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Recovery of Process-induced Damages of Porous Silica Low-*k* Films by TMCTS Vapor Annealing

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1. Introduction

We have recently reported vapor-phase TMCTS (tetramethyl-cyclo-tetra-siloxane)-treated disordered or periodic porous silica low-*k*/Cu single damascene [1]. Details of the vapor-phase TMCTS treatment and the disordered porous silica low-*k* film were also discussed elsewhere [2,3]. This TMCTS treatment can significantly reduce the leakage current and remarkably enhance the mechanical strength. On the other hand, process-induced damages of porous low-*k* films are inevitable and important problems to be solved in order to put the fragile porous low-*k* films into practical use. For instance, ashing damages by oxygen have been widely reported. Among others, the degradation of electrical properties such as the dielectric constant (*k*-value) and the leakage current density should be minimized or recovered.

In this study, we focus on recovery of process-induced damages using TMCTS treatment after exposing the disordered porous silica low-*k* films to ashing, wet cleaning, and half etching.

2. Experimental

The disordered porous silica low-*k* films were produced on 200 mm p-type Si wafers by spin coating, followed by calcination at 698 K in dry air [1]. After calcination, TMCTS treatment at 698 K was carried out to make the porous silica hydrophobic. Thus prepared films were processed as indicated in Table I. For example, A2+T stands for CF_4/O_2 ashing followed by TMCTS treatment at 673 K as "TMCTS recovery process". A1 is equivalent to the case of A2 followed by A3 successively. The processed low-*k* films were characterized as follows: The film thickness and refractive index were evaluated by spectroscopic ellipsometry. The dielectric constant and leakage current density were measured by mercury probe method in nitrogen ambient. The elastic modulus (*E*) and hardness (*H*) were estimated by nanoindentation.

3. Results and Discussion

Table Ⅱ shows a set of film thicknesses evaluated by spectroscopic ellipsometry. Ref stands for an as prepared sample without any processing. Both A1 and A2 processes caused the decease in the film thicknesses by about 10%, presumably due to etching of disordered porous silica by CF_4/O_2 chemistry, while the film thickness was kept almost the same after A3 (O_2 ashing). WC also did not change the film thickness. A3 and WC induced little damage in terms of the film thickness. TMCTS recovery process had little effect on the film thickness. Table Ⅲ shows a set of refractive indices estimated by spectroscopic ellipsometry. Both A1 and A2 decreased the refractive indices, while A3 increased the refractive index owing to the degradation of hydrophobicity by O_2 ashing. The refractive index increase by TMCTS recovery process can be understood qualitatively in terms of film density increase by the incorporation of TMCTS molecules in pores. The changes in the refractive index with the various processes are not very significant. Thus, the degree of *k*-value degradation induced by the processes was further investigated as shown in Fig. 1. The initial *k*-value of the as prepared sample is 2.2. The extent of *k*-value recovery by the TMCTS treatment is also indicated by arrows in Fig. 1. The degree of the recovery was defined as % reduction of degraded *k*-values. For example, the TMCTS treatment after A1, A2, and A3 processes recovered the *k*-value by 52, 23, and 68 %, respectively, indicating that the final degradation of *k*-values is kept within 12 %. In the case of WC and HE, the TMCTS recovery process improved the *k*-value even lower than that of the as prepared sample, so that the degrees of recovery exceed 100%. Figure 2 shows the family of leakage current density (J) versus electric field (E) curves with and without the TMCTS recovery process. As seen in Fig. 2 (a), A1, A2, A3 and HE increased the leakage current density by one or two order magnitude with respect to Ref, while the TMCTS recovery process significantly reduced the increased leakage current density (Fig. 2 (b)). Figure 3 shows the enhancement of the elastic modulus and hardness caused by each process, and the additional TMCTS treatment. A1, A3 and HE largely increased *E*, while the subsequent TMCTS treatment slightly decreased *E*. A2 and WC cause a little increase of *E*, while the subsequent TMCT treatment further increased *E*.

In contrast, the TMCTS recovery treatment after the processes improves the hardness *H* for all the cases.

4. Conclusion

Recovery of process-induced damages of porous silica low-*k* films by TMCTS vapor annealing was examined. The *k*-values degradation can be kept within 12 % by the TMCTS treatment. The leakage current degradation is also suppressed by the TMCTS recovery process. The TMCTS treatment increases both *H* and *E*. It is shown that the vapor-phase TMCTS treatment is effective to recover the process-induced damages of porous silica low-*k* films.

Acknowledgment

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References

[1] Y. Oku, et al., *IEEE 2003 International Electron Devices Meeting, Technical Digest* (2003) 139.
[2] K. Kohmura, et al., *2004 MRS Spring Meeting, F6.2* (2004).
[3] N. Fujii, et al., *2004 MRS Spring Meeting, F4.10* (2004).

Table Ⅰ A list of processes employed in this study.

Abbr.	Process
Ref	As prepared (without processing)
A1	CF_4/O_2 ashing followed by O_2 ashing
A1+T	TMCTS treatment after CF_4/O_2 ashing followed by O_2 ashing
A2	CF_4/O_2 ashing
A2+T	TMCTS treatment after CF_4/O_2 ashing
A3	O_2 ashing
A3+T	TMCTS treatment after O_2 ashing
WC	Wet cleaning (organic acid)
WC+T	TMCTS treatment after wet cleaning (organic acid)
HE	Half etching ($Ar/C_5F_8/O_2$)
HE+T	TMCTS treatment after half etching ($Ar/C_5F_8/O_2$)

Table Ⅱ A set of film thicknesses for processed disordered porous silica low-*k* films evaluated by spectroscopic ellipsometry.

Abbr.	Ref	A1	A2	A3	WC	HE
Thickness (nm)	327.0	293.2	289.8	324.7	330.3	208.7
Abbr.	Ref	A1+T	A2+T	A3+T	WC+T	HE+T
Thickness (nm)	327.0	293.8	291.6	314.2	327.7	194.9

Table Ⅲ A set of refractive indices for processed disordered porous silica low-*k* films evaluated by spectroscopic ellipsometry.

Abbr.	Ref	A1	A2	A3	WC	HE
Refractive Index	1.202	1.197	1.180	1.209	1.207	1.213
Abbr.	Ref	A1+T	A2+T	A3+T	WC+T	HE+T
Refractive Index	1.202	1.212	1.193	1.228	1.204	1.220

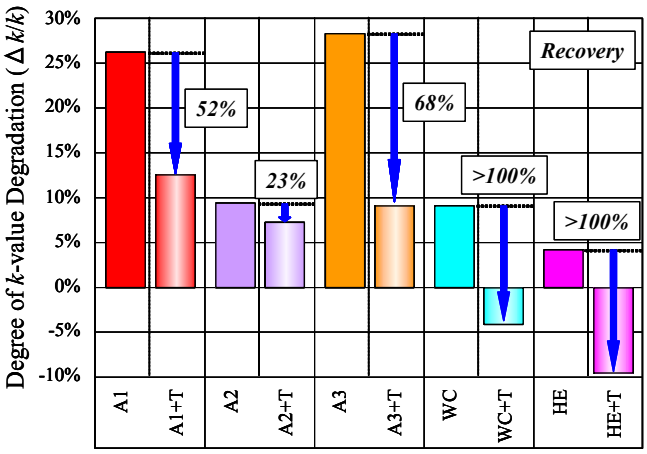

Fig.1 Degree of *k*-value degradation ($\Delta k/k$) induced by each process, A1, A2, A3, WC, and HE. The extent of *k*-value recovery by the TMCTS treatment T is indicated by arrows with %.

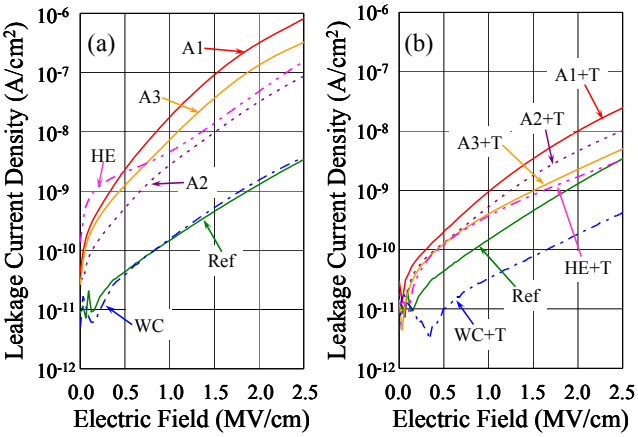

Fig.2 J-E curves of the processed disordered porous silica low-*k* films: (a) without TMCTS recovery process and (b) with TMCTS recovery process.

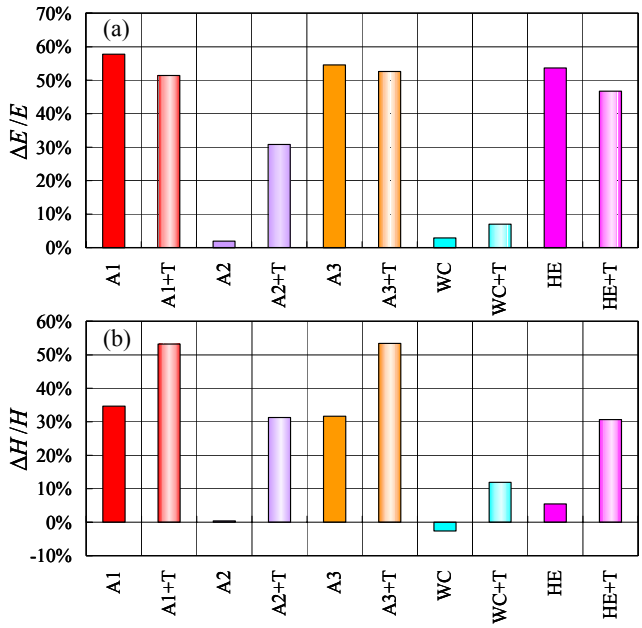

Fig.3 (a) Elastic modulus enhancement ($\Delta E/E$) induced by each process and the subsequent TMCTS treatment. (b) Hardness enhancement ($\Delta H/H$) by the TMCTS treatment after each process.