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Internal Stress Kinetics in Silicon and Silicon Oxide During Ion Irradiation

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Theoretical calculations of ion-induced stress in SiO_2-Si system are done using a model where stress in plane is expressed in terms of elementary volume related to the point defect. Stress - strain dependence is defined taking in account relaxation processes in the ion irradiated solid. It is demonstrated that proposed model describes average stress dependence versus ion dose and energy. In addition to the stress due to radiation defects and implanted ions, additional source of the compressive stress (an increase of thickness of silicon oxide with the increase of ion energy and interface modification due to extra oxygen atoms) is involved

Keywords: ion irradiation, stress, silicon, silicon oxide, amorphisation, point defect, relaxation processes.

1.INTRODUCTION

Ion irradiation induced strain and stress in silicon or silicon oxide is subject of many articles dealing with ion implantation [1 – 7]. Dependence of the stress (or strain) on the ion dose, energy, kind of ions, stress relaxation processes are the key problems that are solved in the recent articles on this subject. Sophisticated experiment [1, 2] were done to study stress in the silica, silicon oxide or silicon induced by light ion irradiation (H^+, He^+, $E = 50 – 430$ keV, $\Phi = 10^{18}$ cm^{-2}), average mass ion irradiation [2] (Ar^+, $E = 80$ keV, $\Phi = 10^{14}$ cm^{-2}) and heavy ion irradiation [3] (Xe^+, $E = 2$ MeV, $\Phi = 10^{14}$ cm^{-2}). It was shown that ion irradiation induces tensile stress in the SiO_2 implanted region [4] (Xe^+, $E = 0.27 – 4$ MeV, $\Phi = 10^{14}$ cm^{-2}) and compressive strain in the silicon [5] (Ar^+, $E = 50 – 175$ keV, $\Phi = 10^{17}$ cm^{-2}). Usually stress in the crystalline silicon is increased with the dose of ion irradiation and maximum values of stress ($10^8 – 10^9$ Pa) is reached in the region of dose close to the amorphisation dose.

In the present paper stress in plane is expressed using elementary volume related to the point defect, and stress - strain dependence is defined taking in account relaxation processes in the ion irradiated solid.

2. THEORETICAL MODEL OF ION INDUCED INTEGRAL STRESS

2.1. Integral stress in silicon

We assume that point defects are the source of strain in the ion implanted surface layer. Elastic forces appear in the vicinity of point defect: vacancies induce compression and interstitial - tension in the crystal lattice. Let's note relative increment of the atomic volume due to vacancy as $\frac{\Delta\Omega_v}{\Omega}$, due to interstitial as $\frac{\Delta\Omega_i}{\Omega}$ and implanted ion as $\frac{\Delta\Omega_{ion}}{\Omega}$ (where Ω is atomic volume in the crystal). Usually $|\Delta\Omega_v| < \Delta\Omega_i$. As a result, Frenkel pair produced by ion irradiation induces local expansion of the lattice. It should be noted as well that expansion of the lattice depends on the concentration of vacancies n_v, interstitials n_i and implanted ions n_{ion}. Taking in account all the components, biaxial strain tensor in plain ($\varepsilon_{11} = \varepsilon_{22} \equiv \varepsilon_{in}$) we can express as following:

$$\varepsilon_{in} = \frac{1}{3}\left(\frac{n_v}{n_0}\frac{\Delta\Omega_v}{\Omega} + \frac{n_i}{n_0}\frac{\Delta\Omega_i}{\Omega} + \frac{n_{ion}}{n_0}\frac{\Delta\Omega_{ion}}{\Omega}\right), \quad (1)$$

where n_0 is particle density in the crystal.

In our model we assume that density of the vacancies and interstitials is the same ($n_v = n_i \equiv n$) and defect concentration at the depth x can be calculated according to:

$$n(x) = F_d(x)\Phi_n(1 - \exp(-\Phi/\Phi_n)), \quad (2)$$

where $F_d(x)$ is the function describing distribution of vacancies and interstitials versus depth, Φ is ion dose and Φ_n is characteristic dose of formation of Frenkel pair.

Ion concentration can be defined from:

$$n_{ion}(x) = F_{ion}(x)\Phi, \quad (3)$$

where $F_{ion}(x)$ is the function describing ion distribution versus depth.

As was mentioned in the Introduction, ion induced stress is proportional to the ion dose (or time of irradiation) in the low ion dose region only. When the dose of ion irradiation reaches amorphisation dose, relaxation process of the stress takes place. Expression for the planar stress relaxation can be found from the Boltzmann - Wolterra's equation [8]:

$$\sigma_{in} = -\left(Y(\varepsilon_{in}(\Phi)) - \int_0^{\Phi}\Gamma(\Phi - \Phi')\varepsilon_{in}(\Phi')d\Phi'\right), \quad (4)$$

where Y is the biaxial elasticity modulus, $\Gamma(\Phi)$ is the nucleus of integral transformation of (4).

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Let's assume that elastic viscous medium can be described using a model of Maxwell:

$$\Gamma(\Phi) = \Phi_r^{-1} \exp(-\Phi / \Phi_r), \quad (5)$$

where Φ_r is a characteristic dose of stress relaxation.

From equation (1) – (4), stress and integral stress S can be expressed as:

$$\sigma_{in} = Y\left(\frac{AF(x)\Phi_r \Phi_n}{\Phi_r - \Phi_n} \left(\exp(\Phi / \Phi_n) - \exp(\Phi / \Phi_r)\right) - \right.$$
$$\left. - D\Phi_r F_{ion}(x)\left(1 - \exp(\Phi / \Phi_r)\right)\right) \quad (6)$$

$$S = Y\left(\frac{AKrE_0}{2E_d} \frac{\exp(-\Phi / \Phi_n) - \exp(-\Phi / \Phi_r)}{\Phi_r - \Phi_n} - \right.$$
$$\left. - D\Phi_r \left(1 - \exp(-\Phi / \Phi_r)\right)\right) \quad (7)$$

Where $A = (3n_0)^{-1} \left(\frac{\Delta\Omega_v}{\Omega} + \frac{\Delta\Omega_i}{\Omega} \right)$,

$D \equiv (3n_0)^{-1} \Delta\Omega_{ion} / \Omega$, $K = 0.6 - 0.8$, E_d is the atom displacement energy and r equals to the part of energy of ion lost in nuclear processes.

2.2. INTEGRAL STRESS IN SILICON OXIDE

In the high dose region (10^{14} cm^{-2}) integral stress in silicon is relaxed down to low values [3]. But at the same time integral stress in silicon oxide keep being as high as a maximum stress in silicon (~10^8 Pa) [4]. To describe this high residual stress, phenomenological parameter ("anisotropic strain" - strain perpendicular to the surface of the sample) is used in [4]. It should be stressed that diffusion like mass transport contributes mainly to the anisotropic strain and stress due to ion implantation induced strain is only a part of the total stress in this case [9].

In this work we assume that residual stress in silicon oxide is due to implanted ions and molecular oxygen accumulation (that is related to the stoichiometry variation of SiO_2) According to our model tensile stress appears in the surface layer of silicon oxide with a lack of oxygen and compressive stress due to implanted ions dominates at deeper layers.

Let's consider thermally formed SiO_2 layer on the silicon substrate. During cooling down of the Si-SiO_2 system, strain due to difference of thermal expansion coefficients is induced in this system. Strain at any temperature T can be expressed as follows:

$$\varepsilon = (\alpha_1 - \alpha_2)(T - T_0), \quad (8)$$

where α_1 and α_2 are the thermal expansion coefficients of silicon oxide and silicon respectively, T_0 is the oxide formation temperature.

The second component of the strain is related to the increase in density of oxide due to ion irradiation. Strain tensor related to the density variation from ρ to $\rho + \Delta\rho$ we express as [4]:

$$\varepsilon_\rho = -\frac{\Delta\rho}{\rho}\left(1 - \exp\left(-\frac{\Phi}{\Phi_\rho}\right)\right), \quad (9)$$

where Φ_ρ is the characteristic dose of densification.

The third component of the intrinsic strain as was discussed is related to the molecular oxygen formation. Due to Si-O bond breaking along the ion track in silicon oxide, atomic oxygen is formed. It can relax and form Si-O bond again, or it can form molecular oxygen that is accumulated at the free tethraedric space. This process saturates at low doses (for the xenon ions this critical dose is 10^{13} Xe/cm^{-2}) and the further increase in density is stopped by the accumulated oxygen. Oxygen vacancies are formed in the silicon oxide if the radiation is continued. In the region of doses 10^{13} Xe/cm^{-2} and higher an additional compressive component appears as a result of oxygen vacancies.

In our model we assume that gradient of stress due to implanted ions is responsible for the pushing out of oxygen from the tethraedric space. Thus, oxygen atoms diffuse in the direction of implanted surface if $x < R_p$ and they diffuse in the direction of SiO_2-Si interface if $x > R_p$, where R_p is projected range of the ions. If the "pushing out" of the oxygen atoms dominates, compressive strain dominates in the surface layer.

Let's assume that the number of O_2 molecules leaving a unit volume of the oxide is linear proportional to the ion current density $F(x)\Phi$ where $F(x)$ is a function describing depth distribution of ions. Let's note the average free tethraedric space as Ω and changes of this space due to pushing of the oxygen molecule as $\Delta\Omega_1$ ($\Delta\Omega_1 < 0$) and corresponding component of the strain tensor in the surface layer ($x < R_p$) as:

$$\varepsilon_1 = \frac{1}{3}\frac{F(x)}{n} N \frac{\Delta\Omega_1}{\Omega}\Phi, \quad (10)$$

where n is density of the tethraedric free volumes, N number of O_2 molecules pushed out by one ion.

In the successive layer ($x > R_p$) oxygen vacancies are not produced in average and compressive stress only due to implanted ions is produced. If the increase of the free tethraedric space due to implanted ions we shall note as $\Delta\Omega_2$ ($\Delta\Omega_2 > 0$) corresponding component of the strain tensor one can express as:

$$\varepsilon_2 = \frac{1}{3}\frac{F(x)}{n}\frac{\Delta\Omega_2}{\Omega}\Phi. \quad (11)$$

Resultant strain tensor can be expressed as a sum of components: thermal component, density component and ion - oxygen component $\varepsilon(x,\Phi) = \varepsilon_T + \varepsilon_\rho + \varepsilon_i$, where $i = 1; 2$. As a result, stress distribution versus depth is not uniform and follows the distribution of implanted ions. First (external) region of the sample is under tensile stress and the second one (internal) is under compressive stress.

Ion irradiation induced stress is elastic in the region of small doses only ($\Phi < 10^{12}$ Xe/cm^2). Further ion irradiation results in the relaxation of the stress like it was demonstrated in the case of silicon. Biaxial stress relaxation during ion irradiation can be described by (4). Combining (4), and (8 – 11), one can write biaxial average

stress (that is measured usually in the experiment (e.g. cantilever technique)) expression

$$\sigma_{in} = -Y\varepsilon_T e^{-\Phi/\Phi_r} + \frac{Y\Delta\rho\Phi_r}{\rho(\Phi_\rho - \Phi_r)}\times$$
$$\times\left(\exp(-\Phi/\Phi_\rho) - \exp(-\Phi/\Phi_r)\right) - \quad (12)$$
$$-\sigma_{sat}\left(1-\exp(-\Phi/\Phi_r)\right)$$

where:

$$\sigma_{sat} = \frac{Y\Phi_r}{6n\delta}\left(\frac{N|\Delta\Omega_1|}{\Omega} - \frac{\Delta\Omega_2}{\Omega}\right) \quad (13)$$

is average saturated stress in the implanted layer. Thickness of the implanted layer δ is defined as the width at the half height of ion distribution $F_{ion}(x)$. It is assumed as well that thickness of the first layer is equal to the one of the second layer: $\delta_1 = \delta_2 \equiv 2^{-1}\delta$.

The first member in (12) describes thermal stress ($\sigma_T < 0$), the second one stress due to densification ($\sigma_\rho > 0$), and the third one - stress due to implanted ions and molecular oxygen (σ_Ω). In the region of high doses the first two members relax to zero and resultant stress is approaching residual saturated stress value.

3. RESULTS AND DISCUSSIONS

3.1 Stress in silicon induced by Ar^+ ion irradiation

In our model we consider Φ_n and Φ_r as the parameters corresponding to the maximum values of integral stress. In our calculations $\Phi_n = 10^{19}$ m^{-2} and $\Phi_r = 2\times10^{18}$ m^{-2} were used.

Dose of amorphisation for silicon at the room temperature equals to $(1.5-4)\times10^{14}$ cm^{-2} for the argon ions with energy 50 – 150 keV. This range of doses corresponds to the maximum of stress and position of the stress is slightly influenced by the ion current density and ion energy according to our calculations. Influence of ion component on the stress level can be found for the high dose region only ($\Phi > 10^{15}$ cm^{-2}). Contribution of this component for the sample temperature equal to the room temperature is not higher than 10 % of the maximum stress value. Integral stress is proportional to the total number of defects and as a result stress is proportional to the ion energy. This fact was found experimentally [5].

3.2. Stress in SiO_2-Si system induced by Xe^+ ion irradiation

Average stress induced by ion irradiation was calculated using (12) and (13). The main parameters used in the calculations are presented in Table 1. Ion distribution versus depth was calculated using standard TRIM program [10]. Displacement energy for the SiO_2 (thickness of SiO_2 layer – 1.8 μm) and silicon (thickness of Si – 300 μm) was 15 eV and 20 eV respectively. Biaxial Young's modulus for the silicon oxide used in our calculation was $Y = 100$ GPa. Mean period of the free tethraedric space in silicon oxide was chosen 1 nm [11] and corresponding density $n = 10^{21}$ cm^{-3}.

Table 1. Values of the parameters used in the calculations: (Φ_ρ is characteristic dose of densification, Φ_r is dose of relaxation of the stress, δ is the effective thickness of implanted layer, $\Delta\Omega_2\Omega^{-1}$ is a parameter describing contribution of the ions to the stress level in the second layer)

E_0 [MeV]	Φ_ρ [4] [10^{12} cm^{-2}]	Φ_r [10^{12}cm^{-2}]	δ [μm]	$\Delta\Omega_2/\Omega$
0.27	7.0	7.8	0.09	11.7
1.25	8.2	9.72	0.26	1.3
2.9	8.7	10.74	0.57	6.1
4.0	11.2	12.6	0.60	38.5

In the stationary case when stress is saturated it can be shown that strain $\varepsilon_1 \equiv N|\Delta\Omega|_1\Omega^{-1}$ doesn't depend on the ion energy and the best fitting of experimental results is obtained if $\varepsilon_1 = 25|\Delta\Omega_1|\Omega^{-1}$ i.e. number of molecules of oxygen pushed out from the first layer by one ion $N > 25$. This value corresponds to the density of molecules of oxygen pushed out from the unit volume $\sim(10^{21}-10^{20})$ O_2/cm^3 when silicon oxide was irradiated with Xe^+ ions ($\Phi = 10^{14}$ Xe/cm^2 , $E_0 = (0.27-4)$ MeV). This value is comparable with the density of molecules of oxygen (10^{20} cm^{-3}) used in [12] when silicon oxide was irradiated by P^+ ions ($\Phi = 2\times10^{16}$ cm^{-2}, $E_0 = 180$ keV).

Contribution of the implanted ions on the strain in the second layer depends on the ion energy (Table 1). This fact can be explained as an influence of implanted ions as well as contribution of oxygen knocked – in the silicon. Additional source of the compressive stress is an increase of thickness of silicon oxide with the increase of ion energy and interface modification due to extra oxygen atoms.

The main results of calculations are shown in Fig. 1 where compressive stress is shown as positive stress and tensile stress as a negative one. Residual stress in SiO_2 - Si system ($\Phi = 0$) corresponds to the thermal stress ($T = 293$ K) and is equal to 3×10^8 Pa. In the very beginning of ion irradiation tensile stress (negative) arises and the reason of this is densification of silicon oxide. At the dose $\Phi = 0.5\times10^{13}$ cm^{-2} resultant average stress is equal to zero. Maximum stress is equal to $(3-4)\times10^8$ Pa and this value is reached at the doses $\Phi_m = 1.2\times10^{13}$ cm^{-2}. Further irradiation ($\Phi > \Phi_m$) reduces stress and stress in the dose region $\Phi \approx 5\times10^{13}$ cm^{-2} is negligible.

Contribution of the oxygen vacancies to the stress level at the first layer and contribution of ions and oxygen atoms at the second layer are essential for the doses $\Phi \le \Phi_r$. They saturate at the doses $\Phi \approx 5\times10^{13}$ cm^{-2}. Saturation stress is not uniform versus depth (both - magnitude and the sign) and its value depends on the ion energy. Average

saturation stress is the tensile one up to energies $E_0 = 3.5$ MeV and it is compressive for higher energies. Saturation stress equals to zero for 3.5 MeV.

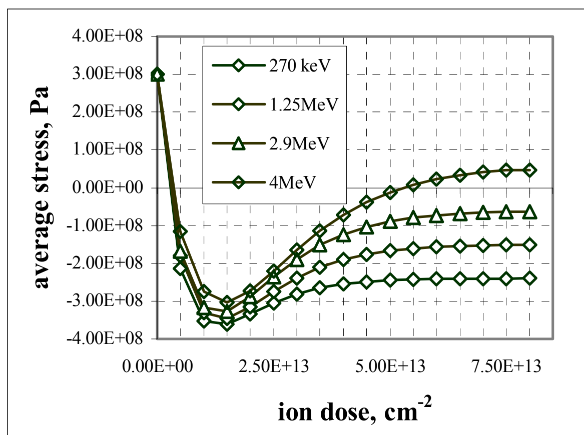

Fig. 1. Calculated dependence of the average stress in the SiO_2-Si system implanted with Xe^+ on the dose and energy of ions

In summary, our proposed theoretical model describes ion induced stress dependence on ion dose, energy, as well as stress distribution versus depth of implanted SiO_2 - Si system.

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