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Dedicated to the memory of Prof. Ulrich Gösele

Interaction of point defects with impurities in the Si-SiO_2 system and its influence on the interface properties

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It has been shown by means of EPR and NMR technique that at the Si-SiO_2 interface at appropriate oxidation temperature (time) local dynamical equilibrium may be achieved. At oxidation temperature 1130 °C the dencity of point defects is less than at lower and higher temperature (1100 °C and 1200 °C) and the content of absorbed impurities (hydrogen, oxygen) diminishes.

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1 Introduction Point defects (PD) density at the Si-SiO_2 interface depends on the oxidation condition. If local dynamical equilibrium between PD is achieved at low oxidation temperature or short oxidation time, it brings about a supersaturation with self-interstitial Si atoms (I) and undersaturation with vacancies (V), while at high oxidation temperature or long oxidation time, the interface is supersaturated by V and undersaturated by I [1]. It may be suggested if it is so, that at an intermediate oxidation temperature (time), where the densities of V and I at the interface are nearly equal and recombination occurs between them during cooling, its equilibrium concentration may be diminished. It has been shown in our previous work that this assumption is valid [2]. The purpose of present work was investigation of PD interaction with impurities (hydrogen and oxygen). Hydrogen is an amphoteric impurity in Si. Depending on the Fermi level position as determined by the shallow dopants, it will assume either a positive or a negative charge state or it my be neutral under nonequilibrium conditions [3]. In the present work hydrogen interaction with PD was studied by means of the EPR and ^{1}H NMR spectra measured on the powdered and crystalline samples with n- and p-type conductivity to separate the surface from the volume and change the Fermi level position.

2 Experimental To separate the PD at the interface from the defects in volume, the EPR and NMR spectra measurements were performed on powdered and crystalline oxidized samples. Si (n- and p-type conductivity) of 10-15 Ωcm resistivity [111] and [100] orientation was used. The oxides were thermally grown in dry oxygen at 1050-1200^0 C. The thickness of the oxide layers was varied (0.2-0.6 µm). EPR spectra were taken on ERS 231 and Bruker ELEXSYS E500 spectrometers. The content of PD and impurities was varied by oxidation temperature, oxidation time, cooling rate and by SiH_4 decomposition in NH_3, ambient up to Si_3N_4 formation of SiO_2. Hydrogen does not penetrate trough Si_3N_4 providing its separation and storage in the Si-SiO_2 structure. To evaluate the content of impurities in the Si-SiO_2 system the chemical shift of hydrogen by ^{1}H NMR spectra and IR absorption spectra where measured on n- and p-type wafers.

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3 Results and discussion. In Fig. 1 the EPR signal intensity dependence on the oxidation temperature for samples with different oxides thickness are shown. It can been seen that for samples with oxides 0.2 μm and 0.5 μm the signal increases with an increase of the oxidation temperature and follows the Arrhenius type temperature dependence with different activation energy. The activation energy of paramagnetic centers determined from the I(1/T) dependence for samples with thin oxides (see (1), Fig. 1) is 3.4 eV that coincides with creation energy of divacancy (3.5 eV).

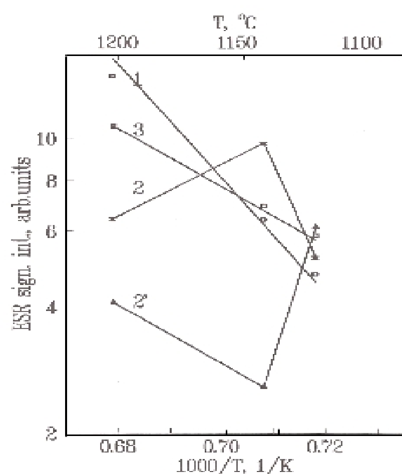

Figure 1 Dependence of the EPR signal intensity on the oxidation temperature, (1), (3) oxide thickness 0.2 and 0.5 μm. respectively, (2), (2') samples with intermediate oxide thickness, (1), (2), (3) P_a centres; (2') P_b-like centres.

For samples with oxides thickness 0.5 μm (see (3), Fig. 1) the activation energy is lower (2.5 eV). The decrease of the PD activation energy with an increase of the oxidation time, may be due to the vacancies generation by voids in volume and its diffusion on the surface. In samples with an intermediate oxides thickness (~ 0.35 μm) (see (2), (2'), Fig. 1), the EPR signal intensity dependence on the oxidation temperature is non-monotonous with a maximum (minimum) at 1130 ^{0}C. A second EPR signal with g~2.002 appears in these samples. These signals may be connected with P_b- or P_b-like centers. It can be seen from the obtained results that reciprocal interdependence between P_a- and P_b-like centers was observed. It allows to suggest that in accordance with the model of PD generation kinetics proposed in [1], at these oxidation temperature and time the local dynamical equilibrium at the Si-SiO_2 interface is achieved, and density of PD follows the mass action laws. It follows from the obtained results, that at this oxidation temperature (1130 ^{0}C) and oxides thickness (~0.3 μm) V > I and the density of absorbed impurities may be diminished. To check these assumption the hydrogen content were measured by means of ^{1}H NMR spectra for samples with oxides thickness 0.25 μm oxidized at 1130 ^{0}C and 1100 ºC (Fig. 2). As can be seen from the obtained results, the content of adsorbed hydrogen in samples oxidized at 1130 ^{0}C is much lower than in case of samples oxidized at 1100 ^{0}C. This results confirms the conclusion that interaction between PD and hydrogen at the Si-SiO_2 interface at appropriate choice of the oxidation condition may be diminished.

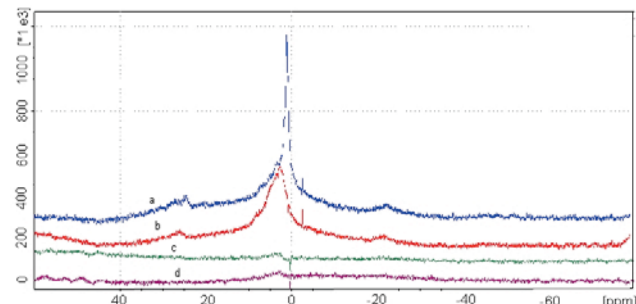

Figure 2 ^{1}H MAS-NMR spectra of Si powder from top to bottom: a) Si-SiO_2, b) Si-SiO_2-Si_3N_4, c)Si(p)-SiO_2, d) Si(n)-SiO_2.

The difference in hydrogen absorption on samples with n- and p-type conductivity oxidized at 1130 ^{0}C is absent (Figs. 2,c,d). To explain the hydrogen interaction mechanism on samples oxidized at 1100 ^{0}C, Si_3N_4 film deposition on SiO_2 was performed. It can be seen that after nitride deposition the content of hydrogen in SiO_2 decreases. Hydrogen content in SiO_2 after Si_3N_4 deposition measured on crystalline samples has shown that in p-type samples the content of Si-H bonds increases and content of O-H bonds decreases.

EPR measurements have shown that after nitride deposition the surface state density becomes lower and EPR signal connected with vacancies in volume increases. This may be connected with change of the internal mechanical stresses after nitride deposition [4].

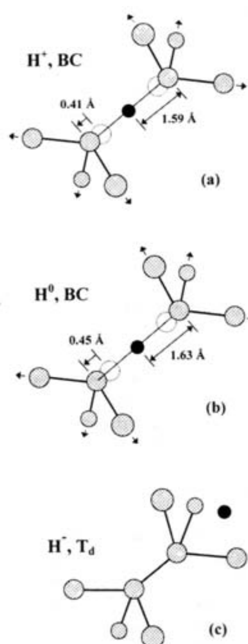

Figure 3 Schematic illustration of the location of H^+(a), H^0(b) and H^- (c) in the Si crystal. Relaxation of the Si atoms, based on calculations are presented [3].

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The obtained results allow to suggest that the differencies in hydrogen absorption on n- and p-type samples are connected with different Fermi level positions at the interface and in volume and are in agreement with the model of hydrogen incorporation in Si [3]. According to this model, the charge state of absorbed hydrogen in samples with n-type conductivity is H^+ and in samples with p-type conductivity is H^-. In Fig. 3 schematic illlustration of the location of hydrogen atoms in Si crystal are presented. As an ionised donor, in the state H^+ hydrogen will find its energetically most stable position in the region of highest electron density. Also, the neutral hydrogen atom will be bonded at bond-centred site. The negative hydrogen ion H^-, will prefer the region of lowest electron density, which is found in an interstitial space. With hydrogen in the bond-centered position, the two Si neighbour atoms in the Si-H-Si three centered bond move outwards from the hydrogen, to minimise the energy. With the positive hydrogen ions situated in a region of high electron density, it is difficult to add one more electron to convert the impurity to the neutral state. A high Fermi level is required to create the neutral state and the (+/0) donor level will be high in the bandgap. Using capasitance-voltage technique, such as deep-level transient spectroscopy, the donor level of single hydrogen was determined as $E_d = E_c - 0.2$ eV. For negative hydrogen bonded on the site with low electron density a lower energy for the level (0/-), may be predicted. Experiment has determined the level to be $E_a = E_c$-0.56 eV, near the midgap position. It has been found in our previous work [5], that samples deflection increases or decreases simultaneously with EPR signal intensity (P_a centers) depending on the oxidation temperature. At 1100 ^{0}C the deflection decreases with an increase of the P_a centers EPR signal intensity, while at 1200 ^{0}C the deflection and P_a centers density increase simultaneously that lndicated the strain (stress) influence on the PD density and vice versa. These results allow to explain the pressure influence in Si on the PD density (VO and VO_2 complexes). the pressure application to Si wafers treated at 1100 ^{0}C increases the PD density) while in wafers treated at 1130 ^{0}C, their density decreases [6].

4 Conclusions It has been found that at oxidation temperature 1130 ^{0}C local dynamical equilibrium between PD at the Si-SiO_2 interface is achieved and their density follows the mass action law in agreement with the pro-poosed in [1] model. This brings about that in samples oxi-diezed at these temperature V > I. Decrease of the PD-impurities (hydrogen, oxygen) complexes density in sam-ples prepared at this temperature (time) may be connected with PD density diminishment.It has been shown that the differencies in impurities absorbtion in samples with n- and p-type conductivity are connected with different Fermi level position at the Si-SiO_2 interface.

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