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ANNEALING BEHAVIOR OF CRYSTALLINE SILICON HEAVILY IMPLANTED WITH OXYGEN AT LOW TEMPERATURE

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The annealing behavior of oxygen-related paramagnetic defects in ion-implanted silicon in the range of 170-1050°C was investigated by means of electron paramagnetic resonance. In as-implanted samples a P_b-like center with principal tensor components $g_{\parallel} = 2.0012$ and $g_{\perp} = 2.0082$ and two isotropic lines with $g = 2.0056$ and $g = 2.0067$, respectively, have been observed. The isotropic lines belong to oxygen-related defects in an amorphous environment (*a*-Si). For annealing above 600°C the *a*-Si centers decrease to below 20% and the P_b-like center becomes the dominant defect. After annealing at 1050°C an intense resonance line with the g value close to that of the conduction electrons has been detected in the sample implanted with $1 \cdot 10^{18}$ cm^{-2} oxygen. This signal is related to a very effective thermal generation of shallow donor centers and a consequent formation of an n-type inversion layer at an interface with a buried SiO_2 layer. In this case Rutherford back scattering and optical spectroscopy indicated formation of a 2250 Å thick buried oxide layer and a high concentration of oxygen in the top Si film.

1 Introduction

The formation of silicon-on-insulator structures by ion implantation of a high dose of oxygen (SIMOX) is a promising technology[1,2] for microelectronic applications. Much work has been devoted to studies on SiO_2 layer formation by high temperature annealing (1200−1350°C) of oxygen-implanted silicon.[3] Relatively little is known about the crystalline-silicon-oxide (*c*-Si-O) system implanted at low temperatures with high oxygen concentration ($1 \cdot 10^{19}$ cm^{-3}−$1 \cdot 10^{21}$ cm^{-3}) and annealed in the temperature range of 400−1000°C. The present contribution focuses on the investigation of such material. In comparison to the behavior of oxygen in Czochralski (Cz) silicon, the specific features of heavily oxygen implanted silicon are related to the formation of a buried SiO_2 layer and to different kinetics of thermal donor generation.[2] The SIMOX Si/SiO_2 interface formed below 1200°C has a significantly smaller gradient of O concentration than the interface obtained by thermal oxidation of Si. High concentrations of (dia- and paramagnetic) defects can accumulate at an interface. Further, the band bending near the Si/SiO_2 interface can generate an inversion layer.[3] In the paper the annealing behavior of the paramagnetic centers generated by high-dose oxygen implantation of crystalline silicon (*c*-Si) was analyzed.

2 Experimental Details

Phosphorus- (4-5 Ωcm) and boron- (16-20 Ωcm) doped Cz silicon samples were implanted with O^+ ions at an energy of 150 keV for the doses of $1\cdot10^{17}$ cm^{-2} and $1\cdot10^{18}$ cm^{-2}. The temperature during the implantations has been estimated as 170°C and 350°C, respectively. The samples were cut along the $\langle 011 \rangle$ direction and annealed in closed quartz ampoules in an argon atmosphere at a pressure of 0.1 Torr. The annealing was performed in steps at temperatures between 170 and 1050°C, in order to investigate the first stages of oxygen precipitation in the high concentration range. In what follows we refer to oxygen-related complexes as SiO_2 precipitates without pretending that the stoichiometric compound is actually synthesized. The magnetic resonance experiments were carried out with an Electron Paramagnetic Resonance (EPR) superheterodyne spectrometer operating at 9 GHz (X-band) and tuned to dispersion. EPR spectra have been measured at 8 K. The EPR spectrum of substitutional phosphorus was used as a reference. The depth and the thickness of the buried oxide layer has been determined by Rutherford Back Scattering (RBS) and optical spectroscopy.

3 Results and Discussions

3.1 Identification of EPR lines

The EPR spectra of the as-implanted samples with a dose of $1\cdot10^{17}$ cm^{-2} show a well-defined anisotropic signal as depicted in figure 1 for magnetic field directions parallel to $\langle 111 \rangle$ and $\langle 011 \rangle$. The non-annealed samples show a dominant defect with trigonal symmetry; the principal values of the g tensor are $g_{\parallel} = 2.0012$ and $g_{\perp} = 2.0082$. These values are close to the result of Barklie *et al.*[4] obtained at room temperature, and also to other measurements performed at liquid helium temperature by Carlos.[5] The observed g value agrees with that of the well-known P_b center and consequently we identify the defect as a P_b-like center. The characteristic ^{29}Si hyperfine structure of the P_b center could only be observed for the annealed samples. The P_b defect is specific to the Si/SiO_2 interface obtained by thermal oxidation of silicon, but was also observed in implanted material.[4] The high concentration of implanted oxygen leads to the formation of SiO_2 precipitates. The P_b-like defects could be located at the border of these SiO_2 precipitates embedded in a partially disordered Si lattice. The defect production rate by implanted ions increases at the end of their trajectory. Because of that the amorphization is more effective in the region with high oxygen concentration. In consequence the anisotropic signals cannot belong to this region, and must originate outside of it where the symmetry of the host lattice is not totally destroyed. However, the fact that the P_b-like defects are present for as-implanted samples, i.e., even without annealing, when a buried SiO_2 layer has not yet been created, means that the P_b centers cannot be confined to the interface only. This observation is relevant for the structure of the P_b center. The EPR spectra of the as-implanted samples contain also two superimposed almost isotropic lines with g = 2.0056 and g = 2.0060-2.0067. Isotropic resonances were also observed by Barklie *et al.*[4] with g = 2.0054 and g = 2.0057. The first line with g=2.0056 is known to be related to *a*-Si defects.[4] The second line increases its intensity when the amorphization process becomes more effective, i.e., for higher doses. This effect is evident in the isotropic spectra of figure 2 obtained for the dose of $1{\cdot}10^{18}$ cm^{-2}. In this case a single broad resonance line is observed. The intensity of this resonance increases after annealing at 800°C. In the same figure the middle arrow indicates the disappearance of the initial tail of the broad line at this annealing stage. The g value indicates that the vanishing resonance line is related to the well-known E' defect,[3,4] found in irradiated silicon dioxide. The observation of the E' defect in as-implanted silicon indicates the formation of large SiO_2 precipitates and/or an amorphous oxide layer below the Si surface for these implantation conditions. The EPR signals persist even after annealing at 1050°C for 30 minutes, and

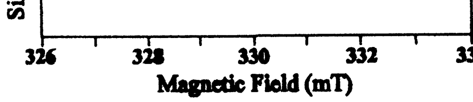

Figure 1: EPR spectra of the as-implanted Si sample, for the oxygen dose $1{\cdot}10^{17}$ cm^{-2}. (a) Magnetic field B || ⟨111⟩, (b) magnetic field B || ⟨011⟩.

a new line arises with its g value very close to that of conduction electrons. Heat treatment of oxygen-rich Si is known to generate the so-called thermal donors. These, however, require annealing temperatures in the vicinity of 450°C and are destroyed at higher temperatures. The unusual generation of a donor by annealing above 1000°C could be related to the band bending at the Si/SiO_2 interface. It has been suggested in the past[3] that the band bending could transform a nonparamagnetic defect into a paramagnetic state. In this case centers close to the interface would be affected, increasing locally the conduction electron concentration. The inversion layer formation in p-type silicon would then be a consequence of the buried oxide layer formation.

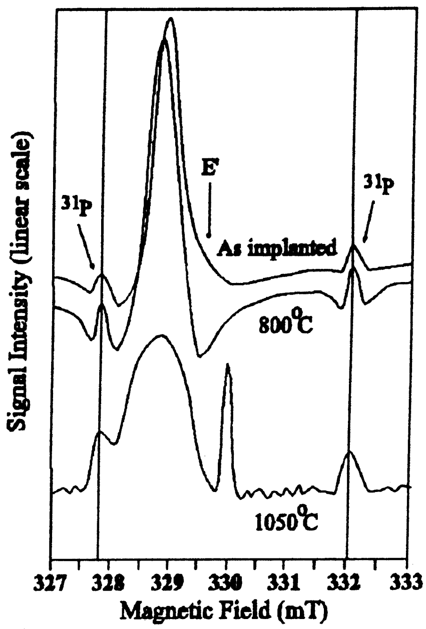

Figure 2: EPR spectra of the oxygen implanted Si sample for the dose $1{\cdot}10^{18}$ cm^{-2}, before and after an annealing step at 800°C for 1h and after an additional one at 1050°C for 0.5h.

3.2 Relative annealing behavior of P_b and a-Si defects

The results obtained for the annealing behavior of the P_b-like centers and the isotropic a-Si defects are given in figure 3 for isochronal heat treatments of 1 hour at 400, 500, 600, 700 and 800°C. The EPR intensity of the individual resonances has been compared to that of the ^{31}P line and normalized to the value obtained for the as-implanted sample. The curve labeled "All" shows the global concentration of all the paramagnetic defects produced by O^+ implantation. The plots labelled "P_b" and "a-Si" show the relative intensity as a percentage of a Si:P standard used in the experiment, of P_b and amorphous-related centers from the corresponding total amount of defects that remain after the annealing step. The P_b intensity has been estimated from the spectra obtained with **B** parallel to ⟨111⟩ (see figure 1).

From the data presented in figure 3 the following conclusions can be drawn:

- The annealing of the a-Si defects is more effective than that of P_b centers.
- In as-implanted samples the P_b concentration is the same as that of the a-Si defects.

- The possible decrease of P_b concentration as a result of the step-by-step annealing procedure from 400°C to 800°C is weak and comparable to the estimated experimental error. Apparently the P_b centers are stable up to temperatures of approximately 800°C.

If one assumes that the P_b-defect concentration is related to the total surface of the SiO_2 precipitates, then the weak annealing temperature dependence of the P_b concentration shown in figure 3 indicates that (for a dose of $1 \cdot 10^{17}$ cm^{-2}) the formation of a buried SiO_2 film is not affected by annealing up to 800°C. It can also be seen that for a temperature range of 200°C to 400°C we have found a detectable increase in P_b concentration. This could indicate that in this temperature range the initially isolated implanted oxygen atoms are thermally activated to form SiO_2 precipitates, increasing in this way the total area of the Si/SiO_2 interfaces.

3.3 The buried oxide layer formation

The profile of oxygen concentration after thermal annealing at 1050°C has been investigated by the RBS technique as presented in figure 4. The existence of the buried SiO_2 layer has been confirmed by the increased yield at around the backscattering energy of 750 keV. The bottom Si/SiO_2 interface was found

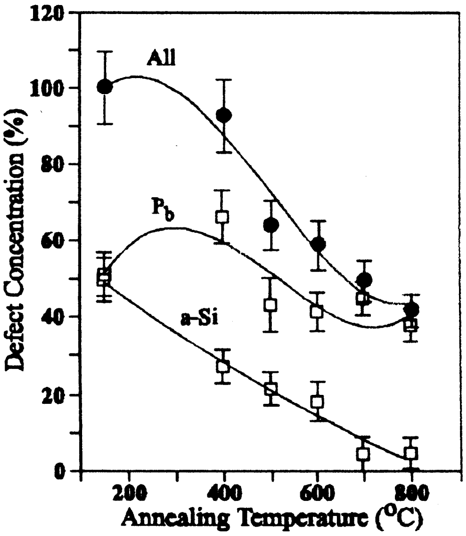

Figure 3: Annealing dependence of the individual defects as observed for the sample implanted with a dose of $1 \cdot 10^{17}$ cm^{-2} of oxygen ions.

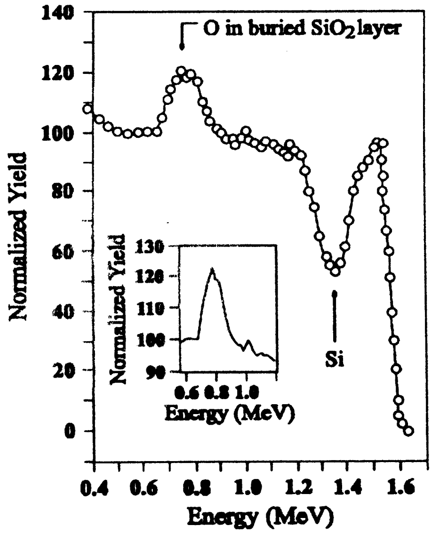

Figure 4: The Rutherford back scattering spectra of the sample implanted with a dose of $1 \cdot 10^{18}$ cm^{-2} after annealing at 800°C for 1h and at 1050°C for 0.5h.

to be sharper than the upper one. The long tail of the distribution profile indicates a high oxygen concentration in the top Si layer. The thickness of the SiO_2 layer and of the top Si film were determined as 2340 Å and 2609 Å, respectively. Similar values were also found from optical spectroscopy: 2150 Å and 2650 Å for the buried SiO_2 layer and the Si top film, respectively. These data were obtained by a fitting procedure of spectra based on the reflectance calculation in the frame of a multilayer optical model.[6] The small discrepancy between both results is related to the oxygen step-profile approximation used in the model. One concludes that after heating the sample at 1050°C a higher oxygen concentration remains in the top silicon layer than in ordinary SIMOX structures, which are annealed at 1350°C.

Acknowledgements

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