Extended Abstracts of the 2001 International Conference on Solid State Devices and Materials, Tokyo, 2001, pp. 24–25

A-2-3

The Effect of Organic Contaminations Molecular Weights in the Cleanroom Air on MOS Devices Degradation—a Controlled Laminar Air Flow Experiment

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

[1]Department of Electronic Engineering, Tohoku University, Aza-Aoba 05, Aoba-ku, Sendai 980-8579, Japan, [2]New Industry Creation Hatchery Center, Tohoku University, [3]Taisei Corporation, [4] Department of Electrical and Computer Engineering Ben-Gurion University of the Negev Beer-Sheva, 84105, ISRAEL

TEL/FAX:+81-22-217-7124 / +81-263-9395 e-mail: ohkawa@sse.ecei.tohoku.ac.jp

1. Introduction

Organic compounds inevitably exist in the cleanroom materials and are emitted from them to the cleanroom air, contaminating the uncompleted devices during inter-equipment transportation. The effects of the *amounts* of organic compounds contaminants on the semiconductor devices electrical characteristics was reported [1,2,3]. Quantified data relating specific *types* of organic contaminations, (i.e. their *molecular weights (Mw)*) and the resulting device degradation, was published by us, for the case of two groups organic compounds, namely *hydrocarbon and phthalic esters contamination* [4]. It was found that the existence of these compounds having Mw>400, in the cleanroom materials, can be acceptable. *An important conclusion was that hydrocarbons and phthalic esters with Mw below that limit should be eliminated from future cleanroom materials.*

Here, the effect of an extended group of phthalic esters, namely - *aromatic esters* contamination, on MOS devices, is perused. Two compounds, with distinctly different Mw, were chosen. One is Di-Octyl-Phthalate (DOP) with Mw=391, i.e., just below the above limit. It exists in the cleanroom within various PVC materials, and is also sprayed by cleanroom air filters manufacturers, on the filters, for testing the filter efficiency against penetration of solid particles. In such a case, the filters may *unintentionally* emit organic contaminants, while stopping solid particles. The second is Tri-Octyl TriMeritate (TOTM), with Mw=564. It is chosen in order to examine its potential, for future use in the cleanroom materials composition and in air filter testing.

2.Experimental

Two Ultra Low Penetration Air (ULPA) filters were sprayed (200mg), one by only DOP and one by only TOTM. A third ULPA filter was not sprayed for use as a *reference.* Just before the deposition of the poly-Si gate electrodes, the gate oxides surfaces of MOS capacitors were exposed to laminar flow of air passing either through the "DOP filter" or "TOTM filter" or the "Reference filter", for 24 hours. This was done in a specially built exposure chamber (air velocity: 0.3m/sec), simulating cleanroom conditions. Thereafter the MOS capacitor fabrication was completed. In the above experiments, in order to ensure that the airflow blown on the gate oxide surfaces, include in each case, *only a single selected contaminant* (DOP or TOTM, or only "reference" air), the cleanroom air was passed first through a chemical filter, to remove other cleanroom air contaminants, and only then it was flown through the intentionally contaminated and the reference ULPA filters, towards the gate oxide surfaces.

3.Results and Discussions

Three test Si wafers with SiO_2 films were exposed to the above filters. Thereafter, each wafer was separately heated to 400°C, under helium flow, and the content of the desorbents from its SiO_2 surface was chemically analyzed by Gas-Chromatogram / Mass- Spectroscopy (GC/MS). **Fig.1 (a)** and **1(b)** show the Total Ion Chromatogram (TIC) of the desorbents from the above SiO_2 surfaces. It shows that the "DOP-SiO_2" desorbed significantly more contaminants (such as DOP, and its byproducts created by the high temperature), than the "TOTM-SiO_2". The chromatogram of the "reference-SiO_2" (not shown) was similar to that of the "TOTM-SiO_2". The anti-oxidant peaks in **Fig.1** originates from desorbents of the inter-equipment wafer-transportation box, adding an unexpected contamination source. **Fig.2** show the current density (J) vs. the electric field (E) characteristics of the above MOS capacitors. Three capacitors were tested for each contamination type (DOP, TOTM, reference). While the difference in the J-E characteristics of the "reference" and "TOTM" capacitors is negligibly small, presenting a well-behaved and overlapped J-E characteristics, the three "DOP capacitors", exhibit a significant different behavior, specifically in the low electric field region. This is well related to the results of **Fig. 1. Fig.3** show the breakdown electric field (E_{BD}) failure frequency (in percent) of the above capacitors, determined from the respective J-E characteristics at the standard current density of $1A/cm^2$ [5]. While the E_{BD} histograms for the "TOTM" and the "reference" capacitors are practically the same, exhibiting *uniform* breakdown at only 13 MV/cm, the "DOP capacitor" exhibit *non-uniformity* of the breakdown fields within a range of 10 MV/cm to 13 MV/cm. **Fig.4** shows the Time-Dependent- Dielectric-Breakdown (TDDB) characteristics of the capacitors. The "DOP capacitors" exhibit the lowest charge-to-breakdown (Q_{BD}) values. **Fig.5** show the gate voltage shift, measured at a constant current stress ($1A/cm^2$), while observing the resulting changes in the gate voltage. Although the differences of the three curves are small, it is noted that they exhibit similar tendency to the results presented in **Figs.2, 3 and 4**, i.e. that the "Reference capacitors" yield the lowest shift, and the "DOP capacitors" yield the highest gate voltage shift.

4.Summary and Conclusion

Simulating in a controlled fashion, the experimental laminar airflow conditions to that of a clean room environment, a distinct observation is made, i.e. that the molecular weight limit (Mw>400) that was found for the hydrocarbon, and phthalic esters organic compounds groups, is valid for the aromatic esters as well. Other organic compounds groups, can be investigated in a similar fashion, *in order to determine, which of them should be excluded from future cleanroom materials.* This may eventually lead to a higher standards for cleanroom air, and higher device yield.

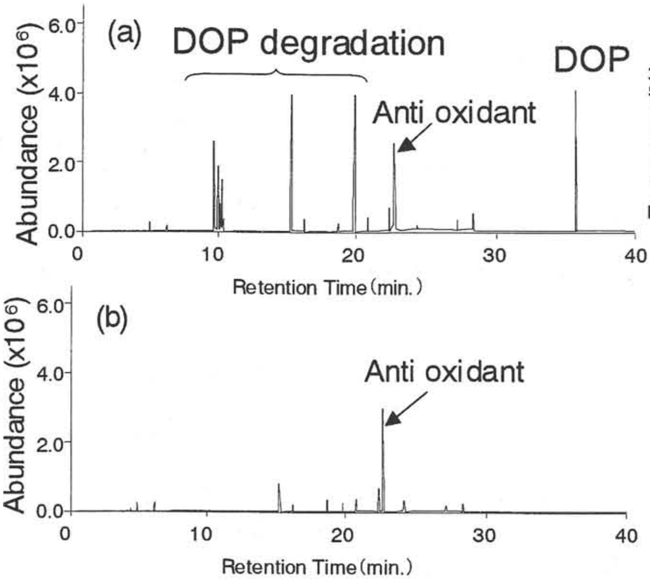

Fig.1 Total Ion Chromatogram (TIC) of desorbents from the SiO_2 surfaces exposed to laminar airflow through: (a) DOP sprayed ULPA filter, (b) TOTM sprayed ULPA filter.

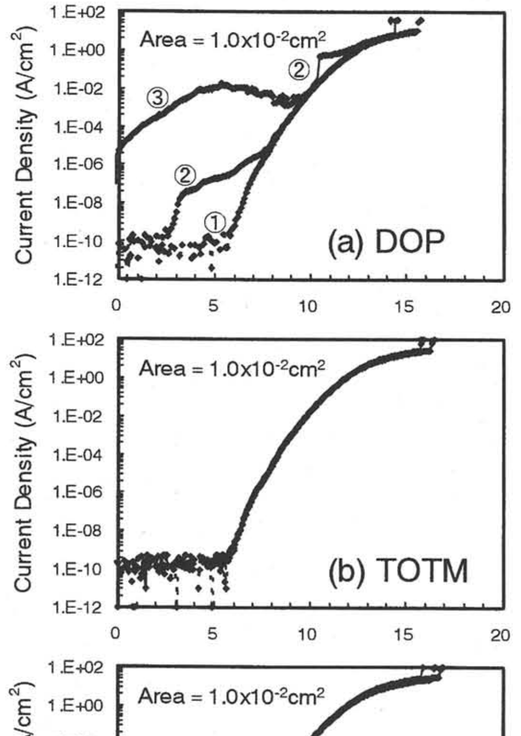

Fig.2 J-E characteristics of MOS capacitors, which their gate SiO_2 surfaces were exposed to airflow passing through one of the following ULPA filters: (a) DOP sprayed, (b) TOTM sprayed, (c) Unsprayed (reference)

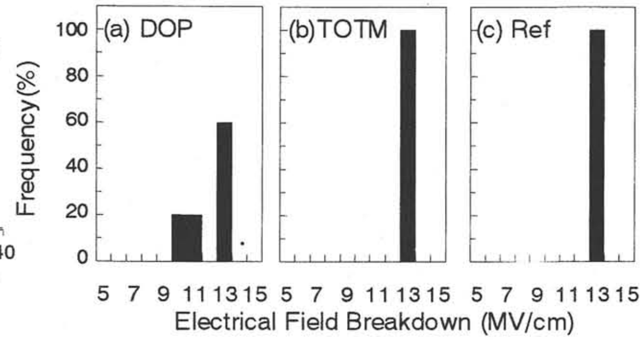

Fig.3 Electrical field breakdown (E_{BD}) failure frequency histogram for the (a) "DOP capacitors", (b) "TOTM capacitors", (c) "Reference capacitors"

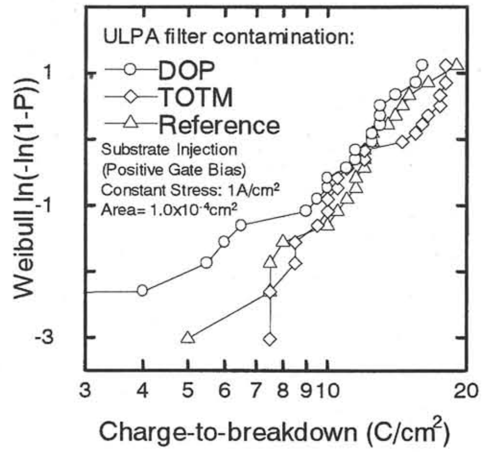

Fig.4 Time-Dependent-Dielectric-Breakdown (TDDB) characteristics of the MOS capacitors exposed to contaminated ULPA filters

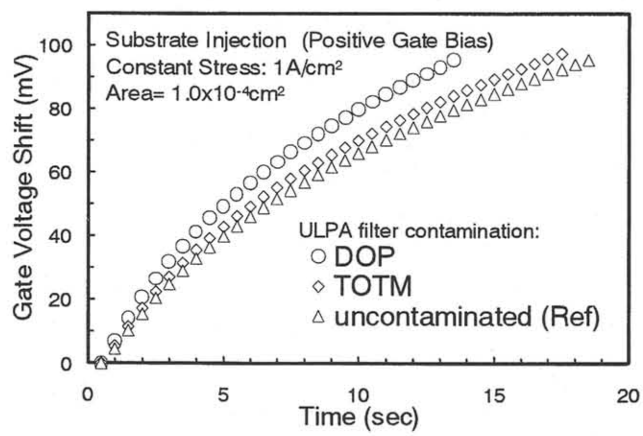

Fig.5 Gate voltage shifts (under constant current stress) of the MOS capacitors exposed to contaminated ULPA filters

References

[1] T. Jimbo, et al, Proc. of 1997 IEEE International Symp. on Semiconductor Manufacturing, E-5 (1997)

[2] K. Tsugane, et al., Proc. of 1997 IEEE International Symp. on Semiconductor Manufacturing, B-13 (1997)

[3] T. Iwamoto, et al., Proc. SPIE, Microelectronic Device and Multilevel Interconnection Tech. II, Vol. 2875, p.207 (1996)

[4] Y. Wakayama, et al.., Proc. of SSDM2000, pp. 550-551

[5] T. Ohmi et al, J. Appl. Phys. 77 (3) (1995), pp.1159-1164