Influence of Humidity on Electrical Characteristics of Porous Silica Films

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1. Introduction

Scaling of interconnects in ultra-large scale integrated circuits has caused the increase of signal delay time due to the increase of interconnect resistance and parasitic capacitance. In order to overcome this problem, copper and porous low-k dielectrics have been introduced. However, porous low-k films absorb moisture, resulting in the degradation of the film properties. Hexamethyldisilazane (HMDS) treatment has been introduced to make the film hydrophobic. In this paper, the influence of humidity and the effect of HMDS on the dielectric constant and leakage current are investigated.

2. Experimental

P-type (100) silicon substrates were oxidized in O_2 ambient at 900°C to form 5nm thick thermal SiO₂. 200nm thick porous silica films were formed on the SiO₂ by spin-coating, pre-baked at 100°C (1h), and cured in N₂ ambient at 400°C (3h). Then, the film was treated in HMDS ambient at 23°C for 24h. Si-OH bonds turned into Si-O-Si(CH₃)₃ bonds [2]. C-V and I-V measurements were carried out for Al/porous-silica/SiO₂/Si MOS capacitors in humid environment. Film thickness and refractive index were measured by spectroscopic ellipsometry. Density of silica was measured by X-ray scattering measurement. The amount of water absorption was measured by thermogravimetry differential thermal analyzer (TG-GTA).

3. Result and discussion

Figures 1(a), 1(b) and 1(c) show schematic diagrams of water distribution models in porous silica films such as effective medium approximation (EMA) model, Rayleigh model and modified Rayleigh model, respectively. Figure 2 shows the effect of HMDS treatment on the dielectric constant as a function of relative humidity (RH). The dielectric constant increased with increasing humidity. It was found that the dielectric constant could be suppressed by HMDS and was saturated at 25% RH. Figure 3 shows the effect of HMDS on the leakage current as a function of humidity. It was found that HMDS could reduce the leakage current to approximately 1/100, and the current was saturated at 5% RH. Leakage current mechanism was investigated as shown in Figs. 4 and 5. Possible leakage current mechanisms are Schottky emission and Poole-Frenkel emission [3]. As can be seen, Schottky or Poole-Frenkel current could be suppressed after HMDS treatment. Figure 6 shows Weibull distribution of the time dependent dielectric breakdown of the porous silica films before and after HMDS at 2.9 MV/cm in N2 at 200°C. It was found that HMDS could improve the reliability of porous silica film. The amount of absorbed H_2O was calculated from measured dielectric constants by three different models such as EMA model, Rayleigh model and modified Rayleigh model. EMA model assumes that silica, pore, and H_2O are distributed at random as shown in Fig. 1(a), so that Clausiuss-Mossotti equation should be as follows,

$$\frac{k_{film} - 1}{k_{film} + 2} = (1 - x)\frac{k_{silica} - 1}{k_{silica} + 2} + (x - y)\frac{k_{air} - 1}{k_{air} + 2} + y\frac{k_{water} - 1}{k_{water} + 2}$$
(1)

,where k_{film} , k_{silica} , k_{air} and k_{water} are effective dielectric constant, dielectric constant of silica, dielectric constant of air and dielectric constant of H₂O, respectively. x is the porosity. y is the fraction of absorbed water. Rayleigh model [4] assumes that cylindrical pore and water are distributed at random in silica as shown in Fig. 1(b), so that the equation should be as follows,

$$k_{film} = k_{silica} \frac{k_{pore} + k_{silica} + x(k_{pore} - k_{silica})}{k_{pore} + k_{silica} - x(k_{pore} - k_{silica})}$$
(2)

$$k_{pore} = k_{air} \frac{k_{water} + k_{air} + y(k_{water} - k_{air})}{k_{water} + k_{air} - y(k_{water} - k_{air})}$$
(3)

,where k_{pore} is dielectric constant of pore (air and water). Modified Rayleigh model assumes that cylindrical pore is distributed at random in silica, and the surface of the inner cylinder wall is covered with H₂O as shown in Fig. 1(c), so that the equation should be as follows.

$$k_{pore} = k_{silica} \frac{1-\gamma}{1+\gamma}$$

$$\gamma = \frac{(k_{silica} - k_{water})(k_{water} + k_{air}) + (k_{silica} + k_{water})(k_{water} - k_{air})(1-y)}{(k_{silica} + k_{water})(k_{water} + k_{air}) + (k_{silica} - k_{water})(k_{water} - k_{air})(1-y)}$$
(5)

Porosity can be calculated from the effective dielectric constant before moisture uptake, assuming that k_{silica} is 4.0, resulting in x=0.271 for EMA model and x=0.315 for Rayleigh models. Figures 7 and 8 show the calculated water absorption as a function of humidity before and after HMDS, respectively. It is found that HMDS treatment could suppress water absorption. The modified Rayleigh model suggests that the least water absorption at the surface of inner wall affects the dielectric constant most and the estimated amount of absorbed water could fit well with measured TG-GTA, which was 3.16 vol% of film at 15% RH. Consequently, HMDS treatment could reduce the water absorption to 1/2.

4. Conclusion

The influence of the humidity and effect of HMDS on the electrical characteristics of porous silica films were investigated. Porous silica films absorb moisture from air, so that leakage current and dielectric constant increased with humidity. It is found that HMDS could reduce the leakage current and the increase rate of the dielectric constant to 1/100 and 1/2, respectively. The amount of H₂O absorption in the porous silica film was calculated and compared with TG-GTA, so that the modified Rayleigh model was found to be the most appropriate for estimating H₂O content in the porous film.

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Fig. 1. Schematic diagrams of water absorption models (a) EMA model. (b) Rayleigh model. (c) Modified Rayleigh model.



Fig. 3. Effect of HMDS treatment on the leakage current at 1.3MV/cm as a function of humidity.



Fig. 6. Effect of HMDS treatment on the time dependent dielectric breakdown of porous silica films at 2.9 MV/cm in N₂ at 200°C.







Fig. 7. Calculated water absorption as a function of humidity for porous silica films before HMDS treatment. EMA, Rayleigh, and modified Rayleigh models are compared.

References

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Fig. 2. Effect of HMDS treatment on the dielectric constant as a function of humidity.



Fig. 5. Poole-Frenkel plot of leakage current for porous silica films before and after HMDS treatment.



Fig. 8. Calculated water absorption as a function of humidity for porous silica films after HMDS treatment. EMA, Rayleigh, and modified Rayleigh models are compared.