[Technical Paper]

Quantitative Adhesion Properties and Interfacial Behavior of SiCN Barrier Layer and Cu Film

Satoko Abe, Teruhisa Baba, Kenichi Ueoka, Yohei Takahashi, Kouji Yoneda, and Jiping Ye

NISSAN ARC, LTD., 1, Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan

(Received July 30, 2012; accepted October 11, 2012)

Abstract

Adhesion of the SiCN barrier layer and Cu film interface is one of the important characteristics that reflect the interfacial structure. NH_3 plasma treatment of the Cu surface is a well-known way of improving adhesion. The results of X-ray reflectivity (XRR) and X-ray photoelectron spectroscopy (XPS) depth profiles indicate that the plasma treatment imparts a difference to the formation of the interface with SiCN. Adhesion properties are regarded as fracture energies measured by double cantilever beam (DCB) and 4-point bending (4PB) techniques. The influence of the NH_3 plasma treatment of the Cu surface on adhesion is quantitatively discussed. The treated samples showed approximately twice the fracture energy of the non-treated samples. After 4PB and DCB measurements, fracture surfaces were investigated by XPS and atomic force microscopy (AFM). The formation of a N-Cu chemical bond on the Cu surface was enhanced as a result of removing oxygen by the plasma treatment. N-Cu chemical bonding contributes substantially to better SiCN/Cu interfacial adhesion.

Keywords: SiCN, Cu, Interface, Adhesion, Fracture Energy, N-Cu Chemical Bonding, Plasma Treatment

1. Introduction

Ultra-large-scale integrated (ULSI) circuits require lower resistivity to obtain higher operating speeds and lower power consumption. Cu is now used as an interconnect material instead of Al, which was used for a long time. Cu exhibits a lower electrical resistivity and a better electromigration resistance. The Cu surface is, however, chemically unstable. Cu easily oxidizes and diffuses in the deposition process environment. Cu wire, therefore, needs to be covered with a barrier layer to prevent diffusion and oxidation. The behavior of the barrier layer/Cu interface is one of the key factors in inhibiting breakdown and ensuring reliability of ULSI circuits. Adhesion properties are closely related to the interfacial behavior of the barrier layer/Cu.

SiCN is now being applied as a barrier layer instead of conventional SiN because the barrier layer is also expected to have a lower dielectric in order to reduce the intrinsic capacitance. Adhesion between SiCN and Cu is, however, drastically lower than that of SiN. Weak adhesion could cause breakdown ultimately. Accordingly, investigation of adhesion properties, which depend on fabrication processes and materials, is always a critical issue. It has been

widely reported that a NH_3 plasma treatment of the Cu surface improves the adhesion of the SiCN/Cu interface.[1] A comparison of adhesion is, however, almost always relative and qualitative. In this study, we measured the fracture energies of the SiCN/Cu interface treated with and without NH_3 plasma using a double cantilever beam (DCB) technique[2, 3] and a 4-point bending (4PB) technique[4] in order to compare adhesion properties quantitatively. X-ray reflectivity (XRR), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used for characterization of SiCN/Cu interfaces. Direct observation of fracture surfaces after DCB and 4PB measurements is especially valuable for obtaining information about the interface. SiCN/Cu interface properties are discussed in relation to fracture energies and an important factor affecting interfacial adhesion is identified.

2. Experimental

2.1 Sample preparation

The multilayer sample includes the SiCN/Cu interface as shown in Fig. 1. Samples with NH_3 plasma treated and non-treated Cu surfaces were prepared for comparison of adhesion properties and behavior of the SiCN/Cu inter-

SiCN 140 nm
Cu 150 nm
TiN / Ti 30 nm
SiO ₂ 300 nm
Si substrate 725 μ m

Fig. 1 Schematic cross-sectional view of multilayer structure.

face. The specimens for XRR and XPS depth profiles were cut into 10 mm squares.

For the specimens subjected to DCB and 4PB measurements, square-shaped bare silicon substrates measuring about 50 mm on one side were used with SiCN epoxy-bonded on the top of the specimens. The sandwich substrates were diced using a high speed wafer saw to fabricate individual specimens with dimensions of 4 mm wide, 50 mm long and 1.45 mm thick.

2.2 Adhesion

Adhesion was quantified as the fracture energy needed for a crack to delaminate the interface. Two different fracture mechanics, namely DCB and 4PB techniques, were used to measure fracture energy.

For fracture energy measurement by the DCB technique under pure Mode I loading, a crack was initiated from a pre-notch machined at the end of the specimen (Fig. 2 (a)). Loading tabs were epoxy-bonded to the notched end of the specimens. Specimens were loaded under controlled displacement at a displacement rate of 1.0 μ m/s. The load-displacement response was linear elastic until reaching a critical load, P_c . After that, the response changed from linear to non-linear when the crack began to propagate. The fracture energy, G_c , was calculated as the critical value of the strain energy release rate, as defined by[2, 3]:

$$G_c = \frac{12P_c^2 a^2}{B^2 h^3 E'} \left(1 + 0.64 \frac{h}{a}\right)^2$$

where a is the crack length, E' is the biaxial modulus of the silicon beams (169 GPa), and B and h are the specimen width and half-height, respectively.

For measurement by the 4PB technique under mixed mode loading, a crack was initiated from a pre-notch at the top center of the specimen into the layered structure (Fig. 2 (b)). Specimens were loaded under a displacement control fixture at a displacement rate of 0.2 μ m/s. The load response became constant and independent of displacement at a critical load, P_c , when the crack began to propagate. The fracture energy of the interface, G_c , was calcu-

Fig. 2 Schematic illustration of (a) the DCB specimen and (b) the 4PB specimen.

lated as the critical value of the strain energy release rate, as defined by[4]:

$$G_c = \frac{21P_c^2 L^2}{16B^2 h^3 E'}$$

where L is a moment arm.

2.3 Characterization

XRR spectra were measured with respect to the mass density of SiCN using a PANalytical X'Pert Pro Materials Research Diffractometer with a parallel Cu $K\alpha_1$ x-ray beam using a germanium monochromator. XPS measurements were performed on a PHI Quantum 2000 XPS system with monochromatic Al $K\alpha$ radiation at 1486.6 eV in order to investigate the depth profile and identify the chemical bonding state of the fracture surface. All the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. Ar ion beam sputtering was used to obtain depth profiles. The sputtering depth was referenced to that of the SiO₂ sputtering rate. Fracture surface roughness was examined using AFM in the tapping mode. The images were processed by flattening to remove the background slope.

3. Results and Discussion

XRR measurements for the samples with and without NH₃ plasma treatment are shown in Fig. 3. The film mass density was derived by fitting the reflectivity data around the critical angle of 0.2 degree. The mass density of SiCN on plasma-treated Cu was 1.93 g/cm³. The same value was obtained for SiCN on non-treated Cu because both critical angles were the same. The plasma treatment did not influence the mass density of SiCN. Both reflectivity curves, however, showed slightly different behavior after the critical angle. Presumably, this different behavior can be attrib-

Fig. 3 X-ray reflectivity of samples with and without the plasma treatment.

Fig. 4 XPS depth profiles of SiCN/Cu interface with and without the plasma treatment. Sputtering depth was normalized to the sputtering rate of SiO_2 .

uted to small variations in the SiCN/Cu interfacial structure and thickness.

Figure 4 shows XPS depth profiles for the NH_3 plasma treated and non-treated specimens. Two major differences are seen in the thickness of SiCN and the oxygen content of the interface. The plasma treated specimens showed a much lower oxygen content around the SiCN/Cu interface. This indicates that the NH_3 plasma treatment was effective in removing the oxidation layer from the Cu surface. XPS depth profiles are commonly used to investigate the interfacial behavior of thin films. They are helpful in understanding the atomic distributions relative to the depth. However, it is difficult to discuss in detail the chemical bonding states obtained on the basis of depth profiles because they are influenced by Ar sputtering.

A schematic illustration of a specimen for adhesion property measurement is shown in Fig. 5. Fracture energies measured by DCB and 4PB techniques are shown in Figs. 6 and 7, respectively. Fracture energy values are summa-

Fig. 5 Schematic illustration of multilayer structure sandwiched between two Si substrates. Directions of crack initiation for adhesion property measurements are indicated by the arrows.

Fig. 6 Fracture energy measured by DCB as a function of crack length for samples with and without the plasma treatment.

Fig. 7 Strain energy release rate measured by 4PB for samples with and without the plasma treatment. Fracture energy was where strain energy release rate reached a plateau.

rized in Table 1. Two different results were obtained from 4PB measurements because cracks could be initiated from two different directions, labeled “4PB-a” and “4PB-b” in Fig. 5. Treated samples tended to show higher fracture energy in every measurement. The results show quantitatively that the plasma treatment was effective in improving adhesion properties. For both treated and non-treated samples, the fracture energies measured with the DCB technique were almost the same as those obtained in 4PB measurements where cracks were initiated from the “4PB-b” direction. 4PB measurements in which cracks were initiated from the “4PB-a” direction, on the other hand, indicated fracture energies twice as high as the other values.

XPS is very sensitive to the surface condition because the typical photoelectron escape depth is less than 5 nm. Characterization of fracture surfaces by XPS revealed SiCN/Cu interfacial failure in nearly every fracture energy measurement. XPS spectra for samples with and without the plasma treatment after 4PB measurements in which cracks were initiated from the “4PB-a” direction are shown in Fig. 8. The fracture surfaces of the Cu film indicate Cu 3s and 3p spectra and those of the SiCN film indicate Si 2s,

2p and N 1s spectra.

The morphology of every fracture surface after fracture energy measurements was observed by AFM. There was no significant difference in the surface roughness of the fracture surfaces. Fig. 9 (a) and (b) show fracture surfaces of the Cu film with and without plasma treatment after 4PB measurements in which cracks were initiated from the “4PB-a” direction. The mean roughness (R_a) values of the Cu film fracture surfaces with and without plasma treatment were 1.0 nm and 1.1 nm, respectively. It is clear that the plasma treatment did not change the surface morphology of the Cu film.

There is no difference for the fracture surfaces in identification by XPS and observation by AFM. The data show that fracture energy was, however, more sensitive to mixed mode loading as is commonly reported.[5, 6] That fracture energy difference, therefore, suggests that the position of the fracture surface moves up or down several nm depending on the crack initiation direction. In order to understand the difference in fracture energies attributable to the plasma treatment, the chemical bonding of the fracture surfaces was examined in detail by XPS. N 1s spectra of the fracture surfaces of the Cu film are shown in Fig. 10.

Table 1 Fracture energies measured by DCB and 4PB techniques.

Technique	Fracture energy	
	Plasma treated	Non-treated
DCB	1.6 J/m ²	1.0 J/m ²
4PB (“4PB-a” direction)	3.7 J/m ²	2.3 J/m ²
4PB (“4PB-b” direction)	1.9 J/m ²	1.3 J/m ²

Fig. 8 XPS spectra for samples with and without the plasma treatment after 4PB measurements where cracks were initiated from the “4PB-a” direction.

Fig. 9 AFM images of the three-dimensional configuration of the fracture surface of the Cu film after 4PB measurements where cracks were initiated from the “4PB-a direction”. (a) Treated sample; (b) non-treated sample.

Fig. 10 The details of N 1s spectra of fracture surfaces of Cu film.

For all of the Cu film fracture surfaces, no N-Si chemical bonding originating from the SiCN film around 397 eV[7] was found. N-Cu chemical bonding near 399 eV[7] was clearly observed only for the fracture surfaces of the Cu film in the 4PB measurements where cracks were initiated from the “4PB-a” direction. The integral intensity of the N-Cu peaks was higher for treated samples than for non-treated samples. Judging from the results of the fracture energy measurements, N-Cu chemical bonding is strongly related to adhesion properties. Si 2*p* and O 1*s* spectra of the fracture surfaces of the SiCN film are shown in Fig. 11. Peaks around 102 eV in Fig. 11 (a) represent Si-N chemical bonding. The three treated samples show relatively sharp peaks. The peaks of the non-treated samples, on the other hand, have a shoulder in the 103 to 104 eV range, which represents Si-O chemical bonding. This tendency is consistent with the O 1*s* spectra shown in Fig. 11 (b). Reduction of oxygen on the Cu surface by the plasma treatment prevented oxygen from being included in the SiCN film at the SiCN/Cu interface. Consequently, the quality of the SiCN film was improved.

Fig. 11 The details of (a) Si 2*p* and (b) O 1*s* spectra of fracture surfaces of SiCN film.

4. Conclusion

Adhesion properties of SiCN/Cu interfaces were investigated quantitatively on the basis of fracture energies measured by DCB and 4PB techniques. NH₃ plasma treatment of the Cu surface was effective in improving interfacial adhesion. Direct investigation of fracture surfaces after DCB and 4PB measurements revealed an important factor in controlling the quality of the SiCN/Cu interface. NH₃ plasma removes oxygen from the Cu surface, thereby promoting the bonding of copper to nitrogen. At the same time, silicon does not bond with oxygen at the interface. As a result, a better quality SiCN film grows at the interface. N-Cu bonding is the most important factor in deriving high adhesion properties of SiCN/Cu.

Conventional measurements of adhesion properties require the use of the same materials, thicknesses and structures for relative comparison. DCB and 4PB techniques, on the other hand, allow quantitative comparisons of different materials, thicknesses and adhesion structures. Furthermore, the combination of these techniques with analyses of fracture surfaces provides important information about the interface of interest and can contribute to better control of the factors governing adhesion properties.

References

- [1] J. Noguchi, N. Ohashi, T. Jimbo, H. Yamaguchi, K. I. Takeda, and K. Hinode, “Effect of NH₃-plasma treatment and CMP modification on TDDb improvement in Cu metallization,” *IEEE Trans. Electron Devices*, Vol. **48**, p. 1340, 2001.
- [2] M. F. Kanninen, “An augmented double cantilever beam model for studying crack propagation and arrest,” *Int. J. Fract.*, Vol. **9**, p. 83, 1973.
- [3] M. F. Kanninen, “A dynamic analysis of unstable crack propagation and arrest in the DCB test specimen,” *Int. J. Fract.*, Vol. **10**, p. 415, 1974.
- [4] P. G. Charalambides, H. C. Cao, J. Lund, and A. G. Evans, “Development of a test method for measuring the mixed mode fracture resistance of bimaterial interfaces,” *Mech. Mater.*, Vol. **8**, p. 269, 1990.
- [5] H. C. Cao and A. G. Evans, “An experimental study of the fracture resistance of bimaterial interfaces,” *Mech. Mater.*, Vol. **7**, p. 295, 1989.
- [6] A. G. Evans, M. Ruhle, B. J. Dalgleish, and P. G. Charalambides, “The fracture energy of bimaterial interfaces,” *Metall. Trans. A*, Vol. **21**, p. 2419, 1990.
- [7] A. V. Vairagar, Z. Gan, W. Shao, S. G. Mhaisalkar, H.

Li, K. N. Tu, Z. Chen, E. Zschech, H. J. Engelmann, and S. Zhange, "Improvement of electromigration lifetime of submicrometer dual-damascene Cu intercon-

nects through surface engineering," J. Electrochemical Society, Vol. **153**, p. G840, 2006.

Satoko Abe received her PhD in metallurgical engineering from Tokyo Institute of Technology. She worked for several years on crystal structures, electric and thermal properties in chalcopyrite semiconductors and metallic superconductors. In 2008, she joined Nissan ARC, Ltd. and started her research dealing with the interface of thin film multilayer structures. Her current research is focused on the relationship between the interface phenomena and electronic structures in wide-gap semiconductors GaN and SiC.

Teruhisa Baba received his PhD in applied physics from the University of Tokyo in 2007 and is the analyst of Nissan ARC, Ltd. near Yokohama, Japan, which offers analytical services for Nissan Motor and many other major advanced R&D companies in Japan. His research focus includes the electron spectroscopic measurement at the solid-state materials, especially the lithium-ion battery electrodes.

Kenichi Ueoka joined Nissan ARC, Ltd. in 2001 and started surface analysis using atomic force microscopy. His research interests are the measurement of the surface potential distribution and the thermal property measurement of localized area using scanning probe microscope technique.

Yohei Takahashi works in Nissan ARC, Ltd. near Yokohama, Japan. His specialties range over various X-ray analyses such as X-ray diffraction, X-ray reflection and small angle X-ray scattering. He is currently working on the structural characterization of the lithium-ion battery electrodes.

Kouji Yoneda joined Nissan Motor Company in 1982 and worked on the research and development of ceramic component. In 1990, he moved to Nissan ARC, Ltd. and is the manager of material analysis department. He specializes in the measurements of the mechanical properties. The focus of his current research is on the fracture mechanism in microscopic area using the acoustic emission technique.

Jiping Ye received his PhD in metallurgical physics from the Tokyo Institute of Technology in 1996 and is the director of Nissan ARC, Ltd. near Yokohama, Japan, which offers analytical services for Nissan Motor and many other major advanced R&D companies in Japan. His research focus includes the quantitative property measurement at the nanoscale and serves on a variety of steering committees that regulate nanoscale property measurement.