

## Electrical Reliabilities of Highly Cross-Linked Porous Silica Film

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### 1. Introduction

In order to lower the resistance-capacitance signal delay and power consumption at the Cu interconnect of large-scale integrated circuits, ultra-low dielectric constant insulator film with  $k < 2.1$  must be developed. Porous silica film is a promising candidate of it. When it is demanded to fabricate it at low-temperature of 350°C, the degree of siloxane cross linkage become poor and its electrical reliabilities are degraded. Fujii et al. proposed the method of adding Cs to the silica skeleton so as to promote the cross linkage [1].

In this work, it is shown that a hydrophobic porous silica film was fabricated and high electrical reliability was insured by the Cs doping technique.

### 2. Experiment

Fig. 1 shows the film fabrication process of porous silica film. Precursor solutions were prepared by the method described in Ref. [2]. In order to promote siloxane cross-linkage of resulting film, cesium (Cs) ion was added to the solution with the amount of 30-wt ppm. After spin coated it on p-type silicon substrates, these were cured under nitrogen vapour at 150 °C and UV light was irradiated at 350°C to remove porogen. Vapor phase treatment with 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) was performed at 350°C to make the pore surface hydrophobic.

### 3. Results and Discussions

The dielectric constants of non-doped and Cs doped film were 1.89 and 2.06, respectively. Porosities calculated from these with the use of Rayleigh equation were 0.58 and 0.52. Fig. 2 represents Fourier transformed infrared spectrum. The peak at 3740 cm<sup>-1</sup> is due to the stretching motion of isolated silanol group (SiOH), and the broad peak between 3500 and 3740 cm<sup>-1</sup> is due to hydrogen bonded silanol group (H-HOSi). These silanol groups were almost eliminated by Cs doping. The other sharp peaks are attributed to the motion of the chemisorbed TMCTS on pore surface. D-type structure (H<sub>3</sub>C-Si(H)-O<sub>2</sub>) of it was decreased but T-type structures (H-Si-O<sub>3</sub> and H<sub>3</sub>C-Si-O<sub>3</sub>) were increased in Cs doped film. So, it is found that the siloxane cross linkage of TMCTS were promoted by Cs doping.

Fig. 3 shows the dielectric constant ( $k$ ) under various relative humidity conditions ( $R_h$ ) at room temperature. The dielectric constant of non-doped film was drastically degraded in humid vapor. This is because that non-doped film had large amount of silanol groups and which adsorbed water at humid vapor, then the large dielectric constant of water (~79) induced the degradation. On the other hand the humidity effect on the dielectric constant of Cs doped film was negligible. It is interesting to evaluate the water adsorption property quantitatively. With the use of modified Rayleigh equation and Kirkwood equation, water adsorption isotherm was obtained from  $k$ - $R_h$  relation [3] as depicted in Fig. 4. By comparing that with BET theory, number density of water adsorption site was determined as 1.31 and 0.13 /nm<sup>2</sup> for non-doped and Cs doped film, respectively as shown in Fig. 5. Therefore, water adsorption site (SiOH) was drastically decreased by Cs doping technique.

It is known that the leakage current of porous silica is due to proton conduction, which increases in proportional to the amount of pore surface silanol group and adsorbed water [4]. Fig. 6 is leakage current density under N<sub>2</sub> ambient. During the constant electric field strength of  $|E| = 1$  MV/cm were applied, the leakage currents were decreased monotonically as a function of time, this is the relaxation current due to proton conduction. Fig. 7 is the result of the same measurement at humid vapor. The leakage current of non-doped film became larger than 1 μA soon after bias voltage was applied. However, that of Cs doped film was almost not affected by water adsorption due to its little amount of adsorbed water and silanol group. At last, mobile ion was searched by triangular voltage sweep (TVS) technique. A peak due to coherent motion of proton was detected in non-doped film, but no peak was detected in Cs doped film as shown in Fig. 8.

### 4. Conclusion

A highly cross-linked porous silica film was fabricated at low temperature of 350°C by Cs doping technique. Pore surface silanol groups were almost eliminated. Dielectric constant and leakage current were hardly

degraded even at high relative humidity condition due to its little amount of adsorbed water and silanol groups.

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### References

- [1] N. Fujii, K. Kohmura, T. Nakayama, H. Tanaka, N. Hata, Y. Seino, and T. Kikkawa, Proc. SPIE, vol. 6002, Nanofabrication: Tech. Dev. Appl. II, 60020N-1 (2005).
- [2] K. Kohmura, H. Tanaka, S. Oike, M. Murakami, T. Ono, Y. Seino, and T. Kikkawa, Mater. Res. Soc. Symp. Proc. Vol. 863, B3.10.1 (2005).
- [3] S-I. Kuroki and T. Kikkawa, J. Electrochem. Soc. 153. G759-764, 2006.
- [4] M. Nogami and Y. Abe, Phys. Rev. B **55**, 12108 (1997).

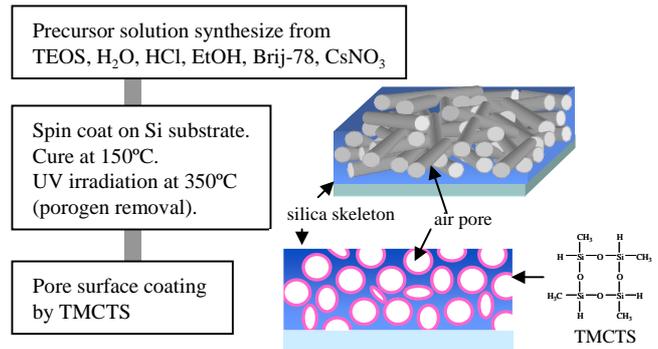


Fig. 1 A schematic diagram of fabrication process of porous silica film. CsNO<sub>3</sub> was added to its precursor solutions to promote the siloxane cross-linkage of the film.

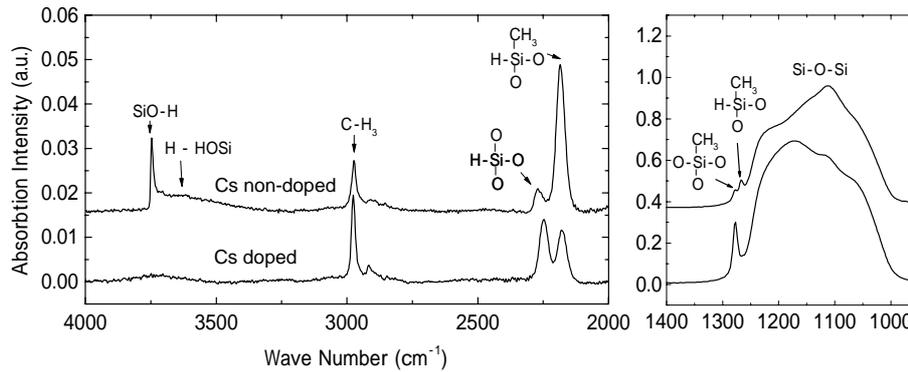


Fig. 2 Fourier transformed infrared spectrum of porous silica films. By Cs doping silanol groups are almost eliminated, and bridged structures of TMCTS are promoted.

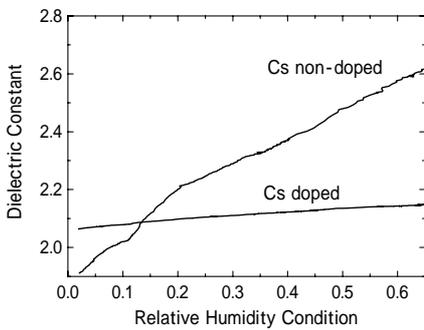


Fig. 3 Dielectric constant as a function of relative humidity conditions. Degradation of dielectric constant is suppressed in Cs doped sample.

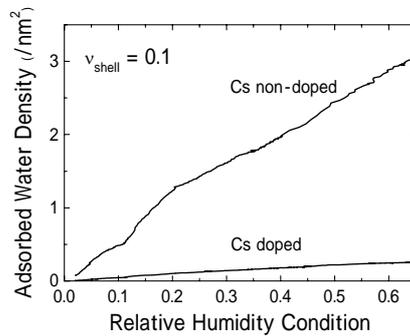


Fig. 4 Water adsorption isotherm which calculated from dielectric constant - relative humidity relation (Fig. 3) with the use of medium approximation theories.

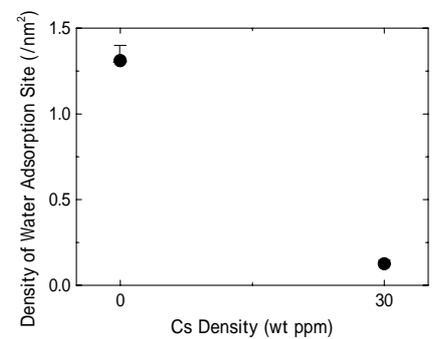


Fig. 5 Number density of water adsorption site. Cs doped porous silica films has few number of adsorption site.

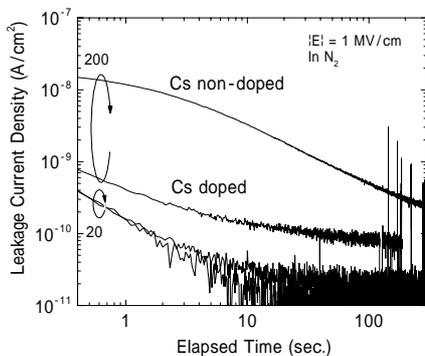


Fig. 6 Leakage current density at N<sub>2</sub> ambient as a function of elapsed time after constant electric field strength is applied. Relaxation current is measured and that is suppressed in Cs doped film.

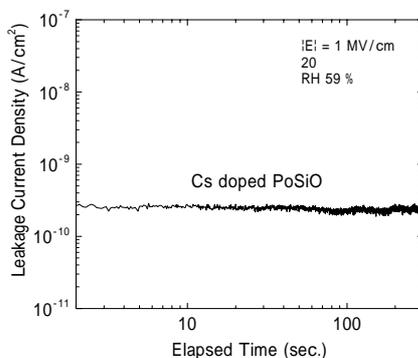


Fig. 7 Leakage current density at humid vapor as a function of elapsed time under a constant electric field strength. Effect of water adsorption on the leakage current is negligible in Cs doped film.

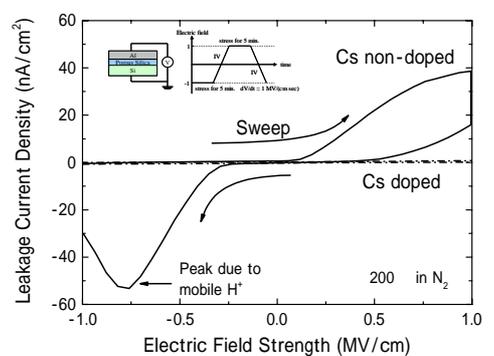


Fig. 8 Leakage current - electric field relation in triangular voltage sweep test for mobile ion detection. Peak due to mobile proton is found in Cs non-doped film, but no peak is found in Cs doped films.