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Evaluation of Surface Contamination by Noncontact Capacitance Method under UV Irradiation

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1. Introduction

In recent years, the gaseous contaminants such as hydrocarbons, acid and alkaline gases (NO_x, SO_x, NH_3) are recognized as harmful for the LSI manufacturing [1]. The H_2O and oxygen cause the natural oxide of Si, which should be avoided for the advanced sub 0.1 μm devices [1]. Therefore, the reliable and accurate method to evaluate the gaseous contaminants adsorbed on the semiconductor surfaces has been strongly desired. We developed the noncontact capacitance method [2], and reported a sensitive method to detect Na ions under UV irradiation [3].

In this paper we report that the surface contaminants such as hydrocarbon or H_2O adsorbed on SiO_2 surface are sensitively detected by the noncontact capacitance method under UV irradiation.

2. Experimental

Schematic diagram of the noncontact capacitance measurement system is shown in Fig. 1. The details of the system are found in Ref. 2. The ac capacitance-voltage (C-V) measurement is carried out at frequency of 500 kHz, and the oxide charge is calculated from the C-V curve. The spot (ϕ~10 mm) UV light is irradiated on the wafer after moving the stage. Every time the virgin position on the wafer was measured. The sample is dry oxidized (at 1000°C) Si (001) wafer with resistivity of 10-15 Ω·cm. In order to change the fixed charge in the oxide the post oxidation anneal is omitted for some wafers. The oxide thickness (d_{ox}) is ranged from ~10 to ~100 nm. For the thickness dependence measurement, the SiO_2 was thinned by the wet etching in a diluted HF. For the contamination measurement, the samples were stored in the plastic box made of polycarbonate or in the measurement system purged with pure N_2 gas.

3. Results and Discussion

A. Photon energy dependence of induced oxide charge

Figure 2 shows an example of the oxide charge after UV irradiation. The light with shorter wavelength induces higher amount of negative charge (ΔN_{ox}). The ΔN_{ox} obeys the exponential law [3]. By fitting the experimental data to the exponential curve, the capture cross section multiplied by the quantum yield (of the photoelectron generation) is obtained [3] and plotted as a function of photon energy in Fig. 3. A clear linear relation is observed and the threshold photon energy (4.1 eV) coincides with the SiO_2/Si barrier height, ϕ_{BH}. This result indicates that the negative charge is induced by the photoelectrons jumped over the oxide barrier and captured at the surface trap states.

B. Storage time dependence of oxide charge without and with UV irradiation

Four kinds of samples were fabricated; *p*-type and *n*-type with different initial fixed oxide charge. d_{ox} is ~10 nm. Figure 4 shows the oxide charge as a function of storage time in the plastic box without UV irradiation. The charge is almost constant with varying the storage time. On the other hand, as shown in Fig. 5 the UV (4.88 eV) induced oxide negative charge, ΔN_{ox}, is relatively large and gradually increases with the storage time at any irradiation energies. The ΔN_{ox} is found to be almost same regardless of the substrate type and the fixed oxide charge (not shown), which suggests that the ΔN_{ox} is determined by the density of adsorbed contaminant on the surface and the contaminant density gradually increases with time.

C. Oxide thickness dependence of UV induced charge

We found that the UV induced negative charge is proportional to the reciprocal oxide thickness as shown in Fig. 6. The reason is discussed in the following section.

D. Mechanism of UV induced charge

The model is shown in Fig. 7. Philip *et al.* [4] proposed that the UV induced charge is limited by the oxide barrier. Initially the conduction band is bent downward to the surface. Then the photoelectrons easily flow to the surface and are captured at the surface traps. The trapped electrons push the oxide conduction band at the surface upward, and then a barrier for the electron, ΔV, is formed as shown in Fig. 7 ①, which limits the electron flow. The UV induced oxide charge ΔN_{ox} is expressed by $\Delta N_{ox}=C_{ox}\cdot\Delta V$, where C_{ox} is the oxide capacitance and $\Delta V=h\nu-\phi_{BH}$ ($h\nu$: photon energy). Since the C_{ox} is proportional to $1/d_{ox}$, ΔN_{ox} is also proportional to $1/d_{ox}$. However, this model is not perfect, namely, the consideration of Fermi level is missing. For relatively thin oxide (~10 nm thick), the tunnel current is not negligible. Therefore, when the filled electron state is located over the Fermi level, the trapped electrons are detrapped and eventually the filled state level reaches the Fermi level (Fig. 7 ②). In this case, the ΔN_{ox} is also proportional to $1/d_{ox}$ because $\Delta N_{ox}=C_{ox}\cdot\Delta V'$, where $\Delta V'$ is defined in Fig. 7.

E. Temperature dependence

The Arrhenius plot of the UV induced negative charge is shown in Fig. 8. The activation energy of 0.15 eV is obtained, which roughly agrees with the hydrogen bond energy [5]. Therefore, the adsorbed contaminants are speculated to be H_2O or hydrocarbon which is bound on the surface with the hydrogen bond.

F. Storage environment dependence

The negative charges induced with and without the UV irradiation are summarized in Fig. 9 (a) for N_2 purge box storage and (b) for plastic box storage. The samples are OH-terminated SiO_2 films [6] (therefore, the behavior of ΔN_{ox} is different from those shown in Figs. 4 and 5 with Si-O-Si termination) treated in diluted HF followed by pure water rinse. For the N_2 purge box storage, the negative charge generated during storage without UV irradiation is relatively small and the UV induced charge is dominant and stable due to the dry N_2 purge, which reduces the H_2O or hydrocarbon adsorption. On the other hand, for the storage in the plastic box the negative charge generated without UV irradiation gradually increases and the UV induced charge decreases. It should be noted that the total amount of the charge is almost constant, which suggests a replacement of initially existing OH bond with H_2O or hydrocarbon.

4. Conclusion

We have developed a new method to evaluate the surface contamination by using the noncontact C-V method under UV irradiation. The availability of this method is demonstrated. The mechanism of the negative charge generation by UV irradiation is proposed.

References

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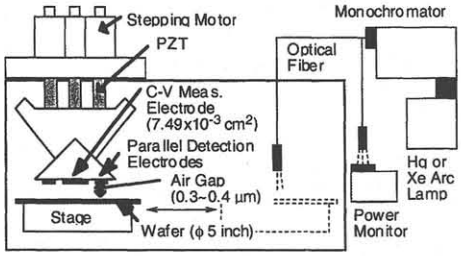

Fig. 1 Schematic diagram of non-contact capacitance measurement system under UV irradiation.

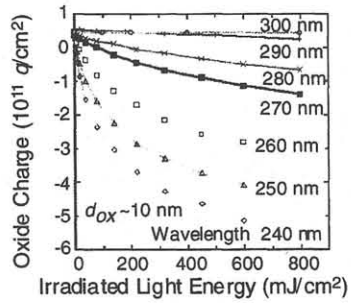

Fig. 2 Example of oxide charge as a function of irradiated light energy with a parameter of light wavelength. q is the electronic charge (1.602×10^{-19} C).

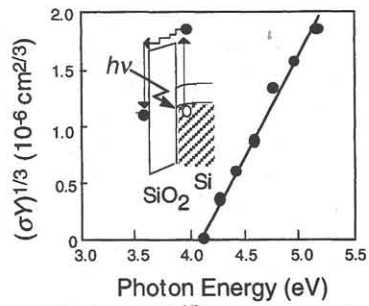

Fig. 3 $(\sigma Y)^{1/3}$ versus photon energy. σ is a capture cross section of surface electron trap. Y is the quantum yield. Threshold energy 4.1 eV coincides with the SiO_2/Si barrier height.

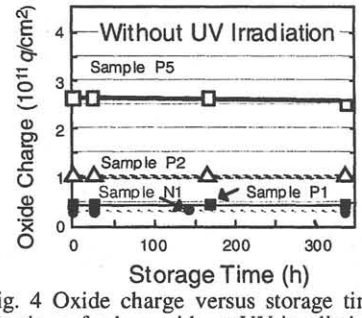

Fig. 4 Oxide charge versus storage time in plastic wafer box without UV irradiation for various samples. P and N mean p- and n-type Si substrates, respectively. The sample is as oxidized wafer (d_{ox}~10 nm), which surface is terminated by Si-O-Si bonds [6].

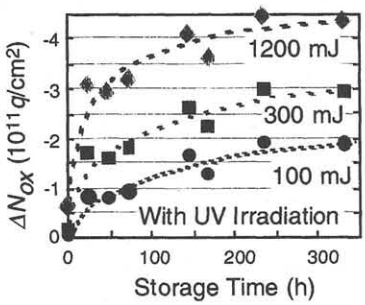

Fig. 5 UV (4.88 eV) induced oxide charge versus storage time in plastic wafer box.

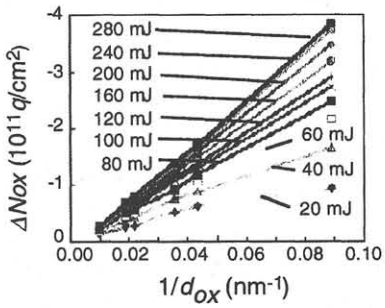

Fig. 6 UV (4.88 eV) induced oxide charge versus reciprocal oxide thickness for various irradiated UV light energies. The positive charge generated during water rinse was subtracted from the raw data.

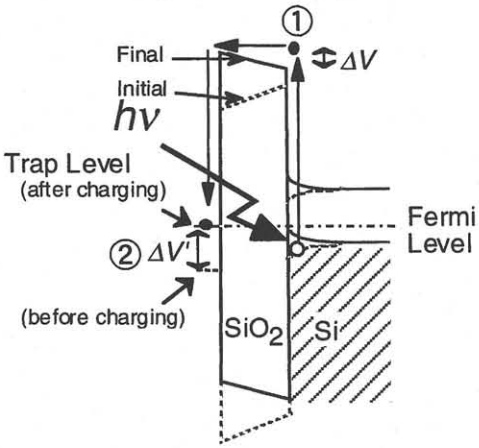

Fig. 7 Proposed model for negative oxide charge generation under UV irradiation. The oxide surface charge is saturated when ① photogenerated electrons can not jump over the oxide barrier or ② the surface charged electron state reaches the Fermi level.

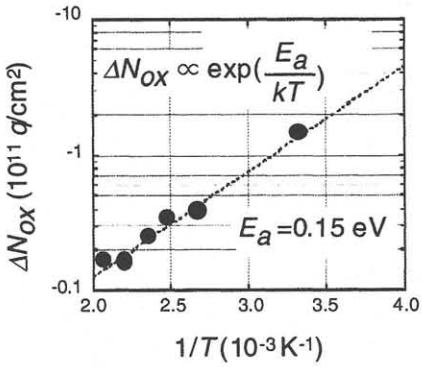

Fig. 8 Arrhenius plot of UV (4.88 eV) induced negative charge. The obtained activation energy 0.15 eV is close to the hydrogen bond energy [5], which suggests that the adsorbate on the surface is H_2O or hydrocarbon.

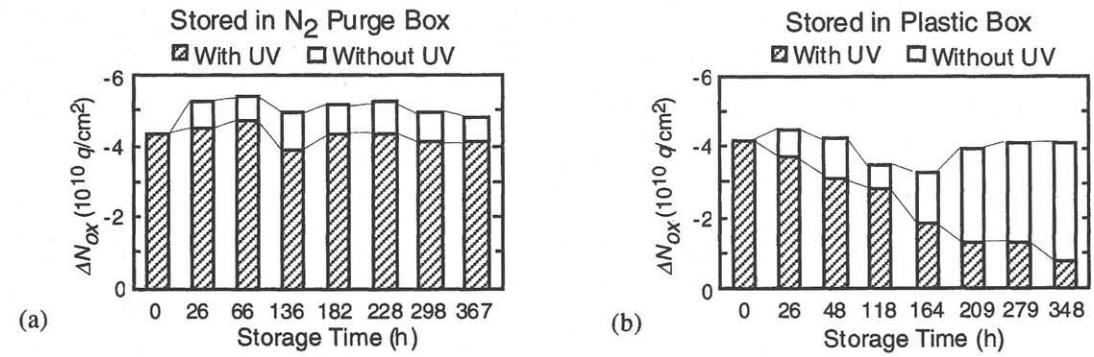

Fig. 9 ΔN_{ox} with and without UV (4.88 eV) irradiation as a function of storage time in (a) N_2 purge box and (b) plastic box (not N_2 purged). Sample is OH-terminated SiO_2 treated in diluted HF followed by pure water rinse and N_2 blow dry.