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Correlation of Carrier Trapping and Oxide Breakdown with H_2O Partial Pressures in Pyrogenic Oxides

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Avalanche injection of carriers into pyrogenic oxides grown with different H_2O partial pressures (PP) on n and p-Si is studied. It is found that the electron trap density increases with PP whereas the hole trap density decreases. The electron trapping characteristics show a 'turn around' effect while the hole trapping shows a weak nonsaturation for large N_{inj}. The oxide breakdown field for n-Si in accumulation shows a correlation with density of trapped holes and hence with PP.

1. Introduction: Carrier trapping in oxides, interface state generation and oxide leakage currents and breakdowns are important factors which can adversely affect MOS VLSI reliability during normal device operation[1]. It is of much interest to understand the basic mechanisms of the above phenomena and to study the influence of device fabrication processes. With these motivations, much effort has been devoted in the past to investigate the effects of, for example, variations in post oxidation[2] and post metallization[3] annealing conditions, exposure to high energy radiations[4] and to moisture[5] on these phenomena. These studies have mostly considered electron traps and properties of dry (and sometimes HCl) oxides. It is also necessary to understand the hole trapping phenomena which can be of importance for CMOS LSI and also for NMOS devices under certain operating conditions.[6] Also considerable work remains to be done to examine the properties and relative merits of other 'clean' oxides such as pyrogenic oxides. In the present paper, we report our results of avalanche injection of both electrons and holes into pyrogenic oxides grown with different H_2O partial pressures (PP) on p and n-Si. It is found that the charge trapping dependence on PP for electrons is opposite of that for holes. Also, the oxide breakdown field increases with PP and decreases with trapped hole density.

2. Experimental: Silicon wafers of both n type (0.07-0.13 Ωcm, (100), P doped) and p-type (0.1-0.3 Ωcm, (100), B doped) were chosen to ensure uniform carrier injection. They were thoroughly cleaned using the standard H_2O_2 based basic and acidic solutions along with dilute HF dips and deionized water rinses. The oxidations were performed at 950°C in an oxidizing mixture of oxygen and hydrogen. Hydrogen gas was introduced into the entry zone of the furnace through a capillary tube at a point maintained above 600°C while dry oxygen flowed through the enveloping tube. The H_2O vapor generated by combustion of H_2 has a partial pressure (PP) given by (2xVol. of H_2)/(2xVol. of O_2 + 1xVol. of H_2). PP was varied from zero to one in steps of 0.25, keeping the total flow rate the same. The oxidation was followed by annealing in dry nitrogen for 20 min. at the oxidation temperature. The oxidation time for these oxidations was so adjusted that the thicknesses, as given by ellipsometry were close to 70 nm. The samples were then metallized on both sides by evaporating aluminium using e-beam. Circular dot pattern (size 1.4 mm dia.) was developed on the front side using standard photolithography. The post metal annealing was done at 450°C

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for 45 min. in dry nitrogen. Also, a group of the dry oxides samples (PP=0.0) were given the following different treatment after post oxidation annealing. The samples in this group proceeded for backside metallization followed by annealing at 450°C in dry N_2. Water vapor was then diffused into the oxides of these at about 180°C for ten to thirty minutes. For this purpose dry nitrogen, bubbled through deionized water kept at 95°C, was passed over the samples. After the front side metallization, some of these samples were annealed at 450°C in dry N_2 while the others were taken straight to carrier injection. Avalanche injection was achieved with the help of a 10KHz saw tooth signal of +ve (-ve) amplitude for electrons (holes). The variation of the amplitude to maintain constancy of injection current, interruption of the injection process for flat band voltage determination and other C/V measurements were all performed on an automated measurement set up based on HP 9825 and IEEE 488 compatible instrumentation. To evaluate the effect of hole injection on the breakdown strength of oxides on n-Si, the MOS capacitor was applied a ramp voltage (about 1v/sec.) and the accumulation I/V characteristics were recorded. The field at which the current value was twice the displacement current was taken as the breakdown field. During our avalanche injection experiments, the electron (hole) injection current was kept at 3.3×10^{-5} Acm^{-2} (1.32×10^{-8} Acm^{-2}).

3. Results and Discussion: Fig.1 shows the hole trapping characteristics (ΔV_{FB}, the flat band voltage shift versus N_{inj}, the no. of holes injected per unit area) for oxides grown with different values of PP while Fig.2 shows the corresponding data for electron injection (the curves for PP between 0.25 and 1.0 are close to each other and are not shown to avoid crowding). The following features are noteworthy: (1) The flat band voltage shifts for hole injection are larger than the corresponding values for electron injection. This presumably reflects the fact that hole capture cross sections are larger. It is also possible that the hole trap density is larger than that for electrons for the same PP. (2) ΔV_{FB}-N_{inj} curves show a weak nonsaturation for large N_{inj} in the case of holes but display the

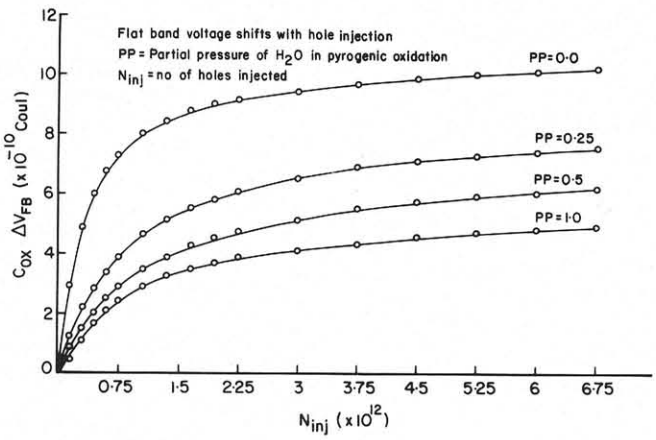

Fig.1. Hole trapping characteristics for pyrogenic oxides on n-Si. ΔV_{FB} is the flat band voltage shift, C_{ox} is the capacitance in accumulation and N_{inj} is the no. of holes injected per unit area. The injection is performed at 200 pA. Note the decreasing ΔV_{FB} with PP for the same N_{inj}.

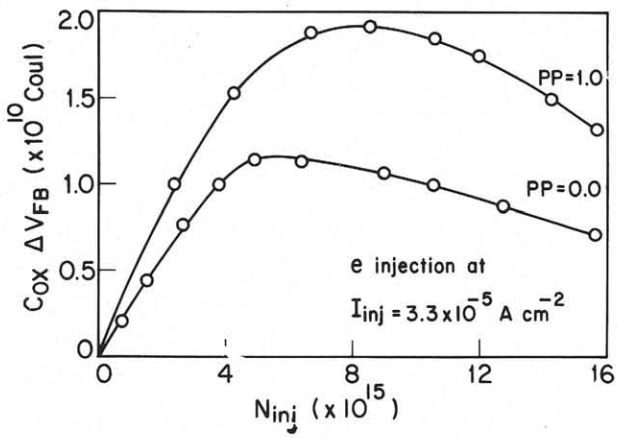

Fig.2. Electron trapping characteristics for pyrogenic oxides on p-Si. N_{inj} is the no. of electrons injected per unit area. Curves for $0.25 \leq PP \leq 0.75$ fall in between those for PP=0 and 1 but are not shown to avoid crowding. The injection is performed at 500 nA. Note that ΔV_{FB} (max) increases with PP.

'turn around' effect for electrons. The turn around effect is believed to be a result of hot electrons dropping into the metal which then injects a hole into the oxide. The weak nonsaturation for hole trapping suggests that flow of holes generates additional traps in the oxides. (3) The most interesting feature of Figs.1 and 2 is that while the electron trapping increases with PP, the hole trapping diminishes. Assuming

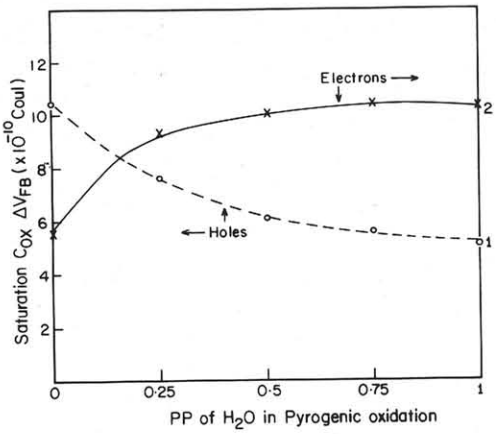

Fig.3. Effective maximum no. of trapped carriers ($\Delta V_{FB}(max)$. C_{ox}) versus H_2O partial pressure in pyrogenic oxides. For holes $\Delta V_{FB}(max)$ = $\Delta V_{FB}(t=90\ min)$.

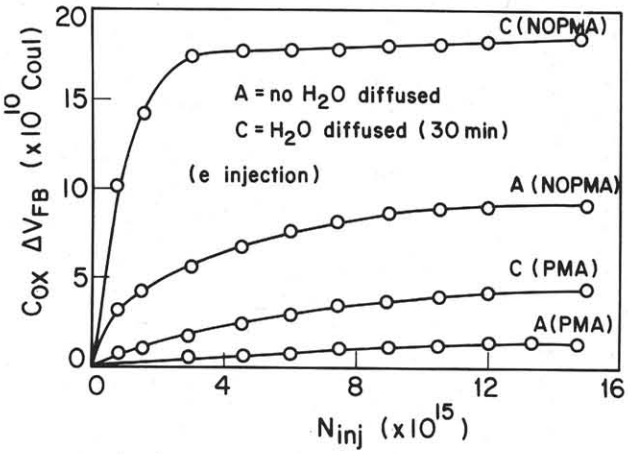

Fig.4 Electron trapping characteristics for water diffused oxides. I_{inj}=500 nA. H_2O diffused into dry oxides for 30 min. at 180°C by bubbling nitrogen through water at 95°C. Curves A (without water diffusion) and curve C (after water diffusion) are shown before and after PMA.

that the same defects are responsible for electron trapping in all the oxides (and similarly for holes), one can conclude that the carrier trap density in these oxides is proportional to the respective maximum flat band voltage shifts. Thus Fig.3 shows the result that electron (hole) trap density increases (decreases) with PP. Since the oxides have slightly different thicknesses as PP is changed and as ΔV_{FB} is proportional to C_{ox}^{-1} ($\Delta V_{FB} C_{ox} \sim d^{-1} \int_0^d x\rho(x)dx$, d=oxide thickness, $\rho(x)$ trapped vol. charge density) we have plotted $\Delta V_{FB}(max).C_{ox}$ against PP. There is a marked difference for PP=0 and PP=1.0 curves in the case of both hole and electron traps. The dependence on PP is seen to be nonlinear. Roughly, the behaviour appears to be of the type $a \pm b\sqrt{PP}$ (+ for electrons, - for holes). It is known[7] that the Si-OH groups have an average density in H_2O grown oxides which goes like $\sqrt{PP}$. It is possible that while the electron trapping defects are related to the above groups, the hole traps are not. To test this, we have injected carriers into 'water diffused' oxides. We are able to reproduce the well known result that the electron trapping increases after water diffusion[5]. The flat band voltage increased, for example, by nearly ten volts in the case of samples which did not undergo PMA (and about four volts which did) in the case of thirty minutes H_2O treatment (Fig.4). For holes, on the other hand, although the flat band voltage did not decrease after H_2O treatment, it certainly showed a behaviour distinct from that seen for electrons in that the shift was negligible both for samples with and without PMA. Presumably, the hole trapping in pyrogenic oxides occurs at defects which are removed by the presence of hydrogen in the network either in Si-H or Si-OH form while electron trapping occurs at OH related defects as previously proposed[5]. Finally, our oxide breakdown experiments on n-Si show that (1) the breakdown electric field depends on the no. of holes previously trapped near the interface. This is related to modification of the electric field profile at the interface by the trapped charge. (2) As the hole trap density bears a correlation with the H_2O partial pressure in the oxides, the breakdown field increases with PP for otherwise identical conditions (see Fig.5).

The results presented above have relevance to the following issues: (1) what is the nature of electron and hole trapping defects in SiO_2? Earlier works have speculated that trivalent Si may act as a hole trap. The other possible candidate is a nonbridging oxygen defect. Both these can trap holes and will be ineffective if bonded to H. These defects are perhaps -vely charged to give large hole capture cross section. Electrons on the other hand can be trapped at Si-OH as suggested by Nicollian et al[5]. (2) what

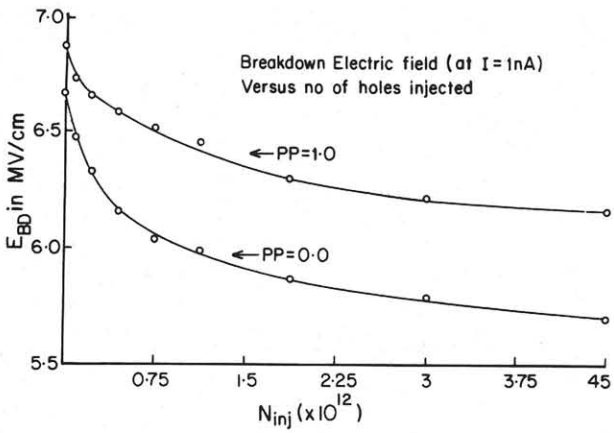

Fig.5. Breakdown electric field for oxides on n-Si in accumulation plotted versus no. of holes previously injected. Hole injection done at 200 pA.

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is the precursor for a large oxide leakage mechanism and subsequent breakdown? One answer seems to be that trapped charges at the interface can lead to these phenomena.

4. Conclusion: In this paper, we bring out an interesting correlation of electron and hole trap densities with H_2O partial pressure in pyrogenic oxides on Si. It is desirable to have oxides with reduced electron and also hole traps (especially as hole capture cross sections are three to four order higher than those for electrons). We find that in pyrogenic oxides which are as clean as dry oxides and which usually have very small Q_{ss} and N_{st}, it is possible to achieve small electron and hole trap densities by selecting proper growth conditions. The results are also expected to throw some light on the nature of electron and hole traps and their relation with presence of hydrogen.

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