Microfluctuations of oxygen impurity concentration as a reason of accelerated oxygen diffusion in silicon

V.B. Neimash[1], O.O. Puzenko[1], A.M. Kraitchinskii[1], M.M. Kras'ko[1], S.Putselyk[1], C. Claeys[2,3] and E. Simoen[2]

[1]*Institute of Semiconductor Physics of NASU, 45, prospect Nauki, 03028, Kyiv, Ukraine*
[2]*IMEC, 75, Kapeldreef, B-3001 Leuven, Belgium*
[3]*KU Leuven, ESAt-INSY, 94, Kardinaal Mercierlaan, B-3001 Leuven, Belgium*

Abstract. Activation energy of thermal donors annealing increases from 1.7 to 2.5 eV on preliminary heat treatment of the Si crystals at 800°C. It is believed that this fact results from the dissolution of oxygen microfluctuations that are considered to be sources of intrinsic elastic strains and thereby to lie at the basis of locally accelerated oxygen diffusion.

Keywords: silicon, thermal donors, diffusion of oxygen, annealing parameters.

1. Introduction

The efficiency of the formation of oxygen containing thermal donors (OTD) at 450 °C depends strongly on the use preliminary heat treatment (PHT) of silicon crystals [1,2]. One of the reasons might be the dissolution during the PHT of some of the OTD nucleation centers, which are always present in the as-grown crystal [3]. According to the Kaizer -Frisch -Reiss (KFR) model [4] the formation of thermal donor complexes, SiO_m, are a result of further oxygen incorporation in already formed SiO_{m-1} complexes. The drawback of this model is the requirement of an enhanced oxygen diffusion at 450 °C by a few orders for the formation of complexes even with $m = 2$. It is even more difficult to explain existence of the OTD microclusters observed in the past [5-8]. A possible explanation may be the assumption that in as-grown Si crystals there exist microfluctuations in the oxygen concentration (OMF), so that the oxygen concentration is strongly localy enhanced [9]. As in this case the oxygen atoms are rather close to each other, the time needed to form complexes is much shorter. Besides that, the oxygen diffusion in strongly strained areas of a crystal, as in the case of the OMF neighbourhood, can considerably differ from that of nonstrained bulk regions. Thus, it is

possible to consider the OMF as nuclei for the OTDs. However, their influence on the kinetics of generation and annealing of the OTD (after a preliminary high-temperature treatment) can essentially differ from the influence of SiO_{m-1} nuclei. The aim of the present work was to determine which of two above described concepts about the nature of the OTD nuclei is in better agreement with the experimental observations. For that purpose, the impact of an initial high temperature heat treatment at 800 °C on the generation and annealing of 450 °C OTDs was studied in detail.

2. Experimental

The studied *n*-type Si had an initial resistivity (ρ) in the range of 150–170 Ohm·cm. Oxygen and carbon concentrations determined by measuring on 10×3 mm^2 samples the infrared absorption spectra in the vicinity of 9.1 and 16.5 μm, were equal to $(8\div10)\cdot10^{17}$ cm^{-3} and $< 5\cdot10^{16}$ cm^{-3}, respectively. Measurements of ρ were carried out by the «four-probes method» at room temperature. Free electron concentration (n_e) was determined through ρ (the value of electron mobility was assumed to be equal to 1350 см^2/ Vs). Total (i.e. all kinds) concentration of thermal donors (N_{td}) was determined from a difference of

(n_i - n_o), where n_o, n_i are concentrations of free electrons in initial and heat treated samples, respectively. Three groups of samples were picked up according to initial ρ: I - 150, II - 160, III - 170 Ohm·cm. Both HT and measurements were carried out with sets of samples in which one sample from each group was included . Isothermal heat treatment at (450±1) °C in the air was applied for generation of the OTD. The treatment step interval was equal to 5÷20 minutes. The measurements were made in the same place of a sample after each step.

3. Results and Discussion

Typical dependencies of N_{td} and dN_{td}/dt versus 450 °C heat treatment duration are shown on Fig. 1 and on 2 for initial samples and for samples, previously treated at 800 °C during 30 minutes, accordingly. It is obvious that generation of OTD is much slowed down after PHT at 800 °C. The IR-absorption band of oxygen after such PHT does not practically change. It testifies to absence of significant changes in phase conditions of the main part of oxygen atoms in crystals under study. The rate of OTD generation (dN_{td}/dt) changes with duration of HT at 450 °C in all cases. It is increased in samples after PHT (800 °C) while in initial samples it is decreased with the rate compared to that in start moment. This result is similar to that observed in [2, 10], and it can be explained with the same efficiency by an influence of the PHT (800 °C) on
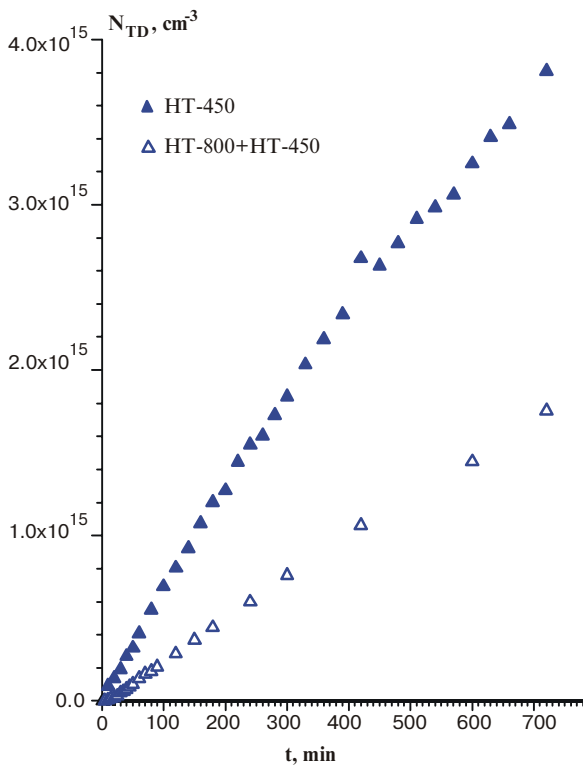

Fig.2. Dependence of thermodonor formation rate on heat treatment time at 450 ^{0}C.

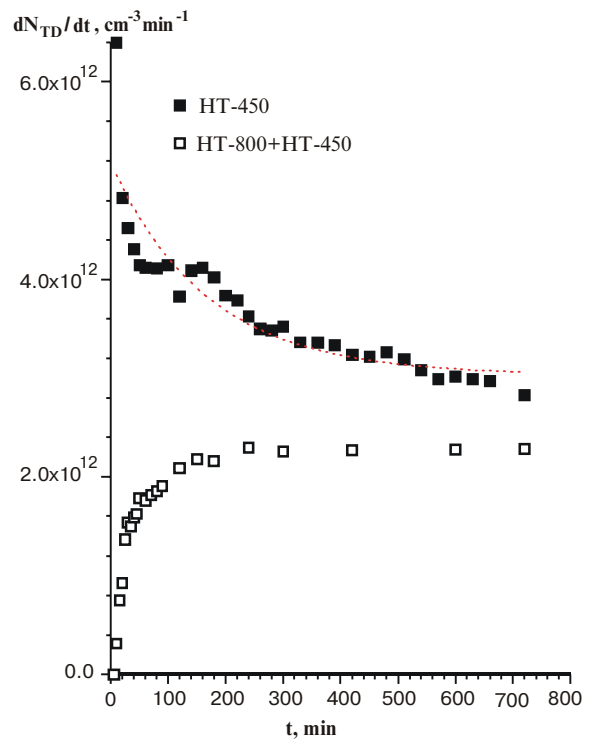**Fig.1.** Dependence of thermodonor concentration on heat treatment time at 450 ^{0}C.

nuclei of both discussed above types of models. In the first case this influence is reduced by dissolution of SiO_{m-1} precipitates. In the second one, by «dispersion» of the OMF as a result of both diffusion and precipitation of oxygen atoms in the another most dense central parts of OMF. To choose that or an other type of nuclei becomes possible with experiment upon the PHT (800 °C) influence on annealing the OTD. Really, if the nuclei are homogeneously allocated SiO_{m-1} precipitates, the PHT (800 °C) can only reduce their number (and the OTD generation rate), but it is not capable to influence on annealing the OTD. If the nuclei are the OMF, then it is possible to expect influence of the PHT (800 °C) on the OTD annealing kinetics because of their mutual influence. In this case, the OTD are in microclusters with large local concentration in a place of OMF localization in an initial crystal [5]. Point defects, being in a deformation field of other defects (for example, the A - centres in areas of clusters after neutron irradiation or close dislocations), can essentially change parameters of annealing [11]. The PHT (800 °C) is capable to reduce local concentration of oxygen in the OMF and, accordingly, local concentration of the OTD in microclusters. Therefore, it is possible to expect change of the OTD annealing kinetics after the PHT (800 °C) owing to decrease of mutual influence of the OTD.

Annealing of the formed at 450 °C OTD was studied by us at two temperatures: 510 and 515 °C. At these temperatures, in addition to annealing of the OTD-450, for-

mation of other kinds of the OTD takes place. However, effective rate of their generation is at least 5 times less than annealing rate of the OTD-450. Therefore, it is possible to neglect their contribution in kinetics of the electron concentration change taking place during annealing. As an example, dependence of thermal donors concentration on annealing time at 515 °C is shown in Fig. 3: without the PHT and after the PHT-800. The same dependence was obtained for annealing at 510 °C. In Fig. 3 points correspond to data of experiment, continuous lines corresponds to computer approximation by an exponential function of the kind $y = A_0 \exp(-t/\tau)$. Numerical values of both τ parameters are shown there.

It is obvious that the experiment is well described by an exponent. It takes place in all twelve samples. It can be seen from figures that the PHT at 800 °C considerably slows down the process of OTD-450 annealing at 510 and 515 °C. As was marked above, this result can provide arguments for the second point of view about a nature of nuclei for formation of the OTD (micro-fluctuation of oxygen concentration). That is, increase of microhomogeneity of spatial distribution of oxygen owing to preliminary PHT (800 °C) results in more microhomogeneous distribution of the OTD as well. In other words, microclusters of the OTD, formed in previously treated at 800 °C crystals, are more lax. As a result, the interdependence of the OTD in the microclusters (by elastic strains) decreases and the effect of accelerated annealing of defects in that clusters is decreased as well.
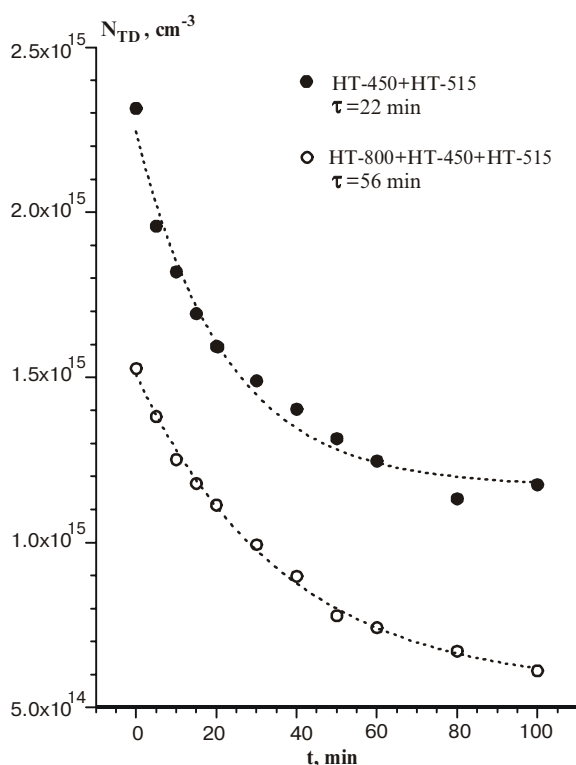
Really, the activation energy (E_a) and frequent factor ν of annealing, determined by us from annealing of the OTD-450 at 510 and 515 °C, are much increased after the PHT at 800 °C. For various groups of samples: $E_a = 1.64 \div 1.88$ eV, $\nu = 6.3 \cdot 10^8 \div 2.3 \cdot 10^7$ s^{-1} without the PHT and $E_a = 2.3 \div 2.47$ eV, $\nu = 1.8 \cdot 10^{11} \div 2.4 \cdot 10^{12}$ s^{-1} after the PHT-800. The rather wide range of values of these parameters (an error of a method: $E_a = \pm 0.05$ eV and $\Delta\nu = \pm 50$ %) is apparently caused in both cases by macroheterogeneous (in scale of distance between probes) distribution of themselves microfluctuation. The following fact can say about it. A generation rate of the OTD can differ by 4 times in measurements with the four-probes method using 1 mm-distance between measuring probes though the integrated concentration of oxygen differs from sample to sample less than 20 %. The results of measurement in a group of 12 samples display the general tendency to increase an activation energy and frequent factor of annealing of the OTD after PHT-800. Such increase is not possible to explain by reduction of concentration of SiO_{m-1} nuclei precipitation. If we assume, that nuclei are the OMF proper, change of annealing parameters is possible to explain by an influence of lattice elastic strains which are caused by both the OMF and the OTD-clusters . The similar approach was used in [11] where influence of dislocations on annealing parameters of radiation defects was examined in Si.

In accordance with the KFR model, diffusion of oxygen atoms is the main factor limiting both formation and annealing processes of the OTD. Hence, the change of E_a can reflect change of conditions for oxygen diffusion. Then the increase of E_a after the PHT-800 means delay diffusion of oxygen in the vicinity of thermodonor clusters and inside them. It can be caused by reduction of local elastic strain of a crystal inside clusters of the OTD owing to a dispersion of oxygen microfluctuation in the course of the PHT-800. As it could be seen from results, $E_a = 2.3 \div 2.47$ eV for «slowed down» (after the PHT-800) diffusion, that is close to a value of activation energy for diffusion of dispersed oxygen [12]. In the case without the PHT-800 we have $E_a = 1.64 \div 1.88$ eV. It corresponds to activation energy of OTD-450 generation [13], and for an explanation of which the assumption about «accelerated» diffusion of oxygen was involved [13]. Being based on obtained results, it is possible to assume that accelerated diffusion of oxygen during generation of the OTD is inherent only for those atoms of oxygen which are placed in strained areas of a crystal inside microfluctuations with high oxygen concentration. Their part in total oxygen does not apparently exceed 1–2 % [9]. However, it is quite enough for explanation of real rates of generation of the OTD in the initial stages. From the point of view of such approach we shall analyse quantitatively obtained experimental results.

Now we shall examine 510 °C annealing of the OTD-450 in samples which have passed PHT-800. Annealing of the OTD-450 (we shall accept that these are SiO_m complexes) at 510 °C proceeds mainly by means of their dissociation since the limiting size of oxygen precipitates in

Fig.3. Dependence of the formed at 450°C OTD on annealing time at 515 °C.

silicon at 450 °C is less than critical size of nuclei for precipitation at 510 °C [14].

Kinetics of defects annealing in approximation of relaxation time can be written down

$$\frac{dN}{dt} = -\frac{N}{\tau} \tag{1}$$

$$\frac{1}{\tau} = \nu \exp(-E_a / kT) \tag{2}$$

where N is defect concentration in moment of time t.

In a case of annealing of thermal donors by way of dissociation, the oxygen atom must move off on some distance Δx from where it could not be captured again. For that, the atom must make $(\Delta x/a_o)^2$ diffusion jumps, where a_o is a distance between neighbour interstitials (~ 5 Å). Then

$$\frac{dN}{dt} = -N \frac{1}{\tau(\Delta x / a)^2} \tag{3}$$

The obtained from experiment value of $\tau = \tau_n$ is a time interval for moving off an oxygen atom on a distance of Δx. It can be determined

$$\Delta x = \sqrt{D_x \tau} , \tag{4}$$

where D_x is diffusion factor of dispersed oxygen. Let's calculate of Δx for different values of D_x that they were obtained by various authors: for $D_x = 0.09\cdot\exp(-2.4$ eV/$kT)$ [15] it was obtained at 510^{0}C: $\Delta x = 30$ Å. For $D_x = 0.07\cdot\exp(-2.44$ eV/$kT)$ [16], $\Delta x = 21$ Å. For $D_x = 0.02\cdot\exp(-2.42$ eV/$kT)$ [14], $\Delta x = 13$ Å. For $D_x = 0.17\times\exp(-2.54$ eV/$kT)$ [17], $\Delta x = 16$ Å. It is clear from these results, that the annealing of thermal donors can be imagined as dissociation of SiO$_m$ complex with following diffusion migration of oxygen atom outside the limit of sphere of deformation interaction between the atom and the SiO$_{m-1}$ rest.

Now we shall analyse the case of annealing of the TD-450 in samples which have not passed PHT-800. Agrees of data [13], activation energy E_a of process of TD-450 accumulation is equal to 1.70 ±1 eV. The same value of E_a is obtained by us from experiment on TD-450 annealing without PHT. The equality of activation energy values for both generation and annealing processes corresponds to the KFR model, in which the annealing of thermal donors (in the course of annealing at higher temperature) is also limited by oxygen diffusion as well as process of their generation. Let's write down a ratio (4) in which an oxygen diffusion factor $D_x = 6.26\cdot10^{-3}\times\exp(-1.8$eV/$kT)$ is obtained from experiment on the TD-450 generation in [14]. Substituting the appropriate experimental value of τ, we receive $\Delta x = 730$ Å. The existence of deformation fields (with energy that is higher than

kT at $T = 510°$ C) of such extent is probably inside microfluctuation of oxygen concentration or clusters of thermal donors which have the sizes about hundreds of Ångströms and local concentration, considerably exceeding the averaged one.

Thus, the quantitative analysis of obtained experimental results testifies in favour of the assumption of acceleration of oxygen diffusion inside the OMF and microclusters of thermal donors. The part of oxygen atoms, being in the OMF, does not exceed several percents from their total amount, therefore the revealing of an accelerated diffusion of oxygen by direct methods is complicated.

The presented analysis of results is only estimate. However, in our opinion, it is sufficient for the following conclusions:

1) Microfluctuations of oxygen concentration with sizes about 700 Å play role of nuclei during generation of the OTD in Si.

2) Both generation and annealing of the OTD, located in microclusters on a place of localization of initial oxygen microfluctuation, are considerably facilitated by acceleration of oxygen diffusion in fields of elastic deformations close and inside microclusters of both the OTD and the OMF.

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