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Copper Ion Drift Rates in Porous Methylsilsesquiazane Dielectric Films

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1. Introduction

Copper (Cu) interconnects have been introduced to ULSI processes [1,2]. In order to improve high-speed performance of ULSIs, low-k interlayer dielectric (ILD) films must be implemented with Cu interconnects [3,4]. However, the drift of Cu ions occurs from the Cu interconnects to a Si substrate through ILDs occurs in the presence of an electric field, resulting in the increase of leakage current. This paper describes determination of copper ion drift rates in porous methylsilsesquioxane (MSQ) films derived from a porous methylsilsesquiazane (MSZ) precursor.

2. Experimental

N-type (100) silicon substrates were oxidized in H_2-O_2 ambient at 900°C to form 50 nm thick thermal SiO_2. Porous MSZ films were formed on the SiO_2 by spin-coating, pre-baking at 150°C (3min) and 280°C (3min), and curing in an N_2 ambient at 400°C for 30 min, consecutively, as shown in Fig. 1. Capacitance-voltage (C-V) measurements [5-7] were carried out for Cu/MSZ/SiO_2/Si MOS capacitors before and after bias-temperature stress tests (BTS) to investigate Cu ion drift rates in porous MSZ films. The amount of charges drifting into the MSZ and SiO_2, shown in Fig. 2, can be calculated from a flat-band voltage shift ΔV_{FB} and leakage current I_{Gate}. ΔV_{FB} is expressed as [8]

$$\Delta V_{FB} = -\frac{1}{C_{acc}}\int_0^{d_1+d_2}\omega(x)\rho(x)dx \qquad (1)$$

, where d_1 and d_2 are the thicknesses of MSZ and SiO_2, respectively. C_{acc} is a series capacitance of MSZ and SiO_2 per unit area. $\rho(x)$ and $\omega(x)$ are the density distribution function of the charges and weight function, respectively. When the charges accumulate as a delta function at the SiO_2/Si interface or at the MSZ/SiO_2 interface, the expressions for ΔV_{FB} become as follows.

$$\Delta V_{FB} = -\frac{q}{C_{acc}}[Cu^+] \qquad (SiO_2/Si) \qquad (2)$$

$$\Delta V_{FB} = -\frac{q}{C_{MSZ}}[Cu^+] \qquad (MSZ/SiO_2) \qquad (3)$$

, where q and $[Cu^+]$ are the electronic charge and the number of Cu ions, respectively. C_{MSZ} is a capacitance of a MSZ film. An energy band diagram of a Cu/MSZ/SiO_2/Si capacitor is shown in Fig. 3, where positive charges accumulate at the MSZ/SiO_2 interface. ΔV_{FB} is also expressed in terms of gate leakage current density J_{gate}:

$$\Delta V_{FB} = -\frac{1}{C_{MSZ}}\int_0^t J_{gate}(\tau)d\tau \qquad (4)$$

3. Results and Discussion

The properties of porous MSZ film are summarized in Table 1. The FTIR spectrum of porous MSZ after 400 °C curing is shown in Fig. 4. Absorption peaks due to C-H (2970, 2850 cm^{-1}), Si-C (1270, 780 cm^{-1}), Si-O (1020 cm^{-1}) were observed. Figure 5 shows flat-band voltage shift and gate current of MSZ films. Measured ΔV_{FB} was smaller than the calculated value by eq.(4) due to the charge distribution in the film. The gate leakage current decreases as Cu^+ ions drift into the MSZ film because the accumulated positive charges Q(t) reduce electric field $E_1(t)$ in the MSZ film as described in eqs.(5) and (6) from Gauss's law and potential equations.

$$E_1(t) = \frac{\varepsilon_2 V_g - d_2 Q(t)}{\varepsilon_1 d_2 + \varepsilon_2 d_1} \qquad (5)$$

$$J_{gate}(t) = \frac{dQ(t)}{dt} = \sigma E_1(t) \qquad (6)$$

, where ε_1 and ε_2 are dielectric constants of MSZ and SiO_2, respectively. V_g and σ are applied voltage and conductivity, respectively. The solution of the differential equation in terms of Q(t) is $Q(t)=a-b\exp(-ct)$. Consequently, $\Delta V_{FB}(t)$ is

$$\Delta V_{FB}(t) = -\frac{q}{C_{MSZ}}[a - b\exp(-ct)] \qquad (7)$$

, where a, b, and c are fitting parameters. Measured ΔV_{FB} as a function of time could be fitted to $\Delta V_{FB}(t)$ as shown in Fig. 6. Cu ion drift rates in porous MSZ were calculated by taking the derivatives of $\Delta V_{FB}(t)$ at t=0. An Arrhenius plot of Cu drift rates in porous MSZ is shown in Fig. 7. The activation energy was 1.28eV.

4. Conclusion

Determination of Cu ion drift rates in porous MSZ was described. The Cu ion distribution in the film could be estimated by comparing measured ΔV_{FB} with the calculated value from the gate leakage current. The Cu drift rate can be determined by taking the derivatives of the fitting curve.

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References

[1] D. Edelstein et al. Int. Electron Device Meet. Tech. Dig. 1997 (IEEE,New York, 1997) p.773.
[2] S. Venketesan et al. Int. Electron Device Meet. Tech. Dig. 1997 (IEEE,New York, 1997) p. 769.

[3] M. T. Bohr. Int. Electron Device Meet. Tech. Dig. 1995 (IEEE,New York, 1995) p. 241.
[4] D. Sylvester et al, Dig. Tech. Pap. Symp. VLSI Technol. 1998 (IEEE,New York, 1998) p. 42.
[5] A. L. S. Loke, C. Ryu and C. P. Yue, IEEE Electron Devices Lett. 17, 549 (1996).
[6] A. S. Loke, J.T.Wetzel, C.Ryu, W-J.Lee and S. Wong, Dig. Tech. Pap. Symp. VLSI Technol. (IEEE, New York, 1998) p. 26.
[7] S. S. Wong, A. L. S. Loke, J. T. Wetzel, P. H. Townsend, R. N. Vrtis and M. P. Zussman, 1998 MRS Meet. Symp. E, Preprint, San Francisco, 1998, Paper E7.1.
[8] S. Mukaigawa, T. Kikkawa, T. Aoki, and Y. Shimizu, Extended Abstracts of SSDM (Japan Society of Applied Physics, Tokyo, 1999) pp.504-505.

Table 1. Properties of porous MSZ

	Dielectric Constant	Refractive Index	Density [g/cm^3]
Porous MSZ	1.8-2.0	1.32	1.0
MSZ	2.5	1.40	1.4
SiO_2	4.0	1.46	2.2

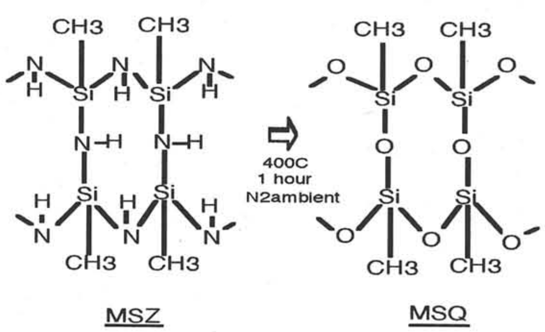

Fig. 1. Molecular structures of porous MSZ and MSQ.

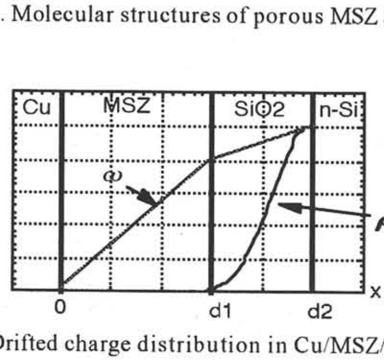

Fig. 2. Drifted charge distribution in $Cu/MSZ/SiO_2/Si$ layers.

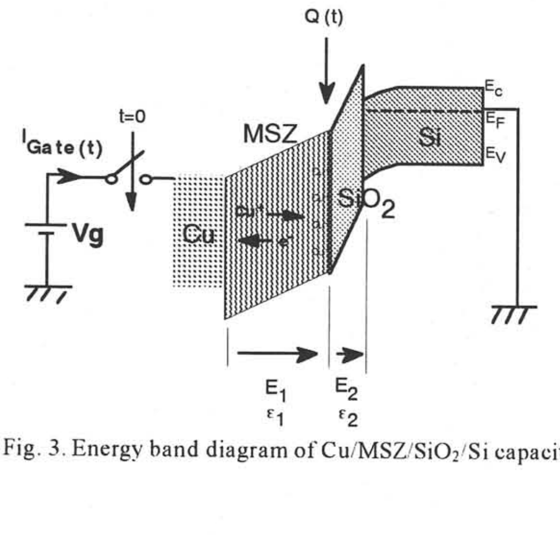

Fig. 3. Energy band diagram of $Cu/MSZ/SiO_2/Si$ capacitor.

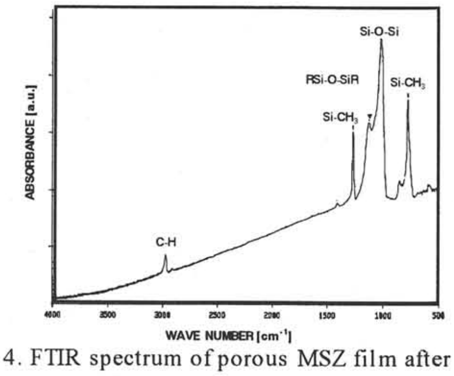

Fig. 4. FTIR spectrum of porous MSZ film after 400°C curing.

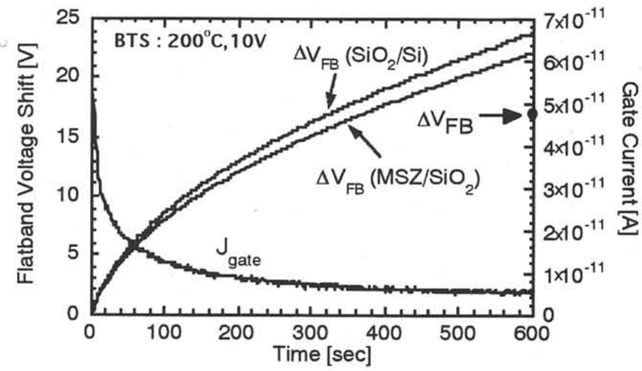

Fig. 5. Measured and calculated flatband voltage shifts and gate leakage current for porous MSZ films.

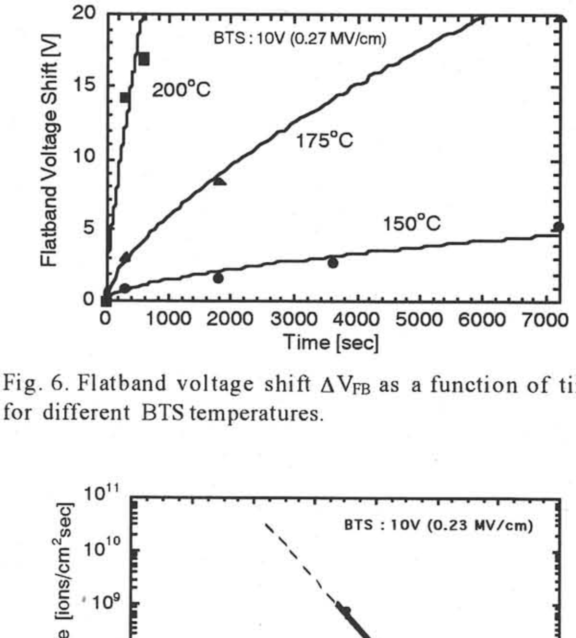

Fig. 6. Flatband voltage shift ΔV_{FB} as a function of time for different BTS temperatures.

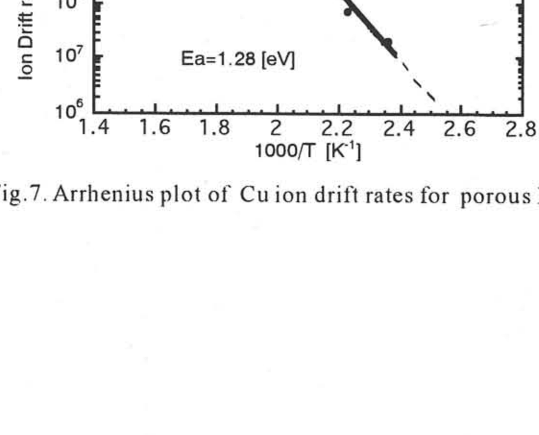

Fig.7. Arrhenius plot of Cu ion drift rates for porous MSZ.