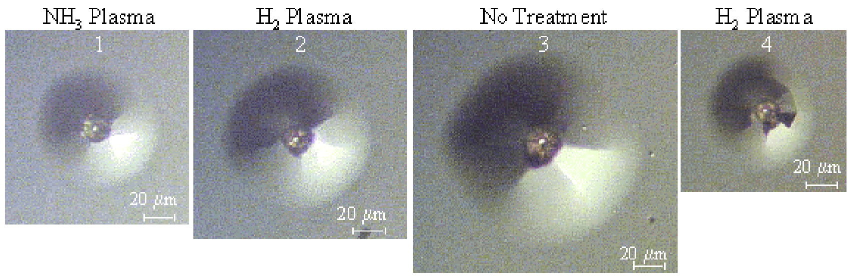


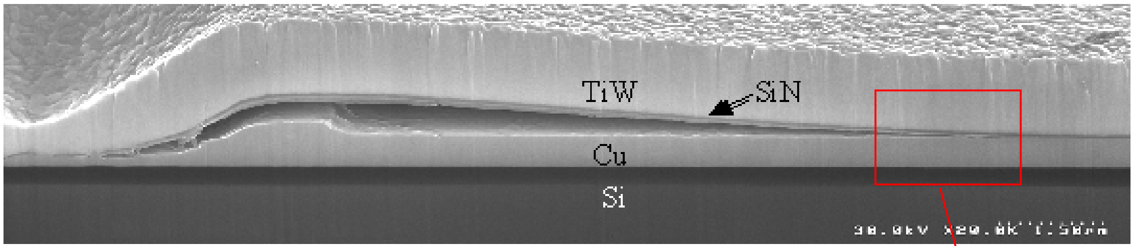
Figure 4. Delamination blisters formed with the use of a TiW superlayer

The methodology of process optimization is an iterative process, in which each iteration is used to optimize a specific set of variables. The process optimization structure used here, takes the order of determining the plasma gas that induces the strongest Cu/SiN interface, followed by optimizing the power input of that reducing gas, followed by optimization of the exposure time for the chosen power input. The nanoindentation adhesion measurements were used to determine which treatment induced the best adhesion of each experimental set.

H_2 and NH_3 plasma treatments of relatively low input powers were first tested to distinguish the Cu/SiN adhesion of each treatment. Figure 3 illustrates nanoindentation induced delamination blisters without the use of a TiW superlayer. Substantial SiN cracking and asymmetric blister formation obscure the blister radius measurement and fail to localize elastic strain energy release to the SiN/Cu interfacial crack.

However, when the TiW super layer is used delamination blisters are observed to be much larger than those generated without, and are symmetric with minimal surface cracking as seen in Figure 4. Figure 4 illustrates that the 4^{th} H_2 plasma etch treatment generated the strongest Cu/SiN interface as seen in the minimum delamination blister radius. The indentations were made to 300mN loads.

An FIB cross section was made of representative blisters to correlate optical blister radii measurements with interfacial crack lengths and to be sure that excessive interfacial crack driving force losses were not generated by extraneous film cracking and plastic flow. Figure 5 illustrates minimal surface cracking, no substrate cracking, and little plastic deformation in the copper delamination substrate. The enlargement of the crack tip illustrates a well-defined crack at the Cu/SiN interface.



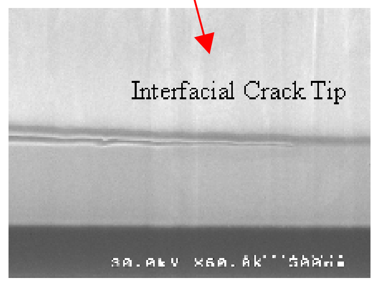


Figure 5. SEM image of FIB blister cross section of patterned Cu/SiN wafer

Using this same indentation methodology, H_2 plasma power level and exposure time parameters were optimized. AFM measurements were used to insure that surface roughness of the Cu surface were within process specifications. Table 2 illustrates the AFM rms roughness measurements that are significantly lower than those generated for NH_3 and N_2 plasma treatments.

Table 2. AFM surface roughness measurements of post-CMP Cu, and H_2 plasma clean

H2 Plasma Power	CMP Rms (nm)	H2 Rms (nm)	G (J/m2)
1	2.753	3.832	3.54
2	2.747	3.75	1.95
3	3.111	3.451	5.29
4	2.97	3.439	5.64

Figure 6 illustrates the practical work of adhesion calculations in units of strain energy release rate (J/m^2). These measurements include plasma composition optimization, plasma power optimization, and plasma exposure time optimization. It should be noted that the plasma exposure time optimization was performed on both blanket and patterned wafers, which is a major advantage of the nanoindentation adhesion measurement technique.

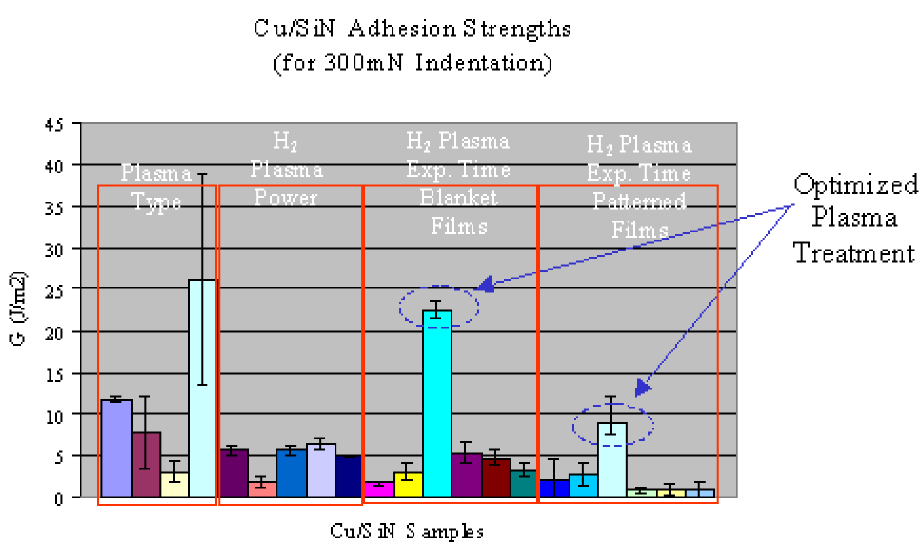


Figure 6. Strain energy release rate calculations (G) for all process variations in Cu/SiN study

CONCLUSIONS

Nanoindentation was used to quantify the practical work of adhesion of oxidized post-CMP copper to an amorphous silicon nitride passivation film. Hydrogen, ammonia, and nitrogen plasma treatments of the post-CMP copper surface may be employed to not only remove the oxide, shown by auger electron spectroscopy, but also to increase the surface roughness of copper, shown by atomic force microscopy. A study of the effects of these three treatments on SiN/Cu adhesion was performed by quantifying the practical work of adhesion of all samples via nanoindentation. Nanoindentation with a conical indenter (1.59 μm tip radius) was used to induce SiN film delaminations from Cu, which were measured and correlated with the practical work of adhesion.[1,2] In order to more reliably and repeatably produce these delaminations a TiW (10%Ti) superlayer was used.[2,3] Mechanical properties, including elastic modulus and hardness of SiN, electrodeposited copper, and TiW measured by nanoindentation are also reported here.

ACKNOWLEDGEMENTS

Many contributors have made this study possible. The authors would like to acknowledge Mike Kottke for his Auger electron spectroscopy work, Bob Carpenter, Arnold Yazzie, Mike Dickenson, and Ha Le for their FIB and SEM work, Cindy Goldberg for her AFM results, John D'Urso, Jeffrey Baker, and Tony Botta for their test structure fabrication work. We would also like to acknowledge Prof. William Gerberich for his assistance.

REFERENCES

1. D. B. Marshall, A.G. Evans, *J. Appl. Phys*., **56**(10), 2632-2638, 1984.
2. M. D. Kriese, W.W. Gerberich, N. R. Moody, *J. Mater. Res*., **14**(7), 3007-3018, 1998.
3. A. A. Volinsky, N. I. Tymiak, M. D. Kriese, W. W. Gerberich and J.W. Hutchinson, *Mater. Res. Soc. Proc*., **539**, pp. 277-290, 1999.
4. J. Noguchi et al., IEEE, 38th Annual International Reliability Physics Symposium, San Jose, CA, 2000, 339-343.
5. G. Raghavan, C. Chiang, P. B. Anders, S Tzeng, R. Villasol, G. Bai, M. Bohr, and D.B. Fraser, *Thin Solid Films*, **262**, 168 (1995).
6. H. Mikazaki, K. Hinode, Y. Homma, and N. Kobayashi, *Jpn. J. Appl. Phys*.,**35**, 1685 (1996).
7. Z. Falkenstein, M.Hakovirta, and M. Nastasi, *Thin Solid Films*, **381**, 84, (2001).
8. G. G. Stoney, Proc. Roy. Soc. Lond. A82 (1909) p. 72.