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EVOLUTION OF STRUCTURAL DEFECTS IN SILICON CAUSED BY HIGH-TEMPERATURE OXIDATION

The dislocation self-organization processes in near-surface silicon layers of Si-SiO_2 during high temperature oxidization have been investigated. It was observed the complex destruction of these layers caused by relaxation of mechanical stresses. We have proposed the defect formation mechanism of near-surface layers in Si-SiO_2 structure. For self-organization processes to be explained, the synergetic method was applied. It was shown that the formation of periodical dislocation structures at the interface is a consequence of the spatial instability of the dislocation distribution in the crystal, their self-organization due to correlation effects between the oxygen diffusing along structural defects and an ensemble of dislocations.

1. INTRODUCTION

Structures Si-SiO_2 are widely used in modern micro and nano – electronics. Electrophysical parameters of these structures depend on many factors. The property of initial semiconductor, silicon dioxide parameters, and the presence of structural defects on the interface can have an effect on the quality of devices based on the Si-SiO_2 structure [1]. Despite a huge number of articles related to this problem, interest in the study and production of the Si-SiO_2 structure is increasing. Due to transition of the active devices elements to nanoscale the quality of the Si-SiO_2 interface plays an important role in electrical processes. Even existence of one dislocation in space-charge zone of the device leads to catastrophic degradation of ten thousands nanoscale elements and as a consequence causes a reduction in quality of functional units [2, 3].

Dislocations in silicon and other semiconductors have been well studied both theoretically and experimentally. Properties of dislocations were under investigation since the initial observations of these extended defects in crystalline semiconductors. Complexity of the investigations was related to large variety of dislocation structures and to strong interaction of dislocations with impurities and other defects [1]. Moreover, previously applied methods for introduction of dislocations to the bulk of the crystal, i.e. plastic deformation, indentation, oxide precipitation etc., were not capable of well-controlled fabrication of dislocations regarding their structure, electro-optical properties, location and state of decoration with impurities. As a result, many important properties of dislocations still remain under discussion. Namely, relations of optical and electrical properties of dislocations with their microscopic structure were not yet well established.

On the other hand, the complex defect structure is formed at near-surface Si-SiO_2 interface during high-temperature oxidization. The disordered silicon layer and the dislocation network layer are both present in this structure. Also, the additional chemical treatment of dislocation networks allowed us to obtain nanostructured silicon surface which fluoresces in a visible spectrum range [4]. Such a periodical structure as a dislocation network is a consequence of self-organization processes of defects at near-surface silicon layers of the Si-SiO_2 interface.

The self-organization of ordered structures is a recurring theme in physics, chemistry, and biology. Spatially periodic patterns, in particular, are observed at length scales ranging from the atomic to the astronomical. Self-organized patterns are rarely perfect; topological defects, such as dislocations and disclinations, are an intrinsic element of their phenomenology.

This paper is devoted to studying of dislocation self-organization processes in silicon during high temperature oxidization. We have been tasked with investigating on the complex defect structure of the $Si-SiO_2$ interface and to determine the mechanism of self-organization processes of dislocations.

2. EXPERIMENTAL RESULTS

The experiments were carried out on p-type Si samples cut from the Czochralski grown wafers. The initial wafers were doped with boron ($N_B \sim 10^{15}$ cm^{-3}). The silicon wafers were oxidized in dry oxygen at 1150C (the oxide thicknesses were about 0.1 – 1.5 μm) followed by etching in a hydrofluoric (HF) acid solution and treatment of the silicon surface by selective etchants (SE). To reveal the deformation-induced defects (dislocations), the surface of samples was selectively etched by the Secco-etchant and the Sirtl-etchant for the (100) and (111) surfaces, respectively.

The following techniques and equipment were used for examination of the silicon surface upon chemical treatment:

- Scanning electron microscopes (SEM) (CamScan 4-D with a Link-860 system of an energy dispersion analyzer; REM-104);
- Auger electron spectroscopy (AES) («Riber» Las-300 spectrometer);
- Optical methods using an MMR-2R microscope;
- X-Ray analysis.

During investigations of near-surface silicon layers of the $Si-SiO_2$ interface the complex defect structure was revealed. Directly below the silicon dioxide there was a layer of disordered silicon. A pattern of the silicon surface upon removed a 1 μm thick dioxide is shown in Figure 1. The tendency is clearly seen for the absence of etch pits typical for a crystalline structure. The irregularly shape pits can be associated with the oxide formed under enhanced diffusion of oxygen along structural defects. We were unable to view the silicon surface using an SEM since the surface was heavily charged. This made it impossible to obtain a reflected electron beam. These results enabled us to conclude that the silicon surface had a highly disordered structure close to a fine-polycrystalline or even an amorphous. X-Ray analysis allowed us to calculate the average sizes of silicon grain. The sizes were about 0.3 – 1 μm and depend on oxidization conditions, the structural defect density and dioxide thickness [5].

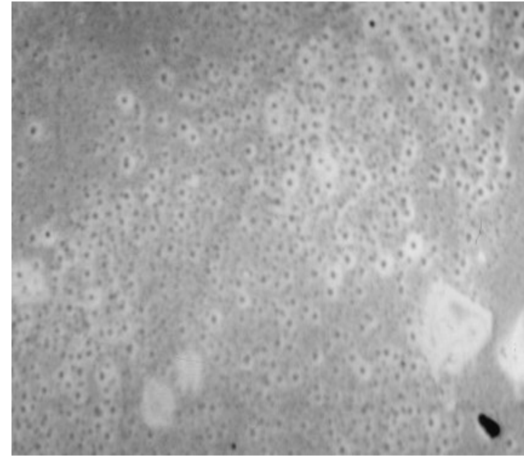

Figure 1. Optical image of the silicon surface after removal of an oxide layer (1 x 1000).

With further 5 minutes of SE, dislocation networks were formed on the silicon surface (Figure 2 (a, b)). The dislocation networks were decorated by SiO_x. This observation is supported by the fact that further etching can be performed without an oxidant. This is also confirmed by an X-Ray analysis and Auger spectroscopy analysis (Table 1). Given the SE velocity is about 3 μm/min ; the depth of dislocation networks was calculated to be about 30 μm for an oxide thickness of 1 μm . The thickness of the silicon layer with dislocation networks was about 10 μm .

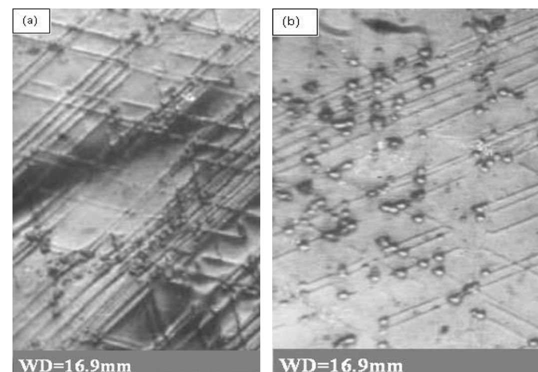

Figure 2. (a) SEM image of a typical dislocation network pattern upon selective etching in the Sirtl-etchant for 10 min. (b) SEM image of a typical dislocation network pattern upon selective etching in the Sirtl-etchant for 15 min.

Table 1. Calculations of Auger-spectra of elements in the dislocation network.

Element	Amount, % [atomic percent]
K	0.00
C	0.452
Na	0.04
Si	95.245
O	3.742

The dislocation networks occur at the disordered silicon – crystalline silicon interface and disappear at the interface between the two nearest silicon layers (Figure 3) [6]. In case of the absence of layered structure, dislocation networks transform in the single dislocations (Figure 4).

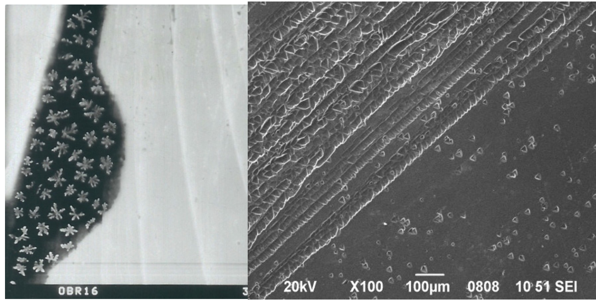

Figure 3. A typical SEM image of the silicon wafer cleavage with a layered structure.

Figure 4. A typical SEM image of single dislocations on the silicon wafer cleavage.

It is known, that dislocations which are generated under the influence of diffusion impurity, form the flat dislocation network that are parallel to the solidification front. Stresses lead to plastic deformations due to a difference of atomic radius of the dopant and silicon (for example: R_{Si} = 1.17 Å, R_B = 0.88 Å, R_P = 1.10 Å). The Wegard's law describes the deformation if the dopant atom penetrates into the crystal (taking into account the sp^3 hybridization) [7]

$$\varepsilon = \omega N, \qquad (1)$$

where ω - Vegard's coefficient (depends on a type of impurity atoms and their lattice position), N – impurity concentration. Besides, stresses in the crystal due to the penetration of atoms with another radius are described by the following equation [8]

$$\sigma = 2\cdot\omega\cdot\mu\cdot\frac{1+\nu}{1-\nu}\left(N_0 - \frac{1}{a}\int_0^a N(y)dy\right), \qquad (2)$$

where μ – shear modules, ν – Poisson ratio, y – the interior plane of the crystal and limited by planes situated at a given distance. Calculations have shown that the stresses (concentration of the impurity) required for Boron at which plastic deformation occurs are about 10^{18} cm^{-3} [9]. A pattern of the dislocation network which was generated under the influence of Boron is shown in Figure 5.

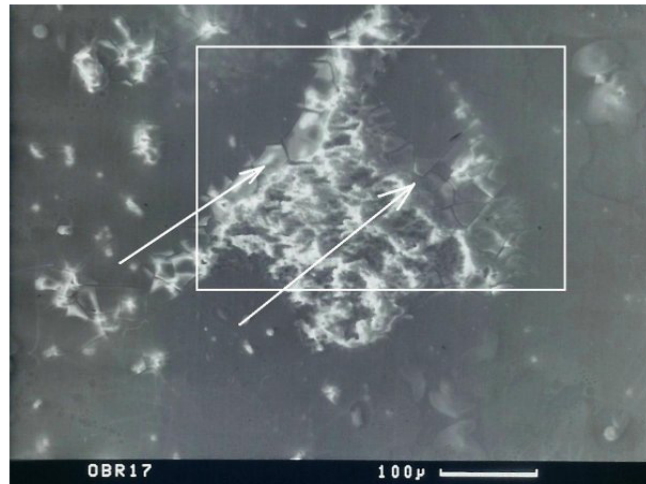

Figure 5. SEM image of a typical dislocation network pattern (concentration of the Boron is 3 10^{18} cm^{-3}).

We can explain the generation of dislocation networks at the silicon in the same initial analysis. The ionized oxygen overcomes the potential barrier at silicon surface and penetrates into the interstices of silicon crystal lattice. The knocking out processes of silicon atoms of the crystal lattice are begun when oxygen ions reach the saturation stage. Silicon atoms diffuse into the bulk due to the impossibility to fill the interstices occupied by oxygen. This process is accompanied by a rapid diffusion of oxygen along the lines of structural defects, thereby raising the level of mechanical stress. Thus, the increasing of mechanical stresses

in the surface layer of silicon at the early stage of oxidation leads first to the elastic deformation and then to plastic deformation respectively. Stresses in silicon layers cause the different types of defects depending on these stresses values. The layer of maximum oxygen concentration is becoming the silicon dioxide with an amorphous structure. Next layer of silicon has highly disordered structure of oxygen-rich nonstoichiometrical oxides. And last layer consists of dislocation networks decorated by oxygen and nonstoichiometrical oxides. It should be noted that the boundary between disordered silicon and dislocation networks is relative because of the disordered silicon consists of grain boundary dislocations.

3. THEORETICAL MODEL

Unfortunately, this empirical theory failed to explain why, in some cases, the dislocations are organized in a strictly periodic structure. For this structuring of the silicon surface to be clarified, we applied synergetic method.

The formation of defect structures like dislocation networks is the consequence of spatial instability of the distribution of dislocations in the crystal and their self-organization. There are two different conditions of behavior of the defect ensemble during plastic deformation. The plastic flow regime takes place for insignificant stresses and low defects density. This regime of plastic flow is carried out autonomously by external influences. At a certain magnitude of the stress, the coherent regime takes place, and the correlations effects between dislocations begin to appear [10-12].

Let us consider the following model (Figure 6). A semi-infinite plane X0Y is an interface Si-SiO_2. Let us fix some plane at a certain depth Z_1.

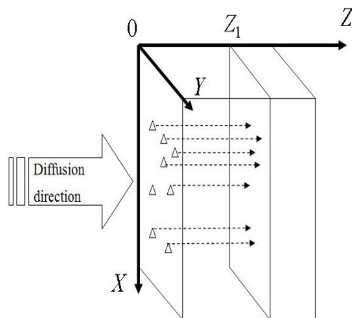

Figure 6. Diffusion model (triangles — dislocations on the surface, dash lines — directions of enhanced diffusion of oxygen).

During high-temperature oxidation in a given plane will be the processes that lead to the formation of structural defects, and to their annihilation. The kinetic equation for the dislocation density N_d in the given plane is

$$\frac{dN_d}{dt} = AN_d - BN_d^2 + CN_d N_o, \qquad (3)$$

where A is a constant characterizing the sources of the generation of structural defects, B is a constant characterizing the sources of the annihilation of dislocations, and here is characterized by a quadratic law [11], C is a constant characterizing the generation of dislocations due to stresses caused by the oxygen penetrated along the dislocation, N_o is an oxygen concentration.

It is obvious, that the concentration of oxygen in the given plane depends on the density of structural defects, along which occurs the enhanced diffusion. Thus, a case of self-consistency between the dislocation density and oxygen concentration takes place. If we assume that the interface XY is a constant source of oxygen then obviously the kinetic equation takes the form

$$\frac{dN_o}{dt} = D\, N_d - EN_o + FN_d N_o, \qquad (4)$$

where D is a constant characterizing the concentration of oxygen diffusing along dislocations, E is a constant characterizing the annihilation channels, F is a constant characterizing the increasing of oxygen concentration due to the generation of new dislocations. Coherent (autocatalytic) regime requires equality sign of the last term in (3) and (4), namely it must be positive to comply with the positive feedback.

We faced with nonlinear system (3)-(4) which does not have an analytical solution. Let us write the equations in dimensionless form

$$\frac{dN_d}{dt} = \frac{N_d}{t_1}\left(1 + \frac{N_o}{\nu} - \frac{N_d}{\theta}\right), \qquad (5)$$

$$\frac{dN_o}{dt} = \frac{1}{t_2}\left(\frac{N_d}{\eta} - N_o\left(1 - \frac{N_d}{\xi}\right)\right), \qquad (6)$$

where $t_1 \equiv 1/A$, $t_2 \equiv 1/D$ are characteristic times of the autonomous change the density of defects;

scales terms $\theta = A/B$ and $\eta = D/\varepsilon$ determine the density of dislocations without oxygen; characteristic densities $\nu = A/C$ and $\xi = D/F$ determine the intensity of the relative influence of defects. Let us introduce the dimensionless density of defects $y = N_d/\xi$, $x = N_o/\nu$ and dimensionless time $z = t/t_2$. Such parameter as $\alpha = t_2/t_1$ determines the ratio of characteristic times $\beta = \xi/\theta$ determines the intensity ratio of the generation and annihilation of defects and $\gamma = \xi/(\nu\eta)$ determines the relative intensities of the relative influence of dislocations and oxygen. In dimensionless quantities the system becomes

$$\frac{dy}{dz} = \alpha y\left(1 + x - \beta y\right), \qquad (7)$$

$$\frac{dx}{dz} = -x\left(1 - y\right) + \gamma y. \qquad (8)$$

As a matter of fact, the nonlinear equations (7)-(8) have the opportunity to be analyzed qualitatively for different values of the parameters α, β, γ. In order to generation rate of defects was greater than their annihilation, the following conditions $\beta > 1$, $\gamma < \left(\sqrt{\beta} - 1\right)^2$ must be met. The phase portrait is shown in Figure 7. Phase curves converge to the point Σ (coherent regime) which has an asymptote $N_d = (\xi/\nu)\left[(t_1/t_2) + (\xi/\theta)\right]^{-1} N_o$. On the one hand, the coherent regime is carried out by a high concentration of oxygen (the bottom of phase portrait). On the other hand, the coherent regime is carried out by increasing of dislocations (the top of phase portrait). However, it requires an initial density of defects (dislocations) exceeding a critical value which depends on many microparameters.

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 silicon region and dislocation network region. Generation of dislocation networks can be explained by accelerated thermodiffusion of oxygen atoms along initial structural defects that are present in silicon before high-temperature oxidation. In order to explain the generation of such periodical dislocation structure, it was applied the synergetic method.

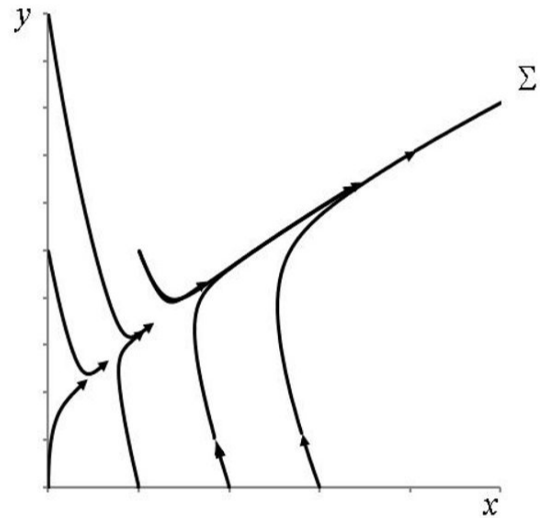

Figure 7. Phase portrait (dimensionless density of defects: y — dislocations, x — oxygen; Σ — coherent regime).

The formation of periodical dislocation structures at the interface is a consequence of the spatial instability of the dislocation distribution in the crystal and their self-organization due to correlation effects (coherent regime) between the oxygen atoms diffusing along structural defects and an ensemble of dislocations. The coherent regime could take place in the case of increasing of dislocations or a high concentration of oxygen.

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Abstract

The dislocation self-organization processes in near-surface silicon layers of Si-SiO$_2$ during high temperature oxidization have been investigated. It was observed the complex destruction of these layers caused by relaxation of mechanical stresses. We have proposed the defect formation mechanism of near-surface layers in Si-SiO$_2$ structure. For self-organization processes to be explained, the synergetic method was applied. It was shown that the formation of periodical dislocation structures at the interface is a consequence of the spatial instability of the dislocation distribution in the crystal, their self-organization due to correlation effects between the oxygen diffusing along structural defects and an ensemble of dislocations.

Key words: dislocations, self-organization, Si-SiO$_2$ structure.

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И. Р Яцунский

ЭВОЛЮЦИЯ СТРУКТУРНЫХ ДЕФЕКТОВ В КРЕМНИ, ВЫЗВАННОЕ ВЫСОКОТЕМПЕРАТУРНЫМ ОКИСЛЕНИЕМ

Резюме

Процессы самоорганизации дислокаций в приповерхностных слоев кремния в Si-SiO$_2$ при высокотемпературном окислении были исследованы в данной работе. Было определено, что появление сложной дефектной структуры вызвано релаксацией механических напряжений.

Было предложено механизм образования дефектов в приповерхностных слоях $Si-SiO_2$. Процессы самоорганизации объясняется, в рамках синергетического метода. Было показано, что формирование периодической структуры дислокации на границе является следствием пространственной неустойчивости распределения дислокаций в кристалле, их самоорганизации за счет корреляций между кислородом, который распространяется вдоль структурных дефектов и ансамбля дислокаций.

Ключевые слова: дислокации, самоорганизация, структура $Si-SiO_2$

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І. Р Яцунський

ЕВОЛЮЦИЯ СТРУКТУРНИХ ДЕФЕКТІВ В КРЕМНІЇ, ЯКЕ ВИКЛИКАНЕ ВИСОКОТЕМПЕРАТУРНИМ ОКИСЛЕННЯМ

Резюме

Процеси самоорганізації дислокацій в приповерхневих шарів кремнію в $Si-SiO_2$ при високотемпературному окисленні були досліджені в даній роботі. Було визначено, що поява складної дефектної структури викликано релаксацією механічних напружень. Було запропоновано механізм утворення дефектів у приповерхневих шарах $Si-SiO_2$. Процеси самоорганізації пояснюється, в рамках синергетичного методу. Було показано, що формування періодичної структури дислокації на границі є наслідком просторової нестійкості розподілу дислокацій в кристалі, їх самоорганізації за рахунок кореляцій між киснем, що поширюється уздовж структурних дефектів та ансамблю дислокацій.

Ключові слова: дислокації, самоорганізація, структура $Si-SiO_2$.