

Ionic Conduction Leakage Current in Porous Silica Films

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1. Introduction

In order to lower RC time delay of ULSI, ultra low-k interlayer-dielectric films must be introduced. One candidate for it is a porous low-k film. However, porous materials adsorb moisture, resulting in degrading its electrical properties. In this work we analyzed the leakage current density (J)-electric field (E) properties of hydrophobic films in humid environment to search mechanisms of increasing water related leakage currents.

2. Experiment

P-type (100) Si substrates were oxidized in O₂ ambient at 850°C to form 6 nm thick thermal SiO₂. 380 nm thick porous silica films were formed on the SiO₂ by sol-gel method, then cured at 150°C in N₂ ambient for 1min and baked at 400°C in air for 3 h. Then the films were annealed in tetramethylcyclotetrasiloxane (TMCTS) and N₂ ambient at 400°C for 1.5 h to make the films hydrophobic. In the same manner the other films were annealed in hexamethyldisilazane (HMDS) and N₂ ambient. The film thickness and refractive index were measured by spectroscopic ellipsometry in vacuum. The porosity calculated from refractive index was 55%. Measurements of electrical characteristics were carried out for Al/porous-silica/SiO₂/Si MOS capacitors in humid environment in clean room. Relative humidity (RH) was varied slowly from 3% to 50% (RH0.06/min.) at room temperature (16°C).

3. Results and Discussion

The amounts of adsorbed water molecules in each porous silica films were estimated from the dielectric constant-RH relation (Fig. 1). Here the dielectric constant was calculated from C-V measurement. By using modified Rayleigh model [1] and Kirkwood theory, we obtained number density of adsorbed water content (N_{H_2O}) [2] as plotted in Fig.2. In this calculation we adopted arbitrary constant values 0.01, 0.1, and 0.2 to volume ratio of water content for porous silica film (x), because we couldn't determine both x and dielectric constant of adsorbed water from only C-V measurement. From Fig.2 there were no difference between the two films at low RH, but TMCTS treated film adsorbed less water content than HMDS treated film above RH25%. Fig.3 shows the Brunauer, Emmett and Teller (BET) plot of adsorbed water. We determined the number density of water adsorption site (N_m) and adsorption energy (E_0-E_L) as tabulated in Table 1. The x dependence of each result was negligible. E_0-E_L of TMCTS treated film is 1.5 times bigger than HMDS treated film, and N_m of TMCTS treated film is 0.7 times smaller than HMDS treated one.

In Fig. 4 we show J at $E=I$ [MV/cm] as a function of RH. In this result there was no difference between TMCTS and HMDS treated films. This indicates physically interacted water within the pores affects the increase of leakage current. Fig. 5 shows the J - E characteristics of TMCTS treated film. Below RH6% J - E characteristics didn't change, but above RH8% it increased with increasing electric field. It is well known that proton can conduct along hydrogen-bonded networks of water within the pores [3]. However, the J - E characteristics did not match ionic conduction current (eq.(1)).

$$J \propto \sinh(qbE / 2k_B T) \quad (1)$$

On the other hand the J - E characteristics well matched Pool-Frenkel (P-F) type current mode (eq.(2)) above $E=0.3$ [MV/cm] as shown in Fig.5, so the ionic carrier density increased by applying electric field.

$$J = J_0 \exp(-E_{Ion} / k_B T) \exp(-q \sqrt{\frac{qE}{\pi k \epsilon_0}} / k_B T) E \quad (2)$$

Here E_{Ion} is total energy to generate ions from molecules. By fitting data of Fig.5 with eq.(2) we obtained permittivity (k) at each RH as plotted in Fig.6. This increasing k reflects water concentration around carrier emission site. The coulomb potential that relates to ionic carrier emission varied with k as plotted in Fig.7. P-F barrier height $U(r_{min})=-q(qE/\pi k \epsilon_0)^{1/2}$ increased as RH increases as shown in Fig.8, so that carrier emission due to applying electric field was suppressed as RH increased. On the other hand, as plotted in Fig.4, E_{Ion} rapidly increased and carrier density increased with growing RH. This behaviour can be explained by following mechanism. As the water concentration around carrier emission site increases, Born energy (eq.(3)) decreases and ionization is promoted.

$$E_{Ion} = -E_0 + E_{Born}$$

$$E_{Born} = (1 - 1/k) q^2 / 8\pi a \epsilon_0 \quad (3)$$

where E_0 , E_{Born} and a are ionization energy in vacuum, Born energy and ion radius, respectively. As represented in Fig.9 $\ln(J_0 \exp(-E_{Ion}/k_B T))$ linearly depended on $1/k$. This behaviour matched eq.(3) and we obtained $a=0.15$ [nm], which corresponds to typical ion radius.

4. Conclusion

The leakage current density versus electric field characteristics of hydrophobic porous silica films in RH3-50% were analyzed and the mechanism of water related leakage current was studied. Ionic conduction leakage currents were measured above RH8%. The J - E characteristics well matched P-F type leakage current

mode. From this result we found following mechanism. Water concentration around the ionic carrier emission site varies the local coulomb field. Then the ionization energy decreases and carrier density increases. However P-F barrier height increases and carrier emission by applying electric field is suppressed.

Acknowledgment

Part of this work was supported by NEDO. The authors would thank Drs. N. Hata for this useful discussion and measurement.

References

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Table.1. Number of water adsorption site per unit volume (N_m) and adsorption energy (E_0-E_L) for each volume ratio of water content to low-k film (x).

	x	N_m [/nm ³]	E_0-E_L [eV]
TMCTS	0.2	0.74	0.083
	0.1	0.80	0.083
	0.01	0.87	0.086
HMDS	0.2	1.01	0.058
	0.1	1.14	0.054
	0.01	1.22	0.057

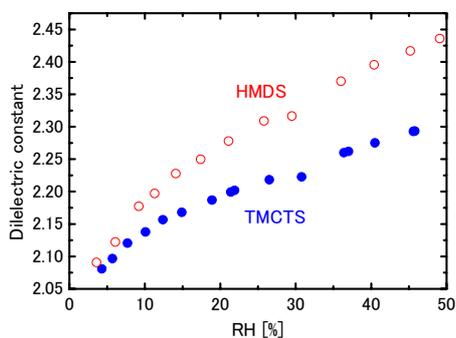


Fig.1. Dependence of dielectric constants of the porous silica on relative humidity.

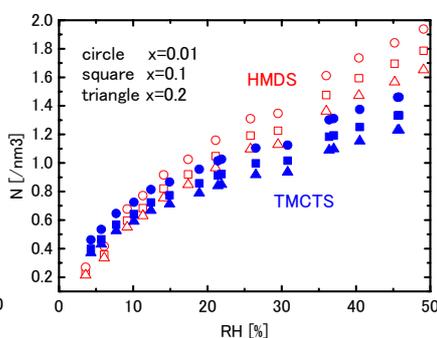


Fig.2. Number density of adsorbed H₂O molecule as a function of relative humidity.

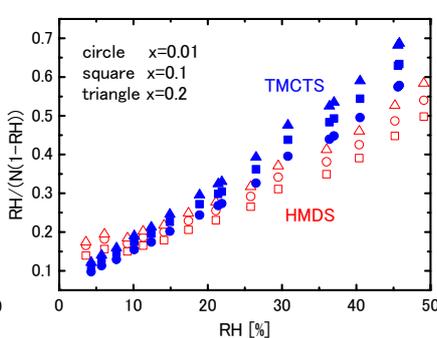


Fig.3. BET plot of adsorbed water for porous silica films.

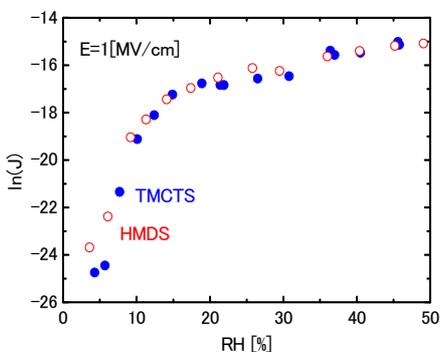


Fig.4. Leakage current density (J) of porous silica films as a function of relative humidity.

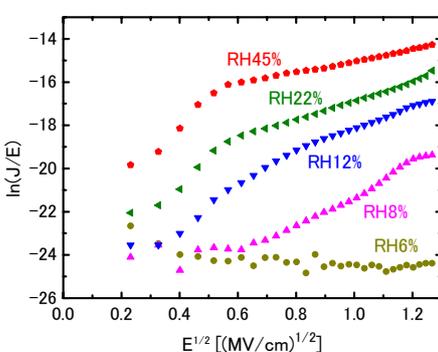


Fig.5. Pool-Frenkel plot of leakage current for TMCTS treated film as a function of relative humidity.

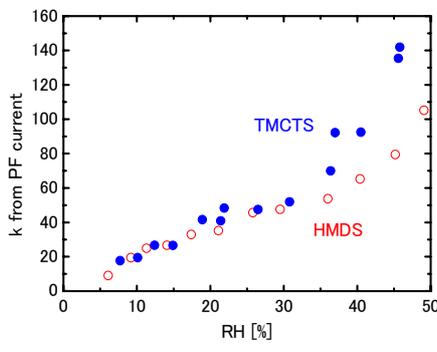


Fig.6. Permittivity from P-F type leakage current of porous silica films as a function of relative humidity.

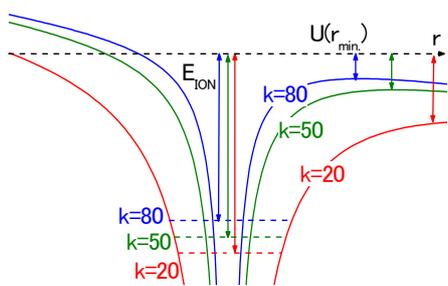


Fig.7. Schematic diagram of local coulomb potential for ionic carrier emission.

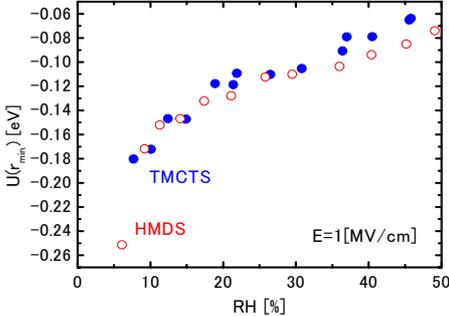


Fig.8. Pool-Frenkel barrier height as a function of relative humidity.

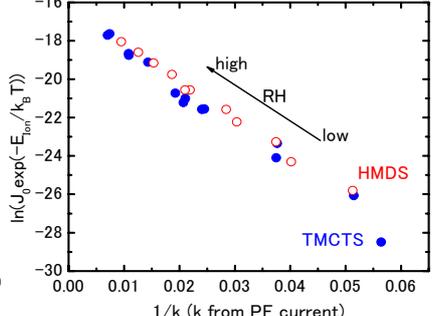


Fig.9. Carrier density for P-F type leakage current of porous silica films as a function of relative permittivity.