Accurate measurement of mechanical properties of nanoporous silica ultra-low-k films

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1. Introduction

In order to reduce the RC time delay of ULSI circuits, low-resistance interconnect metals and ultra low-dielectric constant interlayer films should be used. One candidate of ultra-low-k (ULK) materials is nanoporous silica films, in which main strategy is the reduction of the film density by introducing nanometer sized pores (air) in the base materials [1]. Introduction of pores in silica based materials has serious problems of great reduction of mechanical strength and increasing of brittleness with decreasing material density. The urgent issue in developing nanoporous silica based ULKs is to establish process technology for both reinforcement of pore-walls and high adhesion property of interface between ULKs and surrounding film layers. Especially, the adhesion is directly related to success or failure of chemical mechanical polishing process (CMP) of ULSI interconnects. The accurate evaluation and subsequent improvement of adhesion of brittle low-k films are subjects of great importance for the development of Cu/Low-k interconnect technology.

Recently, 4-point bending test [2] has been widely used to evaluate the adhesion between ULK films and surrounding layers. The 4-point bending technique is easy to analyze, however, it has same problem as traditional 'Scotch tape' test, that is, it can not be applicable for the interfaces stronger than adhesion of epoxy or other glues to construct 'Sandwich' configuration of test samples and its delamination modes are not directly connected to the realistic delamintaion usually observed in the unsuccessful CMP process.

We think that scratch testing reflects the nature of adhesion related to more realistic figure of delamination phenomena in CMP process, and made attempt to apply the scratch method for evaluation of adhesion of ULKs.

2. Measurement Principle

Maltzbender and de With [3] have proposed that adhesion between film and substrate material is characterized by 'adhesion energy'. Their analysis is based on the elastic energy dissipation at the buckling delamination of brittle film on substrate. They formulated the adhesion energy Γ for delamimation as Eq. 1, where, *E* is the Young's modulus of the film, σ_r is the residual stress in the film, *t* is the film thickness, *L* is the radius of the chipped area, *a* is the half width of tip of the chipped area and β is the half of the angle of the chipped area as shown in Fig.1.

$$\Gamma = 1.42 \frac{Et^{5}}{L^{4}} \left(\frac{a/L + \beta\pi/2}{a/L + \beta\pi} \right)^{2} + \frac{t(1-\nu)\sigma_{r}^{2}}{E} + \frac{3.36(1-\nu)t^{3}\sigma_{r}}{L^{2}} \left(\frac{a/L + \beta\pi/2}{a/L + \beta\pi} \right).$$
(1)

We have investigated the feasibility of 'adhesion energy' measurements for nanoporous silica low-k films and correlation among the adhesion energy, Young's modulus and hardness of ULK films.

3. Experimental

We prepared several ULK films on Si (100) substrates. The first sample was the periodic nanoporous silica ULK with k = 2.2 (PPSiO), the second one was the periodic nanoporous silica ULK of k = 1.9 which was hydrophobised by hexamethyldisilaze(HMDS) treatment process (HMPPSiO) [3], the third one was disordered nanoporous silica ULK with nanometer sized pores (DPSiO). For reference, non-porous organic silica film (NPSiO) which was made from same base materials as above three ULKs, and finally hydrosilsesquioxane (HSQ).

Young's modulus and Hardness were evaluated by Continuous Stiffness Measurement (CSM) nanoindentation technique [4] by using Nanoindenter DCM (MTS, TN, USA) with widely used Berkovich type indenter in N_2 atmosphere at room temperature. The relative humidity was kept lower than 1% to avoid the influence of the moisture absorption on mechanical properties of nanoporous low-k film samples. Prior to measurements of nanoindentation of the samples, the frame compliance and the area function of the indenter tip were calibrated using the procedure proposed by Oliver and Pharr, applied to indentations of fused silica grass[4]. Scratch testing were performed with scratch test mode of Nanoindenter XP (MTS, TN, USA) with cube corner shaped indenter in the same environment as nanoindentation measurements.

In evaluation of 'adhesion energy' of the films, the shapes of delaminated areas were observed by a scanning electron microscope (SEM) JSM-5410LV (JEOL, Akishima, Japan) and the observed images were stored in digital files. The geometrical parameters *L*, *a* and β in Eq. 1 were then measured by an image processing software from the SEM images. The film thickness *t* was measured by using a scanning probe microscope (SPM) SPA400 (Seiko, Instruments Inc., Chiba, Japan) from the step height of the peripheral of the chipped area. Magnification of both SEM and SPM were calibrated by using a topography standard material which is traceable to National Institute of Standards and Technology.

4. Results and Discussion

The Young's moduli and the hardness of the films measured as functions of indentation depth by CSM technique. Young's moduli and hardness showed strong depth dependence influenced by substrate stiffness. To deduce the Young's modulus of the film itself from the 'composite modulus', the Young's moduli of the films were estimated by extrapolation to zero depth. The film hardness were obtained from the mean values of those of the plateau region of the depth dependence curves of the 'composite hardness'. The correctness of this procedure was confirmed by the measurements of thermally oxidized SiO₂ layer of thickness of 1 μ m on Si (100) substrate. The accuracy of the measurement for SiO₂ layer was better than 1.5 % for both Young's modulus and hardness.

Table 1 summarizes the results of measurements of Young's moludi and hardness of the samples including the reference SiO_2 .

Fig. 2 shows the Weibull plot of adhesion energy for non-treated sample PPSiO and HMDS treated sample HMPPSiO as examples. One can see that both samples have almost the same adhesion on Si substrate and have similar statistical distribution.

Fig. 3 (a) and (b) show the adhesion energy of 5 samples as functions of Young' modulus and hardness of the films respectively. No correlation between adhesion energy and Young's modulus or hardness is observed even though nonporous organic silica film and HSQ film are included. This results suggests that nanoporous silica ULK films have uniformly planar structure without open pores at the interface with Si substrate.

5. Conclusions

We have successfully measured the accurate and reliable values of Young's modulus and hardness of thin layer of nanoporous ultra-low-k materials.

We also demonstrated the capability of the scratch testing for the evaluation of adhesion property of interface between ULKs and substrate materials. To make this method more easy to use, further investigation concerning the optimization of test conditions is in progress.

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References

[1] N. Nishiyama, S. Tanaka, Y. Egashira, Y. Oku and K. Ueyama,

Chem. Mater. 14, p4229(2002).

- [2] Q. Ma, J. Mater. Res. 12, p840 (1997).
- [3] J. Maltzbender and G. de With, Surf. Coat. Technol. 154, p21 (2002).
- [4] S. Fruehauf, I. Streiter, S. E. Sculz, E. Brendler, C. Himcischi, M. Friedrich, T. Gessner and D. R.T. Zahn, Advanced Metallization Conference 2001, Proceeding of the Conference, p287(2001).
- [5] W. C. Oliver and G. M. Pharr, J. Mater. Res. 7, p1264 (1992).



Fig.1 Scanning electron micrograph of the chipped area after scratching test for HMDS treated nanoporous silica ultra low-k film.

Table 1 Evaluation of Young's modulus and hardness of ultra low-k films.

	Young's modulus(GPa)	Hardness (GPa)
PPSiO	1.84	0.19
HMPPSiO	1.80	0.20
DPSiO	3.58	0.33
NPSiO	9.37	0.90
HSQ	10.28	1.45
SiO ₂	72.08	10.20



Fig. 2 Weibull plot of adhesion energy for non-treated nanoporous silica low-k (PPSiO), (filled circle) and HMDS treated one (HMPPSiO), (open circle).



Fig.3 Adhesion energy plotted as functions of Young's modulus (a) and hardness (b).