

Influence of low temperature chlorinated oxides on the stability and generation-recombination properties of MOS structures

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Abstract. Ion instability and generation lifetime in MOS structures with oxides obtained by dry O_2 oxidation, at $T = 1000^\circ C$, in the presence of $C_2H_3Cl_3$ were investigated. It was found that under these conditions the stability of MOS devices is improved. The generation lifetime increases with increasing oxide thickness (for oxidation time ≥ 50 min), and this increase is more pronounced in the case of chlorinated oxides. The combined effect of chlorinated oxides and the use of PSG results in excellent stability of MOS devices.

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1. Introduction

In recent years the use of chlorine-bearing species by the use of HCl , C_2HCl_3 (trichlorethylene-TCE), $C_2H_3Cl_3$ (trichlorethane-TCA) [1-5, 11] during the oxidation process has gained considerable attention because it has been found not only that it can have both the sodium gettering and passivating effects of phosphosilicate glass (PSG), but also it increases generation lifetime [1, 6, 7], improves the dielectric breakdown characteristics of the oxide and decreases fixed oxide charge and fast surface state densities [4].

Almost all papers concerning the properties of chlorinated oxides report results for oxidation at $T \geq 1050^\circ C$. Some authors claim that the oxidation in chlorinated dry O_2 ambient does not show sodium gettering effect at $T < 1050^\circ C$ (Ref. [8], p. 773). At the same time "low" temperature $< 1050^\circ C$ oxidation is interesting for DMOS, CCD and related devices, in which high temperature oxidation may not be desirable [3].

It is the purpose of this paper to report the stability and generation-recom-

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bination properties of MOS structures with oxides grown at $T = 1000^\circ\text{C}$ in dry O_2 ambient and with a relatively high (2%) concentration of TCA in the stream. Comparison with samples stabilized with PSG is made.

The results were obtained in the course of process optimization of Integrated Circuit fabrication at the Instituto Nacional de Astrofísica, Óptica y Electrónica (INAOE).

2. Experimental procedure

The MOS capacitors were fabricated on n -type, 2 to 5 ohm-cm, (100) oriented CZ grown Si substrates. All wafers were cleaned by a standard RCA process. The oxidation was performed at $T = 1000^\circ\text{C}$ for different times (from 52 to 112 min) in dry O_2 ambient with and without TCA. The chlorine containing ambient was provided by adding 2% TCA to the oxidizing atmosphere. For this purpose dry O_2 was flowing through a quartz bubbler filled with purified liquid TCA. The bubbler was kept at room temperature. Before the oxidation the furnace tube was purified for 2 hours with TCA at $T = 1000^\circ\text{C}$. After the oxidation thermal treatment in an N_2 ambient at $T = 1000^\circ\text{C}$ for 30 min was performed on all wafers.

The advantage of using TCA is that the reaction products of TCA with oxygen give an oxidation ambient equivalent to the one obtained when a three times higher concentration of HCl-gas is used (*e.g.* 0.1% TCA is thus equivalent to 0.3% HCl). On the other hand, the use of TCE results in almost equal amounts of HCl and Cl_2 in the oxidation ambient, which can cause trouble at higher TCE concentration (1%) because of the corrosive character of Cl_2 -gas [11].

Two groups of samples were prepared, with Al and with polysilicon electrodes. 6000 Å of LPCVD polysilicon layer was deposited at $T = 650^\circ\text{C}$. The phosphorus doping of the polysilicon was performed after deposition at $T = 1050^\circ\text{C}$ for 20 min. The polysilicon was oxidized at $T = 1100^\circ\text{C}$ for 30 min. On part of the samples PSG was deposited. After the oxide etch, polysilicon dots were formed by means of photolithography.

The Al film for all the samples with Al electrodes was deposited through a metal mask by means of an electron gun. The back side oxide was stripped and Al was deposited for back contact. All wafers were sintered in an N_2/H ambient at $T = 450^\circ\text{C}$ for 45 min.

The capacitance-voltage (C-V) and the capacitance relaxation (C-t) measurements were performed at 1 MHz using a PAR Model 410 C-V plotter. The generation lifetime evaluation was performed using the "Zerbst" plot [9]. Oxide thickness was measured using a Gaertner ellipsometer.

To investigate device instability we performed C-V measurements under bias-temperature stress (BS), *i.e.* measurements at elevated temperatures with applied voltage on the gate electrode.

After the performance of electrical measurements, the electrodes and the oxide

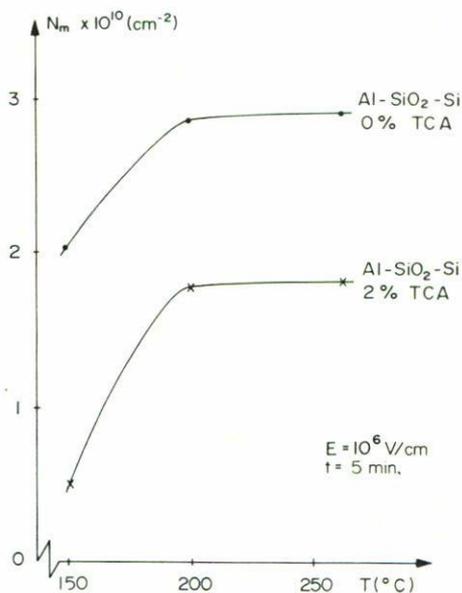


FIGURE 1. Density of mobile oxide charge as a function of stress temperature for $E = 10^6 \text{ V/cm}$ and $t = 5 \text{ min.}$

film were removed. Defects were delineated using the preferential etch described by Secco [10] and were observed in an optical microscope.

3. Results and discussion

a) Stability

The concentration of mobile oxide charge versus the stress temperature in two typical samples oxidize in dry oxygen with and without TCA (with Al electrodes) is shown in Fig. 1. A positive electric field 10^6 V/cm for 5 min was applied during the bias-temperature stress (BTS). The stress time was 5 min because it has been reported that ionic contamination withing an SiO_2 layer can be rearrange in a few minutes at 150°C [3].

It is seen from the figure that even at $T = 1000^\circ\text{C}$ oxidation in the presence of TCA improves device stability. This result brings us to the following hypothesis. It is known that the improving effect of TCA depends not only on the oxidation

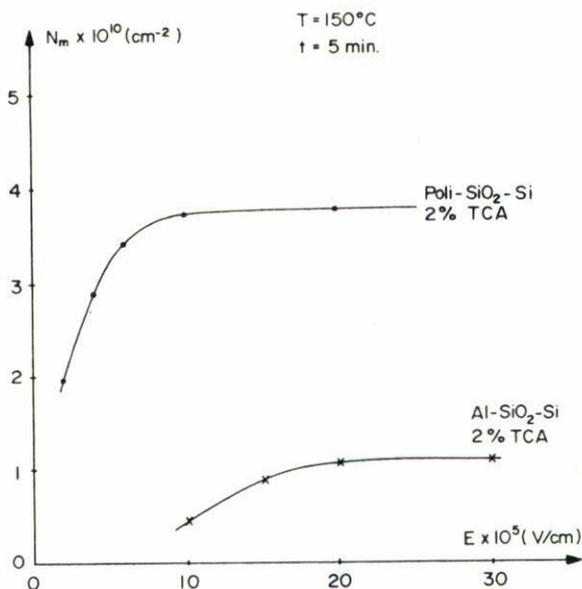


FIGURE 2. Density of mobile oxide charge as a function of applied positive electric field at a temperature of 150°C .

temperature, but also on the concentration of the chlorine [11]. Probably in our case the relatively high concentration of TCA (2%) is responsible for the improvement of the device stability in spite of the "low" temperature.

In Fig. 2 the concentration of mobile oxide charge is shown versus the applied positive field for 5 min at $T = 150^{\circ}\text{C}$ for two samples with Al and polysilicon electrodes and chlorinated oxides. This is typical behavior of all samples. As can be seen from the figure, the sample with a polysilicon electrode shows greater instability compared with the sample with an Al electrode. There are two possible reasons for this behavior. The first reason is that the samples with polysilicon electrodes underwent more technological steps and the probability for contamination in this case is higher. The second reason is that as part of the technological schedule these samples underwent oxidation of the deposited polysilicon at $T = 1100^{\circ}\text{C}$ for 30 min. It is known that if after the oxidation in chlorinated ambient the wafers undergo another technological process step at higher temperature, the stabilization effect of chlorinated ambient oxidation disappears [8]. In our case the second or the first and second reasons are responsible for the results obtained.

The samples oxidized in chlorinated ambient and with a PSG layer on top of the oxide did not show any instability even at $T = 250^{\circ}\text{C}$ for 15 min at $E = +3 \times 10^6 \text{ V/cm}$ BTS. We think that this is due to the combined stabilization and gettering effect of PSG and TCA.

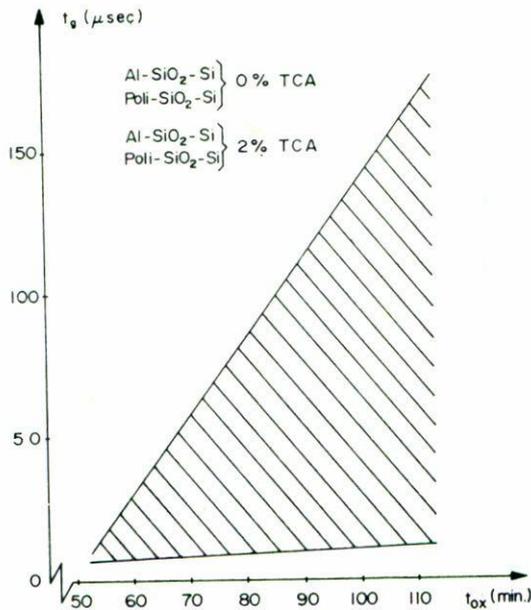


FIGURE 3. Generation lifetime, mean values and the area of scattering, as a function of oxidation time (oxidation in dry oxygen at $T = 1000^\circ\text{C}$).

b) Generation lifetime

The generation lifetime which is extracted from the pulse MOS C-t measurements is highly sensitive to the bulk defect density. Fig. 3 shows the tendency of the generation lifetime (τ_g) to change with the oxidation time. This tendency is common for all type of samples, but it is more pronounced for the samples with Al electrodes and chlorinated oxide. For these an increase of τ_g of up to 80 times with the increase of oxidation time was observed.

The results are presented in this way because of the significant scattering of the data. It is known that usually there is a considerable spread in τ_g values both withing one wafer and between different wafers [12].

On the basis of the results obtained from generation lifetime measurements there are two main conclusions:

- i) Generation lifetime increases with the time of oxidation (for time 52 min and $T = 1000^\circ\text{C}$), and
- ii) the increase of generation lifetime is more pronounced in the case of chlorinated oxides.

After the defect delineation process, it was found that the wafers oxidized in a chlorinated ambient for 52 min have stacking faults (SF) density $2.0 \times 10^{-2}\text{CM}^{-2}$

with $\sim 5 \mu\text{m}$ length. For the wafers oxidized for 78 and 112 min, it was found that the surfaces are normally without defects, except on one or two places where the length of the SF was $\sim 1.5 \mu\text{m}$. On the surface of one of the wafers oxidized for 78 min were found several SF with length between 3 and $35 \mu\text{m}$; it is clear that in this case the defects are due to mechanical damage of the wafer surface. It is well known that mechanical damages of crystal surface are nucleation sites where oxidation-induced stacking faults (OSF) are formed during the oxidation. The results correlate with the results from the electrical measurements.

It is well known that SF are one of the main reasons for the decrease of generation lifetime. Thermal oxidation of silicon usually leads to nucleation and growth of OSF [13-15], and anomalous diffusion of substitutional dopants [16,17]. It has been pointed out that oxidation causes silicon self-interstitials to flow into the crystal [18]. This point of view has been further emphasized by Hu [19]. It is now generally accepted that the OSF growth is intimately related with the Si-SiO₂ interface, which acts as a source of interstitials during oxidation. The OSF shrinkage in an inert ambient occurs because there is no interstitials injection due to the Si-SiO₂ interface, and at high temperatures for long oxidation time when the interface acts as a less efficient interstitials source [20]. Shiraki [21] found that OSF sizes become much smaller when a small amount of HCl is added to dry O₂ than without HCl. The amount of OSF shrinkage is proportional to the chlorine-bearing species concentration, the oxidation temperature and the time. A similar effect was also found for trichlorethylene (TCE) [22] and for trichloroethane (TCA) [11].

It is supposed that during oxidation in a chlorinated ambient Si atoms are removed from the lattice sites by chlorine molecules and vacancies are thus generated. The vacancies recombine with some injected interstitials at the interface or diffuse into the bulk where they recombine with some injected interstitials [23]. Although OSF growth is related to the oxide growth the OSF growth rate is not linearly proportional to the SiO₂ growth rate. Three models [24-26] are proposed to explain this fact but at the present time knowledge of the atomistic details of the Si-SiO₂ interface is incomplete, and it is thus impossible to verify any one of these models.

The observed increase of generation lifetime with the increase of oxidation time, with and without TCA, in our experiment can be qualitatively explained on the basis of the above OSF growth/shrinkage mechanism. It is possible to propose that with the increase of oxidation thickness (*i.e.* oxidation time) interstitials generation at the Si-SiO₂ interface is suppressed. In the case of oxidation in a chlorinated ambient the vacancies generated recombine with the interstitials, which leads to further shrinkage of OSF.

In spite of the "low" oxidation temperature, this explanation in the case of chlorinated oxides is in qualitative agreement with the results obtained in [27], due to the relatively high concentration of TCA in our case. On the other hand it is known that there is correlation between oxide and substrate defects. For instance, it is reported [28] that dry O₂ oxidation at $T = 1000^\circ\text{C}$, in the presence of TCE substantially reduces oxide defects. The authors explain this result by the reduction of SF density in the substrate.

In the case of the samples oxidized only in a dry O₂ ambient, for which increase

of generation lifetime with the increase of oxidation time (for $t = 52$ min) was observed, further investigations are required and these results must be treated with caution.

4. Conclusions

It was found that oxidation in dry O_2 ambient at $T = 1000^\circ C$ with 2% $C_2H_3Cl_3$ does not remove completely, but does decrease substantially, the instability of MOS devices, and it increases generation lifetime.

The combination of chlorinated oxide and a PSG layer results in excellent stability of MOS devices.

Further work is required in clarifying the influence of $C_2H_3Cl_3$ on the electrical properties of "low" temperature dry oxides.

The results of such experiments can give additional information on the dynamics of OSF.

Acknowledgments

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Resumen. Se investigó la inestabilidad iónica y el tiempo de vida de generación en estructuras MOS, cuyos óxidos fueron obtenidos por oxidación en O₂ seco, a temperatura de 1000°C, y en presencia de C₂H₃Cl₃. Como resultado se encontró que bajo esas condiciones se mejora la estabilidad iónica. El tiempo de vida de generación aumenta cuando se aumenta el grueso del óxido (para tiempos de oxidación ≥ 50 min). Este aumento es más pronunciado cuando la oxidación se efectúa en presencia de especies clorinadas. El efecto de combinar óxidos clorinados y PSG resulta en una excelente estabilidad de dispositivos MOS.