Extended Abstracts of the 2000 International Conference on Solid State Devices and Materials, Sendai, 2000, pp. 552-553

LE-2-5

Influence of Organic Contaminant on Breakdown Characteristics of MOS Capacitors with Thin SiO_2

Takenobu Yoshino[1], Shin Yokoyama[1], Tsukuru Suzuki[2] and Toshiaki Fujii[2]
[1]Research Center for Nanodevices and Systems, Hiroshima University, 1-4-2 Kagamiyama, Higashi-Hiroshima 739-8527 Japan
Phone: +81-824-24-6265, Fax: +81-824-22-7185, e-mail:yoshino@sxsys.hiroshima-u.ac.jp
[2]EBARA, Co., Ltd., 4-2-1, Honfujisawa, Fujisawa 251-8502, Japan

1 Introduction

Recently, a molecular contaminant control is becoming of necessity in advanced ULSI manufacturing processes. We have investigated the influence of the organic contamination on the reliability of the ultra-thin SiO_2 gate oxides (~5 nm thick) of metal-oxide-semiconductor (MOS) devices. As a result, we found that the organic molecules on Si surface enhances the appearance of so called "soft breakdown (SBD)" [1–4], resulting in lower reliability of gate oxides. We have also demonstrated a practical performance of the contaminant-elimination unit called "UV/photoelectron cleaning unit" [5].

2 Experimental

The MOS capacitors were fabricated on 2 inch p-Si(100) substrate as shown in Fig. 1. LOCOS isolated wafers were intentionally stored for 12 h before (pre-contaminated) or after (after-contaminated) gate oxidation in commercial polycarbonate (PC) box, newly developed plastic (new plastic, which emits less organic gases) box, new plastic box with UV/photoelectron cleaning unit (new plastic/UV) as shown in Fig. 2, and SUS/UV box. The gate oxides for all samples including a non-stored control sample were formed in the same batch in wet condition at 850°C for 140 s, resulting in an oxide thickness of 5.1 – 5.4 nm. Then, n^+poly-Si gate was formed.

The effect of contaminant on the breakdown characteristics was examined as follows: (i) time dependent dielectric breakdown (TDDB) under constant gate current of $0.1 A/cm^2$ was measured, (ii) the current-voltage (I-V) characteristics were measured by applying a saw-tooth-shaped bias voltage [4], where the maximum bias voltage was gradually increased by 0.02 V above 6.6–6.8V.

3 Results and Discussion

3.1 Reliability of the gate oxides

The organic contamination species in the wafer boxes and on the Si wafers were measured by a total ion chromatogram spectrum. The results are shown in Fig. 3 and Table 1. The hydrocarbon (HC) such as phthalic acid (DBP and DEP) etc. adsorbed on Si wafer was dramatically decreased below detection limit by using the UV cleaning unit.

Weibull plots of the cumulative failure for the fabricated MOS capacitors are illustrated in Fig. 4. For samples stored in the new plastic/UV box, the reliability is much superior to that stored in the conventional plastic boxes, and is as high as that stored in the SUS/UV box of less contamination level. Especially, for after-contaminated samples stored in new plastic/UV box, the reliability is comparable with the control sample. These facts suggest that the reliability of gate oxide is more sensitive to the HC on Si surface before gate oxidation than that on the oxide before poly-Si deposition.

3.2 Process dependence of the appearance of SBD

Figure 5 displays the typical I-V curves of MOS capacitor with stress induced leakage current (SILC) and soft breakdown (SBD). The values of V_{oxi} and V_{oxc} in Fig. 5 indicate the cross points where SILC and SBD branch from the initial I-V curve, respectively. They are essentially independent of both of the storage process and kinds of wafer box. In addition, no systematic variations were found in the magnitude of current for both of SILC and SBD modes. However, as shown in Fig. 6, the value of n_{sweep}, which is the sweep number between V_{oxc} and V_{SBD} on which SBD occurs, largely depends on the storage conditions. That is, the value of n_{sweep} for pre-contaminated samples is approximately half of that for after-contaminated and control samples. In addition, for the pre-contaminated samples, more than 60% capacitors turn into SBD, while that for after-contaminated and control samples do at most 30% and the other directly meet HBD without showing SBD (Fig. 7). It should be emphasized that the SBD tends to more easily occur for pre-contaminated samples than after-contaminated and control samples. In other word, the HC on Si–SiO_2 interface strongly enhances the appearance of SBD.

3.3 Model of hydrocarbon enhanced SBD

According to Hasegawa et. al., Si–O–Si bonds in the oxide are released as O_2 molecules and Si–Si bonds under the stress current, resulting in the formation of SBD current path [2, 6]. For the pre-contaminated samples, the HC is involved into the oxide film during the gate oxidation process and the silicon sites are partly substituted by carbon atoms and C–H bonds. One possible model is suggested from the difference in the bond energy between C–O and Si–O bonds. The bond energy of 84.0 kcal/mol for C–O bond is weaker than that of 88.2 kcal/mol for Si–O bond. Hence, as illustrated in Fig. 8, the high voltage stress tends to break C–O bonds, then the Si–C conductive bonds are formed. Thereby, the SBD path formation is enhanced in pre-contaminated samples.

4 Summary

The electronic properties of MOS capacitors intentionally contaminated in various wafer boxes before or after gate oxidation were compared. We found that the appearance of SBD is more sensitively affected by the HC on Si surface rather than that on SiO_2 surface. We proposed that the HC on Si surface strongly enhances the formation of the conductive interface filament or trap sites that lead to the percolation SBD path [3, 4]. We also found that the injected charge at which the gate oxide meets the HBD is significantly improved by attaching the UV cleaning unit to the new plastic box, which implies the practical use of the new plastic/UV wafer box.

Acknowledgment

The authors would like to acknowledge to W. Mizubayashi for helpful discussions. This work was financially supported by New Energy and Industrial Technology Development Organization (NEDO).

References

[1] K. Okada et. al., *Ext. Abst. SSDM*, 565 (1994).

[2] M. Hirose, Mater. Sci. Eng. B **41**, 35 (1996).

[3] M. Houssa et. al., J. Appl. Phys. **85**, 4351 (1998).

[4] W. Mizubayashi et. al., *Ext. Abst. SSDM*, 318 (1999).

[5] S. Yokoyama et. al., *Proc. of ISSM*, 169 (1999).

[6] E. Hasegawa et. al., J. Electrochem. Soc. **142**, 273 (1995).

[7] T. Wakabayashi et. al., *Meet. Abst. Inst. Electrical Eng. Jpn.*, 55 (1996), in Japanese.

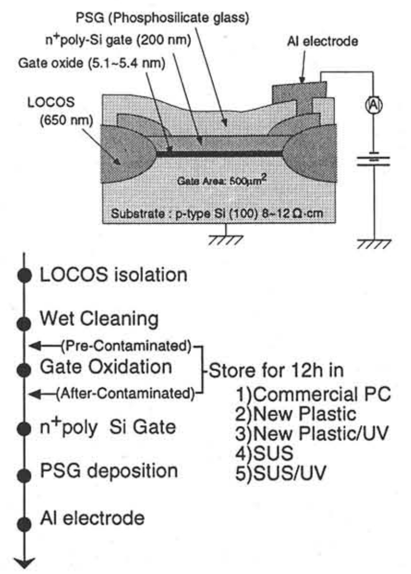

Fig. 1: Structure and fabrication procedure for the MOS capacitor.

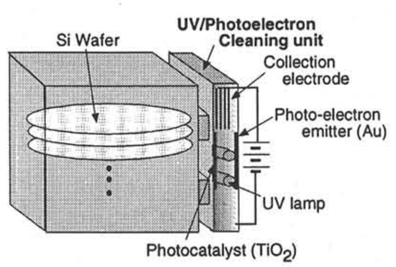

Fig. 2: Illustration of 300 mm wafer box with UV/photoelectron cleaning unit, in which twenty five 300 mm wafers can be stored.

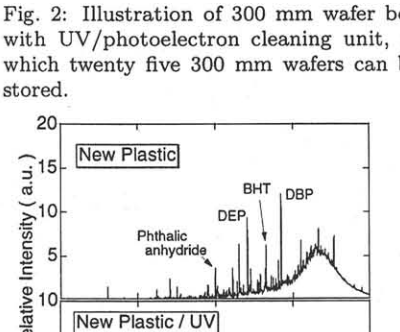

Fig. 3: TIC spectrum for Si wafer stored for 48 h in new plastic and new plastic/UV wafer boxes.

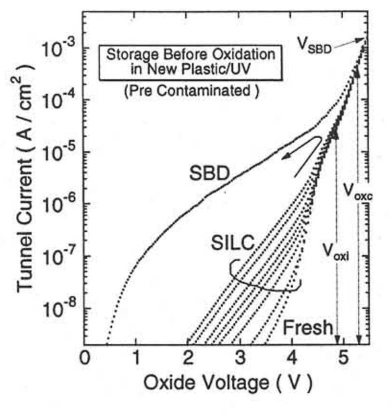

Fig. 5: Typical I-V curves of the fabricated MOS capacitor.

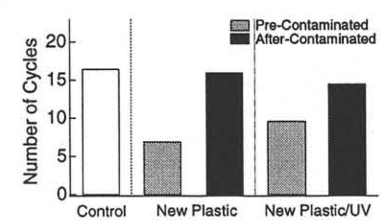

Fig. 6: Sweep number between V_{oxc} and V_{SBD}.

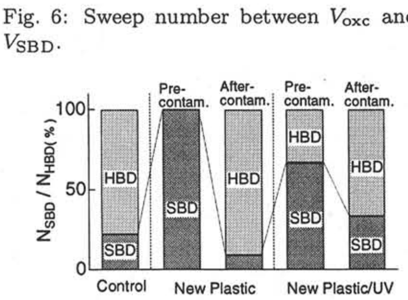

Fig. 7: Ratio of sample numbers that turned into SBD and HBD.

Table 1: Quantitative organic compounds detected in box air and on Si wafer stored for 7 days in various boxes. The adsorption is saturated for the storage 10–20 h [7]. Therefore, these data roughly estimate the contamination levels for the MOS capacitor samples. The contamination level of 1 ng/cm^2 for on-wafer is approximately equal to $\sim$0.02 mono-layer-carbon/cm^2.

	P. C.	New Plastic	New Plastic/UV	SUS/UV
In box (μg/m^3)	–	120	5.3	$\leq$ 0.1
On wafer (ng/cm^2)	1.3	5.1	$\leq$ 0.1	$\leq$ 0.1

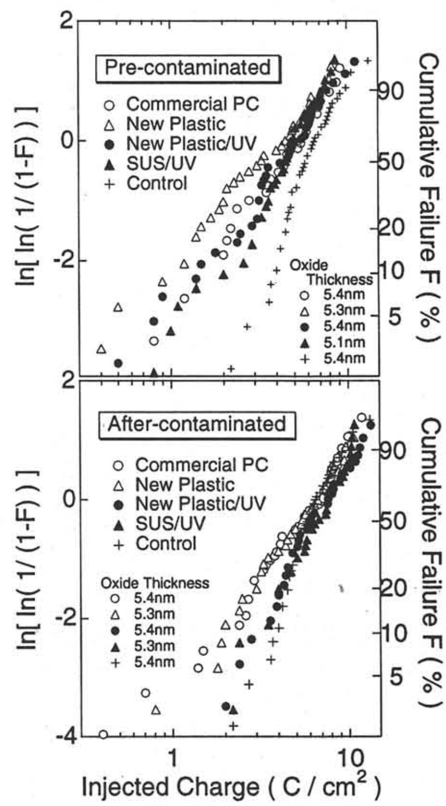

Fig. 4: Weibull plots of the reliability of MOS capacitors fabricated under various contamination levels.

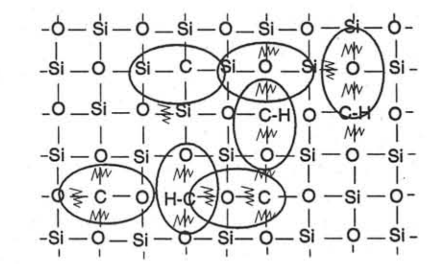

Fig. 8: Model for the SBD for organic contaminated SiO_2.