Extended Abstracts of the 2000 International Conference on Solid State Devices and Materials, Sendai, 2000, pp. 550-551

LE-2-4

The Effect of Organic Compounds Contamination on the Electrical Characteristics of Ultra-Thin Gate Oxide Films

Yoshihide Wakayama[1], Takeshi Ohkawa[1], Osamu Nakamura[1], Sadao Kobayashi[3], Shigetoshi Sugawa[1], Herzl Aharoni[2,4], Tadahiro Ohmi[2]

[1]Department of Electronics Engineering, Graduate School of Engineering, Tohoku University, Aza-Aoba 05, Aramaki, Aoba-ku, Sendai 980-8579, Japan,
Tel: +81-22-217-7124, Fax: +81-22-263-9395, E-mail: wakayama@sse.ecei.tohoku.ac.jp
[2]New Industry Creation Hatchery Center, Tohoku University, [3]Taisei Corporation, [4]At leave from the department of Electrical and Computer Engineering Ben-Gurion University of the Negev Beer-Sheva, 84105, ISRAEL

1. Introduction

Organic contaminations are known to adsorb on wafer surfaces when they are exposed to microelectronics manufacturing cleanroom air, and degrade the reliability of ULSI devices [1]. Published papers, however, mainly discuss the relation between the contaminants *concentration* and resulting device degradation. In this research, the emphasis is on the investigation of the effect of the *type* and *molecular weight* (Mw) of the organic contaminants, which are adsorbed on the gate oxide surface, on the electrical characteristics of the MOS structure.

2. Experimental

Two groups of controlled contamination experiments were made. In the first group, the amounts and molecular weights of contaminants desorbed from the oxide surfaces (SiO_2) contaminated by two sources were determined. One source was solid wax (A) composed of aliphatic hydrocarbons (C_nH_{2n+2}) with n=10-30, and the second was polyvinyl chloride (PVC) sheet (B) containing phthalic acid esters. Table I lists the substances used as a test contamination sources, including their molecular weights and formulas. They were chosen as contamination sources since they are usually airborne in the cleanroom atmosphere. Hydrocarbon contaminants originate in the cleanroom from oils, synthetic rubbers, solvents, etc., and phthalic acid esters originate from electric cables insulator sheath, floor PVC materials, air filters, etc. Each of the above contamination sources was separately stored in a closed vessel with Si wafer with oxide film for 24 hours, resulting adsorption of the respective chemical compounds on the oxide surface. These wafers were moved to another vessel (quartz) and there their adsorbed compounds were thermally desorbed under He gas flow. Their gas phase organic content was analyzed by Gas Chromatography-Mass Spectroscopy.

In the second group of experiments, MOS capacitors breakdown properties were examined. Their oxide thickness was typically 5nm, grown by a newly developed catalytic water vapor generator, which produce ultra clean high density H_2O vapor [2]. Prior to the deposition of the poly-Si gate electrode the surfaces of the gate oxides were each intentionally contaminated by only a single compound, i.e. C20 or DIDP, for 3 hours. Identical reference MOS capacitors were fabricated, in which their oxides were exposed only to the cleanroom air during transportation between the furnaces.

3. Results and Discussion

The ion chromatogram of the detected gases (C_n), which were desorbed from the oxide surface that was exposed to aliphatic hydrocarbon wax (A) is shown in Fig.1. The content of the gas detected from the contaminants desorbed from the oxide surface that was exposed to the phthalic acid esters (contained in the PVC sheet–B) yielded the ion chromatogram shown in Fig.2. Fig.3 and Fig.4 show that a clear correlation exists between the amounts of detected organics and their molecular weights. It is noted that Fig.3 and Fig.4 exhibit similar distributions. However, while C20 was detected in large quantities, the DIDP was below the detection limit. The breakdown electric field (E_{BD}) characteristics in Fig.5 show no essential differences between the contaminated and the reference capacitors. The same was true for the leakage current. However the charge-to-breakdown (Q_{BD}) characteristics which is a more sensitive parameter, did show noticeable degradation of the contaminated capacitors with respect to the reference capacitors as shown in Fig.6, which also show that both characteristics are similarly degraded. The possibility that other contaminants may affect E_{BD} and leakage current is investigated.

4. Conclusion

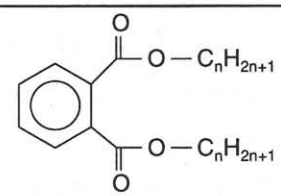
The fact that Q_{BD} of the C20 (Mw=282) MOS capacitors and the DIDP (Mw=446) MOS capacitors exhibit similar degradation *despite the fact that a large difference exists in their molecular weights and quantities* (Fig.3, Fig.4), imply that the contaminant type and the molecular weight are important as causes of device degradation and not only the concentration. This is seen by the fact that large amount of C20 was detected in the desorption experiments, while the quantity of DIDP was below detection limit. Concentration is more important as a criterion to evaluate the contamination influence on device performance exposed to various concentrations of the same contaminant type.

References

[1] T. Hayashi, T. Ohmi et al, The proceding of 31st Conference on VLSI Ultra Clean Technogies, Tokyo, Japan, pp.161~170 (1997)

[2] O. Nakamura, T. Ohkawa, T. Ohmi: Proceedings of the 9th International Conference on Production Engineering, Osaka, Japan, pp.426~431 (1999)

Table 1 Composition of contamination test sources

Contamination Test Sources	Contaminant mixtures	Molecular weight	Chemical Formula
A: hydrocarbons (contained in the Wax)	C10,C12,C14,C16,C18,C20, C22,C24,C26,C28,C30	142 – 422	C_nH_{2n+2}
B: Phthalic Esters (contained in the PVC)	Diethyl Phthalate(DEP)	222	
	Dibutyl Phthalate(DBP)	278	
	Dihexyl Phthalate(DHP)	363	
	Dioctyl Phthalate(DOP)	391	
	Diisodecyl Phthalate(DIDP)	446	DEP:n=2, DBP:n=4, DOP:n=8, DIDP:n=10

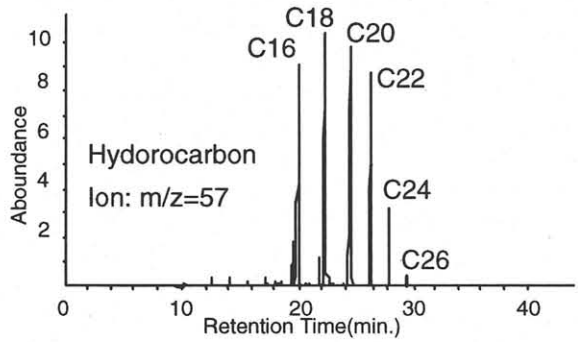


Fig. 1 Ion chromatogram of desorbants from the oxide surface which was exposed to source A (wax)

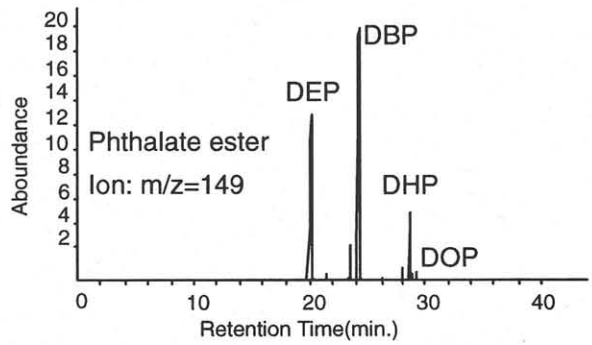


Fig.2 Ion chromatogram of desorbants from the oxide surface which was exposed to source B(phthalic acid esters)

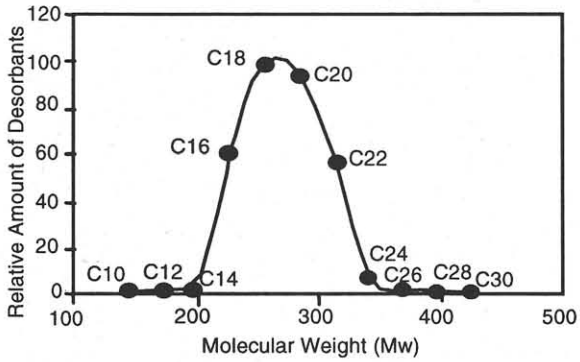


Fig. 3 The relative amount of desorbants from the oxide surface which was exposed to source A (hydrocarbons) as a function of their molecular weight

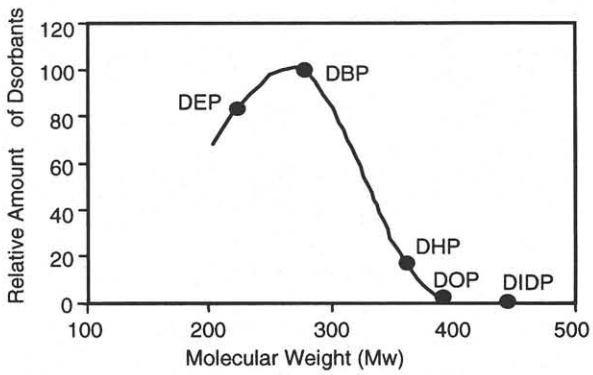


Fig. 4 The relative amount of desorbants from the oxide surface which was exposed to source B (phthalic acid esters) as a function of their molecular weight

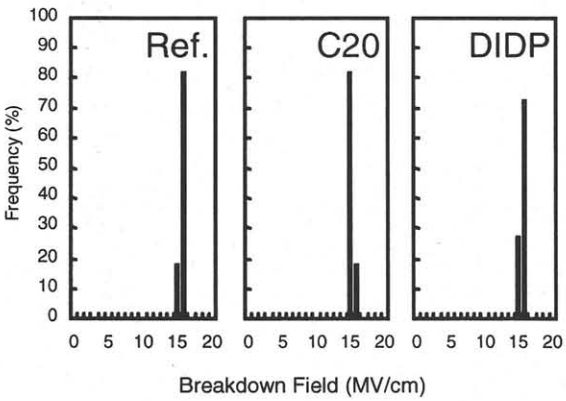


Fig. 5 MOS Capacitors breakdown field (E_{BD}) characteristics (substrate injection)

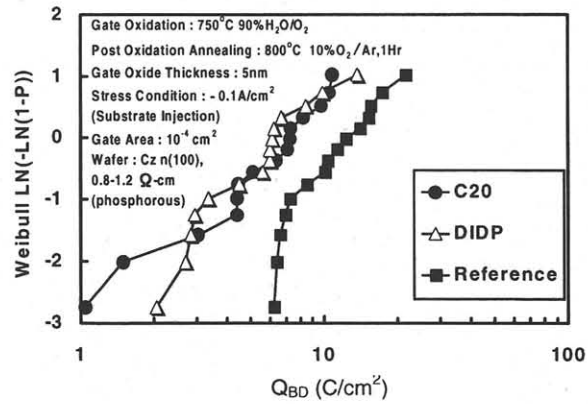


Fig.6 MOS capacitor charge-to-breakdown (Q_{BD}) characteristics (substrate injection)