Oxygen precipitate positive charge evolution upon annealing of oxygen implanted silicon

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Abstract. Oxygen precipitates (OPs) formed by the annealing of oxygen implanted silicon samples at diverse temperatures in the ranges from 700°C to 1100°C have been investigated with capacitance-voltage and transmission electron microscopy techniques. An increase of the OP sizes with the increasing temperature was found to accompany with a decrease of the OP embedded positive charge being inversely proportional to the formers. The obtained result showed that the positive charge is localized in SiOₓ shell of predominantly stoichiometric OP core.

1. Introduction

It is well known that oxygen precipitates (OPs) in silicon can change their size, shape and an average composition depending on the annealing conditions. During many decades the variation of the SiOₓ OP composition has been investigated on an empirical level but recently Kot and Kissenger [1] showed that the structure of the OP is non-uniform consisting of the internal SiO₂ amorphous nucleus bounded by a SiO shell outside (see also Vanhellemont [2] for recent review and the model).

The study of the electrical and recombination characteristics of OPs in silicon revealed that they possess an embedded positive charge (EPC) [3] and an extended distribution of energy states in the silicon band gap [4, 5] as well as a broad luminescence band at around 0.84 eV [6] that were associated with the OPs/silicon interface. From the OP core-shell structure described above [1] it is natural to assume that the EPC and the trap states are confined at the SiO interface and the former value has to follow the variations of the OP sizes upon annealing.

Oxygen implanted samples obtained with the appropriate ion energy are a good model object to quantify EPC by means of the capacitance-voltage (CV) measurements. In this paper we combined such measurements with transmission electron microscopy (TEM) estimation of OP geometry to find out the relationship between EPC value and characteristic OP sizes that was varied upon annealing.

2. Experimental

n-type (Nᵣ=1.5x10¹⁵ cm⁻³) Cz-Si wafers with the surface orientation (100) were used for investigations. The first series of the samples was implanted by oxygen with energies of 350/225/150 keV and doses 1.5x10¹⁵/0.9x10¹⁵/0.7x10¹⁵ cm⁻², to create nearly constant oxygen profile in the depth from 300 to 800 nm from the surface (in the following “multi-energy” (ME) samples). The second series of the sample was subjected to oxygen implantation with energy 150 keV and with doses 1.5x10¹⁵ cm⁻² to
create an oxygen layer at a depth about 400 nm (in the following “single-energy” (SE) samples). Wafers were subjected to the annealing in the clorine-contained atmosphere for 0.5h at the temperatures 700°C, 800°C, 900°C, 950°C, 1000°C, 1100°C. The sample without implantations and annealing was used as a reference.

For electrical measurements gold Schottky contacts were evaporated on the implanted surface whereas InAl ohmic contacts were rubbed on the backside of the samples. The total value of EPC was retrieved from the data of capacitance-voltage measurements at room temperature.

The thin cross-section foils for TEM investigations were fabricated by mechanical polishing with the subsequent polishing by low-energy Ar ions irradiation.

3. Results
Examples of TEM images of the cross-section of ME-samples annealed at 700°C, 950°C and 1100°C are shown in figure 1 A, B, C respectively. A variation of extended defect structure upon the annealing is obvious. The main feature of the sample annealed at 700°C is the dot-like contrasts of an average size of about 5 nm (fig. 1 A). They distributed rather uniformly within a layer 300-800 nm from the surface coinciding well with the expected distribution of implanted oxygen making the most probable interpretation of the contrasts as nuclei of OPs. The absence of extended defects is due to a low annealing temperature which is not sufficient for the aggregation of implantation-induced point defects.

![Figure 1. TEM images of ME-samples annealed at A) 700°C, B) 950°C, C) 1100°C. A) Dark-field, B, C) bright-field images.](image)

Annealing at 950°C for a half-hour (fig. 1 B) resulted in the appearance of lens-like contrasts of oxygen precipitates with averaged sizes of about 30 nm and of Frank dislocation loops. The shapes of every particular OP could not be defined accurately due to their high density but according to previously obtained data, in the temperature range 900°C-1000°C the OPs, besides growth, can transform from discs form into octahedral one [7]. The half-hour annealing at 1100°C (fig.1 C), as well as prolonged annealing at 1000°C [4], led to an increase of OPs sizes to about 50 nm and to appearance of long segments of gliding dislocations.

Fig. 2 A represents inverse square capacitance, C, of the diodes as a function of applied voltage, V, measured at room temperature. At sufficiently high reverse bias the dependences C^2(V) are linear and their slopes are nearly equal for all implanted and annealed (except at 700°C) as well as for reference sample which indicates the constant value of the net-donor concentration in the bulk. The extrapolation of the linear parts of the curves to zero value of C^2(V) (see arrows in fig. 2 A) gives the effective built-in voltage value, V_b. It is of about V_{b,ref} = +0.7 V for reference sample but has a negative value for all implanted and annealed samples indicating the presence of an excess positive charge in the implanted region that decreases with the increase of the thermal treatment temperature.

The concentration of the EPC confined in the implanted region from x_1 to x_2 can be calculated from built-in voltage changes (\Delta V = V_b - V_{b,ref}) as [8]:

\[ C^2(V) = \frac{C^2(0)}{V_b^2} \text{ for } V < V_b \]
\[ C^2(V) = \frac{C^2(0)}{V_b^2} \text{ for } V > V_b \]
and accordingly, decreases 1.6-

2.1, and 4.0.

2.2, 8.0, and 10.0.

1.0, 0.8, 0.6, 0.4,

0.2, 0.1, 0.0.

1000 -

900 -

800 -

700 -

600 -

500 -

400 -

300 -

200 -

100 -

0-

10
20
30
40
50
60
70
80
90
100
110

[O+] = \frac{2e\epsilon_0 \Delta V}{e(x_2^3 - x_1^2)}

For the implanted sample annealed at 700°C, the positive charge concentration was so large that the internal edge of the implanted region, and linear part of C²(V) dependence, could not be reached at any applied reverse voltages due to increased leakage current. In this case the applied voltage maximum value was taken for the charge estimation.

The presence of the excess positive charge became apparent also in the net-donor concentration profiles shown in fig. 2 B. The profile shapes for all ME-samples and SE-900°C coincide well with expected implanted oxygen ones. At lower annealing temperatures, the apparent donor concentration exceeds the bulk value by two orders of magnitude but the profiles are shifted closer to the surface than expected. This might be due to the contribution of the electron trap response that increases the measured value of capacitance, and accordingly, decreases the calculated depth values. Nevertheless, one can show that such effect does not distort significantly the defined total charge value.

The dependence of the EPC per implanted oxygen on the annealing temperature is presented in figure 3 A. One can see that the values retrieved by two estimated method coincide well for the samples annealed at T ≥ 800°C. Though there is a difference between the data for the sample annealed at 700°C, the EPC in this sample significantly larger than in other ones. For all annealing temperatures, the EPC per implanted oxygen atom is very small, less than 4x10⁻³, that indicates the most part of implanted oxygen remains neutral.

Figure 3. EPC per implanted oxygen atom in elementary charge units retrieved from the net-donor concentration profiles (open dots) and from the diode built-in voltage changes (filled squares) as functions of the annealing temperature (A) and of the inverse average precipitate radius (B).

4. Discussion
At all annealing temperatures (700°C-1100°C) after oxygen implantation and annealing silicon wafers, the embedded positive charge was detected. According to our TEM results the samples annealed at temperatures above 800°C contain well distinguished OPs. For such kind of the samples the EPC can be formed only by the OPs as the thermodonors as well as most clusters of intrinsic defects disappear at heat treatments above 600°C[9]. New thermodonors, which have been found at such high-temperature RTA treatment [10], was shown not to change their concentration upon annealing above 700°C and could not be, thus, responsible for the strong charge variation observed in this work (see figure 2 A).

For the 700°C annealing sample where only defects with a rather small size were registered by TEM, the complexes of intrinsic point defects like 113 (rod-like) defects [11] could be also candidates for the EPC. However, for the best of our knowledge, there are no data available about the charge state of the rod-like defects and we assume that in that case also the EPC is mainly localized on the states of small OPs.

The OPs states, localizing on the interface precipitate-silicon [3] as well as the positive charge can be caused by broken bonds due to the oxygen deficit on the interface SiO$_x$ states [1]. At the same time, SiO$_2$ nuclei [1] of precipitate due to the absence of broken bonds should be neutral or nearly neutral. According to these considerations, the EPC must be proportional to the ratio of the SiO$_x$ molecules quantity in the shell to the total amount of oxygen in the OPs. For a small shell thickness and sphere-like OPs a linear EPC dependence on an inverse OP radius is expected and the slope of this dependence determines the total oxygen concentration contained in OPs.

The results of the calculation of the dependence taking SiO shell thickness of 1 nm and the experimental data on the inverse radius of precipitates determined from the TEM results is shown in figure 3 B with a solid straight line with the line slope as the only fitting parameter. A good agreement between the model and the experimental data indicates that the total amount of oxygen in OPs conserves upon annealing. It should be noted that for disc-like OPs expected at low annealing temperatures [12], the model is still valid except small changes in the line slope and its intersection with abcissa that can not be distinguished based on available data.

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