

Interaction of point defects with impurities in the Si-SiO₂ system and its influence on the interface properties

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Abstract. Point defect (PD) generation, redistribution and interaction with impurities in the Si-SiO₂ system are studied during the formation process by electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectra. The type and density of the point defects that are generated in the Si surface layer during thermal oxidation depend on the oxidation conditions: temperature, cooling rate, oxidation time and impurity content. The difference between interface properties of n- and p-type wafers could be related to different Fermi level position at the interface and to different PD densities in the volume.

Introduction

Point defects density at the Si-SiO₂ interface depends on the oxidation condition (oxidation temperature and duration, cooling rate and nature of ambient). If local dynamical equilibrium between PD is achieved at the Si-SiO₂ interface at low oxidation temperature or at short oxidation durations, it leads to the super-saturation with self-interstitial Si atoms and to the under-saturation with vacancies. At the same time at high oxidation temperatures or long oxidation durations the interface is supersaturated by vacancies and under-saturated by self-interstitials [1]. At an intermediate oxidation temperatures (durations) where the densities of vacancies and interstitials at the interface are nearly equal and recombination between them occurs during cooling, their equilibrium concentrations are diminished [2].

The goal of the present work was the investigation of PD interaction with impurities (hydrogen, oxygen). Hydrogen is an amphoteric impurity for Si. Depending on the Fermi level position as determined by the shallow dopant, it will have either a positive or a negative charge state or it could be neutral under non-equilibrium conditions [3]. In the present work PD interaction with impurities was studied in use of the EPR and NMR spectroscopy IR absorption spectroscopy and samples deflection measurements. EPR and NMR measurements were performed for both, powdered and crystalline oxidized samples to separate the PD at the interface from the volume PD. Additionally experiments to improve the Si-SiO₂ interface properties by annealing films under enhanced hydrostatic pressure and laser irradiation were made. The concentration of impurities, including hydrogen, was varied by oxidation ambient, impurity type (B, P) and by decomposition of SiH₄ in NH₃ ambient up to formation of Si₃N₄ on SiO₂.

Experimental

Si wafers (n- and p-type conductivity) of 10-15 Ωcm resistivity and with [111] and [100] orientation were used as initials in our experiments. The oxides were thermally grown in dry oxygen at 1050 – 1200 $^{\circ}\text{C}$. The thickness of the oxide layers varied between 0.2-0.6 μm . EPR spectra were taken in use of ERS 231 and Bruker ELEXSYS E500 spectrometers. The concentration of PD and impurities was varied by oxidation temperature and duration, by cooling rate and by deposition of Si_3N_4 onto SiO_2 . Hydrogen does not penetrate through Si_3N_4 providing its separation and storage in the Si-SiO₂ structure. To evaluate the concentration of impurities in the Si-SiO₂ system the chemical shift of hydrogen by ^1H NMR spectra and IR absorption spectra was measured.

Results and discussion

The dependence of EPR signal intensity on the oxidation temperature for samples with different oxides thicknesses is shown as Fig.1. For samples with thickness of oxide layers between 0.2 and 0.5 μm the EPR signal increases with an increase of the oxidation temperature and follows the Arrhenius type temperature dependence with different activation energy. From the dependence of the EPR signal intensity on the oxidation temperature the activation energy of P_a centers was determined to be ~ 3.5 eV. It coincides with the creation energy of divacancies in Si and oxygen vacancies in SiO_2 . Decrease of the PD activation energy with an increase of the oxidation time (2.5 eV) could be due to the generation of vacancies in volume by voids and their diffusion to the surface. In samples with an intermediate thickness of oxide layer (0.35 μm) the EPR signal intensity dependence on oxidation temperature is non-monotonous and a second EPR signal (P_b) appears. Reciprocal interdependence between P_a and P_b centers was observed. At the oxidation temperature of 1130 $^{\circ}\text{C}$ the interstitial atom density at the interface is lower than the vacancy's one, and the density of absorbed impurity could be diminished (see Fig.1).

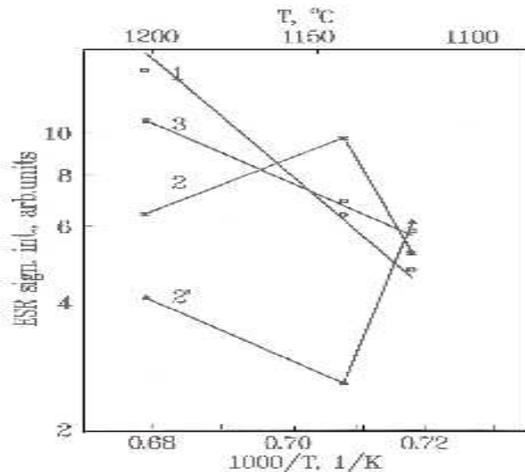


Fig. 1. 1, 3 – oxide thicknesses 0.2 and 0.5 μm respectively, 2, 2' – samples with intermediate oxide thickness, 1, 2, 3 – P_a centers; 2' – P_b -like centers.

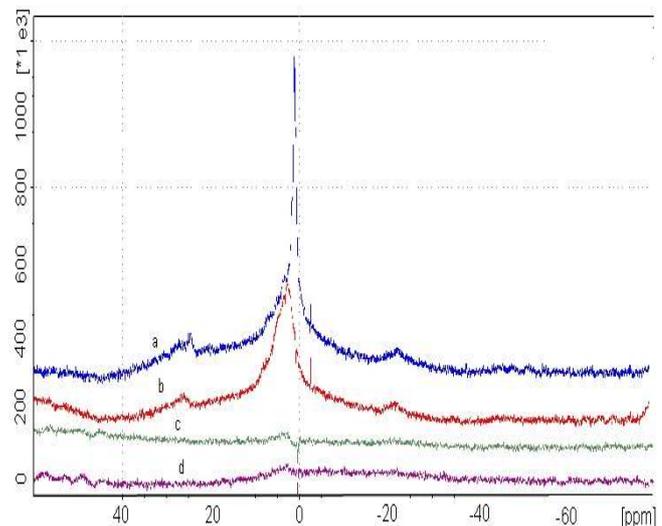


Fig. 2. ^1H MAS-NMR spectra of Si powder from top to bottom: a) Si-SiO₂, b) Si-SiO₂-Si₃N₄, c) Si(p)-SiO₂, d) Si(n)-SiO₂. a, b-oxidation at 1100 $^{\circ}\text{C}$. c, d- oxidation at 1200 $^{\circ}\text{C}$.

The ^1H NMR spectra of p- and n-type powdered samples are shown as Fig.2. The content of absorbed hydrogen in samples oxidized at 1130 $^{\circ}\text{C}$ is lower than in samples oxidized at 1100 $^{\circ}\text{C}$ (Fig.2 c, d). The content of hydrogen in SiO_2 decreases after Si_3N_4 deposition (Fig.2, b). This could be due to the change of the mechanical stresses related to the opposite sign of the thermal expansion coefficients of Si_3N_4 and SiO_2 on Si.

It was established that hydrogen content in SiO₂ on p-type Si is higher than in SiO₂ on n-type Si. It could be explained by the difference in hydrogen absorption and by its redistribution on n- and p-type Si due to its interaction with PD. Hydrogen content measured on n- and p-type powdered samples by NMR spectra indicated that the observed differences are higher than for crystalline samples. Hydrogen contents on n- and p-type crystalline samples determined by NMR spectra indicate that the content of Si-H bonds increases and the content of O-H bond decreases in p-type samples compared with n-type samples. EPR measurements confirm that the surface state density becomes lower and EPR signal connected with vacancies in volume increases after nitride deposition. This could be connected with the change in the internal mechanical stresses after nitride deposition [4].

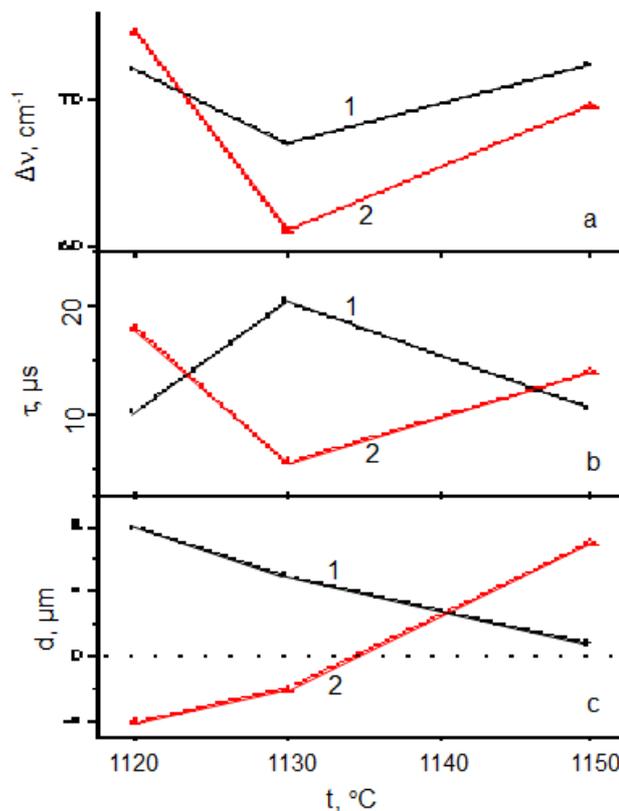


Fig.3. SiO₂ IR absorption 1100cm⁻¹ line width (a), charge carriers life time (b), samples deflection (c) dependence on the oxidation temperature. 1-initial sample, 2-after treatments under pressure.

The influence of the samples treatment under hydrostatic pressure on the interface properties are shown as Fig. 3. Annealing under enhanced hydrostatic pressure results increase (decrease) in the minority charge carriers generation lifetime depending on the PD density in the initial samples (3, b). This could be related to the change of the internal mechanical stresses under hydrostatic pressure and to compressive or tensile stresses appearing at the interface (c). Narrowing of the SiO₂ IR absorption 1100 cm⁻¹ line-width ($\Delta\nu$) under pressure (a) may be related to the diminish of stresses in (c) and indicates the possibility to improve interface properties by means of hydrostatic pressure.

CV characteristics of the MNOS structures are shown as Fig. 4 and Fig. 5. It can be seen that in MNOS structures oxidized at 1130°C the shift of CV curves after bias-temperature treatments (1130°C, +100V, 20min) diminishes and there are no differences in reliability between Si(n) and Si(p) samples.

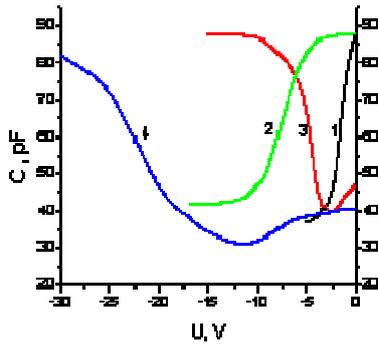


Fig.4. C-V plots for MNOS structure on n-type Si (1, 2) and p-type Si (3, 4) oxidized at 1100⁰C before (1, 3) and after(2, 4) BT treatments.

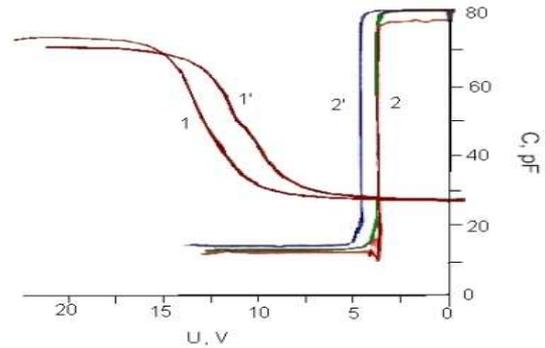


Fig.5. C-V plots for MNOS structure on n-type Si (2, 2') and p-type Si (1, 1') oxidized at 1130⁰C before(1, 2) and after(1', 2') BT treatments.

Laser irradiation allows modifying the stresses at the interface.

Conclusion

It was found that the PD density at the Si-SiO₂ interface diminishes at oxidation temperature 1130⁰C. This means that in samples with thickness of oxide layer ~0.35 μm prepared at this temperature the density of PD-impurities (hydrogen, oxygen) complexes e diminished and the reliability improved.

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