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Radiation-Induced Ordering in MOS Structures with Zinc-Doped Oxides

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The paper presents the results of investigation of radiation-induced effects in MOS structures doped with moderate amounts of zinc. It is shown that post-irradiation low-temperature annealing can result in the improvement of the Si-SiO_2 interface parameters. Both the density of surface states and the minority carrier generation lifetime are improved after the irradiation-then-annealing treatment when compared to those of simply PMA annealed MOS structures. A simple model for explanation of the observed "radiation-induced ordering" effect is also presented.

1. INTRODUCTION

Electrophysical properties of thermal silicon dioxide and its interface with silicon depends, among other factors, on the presence of foreign atoms (other than silicon and oxygen) in the MOS system. For this reason many attempts have been made to improve properties of MOS systems by means of intentionally introduced impurities. Frequently, however, such a treatment while improving some parameters degrades others, e.g. hot-electron immunity or radiation hardness [1].

In our investigations we have studied electrophysical and radiation properties of MOS structures with thermal oxides doped with zinc. The choice of zinc was based on its good solubility in silicon and its healing action on dislocation loops in the near-surface silicon region. Recently, the detailed studies of the Si-SiO_2 interface morphology [2] confirmed that the presence of zinc during oxidation results in a low level of the surface roughness and leads neither to the formation of interface voids nor to the generation of defects responsible for early breakdowns. In our previous work [3] we have shown that zinc slightly improves electrophysical parameters of the Si-SiO_2 system, and we have found that zinc-related centers in the oxide exhibit donor properties and during irradiation effectively capture positive charge. In spite of this degradation, a small amount of zinc improves radiation hardness of the Si-SiO_2 interface and the near-surface silicon region.

In the present paper we report an improvement of the Si-SiO_2 interface parameters as the result of post-irradiation low-temperature annealing in zinc doped MOS structures. We have found that the presence of zinc enhances effect of the so-called "radiation stimulated ordering" [4] in which radiation-then-annealing traetments result in lower values of both the density of interface states and the oxide charge when compared to those of simply post-metallization annealed (PMA) structures.

2. EXPERIMENTAL

Experiments were carried out on Al-gated MOS capacitors. N-type, 4.5 Ωcm (111) oriented silicon wafers served as substrates. Oxide films of 70-80 nm thickness were formed in wet oxygen at 950°C. Zn atoms were introduced into the hot zone in the form of aqueous solution of $ZnCl_2$. The zinc contents in the oxidizing ambient varied from 0 to 0.0025%. Higher concentrations resulted in oxides of poor quality.

Our SIMS data confirmed the presence of zinc in the doped oxides (a linear decrease of its concentration from the outer oxide surface toward the interface) and showed that there was no pile-up of the impurity near the silicon surface.

All the structures passed PMA (N_2, 400°C, 30 min) and then were γ-irradiated from Co-60 source. Density of surface states D_{it} and minority carrier generation lifetime τ_g were determined from high-frequency C-V and C-t measurements.We used the lifetime τ_g to characterize the near-interface silicon region, since τ_g is inversely proportional to the density of defects (generation-recombination centres).

In order to investigate the effect of annealing of radiation-induced defects, post-irradiation annealing in nitrogen was applied at 350°C for 30 min.

3. RESULTS AND DISCUSSION

Electrophysical parameters of MOS structures (the oxide charge Q_{ot}, the density of surface states D_{it}, and the generation lifetime of minority carriers τ_g) with the reference and the zinc doped oxides are collected in Table 1. It can be seen that the doping, within the range of applied doses, does not affect values of parameters - they are comparable to those of the reference sample or even sligtly lower for the zinc containing samples.

Table 1. The zinc contents in oxidizing ambient and corresponding initial parameters of structures under test.

Zinc contents, %	Q_{ot}, cm^{-2}	D_{it}, eV^{-1}cm^{-2}	τ_g, μs
0	4.8×10^{11}	5.7×10^{11}	45
0.0005	4.2×10^{11}	5.7×10^{11}	40
0.001	4.3×10^{11}	5.0×10^{11}	86
0.0025	3.9×10^{11}	5.2×10^{11}	55

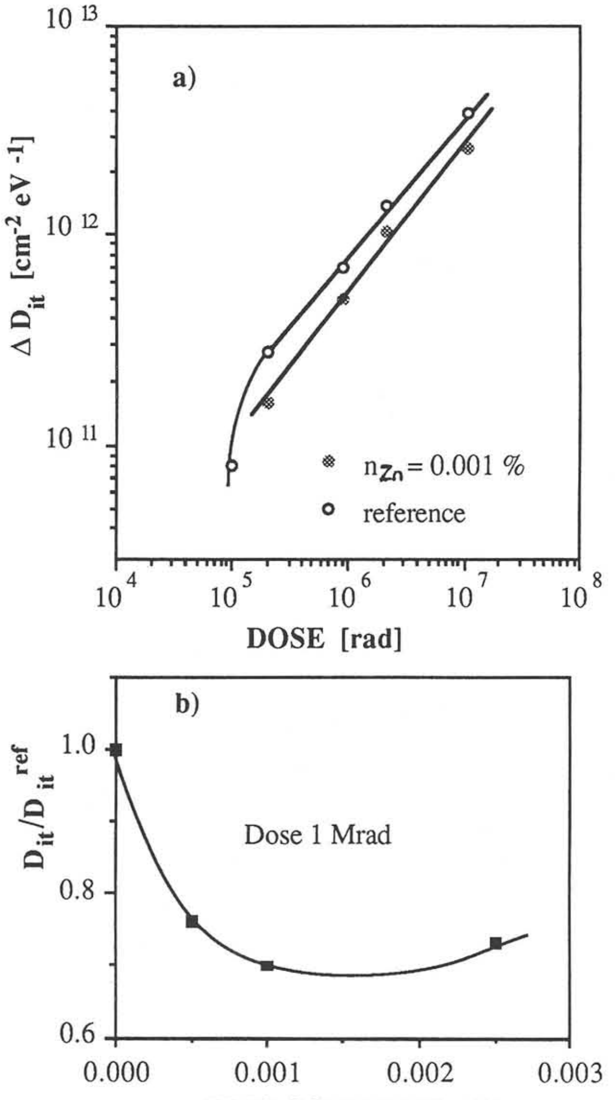


Fig. 1. Radiation-induced generation of interface states: a) dose dependence for the Zn-doped (0.001% of Zn in oxidizing ambient) and the undoped samples;
b) normalized D_{it} for the irradiated structures vs zinc contents (D_{it} ^{ref} refers to the undoped structures).

As we have already reported [3], the presence of moderate amount of zinc can, however, improve radiation hardness of the Si-SiO_2 interface and the near-surface silicon region. This effect is shown in Fig. 1(a), where dose dependence of radiation-induced surface states density is plotted for 0.001% zinc content in the oxidizing ambient. From Fig. 1(b) one can see that this amount of zinc is optimal from the point of view of radiation hardness. The generation of defects in the near-surface silicon region under the influence of ionizing radiation is also inhibited when zinc is present (see Fig. 2).

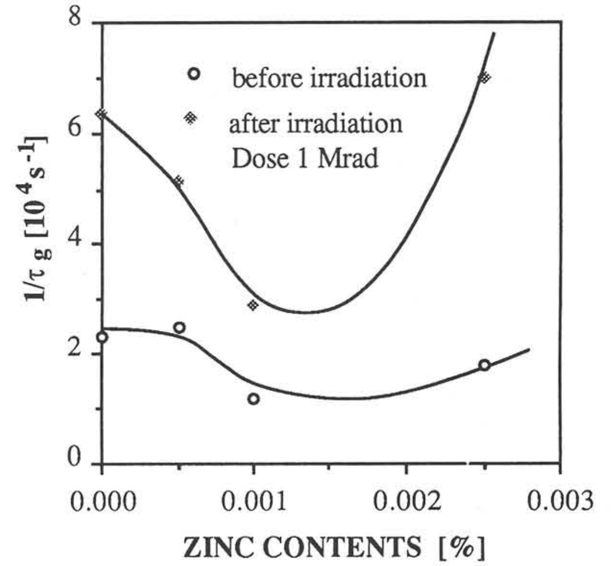


Fig. 2. Reciprocal minority carrier lifetime vs. zinc contents for non-irradiated and gamma-irradiated MOS structures.

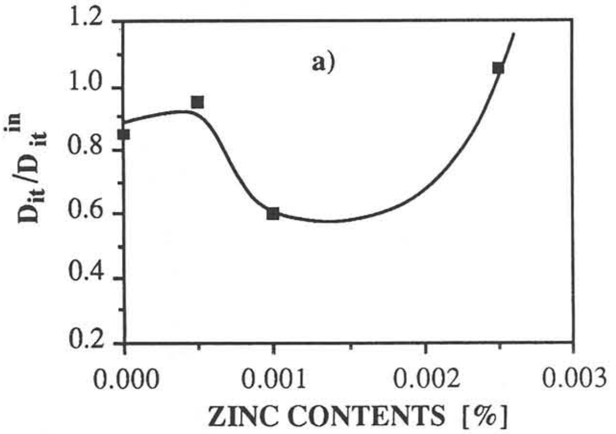
The effect of radiation-stimulated ordering was investigated in 1Mrad irradiated samples after additional annealing in nitrogen. It has been found that under such conditions the strongest effect is observed for zinc contents 0.001-0.0015% in the case of the interface and for 0.0005% in the case of the near-surface silicon. The relative improvement of D_{it} and τ_g (comparing to their initial values) is shown in Fig.3. It should be noted that the effect, although much smaller, can be observed for undoped systems as well.

The data presented in Fig. 3 indicate that the post-irradiation annealing involves some additional mechanisms which do not pass during PMA (without pre-irradiation).

Zinc atoms in silicon act as double donors with corresponding deep levels inside the energy gap of silicon. One can then expect that the presence of zinc near the Si-SiO_2 interface results in appearence of zinc-related states. Then we would have two types of interface states: zinc-related states and those "intrinsic" ones, originating from interface disorder. If this is the case, the latter are strongly supressed in the zinc-doped structures, since the observed resulting densities of interface states are comparable for the doped and the undoped samples (Table 1).

During the irradiation additional states are generated via bond breaking at the interface. The generation is lower when zinc is present, due to lower level of mechanical stress [3]. The subsequent thermal treatment leads to annealing of radiation-induced states either via restoring of broken bonds or via hydrogen saturation of dangling interface bonds. (Hydrogen is released under the influence of radiation in the oxide bulk from both Si-H and SiOH groups [5]). This effect can be even stronger in undoped structures, since the contribution of "dangling bond" states is much higher in this case.

On the other hand, low-temperature hydrogen annealing was found to passivate all zinc-related states located in the Si band gap [6] (the corresponding levels move out of the band gap). In the case of our "wet" oxides, the concentration of hydrogen released during irradiation may be very high. Hence, if the initial concentration of zinc-related states in the total interface state density was significant before irradiation/annealing treatment, the final value of D_{it} can be considerably reduced.



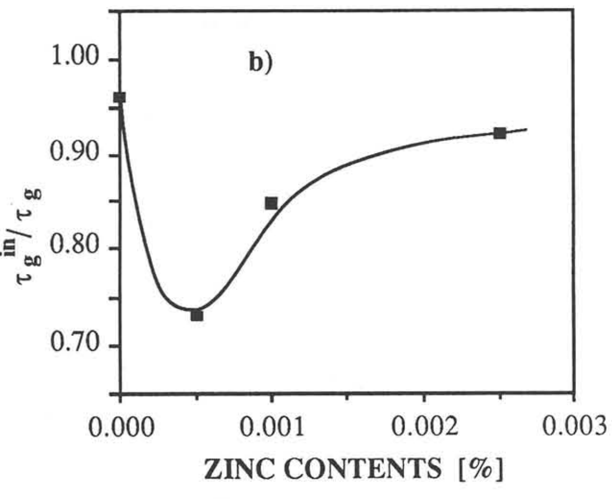


Fig. 3. Radiation-stimulated improvement of the Si-SiO_2 interface and the near-surface silicon in the MOS structures with oxides grown with various contents of zinc (after 1 Mrad and 30 min annealing at 350°C):
a) relative changes of the density of interface states;
b) relative changes of the minority carrier lifetime (parameters indexed with "in" correspond here to initial values for as-processed samples).

As far as the near-surface silicon region is concerned, the density of defects which serve as generation-recombination centres (whose density in turn determines τ_g) may be reduced during post-irradiation annealing via interaction of primary radiation defects with stacking faults, dislocations, and other structural defects initially present in silicon.

From Fig. 2 one can learn that the concentration of 0.001-0.0015% of Zn in oxidizing ambient seems to be the most beneficial to τ_g. This concentration was found also to be optimal for radiation hardness of τ_g, which can be due to lower level of mechanical stress in the presence of zinc. During the post-irradiation annealing defects of radiation origin interact with structural defects and their passivation (or anihilation) takes place, which can be observed in Fig. 3(b) as the increase of τ_g. It can be seen that this passivation is the most effective for the zinc content of 0.0005% in the oxidizing ambient. It seems that for higher Zn doses the number of available intrinsic defects (not decorated with zinc), which may interact with radiation-induced defects is insufficient.

From the results obtained we have also concluded that for zinc contents in oxidizing ambient of about 0.0025% and higher deterioration of radiation hardness of the interface region takes place. The observed improvment effect is not observed, too. Since we found the oxide quality decreasing at the zinc dose above 0.0025%, it seems that phase equilibrium limit corresponds to this concentration. The influence of irradiation (known as strong exciting factor) might then result in phase transformations and precipitation of zinc at the interface.

4. REFERENCES

1) P. V. Dressendorfer: *Ionizing Radiation Effects in MOS Devices and Circuits*, eds. T.-P. Ma and P. V. Dressendorfer (J . Wiley, New York 1989) p.333.
2) S. Verhaverbeke, M. Meuris, P. W. Martens, M. M. Heyns, A. Philipossian, D. Graf, and A. Schnegg: *Tech. Dig. Int. Electron Devices Meeting*, 1991, p.71.
3) T. Brożek, V. Y. Kiblik, O. I. Logush, and G. F. Romanova: *Proc. 7th Int. Conf. Insulating Films on Semiconductors* 1991 (A. Hilger, IOP, Bristol 1991), p.227.
4) M. N. Abuladze, A. B. Gerasimov, and V. G. Litovchenko: Fiz. Tekh. Poluprov. (USSR), **8** (1974), p.791.
5) D. L. Griscom: J. Appl. Phys. **58** (1985), p.2524.
6) P. Stolz, G. Pensl, D. Grunebaum, and N. Stolvijk: Mat. Sci. and Eng. **B4** (1989), p.31.