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Complex destruction of near-surface silicon layers of Si-SiO_2 structure

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Abstract. The structure of near-surface silicon layers of Si-SiO_2 has been investigated. It was observed the complex destruction of these layers caused by relaxation of mechanical stresses. The magnitude of mechanical stresses depends not only on parameters of silicon dioxide and silicon but on presence of initial defects in silicon. We have proposed the defect formation mechanism of near-surface layers in Si-SiO_2 structure, and it has been revealed the influence of impurities on this process.

Keywords: Si-SiO_2 structure, dislocation, defect, mechanical stresses.

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1. Introduction

Silicon has long been synonymous with semiconductor technology. This unique role is largely related to remarkable properties of the Si-SiO_2 interface. Si-SiO_2 systems currently are important and still in the lead position for sub-micrometer electronic devices. That is why there exist a lot of works dealing with investigation of this structure.

The main part of electronic processes in Si-SiO_2 structure happens in near-surface layers, and it requires the detailed structural and impurity investigation of these layers. Understanding the structure of near-surface layers of silicon in Si-SiO_2 systems is serious problem of great importance for microelectronic applications. The up-to-date concept represents interface Si-SiO_2 originating in the course of thermal oxidation as some transition layer with a variable chemical and structural composition. It is supposed that at the boundary surface of monocrystalline silicon there is a monoatomic layer of non-stoichiometrical SiO_x ($1<x<2$). Then the intermediate layer of SiO_2 follows with major internal mechanical stresses that are transfered into amorphous SiO_2 [1, 2]. Also, there is a known model representing the interface Si-SiO_2 in the form of three-layered structure: silicon dioxide, transition layer of non-stoichiometrical SiO_x with the thickness of 1 to 3 nm and hard destructed layer of silicon with a thickness close to few micrometers [3, 4]. However, in some cases the destruction of near-surface silicon layers and generation of dislocation structures happen in the form of dislocation networks [5]. These silicon layers are expanded from the interface to abnormally long distances up to 10-30 μm. The real structure and depth of these layers have not been ascertained yet. It is still not revealed the correlation between the difference in parameters of these layers that appear after oxidation process and characteristics of initial silicon. Therefore, the aim of this work was to investigate the silicon near-surface layers in Si-SiO_2 structure and to determine the parameters that influence on generation of complex defect structure during high-temperature oxidation.

2. Samples and experimental technique

Silicon wafers of n- and p-types with different orientation and dioxide thickness (range 0.1 – 1.5 μm) grown in dry oxygen atmosphere at the temperature 1150 °C were researched (oxygen consumption was about 10 liters per minute). Investigation of silicon surface after removal of dioxide was carried out by scanning electronic microscopy (electronic scanning microscope “Cam-Scan” with “Link-860” X-ray microanalysis, by using the ZAF program for calculation), by optical methods (metallographic microscope MMR-2R), by Auger spectrometer LAS-3000 (beam diameter – 5 μm), by X-ray technique based on DRON-2 with silicon grating monochromator (voltage 16 kV, current 2 mA).

SiO_2 was etched off in hydrofluoric acid followed by washing in deionized water. To detect structural defects, the silicon surface layer-by-layer etching away

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with selective Sacco (for surface 100) and Sirtl (for 111) etchants with preliminary treatment in Karo intermixture and peroxide-ammonia solution was performed. This preliminary procedure improves developing properties of selective enchants [3].

3. Results and discussion

Fig. 1 shows the typical silicon surface received after removal of dioxide in HF and 5 min etching of silicon (the thickness of dioxide was 1 μm) in selective Sirtl etchant. It is well seen that etch pits typical for dislocations and stacking faults are absent. The presence of such pits on silicon surface is usually related with etched dioxide that appeared at the accelerated thermodiffusion of oxygen atoms along initial structural defects of silicon (Fig. 2). The attempt to have an electron image of the silicon surface was impossible by reason of charging as a result of dielectric properties of this one. Therefore, we conclude that these layers consist of polysilicon, block boundaries of which contain unsaturated bonds with a small fill factor for charge carriers. The thickness of this layer depends on the dioxide thickness and quality of silicon. As shown using the Auger-analysis, the certain property of these layers is high amount of dissolved oxygen, and the oxygen concentration increases with growth of the dioxide thickness.

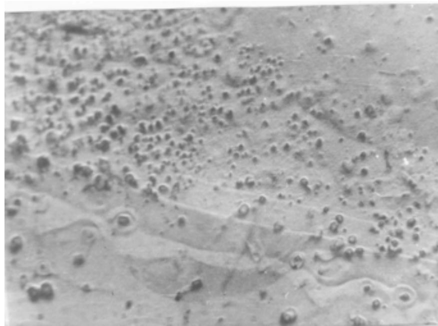

Fig. 1. The optical image of silicon surface (magnification is 1000-fold).

Fig. 2. The SEMS image of initial structural defects (dislocations) in Si.

After etching the silicon surface (up to 5 min), dislocation networks were revealed (Fig. 3) (with the dislocation density up to $10^{10}\,\mathrm{m}^{-2}$), which have included 60° as well as partial dislocations and was decorated by oxygen (Fig. 4). Appearance of typical structural defects testifies to occurrence of a normal crystalline structure. After 5 min etching, separate dislocations and glide lines appear instead of dislocation networks (Fig. 5). This complex structure of disordered silicon is generated as a result of non-stoichiometrical SiO_x origination during enhanced diffusion of oxygen along initial dislocations. Non-stoichiometrical SiO_x causes an additional strain and additional glide polygonization of silicon. As a result, the destructed silicon layer is separated into layers consisting of disordered silicon and the layer containing dislocation networks. These layers contain different energy-level density, capable to capture electrons, i.e., between these layers there is a magnitude jump of the electron trapping level density. This effect is cleared up in electron microscope investigations of near-surface silicon layers. Therefore, the near-surface silicon layers of $Si\text{-}SiO_2$ structure could be represented in the following manner (Fig. 6).

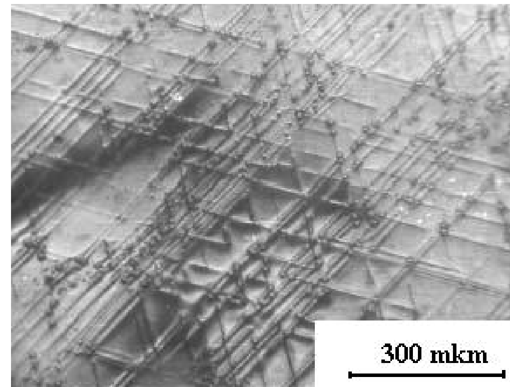

Fig. 3. Image of the dislocation network in *p*-Si obtained after selective chemical etching with Sirtle (depth of analysis L = 15 μm).

ENERGY
3.1
TOTAL AREA = 91996
Peak at 8.086 keV
FIT INDEX = 19.62

ELMT	ERROR (WT %)
Pt	.433 not used for ZAF
Si	.328
Cl	.120 < 2 sigma
Na	.082 < 2 sigma
K	.104 < 2 sigma
Al	.095 < 2 sigma

20.00 kV

Last elmt analysed, NORMALISED

ELMT	% ELMT	ATOM%
K	.000	.000
Cl	.000	.000
Na	.079	.094
Si	93.202	92.812
O	6.304	6.656
Al	.531	.538
TOTAL	100.016	100.000

Fig. 4. X-ray analysis of the dislocation network (concentration of oxygen atoms is 6.6%).

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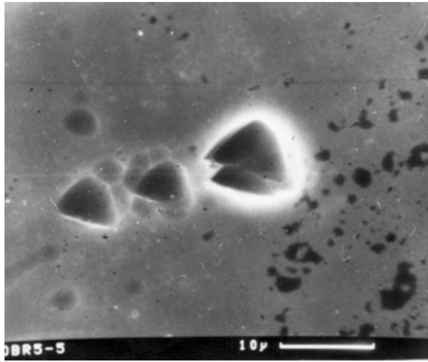


Fig. 5. The electron image of separate dislocations (magnification is 2300-fold).

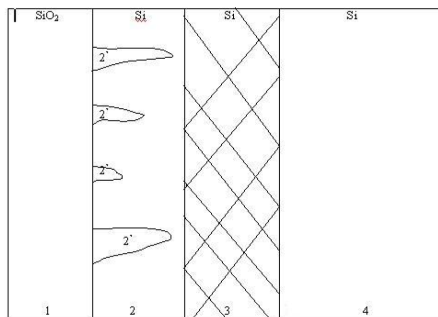
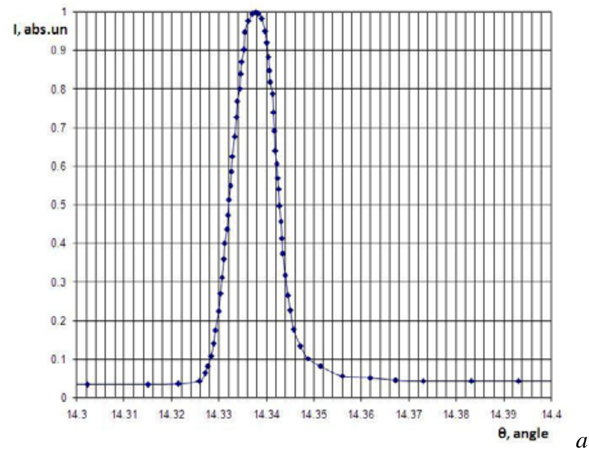


Fig. 6. The near-surface silicon model of $Si-SiO_2$. *1* – SiO_2 layer, *2* – disordered silicon layer, *2′* – internal SiO_2 generated due to accelerated thermodiffusion of oxygen, *3* – dislocation networks, *4* – silicon.

To confirm this complex structure of silicon near-surface region, X-ray diffraction method was used. Rocking curves are presented in Figs 7a and 7b. The slope of a curve is explained by presence of the second reflective layer. It can be noted the overlay of “little” rocking curve in Fig. 7b. By means of Gaussian function approximation the maximum and the half-width of “little” curve were determined, which enabled to calculate other parameters of silicon. The shift of the maximum and curve broadening as compared to the ideal standard specimen are determined by some physical reasons such as macrostress and microstress. Macrostresses are caused by the interface stress, and microstresses are caused by the polycrystalline structure. If we know the curve broadening β_1 and β_2 of 2 orders in reflection for the same reflection plane, we can make qualitative evaluation and determine what parameters influence on curve broadening [4]. Using the following expression

$$\frac{\cos\theta_1}{\cos\theta_2} < \frac{\beta_2}{\beta_1} < \frac{\mathrm{tg}\,\theta_2}{\mathrm{tg}\,\theta_1}, \qquad (1)$$

where θ are the angles of reflection, β – half-width of the rocking curve. We obtained the inequalities 1<1.11<3.35. Therefore, the dispersion in layer structures has main influence on curve broadening.



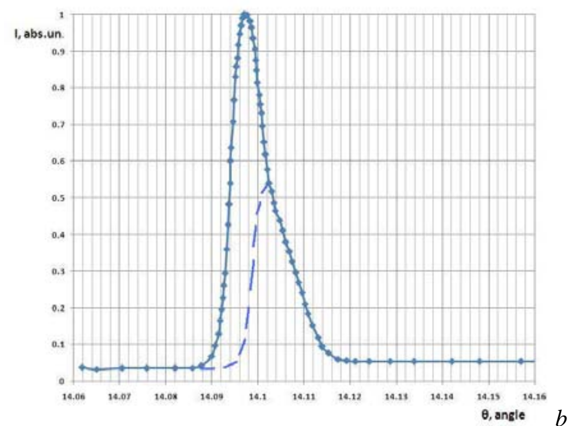


Fig. 7. The rocking curves for oxide thicknesses 0.15 μm (a) and 1.5 μm (b).

According to the expression [4]

$$D = \frac{\lambda}{\beta\cos\theta}, \qquad (2)$$

where λ is the wavelength, we calculated *D* – the crystallite size. It was close to 0.5-0.8 μm and proportional to the oxide thickness. The grain-boundary angle was in the range 0.005° to 0.008°.

Formation of the given complex defect structure is possible, if magnitudes of mechanical stresses are higher than the yield stress for silicon. Calculation shows that it is observed only at the silicon dioxide – silicon interface [5]. The abnormally deep mechanical stresses can be explained by accelerated thermodiffusion of oxygen atoms along initial structural defects. In this case, the oxygen diffusivity along structural defects is higher by 3 to 4 orders than that for bulk.

4. Conclusions

Thus, as shown by experimental investigations, the near-surface layers of silicon at the silicon – dioxide interface has a complex structure and consist of polycrystalline

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silicon region and dislocation network region. The thickness of layers and the size of crystallites in disordered layer depend on mechanical stress, which is related with electrophysical parameters of silicon, the oxide thickness and presence of initial defects in crystal. The abnormally high values of stresses passing round deep into silicon from the interface can be explained by accelerated thermodiffusion of oxygen atoms along initial structural defects that are present in silicon before high-temperature oxidation.

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