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Effect of ageing on x-ray induced dopant passivation in MOS capacitors

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Abstract. Boron and phosphorus passivation in silicon metal-oxide-semiconductor (MOS) capacitors under x-ray irradiation follows a power law in the form $\Delta N/N_0 \sim (\text{dose})^{\alpha}$, with $\frac{1}{2} \leqslant \alpha \leqslant 1$, depending on processing parameters and the device history before irradiation. The minimum x-ray dose for observation of dopant passivation in fluorinated p-type MOS capacitors is smaller when the time interval between fabrication and subsequent irradiation increases. We reason that room-temperature ageing within this timescale is a result of either adsorption of water or gradual reactions of fluorine with hydrogen, silicon or oxygen-related species in the neighbourhood of the SiO_2/Si interface.

1. Introduction

In the past few years, the radiation response of metal-oxide-semiconductor (MOS) devices has been found to change significantly when these structures are exposed to pre-irradiation stress treatments at elevated temperatures [1–3]. As a consequence, the study of long-term ageing effects in these devices, which are alterations in their response that occur from the time of fabrication and qualification for system use to the operational end-of-life, is focusing on the role of pre-irradiation temperature stress [3]. The available data indicate that, for some technologies, ageing may increase radiation-induced device degradation, potentially leading to device and/or system failure during the ageing period. Thus, ageing effects have emerged into device technology as a key research subject for important improvements on radiation hardness and test methods accounting for potential device degradation.

However, further understanding and characterization of associated ageing mechanisms are still needed [3]. Many aspects of ageing-related improvements or degradation in the performance of MOS devices are still not well understood yet. It has been suggested that the mechanism responsible for ageing effects is possibly associated with thermal activation and/or diffusion of molecular hydrogen [2, 3]. A substantial number of experimental data has been explained by models involving the motion of hydrogen-related species in the oxide and their subsequent interactions at or near the SiO_2/Si interface [4–7]. However, the details of these processes are not completely explained [6–8]. One of the detrimental effects caused in MOS devices by hydrogen migration is dopant passivation, a phenomenon which was extensively studied in the past [9–11] and which continues to be a topic of great interest. Dopant passivation is associated with other detrimental effects observed in MOS devices, for example, $1/f$ noise, post-irradiation interface-trap buildup [12], and tunnelling-assisted post-irradiation dopant passivation [13]. In the latter, tunnelling electrons from the substrate not only anneal the oxide charge, but also release hydrogen-related species which pile up in a region close to the SiO_2/Si interface, triggering dopant passivation. An accumulation of hydrogen in the oxide separated from the silicon substrate by a layer with reduced hydrogen concentration has been observed in studies of hydrogen depth profiles in non-irradiated [14, 15] and irradiated MOS structures [16]. Furthermore, tunnelling mechanisms and reactions involving hydrogen are dominant degradation mechanisms in current and future integrated circuits designed to operate at lower power supply voltage and using very thin oxides [17, 18]. Recently, evidence was reported suggesting that an x-ray irradiation threshold dose delivered prior to the observation of dopant passivation seemed to depend on the sample ageing history between device fabrication and irradiation [13].

The aim of this work is to present experimental results that allow a better understanding of the improvement/degradation mechanisms caused by ageing on dopant passivation in MOS devices. It will be shown that ageing affects dopant passivation in p-type devices in a way consistent with a mechanism involving gradual reactions of fluorine with hydrogen, silicon or oxygen-related radicals in the neighbourhood of the interface.

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2. Experimental details

The MOS capacitors used in this work were fabricated using Czochralski-grown, p-type (boron-doped) and n-type (phosphorus-doped) silicon wafers, (100) oriented, 2 in diameter and resistivity 1 Ω cm. The wafers were cleaned with VLSI grade chemicals, following a standard RCA cleaning process, except for the last step in which the wafers were immersed in an HF dip solution, 3% HF in deionized water, before furnace loading. The HF dip is known to leave the silicon surface hydrophobic, therefore aiding in cleaning the surface and removing all possible native oxide. Further, these samples have relaxed the intrinsic stress at the Si/SiO_2 interface, producing devices that are up to one order of magnitude improved in their radiation hardness [19]. The oxides used in the experiments were grown in dry O_2 in a Thermco MB-80 furnace at 1000 °C, followed by an *in situ* dry N_2 annealing at the growth temperature for 30 min, resulting in thicknesses in the 500–700 Å range, measured using an Auto El-IV Rudolph ellipsometer at several wavelengths. For each oxidized wafer, ten points were measured along its diameter to verify oxide uniformity, which was better than 3% in most cases. Aluminium films approximately 2000 Å thick were thermally evaporated from a tungsten boat onto the oxide surface and photolithographically defined to form circular gates with areas ranging from 1.0×10^{-3} to 2.5×10^{-2} cm^2. After backside metallization with aluminium (300 Å thick), the wafers were annealed in forming gas (8% H_2, 90% N_2) at 400 °C for 30 min.

For the study of the ageing effect, more than 20 wafers were processed to fabricate, simultaneously in each wafer, about 100 test chips containing sets of seven capacitors with different areas. Two to four test chips were selected from each wafer. The capacitors were characterized by high-frequency and quasi-static capacitance–voltage (CV) measurements. The devices used in the experiments had a background level of interface traps below 2×10^{10} cm^{-2} eV^{-1} and a few millivolts (or less) of hysteresis in the HFCV curve before irradiation, indicating low mobile ion concentration and high interface quality. The test chips were stored, at 25 °C in a vacuum dessicator, for varying periods, from several weeks to more than one year, and then irradiated. The radiation source was an x-ray beam generated from a W target bombarded by 40 keV, 20 mA electrons. Bias was not applied during irradiation or storage. All capacitors of each test chip were irradiated simultaneously. Before the irradiation with high doses of x-rays, the uniformity of electrical characteristics and radiation hardness of the devices in each test chip were evaluated at a lower dose (1 Mrad (Si)), so that all capacitors subjected to high doses had similar radiation hardness at lower doses. The radiation hardness at lower doses was evaluated from the generation of interface traps and oxide charge.

3. Results and discussion

The characteristic trends of the ageing effects in p-type MOS capacitors for different time intervals are described by the behaviour of the normalized dopant passivation $\Delta N/N_0$, where N_0 is the substrate doping measured in each device prior to irradiation and ΔN are the changes in substrate doping measured in each device after irradiation. The procedure to calculate $\Delta N/N_0$ is described elsewhere [20]. The maximum–minimum high-frequency capacitance method [21] was used to obtain the average doping values for each capacitor, before and after irradiation.

Figures 1 and 2 show the characteristic trend of the ageing effect in p-type MOS capacitors under different time intervals, the former for samples aged for 1 month and 8 months after processing, and the latter for samples aged for 1 year. Each test chip used during the measurements to obtain these results consists of a set of seven capacitors with areas in the range $1.6 \times 10^{-3} - 2.5 \times 10^{-2}$ cm^2. Data for the largest and smallest capacitors analysed in these test chips are shown in figure 1. The curves obtained with the experimental points for capacitors with intermediate areas lie between the curves obtained with the largest and smallest capacitors. When the time interval between fabrication and irradiation is about 1 month or less, the threshold doses for the passivation effect to appear are generally high (up to several hundred Mrad (Si)) and the larger the device area, the lower the threshold dose. This is shown with open symbols in figure 1, obtained with a test chip stored for 1 month after fabrication. When the time interval between fabrication and irradiation increases to several months, the threshold dose decreases substantially and samples with larger areas may have threshold doses of just a few Mrad (Si). This is shown by the data represented by solid symbols in figure 1, obtained with a test chip stored for 8 months. When the time interval between fabrication and irradiation is long (about 1 year or more), the threshold doses are quite low, regardless of the device area, as illustrated in figure 2. By comparing figures 1 and 2, it is also possible to observe that the values of $\Delta N/N_0$ tend to be less dependent on the device area.

It is not possible to detect dopant passivation in fluorinated p-type MOS capacitors below a minimum threshold dose. In previous work [13, 20], the existence of a threshold dose was found to be associated with the presence of fluorine species at the Si/SiO_2 interface. It was suggested that the threshold dose would be a function of the time interval between sample fabrication and irradiation, and that its existence should be associated with the presence of fluorine species at the Si/SiO_2 interface [20]. The fluorine species at the interface may react and capture atomic hydrogen, which may be responsible for dopant passivation. The hydrogen atoms that escape to be captured by (react with) fluorine can migrate through the SiO_2/Si interface into the silicon and passivate the acceptor. This behaviour is in agreement with previous reports and models involving reactions of atomic hydrogen with chlorine [22] and fluorine [23] at the interface. According to this picture, both the quantity of hydrogen available for migration and the probability of its capture are important factors for dopant passivation.

Therefore, the decrease of the threshold dose and the size dependence on the ageing time described above may have two probable causes: (i) adsorption of water on the oxide during storage and/or (ii) gradual reactions of the fluorine with hydrogen, silicon or oxygen-related radicals at the interface. Adsorption of water during

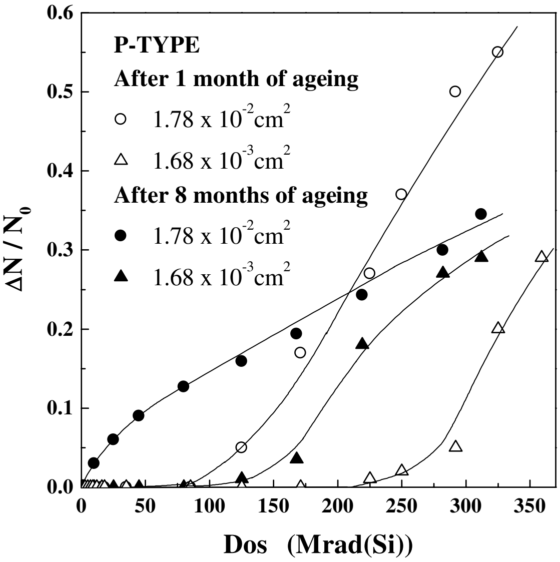

Figure 1. Dopant passivation dependence on the x-ray dose in p-type MOS capacitors aged for one month and eight months after fabrication. Initially, the minimum doses for dopant passivation observation (threshold dose) are high and the larger the device area, the lower its threshold dose. The threshold dose tends to decrease when the time interval between fabrication and irradiation increases. The oxide thickness is 550 Å.

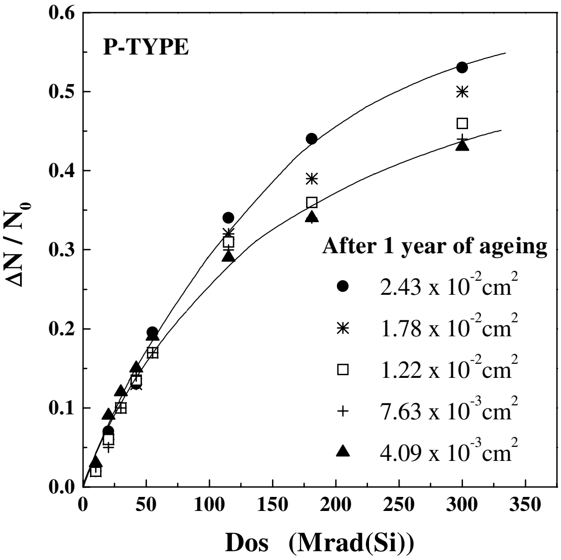

Figure 2. Dopant passivation dependence on the x-ray dose in p-type MOS capacitors aged for one year after fabrication. For long-aged devices, the threshold doses are very low regardless of the device area. The oxide thickness is 660 Å.

storage may increase the hydrogen concentration available for migration and reaction, thus speeding the onset of the dopant passivation. However, mechanism (i) may be less probable since Krauser *et al* [14, 15] have reported that no change in the hydrogen distribution profile could be measured while storing oxidized Si wafers in a clean-room environment over a period of 5 months [15]. With respect to mechanism (ii), Wang *et al* [24] showed that the radiation hardness of MOS capacitors containing fluorinated or chlorinated oxides gradually improved on storing the capacitors at room temperature or at elevated temperatures. Shaneyfelt *et al* [1] also observed less radiation-induced interface trap buildup after storage at elevated temperatures. Wang *et al* [24] have proposed that the improvement in radiation hardness could be due to reactions of fluorine species near the interface. These reactions could improve the radiation hardness in two ways: (a) replacement of Si–H bonds by stronger F–H bonds, and (b) gradual strain relaxation at the interface by conversion of low-fold member rings in the oxide into larger rings. The experimental results presented in this paper seem to be consistent with these ideas. Gradual reactions of the fluorine with hydrogen, silicon or oxygen-related radicals at the interface may accelerate dopant passivation if they cause a reduction in the quantity of fluorine available for reaction and capture of atomic hydrogen migrating during irradiation. Also, in a recent theoretical study on the diffusion of atomic hydrogen in crystalline and amorphous SiO_2, Bongiorno *et al* [25] indicate that the diffusion process is trap limited by the low-fold member rings. Trapping within a ring is stronger for low-membered rings and this suggests that the conversion of low-fold member rings in the oxide into larger rings may accelerate the migration of atomic hydrogen through the interface and, consequently, accelerate dopant passivation. Moreover, the strain relaxation caused by these reactions explains the trend towards a decreasing influence of device area on dopant passivation.

So far, only results obtained in p-type MOS capacitors have been discussed. There is, however, a lack of results in the literature concerning high-dose radiation effects associated with dopant passivation and ageing in devices fabricated with n-type substrates. Few studies of phosphorus passivation in MOS devices have been reported so far. Phosphorus passivation was not detected in experiments with MOS capacitors under electron irradiation [28] and avalanche hole injection [29], but evidence of phosphorus passivation was reported in MOS capacitors after high doses of x-ray radiation by Wei and Ma [27].The results discussed below confirm phosphorus passivation in MOS capacitors even at low x-ray doses.

Figure 3 shows the dopant passivation effect in some non-aged fluorinated n-type MOS capacitors. After fitting of a large number of data from a variety of irradiated samples, it was found that the dopant passivation dependence on the irradiation dose obeys the following universal power law: $\Delta N/N_0 \sim (\text{dose})^{\alpha}$, where $\frac{1}{2} \leqslant \alpha \leqslant 1$. The specific value of α depends on the processing parameters and the device history before irradiation. This behaviour is similar to that previously found in p-type Si substrate capacitors [19]. However, in n-type Si the maximum relative passivation is of lower intensity. Figure 3 shows a maximum degree of passivation around 30%, which is similar to values obtained previously in plasma [26] and x-ray experiments [27].

Figure 4 depicts the changes in the CV curves of an n-type capacitor with area 1.78×10^{-2} cm^2 that has been subjected to the dopant passivation effects shown in figure 3. The curves represent the high-frequency (solid curves) and quasi-static (dashed curves) device characteristics measured at room temperature (*a*) just before irradiation, and after total x-ray irradiation doses of (*b*) 105 Mrad (Si) and (*c*) 482 Mrad (Si). From the quasi-static CV curves, one can notice the fast

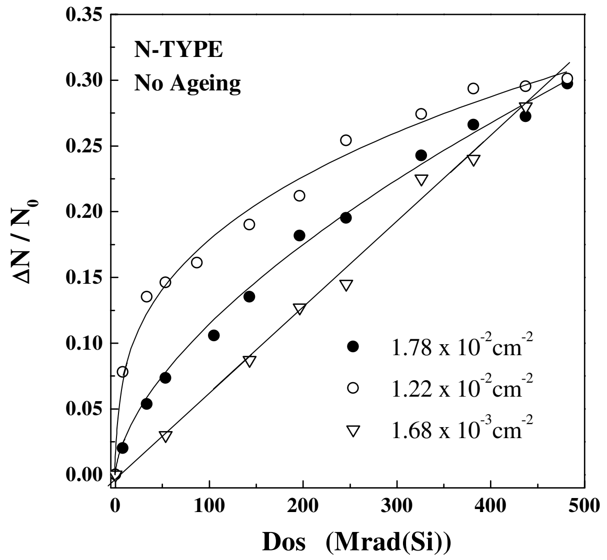

Figure 3. Dopant passivation in freshly processed fluorinated n-type MOS capacitors as a function of total x-ray dose for devices with varying gate areas. The oxide thickness is 560 Å.

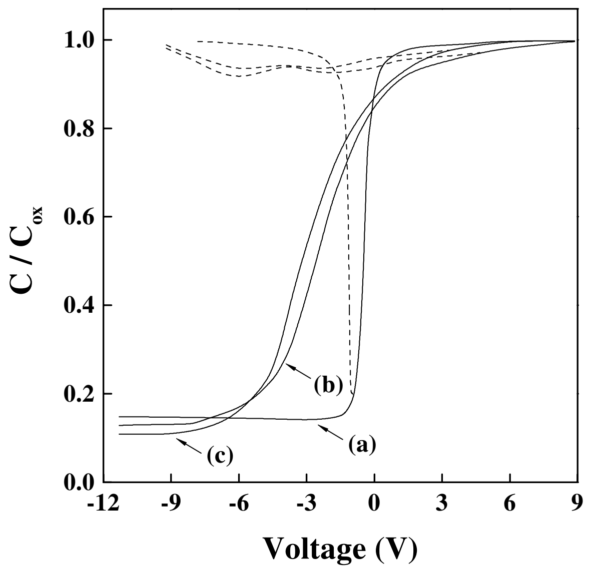

Figure 4. Normalized high-frequency (solid curves) and quasi-static (dashed curves) CV curves of capacitors (*a*) before irradiation, (*b*) after exposure to 105 Mrad (Si) and (*c*) after exposure to 482 Mrad (Si). The capacitor area is 1.78×10^{-2} cm^2; the dopant passivation behaviour with the irradiation dose is shown in figure 3.

saturation of the density of interface traps in the Si bandgap due to the high doses of ionizing radiation. Analysing the high-frequency curves, two effects can be distinguished: (i) the negative voltage shift, due to the generation of positive oxide charge, and (ii) for the doses presented, the decrease of the values of the inversion capacitance for higher doses of ionizing radiation, reflecting the donor passivation.

It is not clear why phosphorus passivation was not detected after electron irradiation [28] or avalanche hole injection [29], but can be detected under x-ray irradiation as reported by Wei and Ma [27] and confirmed in the results above. It may be possible that the hydrogen-related species that cause passivation in n-type Si are somehow more effectively generated or transported under x-ray irradiation. In our studies we observed another interesting fact: in freshly processed (non-aged) p-type fluorinated samples, the threshold doses are generally high, up to 300 Mrad (Si) [13, 20], and it is possible to study the effect of ageing on the threshold dose. However, in contrast with the p-type samples, we could not observe high threshold doses after various experiments with non-aged and aged fluorinated n-type samples. Consequently, it was not possible to study the effect of ageing on the threshold dose for n-type capacitors. This may be another indication of differences in the process of charge generation and trapping or hydrogen transport in the oxide and at the interface in n- and p-type MOS capacitors, which could reflect on the dopant passivation kinetics. These differences would lead to important implications in the radiation response of complimentary circuits combining n- and p-channel devices. Further investigation is therefore necessary to clarify these issues. It is necessary to perform additional experiments and investigate in more detail the influence of irradiation bias, annealing bias, annealing temperature and radiation type, for example.

4. Concluding remarks

Boron and phosphorus passivation in n-type MOS capacitors exposed to x-ray doses up to 500 Mrad (Si), similar to that of p-type capacitors, also follows the power law $\Delta N/N_0 \sim (\text{dose})^{\alpha}$, where $\frac{1}{2} \leqslant \alpha \leqslant 1$, with the specific value of α depending on the processing parameters and device history before irradiation. The donor passivation degree was shown to be similar to those obtained in previous plasma and x-ray experiments. We studied the influence of the time interval between sample fabrication and irradiation (room-temperature ageing effect) on dopant passivation in fluorinated p-type MOS capacitors after high doses of x-ray radiation. The minimum dose for observation of the dopant passivation (threshold dose), as well as the passivation degree dependence on area tends to decrease when the time interval between fabrication and irradiation increases. Two possible ways for ageing to affect passivation were discussed: (i) adsorption of water, which may increase the concentration of hydrogen available for passivation, and/or (ii) gradual reactions of the fluorine with hydrogen, silicon or oxygen-related species at the interface, which may decrease the concentration of fluorine available for hydrogen capture during irradiation. The latter mechanism is more consistent with previous experiments showing less radiation-induced interface trap buildup after ageing, and explains the trend towards a decreasing influence of the device area on dopant passivation.

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