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Anomalous Behavior of Interface Traps of Si MOS Capacitors Contaminated with Organic Molecules

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1. Introduction

Recently, influences of organic gas contaminants on the Metal-Oxide-Semiconductor (MOS) devices are attracting much attention. According to the International Technology Roadmap for Semiconductors [1], it will be required by 2018 year that the quantity of the adsorbed organic molecules on Si surface should be less than 1 ng/cm^2. However, the influences of organic molecules on the characteristics of MOS devices are not yet understood well. We have reported the influences of organic contaminants on the reliability of gate insulators and interface traps of MOS devices [2-4]. Recently, we found that the interface traps are generated by the reverse bias stress for the organic contaminated samples, and they are self healed after stop of the bias stress [3]. In this paper, we have investigated this phenomenon further in detail by changing the contamination level and measurement temperature. As a result, we newly propose a model for the self-healing of the interface traps.

2. Experiment

We fabricated MOS capacitors by oxidizing (5 nm) Si wafers after SC-1 cleaning with the different surface contamination levels. Three kinds of samples were fabricated. (1) Stored in Front Opening Unified Pod (FOUP) made of plastic for 24 h (highest contamination level). (2) Stored in FOUP with cleaning unit consisting of TiO_2 photocatalyst and ultra-violet lamp [2] for 24 h (medium contamination level). (3) Immediately oxidized without storage (control samples). And then the capacitors were fabricated as shown in Fig. 1. Capacitance-Voltage (*C-V*) measurements were carried out at 1 kHz.

3. Results and Discussions

3.1. Evaluation of current induced interface traps

C-V characteristics for samples with different contamination levels after reverse bias stress (V_G=+10 V, E_{ox}=2.04x10^7 V/cm, current=5.37x10^{-8} A/cm^2) are shown in Fig. 2 with a parameter of stress time. Although the oxide field is over the breakdown field, the Si depletion layer limits the current. Therefore, the breakdown does not take place immediately, but the interface trap density gradually increases as shown in the positive bias region in the figure. The interface trap density (D_{it}) generated after 1 h stress is calculated by the capacitance method [3] and plotted in Fig. 3. The trap density is higher for the higher contamination level as expected. Figure 4 and Table 1 show an example of the kind and amount of organic molecules adsorbed on the Si wafer stored in FOUP for 6 h. The measured organic contamination level is consistent with the result of the contact angle of pure water on SiO_2 (Fig. 5). The generated interface traps are healed with the time after stop of the bias stress as shown in Fig. 6. Figure 7 shows the time dependence of D_{it} calculated from Fig. 6. The D_{it} decays roughly exponentially. The temperature dependence of the healing time constant (τ) is plotted in Fig. 8 and the activation energy of ~0.05 eV is obtained, which is only a half of the hydrogen bond energy [5].

3.2 Model of interface traps

The proposed model for the interface traps associated with the organic contamination is shown in Fig. 9. Hirose *et al.* reported that the oxide stress is concentrated within 3 nm from the interface and the conductive filament is likely to be formed in this region [6]. The organic contamination may additionally supplies carbon and hydrogen atoms to the interface and the structure deformation is further enhanced due to the short bond length of C-O bonds than that of Si-O bonds [3]. When electrons flow through this region, some of electron energies are transferred to the SiO_2 lattice and the defects will be generated, which leads to the generation of interface traps. When the current stress is removed, the healing of structure defects takes place. One possible explanation is that the defect healing is caused by the hydrogen termination of the Si- , C- and/or O- dangling bonds. The structural deformation at the interface may reduce the hydrogen bond energy and the small activation energy (0.05 eV) is observed. The further study is necessary to fully understand the mechanism.

4. Conclusion

We have measured the influence of the organic contamination on MOS capacitors and the statistical distributions of the interface trap densities are shown. The self-healing of the current induced traps is analyzed and the model associated with the hydrogen bond is proposed. These results are useful for determining the acceptable organic contamination levels to the actual devices.

References

[1] The ITRS, Semiconductor Industry Association, 2003.
[2] T. Yoshino, *et al.*, Jpn. J. Appl. Phys. **40** (2001) 2849.
[3] T. Yoshino, *et al.*, Jpn. J. Appl. Phys. **41** (2002) 4750.
[4] Q. D. M. Khosru *et al.*, Jpn. J. Appl. Phys. **42** (2003) 1429.
[5] L. Pauling, *The Nature of the Chemical bond* Chap. 12.
[6] M. Hirose, Materials Science and Engineering **B41** (1996) 35.

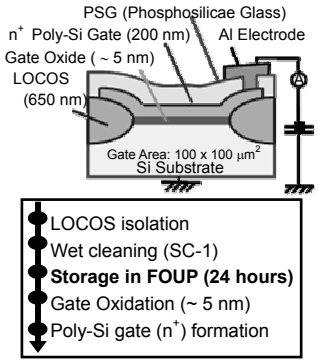


Fig. 1 Cross sectional structure and fabrication procedure for MOS capacitors.

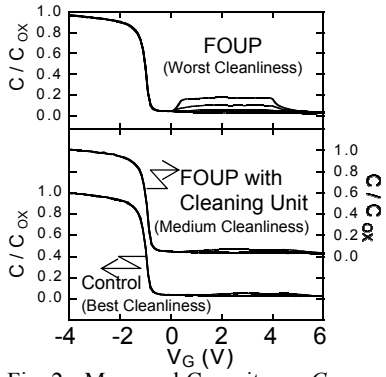


Fig. 2 Measured Capacitance C as a function of gate voltage V_G for samples with different contamination levels.

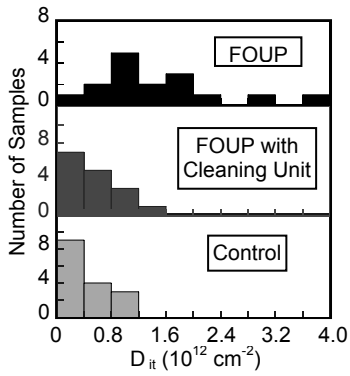


Fig. 3 Interface trap density (D_{it}) histogram of MOS capacitors after current stress for 1 hour.

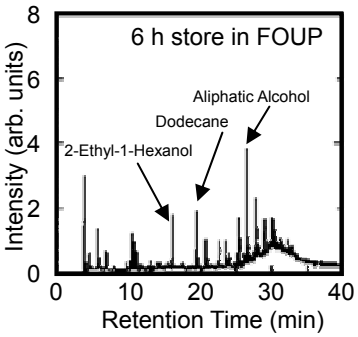


Fig. 4 Total ion chromatogram for Si oxide stored for 6 hours in FOUP.

Table. 1 Quantitative organic compounds (hexadecane equivalent) adsorbed on Si wafers, fresh and stored for 6 h measured by GC/MS method. (Unit: ng/cm^2)

	After Storage	Before Storage
BHT	ND*	0.006
Aliphatic Alcohol	ND	0.062
PGMEA	ND	ND
2-Ethyl-1-Hexanol	0.039	0.029
DBP, DOP, DEP	ND	ND

*ND means "Not Detected".
BHT: di-buthylhydroxytoluene,
PGMEA: propyleneglycol monomethyl ether acetate,
DBP: dibutyl Phthalate, DOP: dioctyl phthalate

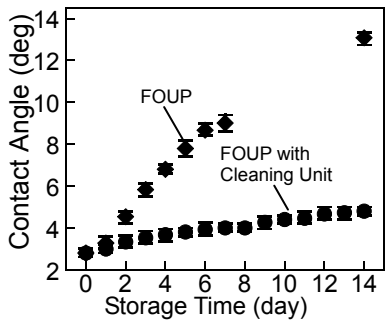


Fig. 5 Contact angle for SiO_2 surface stored in FOUP as a function of storage time.

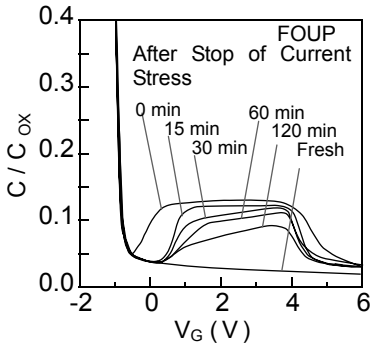


Fig. 6 Capacitance change after removing current stress.

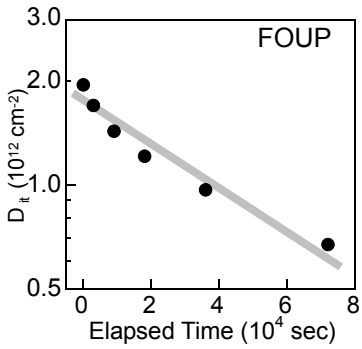


Fig. 7 D_{it} as a function of elapsed time after removing current stress for 1 hour.

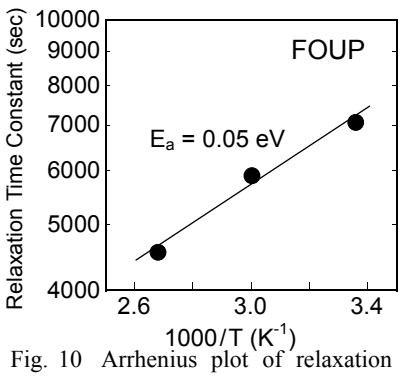
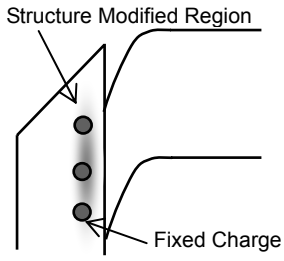
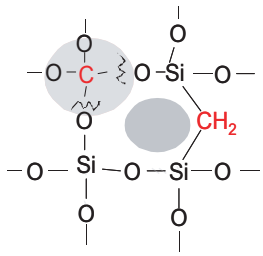


Fig. 10 Arrhenius plot of relaxation time constant (τ) versus reciprocal substrate temperature.



(a) Energy band diagram of MOS capacitor.



(b) Model of the defects in SiO_2 by organic contamination.

Fig. 11 Model for generation and self-healing of interface traps in organic contaminated SiO_2 film.