

FORMATION KINETICS OF THE AL-RELATED SHALLOW THERMAL DONORS: A PROBE FOR OXYGEN DIFFUSION IN SILICON

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Abstract. In this paper we investigate in detail the formation kinetics of the new type of shallow thermal donors, the K-donors, found in Al-doped silicon. A modeling of this kinetics in terms of diffusion controlled chemical reactions of oxygen and aluminum provides a new insight into the problem of oxygen diffusion in silicon at annealing temperatures of about 450 °C.

Introduction.

Thermal donors (TD) in silicon belong, since their discovery in the 1950's [1], to the most intriguing and most studied defect systems in solids. There has been a lot of information gathered during the 40 years of research: the multi-species character of the TD has been evidenced by the IR-absorption measurements and ENDOR and magnetic circular dichroism measurements demonstrated the C_{2v} symmetry of TD and probable constituting elements (oxygen, Si-interstitials) of the defect core [2].

However, no definite undisputed model of TD structure exists at present, because other main problems related to the thermal donors, that of generation kinetics of the TD and the oxygen diffusion at TD annealing temperatures (350-500 °C) still lack a consistent explanation [2]. The activation energy of isolated oxygen diffusion has been estimated to be of the order of 2.5 eV over a wide temperature range [3]. This does not seem to account for the oxygen agglomeration data at TD annealing temperatures - the diffusion of oxygen atoms creating thermal donors should have activation energy of about 1.8 eV, i.e. the diffusion coefficient at 470 °C should be more than 2 orders of magnitude higher than the diffusivity of isolated oxygen [2].

Even less is known about other defects, which, similarly to the TD, are generated during oxygen agglomeration: the shallow thermal donors (STD). They were observed for the first time in the mid eighties by photo-thermal ionization spectroscopy [4]. The binding energies of these single shallow donors are about 30 meV below the conduction band, while the TD double donors have binding energies of the order of 60 meV and 150 meV in TD^0/TD^+ and TD^+/TD^{++} charge states, respectively. Recent comparative studies carried out with infrared absorption and ENDOR techniques tentatively related the STD to the NL10 defect and showed that their generation does not depend on co-dopant species but only on the initial Fermi level position [5].

Infrared transitions attributed tentatively to a new member of the STD-family, called the K-donor, have been found recently in the Al-doped silicon [6]. The defect is generated simultaneously, though with different kinetics, with other shallow thermal donors. It has a very similar binding energy, but, contrary to other shallow thermal donors, it exhibits a metastable behaviour. The K-donor was believed to contain aluminium as it has been found only in Al-doped samples [6].

In this paper we present results of the generation kinetics of the oxygen agglomeration related centers in Si. The creation process of the K-donors, the STD and TD can be linked to a more general problem of oxygen diffusion in silicon at TD-annealing temperatures. Several models of possible generation mechanisms based on the second order, diffusion controlled reaction kinetics have been proposed and their results compared to the experimental data. It seems that the investigation of thermal donor formation in terms of a nonlinear reaction-diffusion process can provide a new insight into the still unsolved problem of the oxygen diffusion and precipitation at 450 °C.

Experimental results and models of the thermal donor generation kinetics .

The generation kinetics of the thermal donors was measured in boron ($N_a - N_d = 1 \cdot 10^{16} \text{ cm}^{-3}$) and aluminium ($N_a - N_d = 4 \cdot 10^{15} \text{ cm}^{-3}$) doped Cz-Si samples (WASO-grade) at 470 °C in the nitrogen atmosphere. The initial oxygen concentration was $N_{ox} = 1 \cdot 10^{18} \text{ cm}^{-3}$ and the samples undergone an oxygen dispersion treatment at 1350 °C. By means of the FTIR spectrometer (Bomem DA3) infrared absorption bands of the TD, STD and K-donors were measured at the resolution of 1 cm^{-1} . The relative concentration of the generated species was drawn from the strength of the IR-bands.

Of several TD absorption bands observed some could be attributed to that already identified in [7] and [8]. Some of them were not reported in literature. They were all named according to the nomenclature of ref. [7]. A total of 10 different TD species (from TD₅ to TD₁₅) could be resolved and their kinetics monitored during several annealing steps at 470 °C (the details of the IR spectra and the identification of different species can be found in [5]). The several STD absorption lines, were more difficult to resolve in the absorption experiment due to their low absorption strength but the kinetics of the deepest of them (the F, G and the K absorption bands) could be monitored in sufficient detail for B- as well as for Al-doped Si samples.

The absorption of the K-donors exhibits metastable behaviour. A photo-excitation experiment [6] showed that the metastability of this defect is very similar to that found for DX centres in AlGaAs.

The generation kinetics of each species approximately follows (at its beginning) the power law $n(t_{\text{anneal}}) \sim t_{\text{anneal}}^p$ where n is the TD concentration and t_{anneal} is the annealing time (Fig. 1). The power p for all TD⁰ and STD species ranges from 1.3 to 1.7 for the Al-doped samples and from 1.5 to 2.3 for the B-doped samples. The power p does not show any dependence on the thermal donor number. It seems that a constant (average) value of p is characteristic for all the thermal donors observed. The deviation from this value is being due to the fact that it was impossible to estimate the exact “star-tling point” of the generation kinetics for all different TD’s and thus to estimate exactly the “initial slope” power p of each kinetics curve. The average power p_{av} seems to be somewhat higher for the B-doped samples ($p_{av} = 1.8$) than for the Al-doped samples ($p_{av} = 1.5$) but this again can be explained with different conditions of the “initial slope” measurements for both types of samples. For B-doped samples (higher doping level, shallower acceptor) the absorption bands could be observed at the very initial stage of the agglomeration (apparently larger slope). For the Al-doped sample (lower doping level, deeper acceptor) the “first” absorption bands resolved could only be measured for a later (than for B-doped samples) agglomeration stage. The power p for the shallow thermal donors has been found to be approx. 1 for both types of samples.

The K-donors kinetics differ markedly from those of the other donors: they have the “initial slope” power $p = 0.6$ and exhibit a pronounced saturation behaviour in contrary to the generation kinetics curves of the TD and STD where the saturation behaviour could be only tentatively (because of possible errors of the absorption coefficient measurement) attributed to a few species for both types of samples (Fig. 1).

There have been several attempts to model the generation kinetics of TD-related centers [9] [10]. One general assumption of all these models was that the annealing time dependence of the TD generation is a process of stepwise

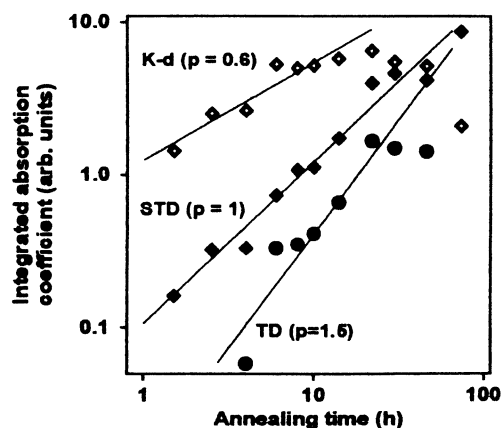


Fig. 1 The generation kinetics of the K-donors (K-d), shallow thermal donors (STD) and thermal donors (TD). The data presented are „as measured” with no further scaling. The two points (for highest annealing times) of the K-donor and STD curve and one for the TD curve are quite unreliable because of the measurement below the 5% transmission limit. The apparent saturation for the TD curve could thus be an artefact.

agglomeration of single oxygen atoms on seed centres which should be the "first" thermal donors. Thus, each of the species observed in the absorption experiment (TD1, TD2 etc.) would "contain" a different number of agglomerated oxygen atoms. Each of the reactions was assumed to be diffusion limited and to follow a second order kinetics. The rate coefficients were constant of the type: $k = 4\pi DR$ where D - sum of diffusion coefficients of reacting species (usually a multiple of the oxygen diffusion coefficient D_{ox}), R - "interaction radius" - the distance from the seed within which an irreversible agglomeration of the single oxygen atom takes place. In some of these models [9] the order of the kinetics was reduced by assumption that the oxygen concentration (N_{ox}) was much larger than the TD concentration and therefore constant during the agglomeration process. The task was to solve a system of coupled differential equations - each of them describing the growth process of a single TD-species.

Such a mathematical procedure (even without the assumption of $N_{ox} = \text{const}$) is not able to describe the time dependence of the TD annealing kinetics observed in our annealing experiment. A simple numerical test - solving of 10 coupled equations - showed that the initial slopes of the generation kinetics *do* depend strongly on the "sequence number" of the TD-species. Secondly, assuming an initial oxygen concentration of $1 \cdot 10^{18} \text{ cm}^{-3}$, a dimer seed, $D = D_{ox} = 5 \cdot 10^{-19} \text{ cm}^2/\text{s}$ (a 470 °C extrapolation of higher temperature diffusion data) and $R = R_{ox} \sim 5 \text{ \AA}$, the yield of already the fifth TD-species would have been under the sensitivity limit of any spectrometer ($N_{TD5} < 10^{12} \text{ cm}^{-3}$) thus the TD6 - TD15 species would not be accessible for the observation. Increasing of the rate constant (i.e. D_{ox} or R_{ox}) helps to improve the yield but the strong dependence of p on the TD sequence number remains. A further improvement, especially when large interaction radii are assumed, can be achieved

by introduction of the time dependent reaction rate [11]: $k = 4\pi DR \left(1 + \frac{R}{\sqrt{\pi Dt}} \right)$.

The dependence of the "initial slope" powers on the TD sequence number is less striking but still present. Eventually, it seems that for implementing the above model to the description of the TD generation kinetics a diffusion coefficient of oxygen or an "interaction radius" R_{ox} (or both) are needed which are much higher than "reasonable" values of $D_{ox} \sim 5 \cdot 10^{-19} \text{ cm}^2/\text{s}$ and $R_{ox} \sim 5 \text{ \AA}$. The result however is still not satisfactory.

Instead of modelling a complex process consisting of several consecutive reactions one can attempt to investigate the K-donor kinetics only. It seems that it is quite distinct from the other TD's and STD's generation processes: the annealing curve is markedly different from that of the other defects ($p = 0.6$!) and the K-donor is observed only in Al-doped samples which strongly suggest that the K-donor must be an oxygen-aluminium complex.

We tested four relatively simple reaction schemes based on two assumptions: a) the K-donor generation is independent of the TD and STD generation, b) the Al-atoms act as quasi-immobile seed-centers for fast diffusing oxygen atoms: the diffusivity of aluminium in silicon at the TD-annealing temperature is three to five orders of magnitude lower than that of oxygen [12].

The reaction schemes for 1 or 2 agglomerating oxygens are as follows: a) $\text{Al} + \text{O} \rightarrow \text{K-donor}$, b) $\text{Al} + 2\text{O} \rightarrow \text{K-donor}$, c) $\text{Al} + \text{O} \rightarrow \text{Intermediate}$, $\text{Intermediate} + \text{O} \rightarrow \text{K-donor}$, d) $\text{O} + \text{O} \rightarrow \text{O}_2$, $\text{O}_2 +$

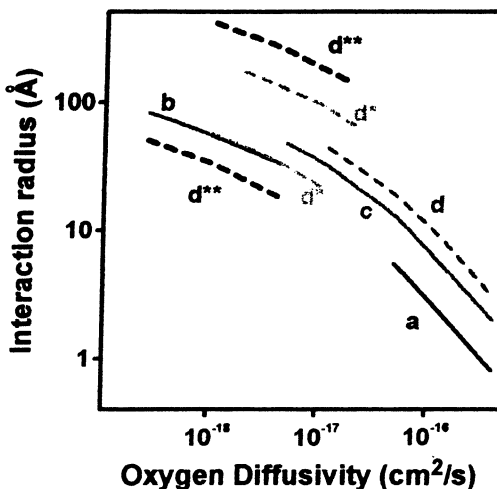


Fig. 2. The interaction radius R vs the diffusivity D for various K-donor generation mechanisms (explanation of the symbols can be found in text).

Al $\rightarrow$ K-donor. Each of the schemes is described by a set of first order nonlinear differential equations with rate coefficients as in [11]. The annealing time dependence of the K-donor concentration - $n_K(t_{\text{anneal}})$ - for all above the reaction schemes depends on only 2 parameters - R_{ox} , D_{ox} of the single oxygen atom. For the solution of the scheme d) a simplifying assumption was made: the reaction rate of the molecule formation is by a constant factor f smaller than the rate for the K-donor formation reaction. In this way, the model of fast diffusing ($D_{O_2} > D_{ox}$) oxygen molecule [13] could be tested.

Each theoretical $n_K(t_{\text{anneal}})$ dependence was fitted to the experimental K-donor generation kinetics and values of R_{ox} and D_{ox} have been obtained. A comparable fit quality has been obtained for different R_{ox} - D_{ox} pairs for each agglomeration mechanism. Therefore, not a single (R,D)-pair but a R vs D curve connecting values of diffusivity and interaction radius could be estimated for the particular mechanism. The results obtained from the best fit to the experimental K-donor annealing kinetics for the particular agglomeration mechanism are displayed in Fig. 2.

As one can see, for any considered model, it is not possible to obtain an interaction radius of the order of the lattice constant of silicon ($R \sim 5 \text{ \AA}$) without assuming very high diffusivities of the isolated oxygen. On the other hand, if one assumes oxygen diffusivities to be of the order of that estimated from Ref. [3] the interaction radius becomes large and the reaction mechanism has to involve two consecutive reactions.

Even the model of fast diffusing oxygen molecules does not provide a sufficient improvement. The R(D)-curves for this mechanism have been estimated at three different ratios f of the K-donor formation rate to the oxygen molecule formation rate (Fig. 2). In the case when this ratio is larger than 1 a pair of curves is obtained. The $Ro_2(Do_2)$ -curve representing the K-donor formation (the Al + O_2 reaction) is shifted up with respect to the one for the oxygen-molecule formation $R_{ox}(D_{ox})$ (curves labeled d^* at $f = 6$ and d^{**} at $f = 32$ in Fig. 2). For $f = 1$, $Ro_2(Do_2) = R_{ox}(D_{ox})$ (curve d) and the mechanism of "fast diffusing O_2 molecule" is comparable to the subsequent addition of oxygen atoms to the seed. As the ratio f increases, the diffusion coefficient of oxygen - D_{ox} can be "reduced" to the value of Ref. [3] but, on the other hand, the interaction radii R_{ox} - for the molecule formation and Ro_2 - for the Al + O_2 reaction remain as high ($\sim 70 \text{ \AA}$) as for other, simpler mechanisms or grow rapidly to a completely unrealistic $Ro_2 \sim 300 \text{ \AA}$, respectively.

If one assumes that the diffusivity of oxygen is of the order of $D_{ox} \sim 5 \cdot 10^{-19} \text{ cm}^2/\text{s}$, a very high interaction radius for all considered reaction mechanisms is obtained. A simple Coulomb attraction of the reacting species (if they were of the opposite sign and Al is certainly a negatively charged acceptor at 470°C , when the K-donor is generated) could be the "interaction" of which the "radius" has to be estimated only if it overcame the mean energy of the species (kT value at $470^\circ\text{C} \approx 64 \text{ meV}$). In this case however the interaction radius not larger than $20 \text{ \AA}$ would be sufficient and a diffusivity of the order of $3 \cdot 10^{-17} \text{ cm}^2/\text{s}$ will be required (Fig. 2).

All the mechanisms considered above for the TD as well as for the K-donor (regarded as an aluminium-oxygen complex) formation are based on one common general assumption: the formation process consists of a series of consecutive reactions in which single diffusing oxygen atoms (or oxygen molecules) are trapped by seed centres - oxygen atoms or dimers in case of the TD-formation or an Al-atom in the case of the K donor generation. The mechanisms require an oxygen diffusivity being two orders of magnitude higher than the value

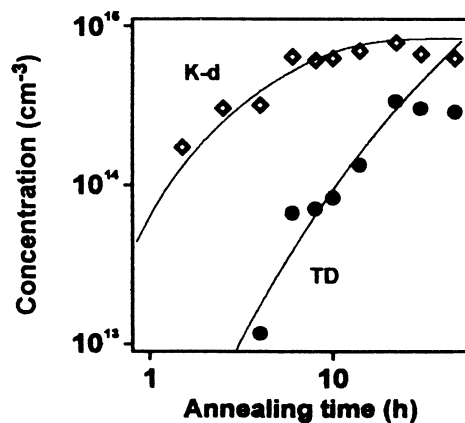
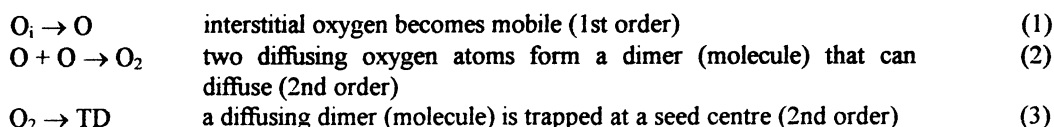


Fig. 3. A simulation of the K-donor and TD generation during dimer creation and concurrent dimer trapping reactions.

expected from direct oxygen diffusion measurements [3] at temperatures higher and lower than 470 °C. This seems to be consistent with several indirect estimates of D_{ox} at TD formation temperatures [2].

However, we can propose an other simple mechanism which models basic features of the measured TD and K-donor kinetics and *does not* require either an oxygen diffusivity value higher than that estimated according to ref. [3] or a high value of “interaction radius”. It consists of the following three reactions:



Following rate parameters have been chosen: for the reaction (1) a constant rate is assumed, sufficiently high to provide a constant concentration (equal to the initial oxygen concentration) of diffusing oxygen atoms throughout the entire duration of the reaction time (that all oxygen atoms present in the sample can diffuse was implicit also in the mechanisms discussed above). For the reactions (2) and (3) time dependent reaction rates [11] have been assumed. The reaction (3) represents in fact several *concurrent* trapping reactions (8 in our simulation). The diffusivity D in (2) and (3) has been put equal to the oxygen diffusivity value of $5 \cdot 10^{-19} \text{ cm}^2/\text{s}$ for simplicity, although a *lower* diffusivity for the dimer would not essentially limit the efficiency of the entire process. The radius R was chosen to be 1.5 Å for both reactions. The concentration of the seed centres is $1.5 \cdot 10^{20} \text{ cm}^{-3}$ (!). The numerical solution of the differential equation set for reactions (1)–(3) are displayed in Fig. 3 versus the experimental data of the K-donor and TD kinetics. The experimental points are not any more in arbitrary units but were scaled to give „reasonable” concentration values of the K-donors and the particular TD species. This scaling is of course somewhat arbitrary as there is no direct relation of the TD-absorption coefficient and TD-concentration. The criterion was that the lowest concentration values correspond to the detectivity limit of the spectrometer setup used and the relations of Fig. 2 are conserved. One sees that the simulation remarkably well corresponds to the experiment. The only (quickly) saturating annealing curve is that of the K-donor kinetics. The TD generation curve is far from saturation.

The model was proven to work well simulating the *entire* kinetics of oxygen agglomeration i.e. for several TD and STD species and the K-donor simultaneously. A fit to the scaled experimental data could be obtained by retaining the R and D values given above and varying only the seed center concentration. The value of this concentration determines the particular value of the „initial slope” power p . The seed centre concentration was found to be approximately of the order of $1 \cdot 10^{20} \text{ cm}^{-3}$ for all TD species and of the order of $5 \cdot 10^{18} \text{ cm}^{-3}$ for the STD. Similar results were obtained also for three different scalings of the experimental data.

A very interesting property of the model has also been found: the concentration of all the TD-related centres goes below the 10^{12} cm^{-3} as the initial oxygen concentration becomes lower than $O_i \sim 1 \cdot 10^{16} \text{ cm}^{-3}$. This agrees well with the experimental finding that the TD's are observed only at higher oxygen concentrations [2].

Discussion

In a previous paper [14] it was argued that a physical reason for the very high oxygen diffusivity at TD annealing temperatures found for models based on the *consecutive* agglomeration of oxygen atoms might be expected due to the metastable behaviour of the “early” TD and the K-donors. The metastability mechanism of the K-donors and TD are similar and both remind of the metastable behaviour of the so called DX-centres in AlGaAs [15]. The DX-type metastability found for the K-donors and TD defects are signs that this defect may be a very good candidate for an intermediate diffusion step (saddle point) in the diffusion process of oxygen at the TD annealing temperatures. By

an analogy, the DX centre configuration in GaAs:Si has been found to be a low energy saddle point for the vacancy-mediated Si diffusion in GaAs [16], for which a substantial lowering of the migration barrier is expected.

Now, it seems that a powerful alternative explanation can be proposed - the model of *concurrent trapping* reactions. The high oxygen diffusivity would no longer be needed. Instead, a high concentration of trapping centres would be welcome. This can be easily provided by the silicon atoms themselves - they are present in sufficient quantity in the Si-sample. According to a recent theoretical model [17] of the TD centre structure two oxygen atoms and one Si interstitial build the core of the TD-species. One could imagine that the moving oxygen dimer (the dimer diffusivity can be of the order of the oxygen diffusivity or lower !) becoming trapped by the silicon atom pushes it out of the substitutional into the interstitial position and the lattice relaxation involved stabilizes this configuration immobilizing the dimer. The immobilized dimer would be the thermal donor centre. Each centre would form nearly the same way independently from the others. The “initial slope” power would thus be the same for each thermal donor and would not depend on the TD “sequence number”. The differences in binding energy observed for the TD-species would then have its origin in the different central cell structure of each thermal donor being due to unavoidable slight variations in the centre short range potential and symmetry after the (trapping) relaxation of the three atom complex.

The K-donor in turn would then represent a dimer “loosely” bound to the silicon lattice (or aluminum) atoms. The “loose” bond would then be responsible for large relaxation phenomena observed for the K-donors.

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