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## FORMATION KINETICS OF THERMAL DONORS IN SILICON\*

JEFFREY T. BORENSTEIN(a), DAVID PEAK(b) and JAMES W. CORBETT(a)

(a) Physics Department, SUNY/Albany, Albany NY 12222, USA.

(b) Physics Dept., Union College, Schenectady NY 12308, USA.

## ABSTRACT

The kinetics of thermal donor formation in Czochralski-silicon at ca. 450° C are explained by a simple model based on the work of Suezawa and Sumino which derives forward and reverse reaction rates for each electrically active species from the general features of the infrared electronic absorption spectra. The model, which is independent of the chemical nature of the thermal donor core, assumes that all thermal donors beyond the first donor species are chemically stable at the donor formation temperature, and approximates the reactions for species smaller than the first thermal donor as being in chemical equilibrium. The model is shown to be consistent with both sets of the available IR spectra of thermal donors (Oeder-Wagner and Suezawa-Sumino) when differences in the annealing temperature and initial oxygen concentration are taken into account.

## INTRODUCTION

The discovery of oxygen-related donor states in Czochralski-silicon annealed at 400-500° C [1] has led to thirty years of efforts to model the formation kinetics of these defects. In 1958 Kaiser, Frisch and Reiss (KFR) [2] proposed a model which was capable of explaining many of the experimental results concerning these defects, and they argued that the dominant thermal donor species was a four-oxygen complex of unspecified configuration. The KFR model required a forward reaction rate for donors which is orders of magnitude above the value expected from the now known diffusion coefficient of oxygen in dispersed silicon [3].

Recent infrared absorption measurements [4-7] have revealed that the thermal donors comprise a hierarchy of at least nine divalent defects with successively shallower ground states. Therefore, it has become necessary to provide more sophisticated kinetic models which are capable of explaining the formation rates of each distinct species. One such model is that of Ourmazd, Schröter and Bourret (OSB) [8], which is capable of fitting the IR annealing data of Oeder and Wagner [6]. Like the KFR model, their theory also requires a diffusion coefficient for oxygen which is much higher than the experimental value. OSB argued on the basis of their best-fit that the thermal donor core, or first electrically active species, contains five oxygen atoms.

In this paper we introduce a kinetic model based upon an approximate scheme proposed by Suezawa and Sumino (S+S) [7], and successfully apply it to the IR data of both Oeder and Wagner [6] and S+S [7]. The present formulation differs

from the aforementioned models in that the kinetic fitting yields rate constants for the thermal donor formation reactions without defining a specific chemical structure for each donor species. The number of free parameters in our model is reduced by making certain approximations which allow reaction constants to be determined by the individual donor growth rates and equilibrium values. We conclude that the forward reaction rates for some of the thermal donors are higher than the values predicted by employing the known oxygen diffusion coefficient in standard kinetic theory [9], which yields rate constants of the form

$$k_i = 4\pi R_i D, \quad (1)$$

where  $R_i$  represents the capture radius for the  $i^{\text{th}}$  reaction

and  $D$  is the effective diffusion coefficient. A clear determination of the temperature-dependence of thermal donor formation is difficult, since the S+S and Oeder-Wagner annealing temperatures differ by only a few degrees, but we show that both kinetic studies can be described using as the diffusion coefficient for all the reactions the value for "as-provided" material measured by Stavola *et. al.* [10]. Since the model finds that the kinetics can be explained provided that the forward reaction rates vary widely between species, we attribute the variation to differences in the effective capture radii.

The model which we present does not require, or suggest, the identity of the core species; therefore, we will not speculate on the structure of the thermal donors. Further evidence regarding both the coupling of donor formation to native defects and the influence of thermal history will be required before kinetic models can be directly correlated with structural models.

#### KINETIC MODEL

The standard form of oxygen-donor kinetic models is based upon an aggregation scheme, in which each successively shallower defect is created by the incorporation of an additional oxygen atom into a defect core. Rate equations involving forward reaction terms and dissociation terms are solved numerically, with the rate constants and the oxygen cluster species corresponding to the first thermal donor treated as parameters.

An alternative to this approach is one in which the general features of the thermal donor annealing curves are analyzed so that a more direct way of determining the rate constants can be achieved. This type of approach was proposed by S+S [7], in which absorption coefficient annealing curves are fit to analytically-determined expressions derived from a set of approximations. We will proceed to apply such a scheme to the IR data of S+S and Oeder and Wagner [6], but first we note a modification in interpretation of the infrared spectra which is necessary [11] to bring the S+S experimental results in line with those of Oeder and Wagner and Pajot *et. al.* [5].

The ladder of increasingly shallower ground states seen by Oeder and Wagner, Pajot *et. al.* and S+S are nearly identical; the only significant difference between the three studies is the presence of the second electrically active species (TD-2) in the S+S measurements. Removal of this level yields excellent agreement between the three groups. Further evidence suggesting that the S+S TD-2 does not belong to this thermal donor series is provided by the ground state ladder predicted by the perturbation model of Corbett *et. al.* [12] and Borenstein *et. al.* [13].

Once this correction has been made, the thermal donors seen by S+S can be re-labelled TD-1 thru TD-5. The modified kinetic curves for the neutral donors appears in Fig. 1.

The model we present here is based on the set of assumptions originally proposed by S+S [7]. The major postulates of the model are:

- 1) The forward and reverse reactions for the saturated species are in equilibrium.
- 2) The reverse reactions for all higher-order species (above the last equilibrated reaction) can be ignored.
- 3) The interstitial oxygen concentration remains constant during the early stages of annealing.

These approximations lead to analytic expressions for the concentrations of all clusters  $O_n$  with more oxygen atoms than the largest saturated species. The result of assuming that the forward and reverse reactions for all species up to and including the largest saturated cluster ( $n$ ) are in equilibrium is that the concentration of  $O_n$  can be expressed:

$$O_n = K O_1^n, \quad (2)$$

$$\text{where } K = \frac{k_{(n-1)} k_{(n-2)} k_{(n-3)} \dots k_1}{k_{-(n-1)} k_{-(n-2)} k_{-(n-3)} \dots k_{-1}}. \quad (3)$$

The time-variation of the higher-order species is given by:

$$O_{n+1} = (k_n O_n / k_{n+1}) [1 - \exp(-k_{n+1} O_1 t)], \quad (4)$$

$$O_{n+2} = (k_n O_n / k_{n+2}) G_2, \quad \text{with} \quad (5)$$

$$G_2 = 1 + (k_{n+1}/W) \exp(-k_{n+2} O_1 t) - (k_{n+2}/W) \exp(-k_{n+1} O_1 t),$$

$$\text{and } W = (k_{n+2} - k_{n+1}),$$

and  $O_{n+3} = (k_n O_n / k_{n+3}) G_3$ , where

$$G_3 = 1 - (k_{n+2} k_{n+3} / Z_1) \exp(-k_{n+1} O_1 t) \\ + (k_{n+1} k_{n+3} / Z_2) \exp(-k_{n+2} O_1 t) \\ - (k_{n+1} k_{n+2} / Z_3) \exp(-k_{n+3} O_1 t),$$

$$\text{where } Z_1 = (k_{n+2} - k_{n+1})(k_{n+3} - k_{n+1}),$$

$$Z_2 = (k_{n+2} - k_{n+1})(k_{n+3} - k_{n+2}),$$

$$\text{and } Z_3 = (k_{n+3} - k_{n+1})(k_{n+3} - k_{n+2}), \quad (6)$$

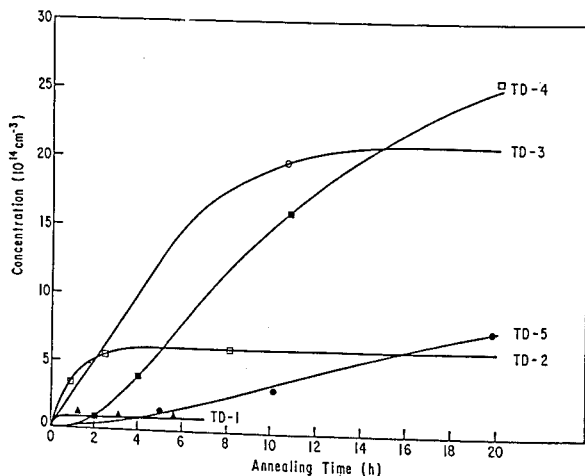


Figure 1. Concentrations of the TD series of S+S versus annealing time at  $471.3^\circ \text{C}$ , with TD-2 as identified by S+S removed from the series. Donors are labeled starting from the deepest level in the ladder. The calibration of absorption coefficients versus concentration follows that of OSB, and assumes that the oscillator strengths for all donors are equal [7].  
Initial oxygen concentration =  $7.85 \times 10^{17} \text{ cm}^{-3}$ .

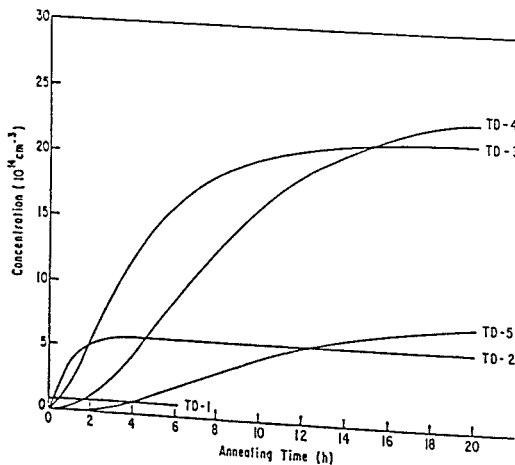


Fig. 2 Best-fit to the S+S spectra of Fig. 1.

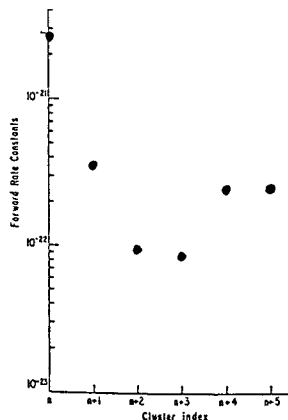


Figure 3. Forward rate constants for the best-fit shown in Fig. 2. The parameter  $k_n$  denotes the rate coefficient for  $O_n \rightarrow O_{n+1}$ .

and an expression containing four exponentials for  $O_{n+4}$ .

The rate constants  $k_j$  can be viewed as parameters, but one can see from the expressions for the concentrations that these parameters depend directly upon the equilibration-value and -time for each species. The rate constants are interrelated and can be determined from the data, rather than by a trial and error fitting. For example, the quantity  $k_{n+1}$  is determined by the rate at which  $O_{n+1}$  reaches equilibrium, provided that its growth rate can be characterized adequately by an exponential. Once this value has been determined, the saturation level of  $O_{n+1}$  determines the quantity  $k_n$ . Each successive complex contains one new parameter, and its value is determined by the saturation value of the complex. The growth rate of the complex will then be completely determined, without the luxury of an additional free parameter.

One important feature of the model is that the concentrations of the various thermal donors may be predicted without choosing a specific number of oxygen atoms in each cluster. The only place that the number of oxygen atoms in a given cluster appears is Eqn. (2), and its value depends upon a freely varying rate constant in front.

The remaining parameter in this model is the choice of which thermal donor corresponds to the largest "initially" saturated complex ( $O_n$ ). This correspondence determines

which thermal donor is the last with significant reverse reactions. Only when the correspondence  $O_n \leftrightarrow \text{TD-1}$  (the first thermal donor) was employed could a good fit to the data be obtained.

The best-fit which resulted from this approximation is shown in Fig. 2, with the appropriate rate constants appearing in Fig. 3.

This model can be modified in a simple way so that it may be compared to other experimental data. Rather than find new rate constants, we can simply adjust the initial oxygen concentration, and assuming that the rate constants have the form (1), we can adjust the temperature-dependent diffusion coefficient,

$$D = 4.00 \times 10^{-4} \exp(-1.95/kT) \quad (\text{cm}^2/\text{sec}), \quad (7)$$

as well. Figure 4 illustrates the results of such an adjustment applied to the data of Oeder and Wagner [6]. It is clear that the general features of the model are retained, especially the low value of TD-1 with respect to higher order complexes. Furthermore, detailed differences between the Oeder-Wagner and S+S data are reproduced by the model; e.g. the convergence times for TD-3 and TD-4.

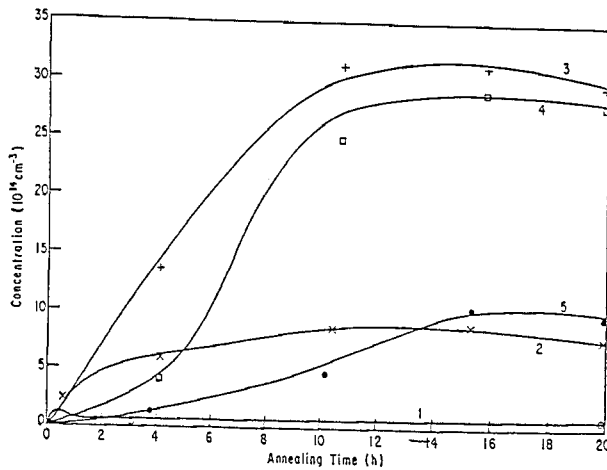
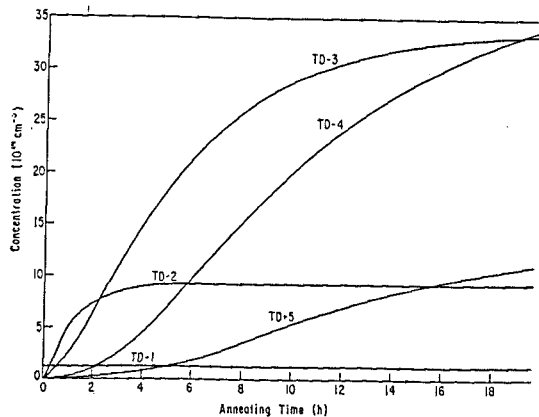


Figure 4. (a) Concentrations of the thermal donor series of Oeder and Wagner [6] versus annealing time. Calibration of absorption coefficients versus concentrations follows OSB.



(b) Best-fit to the infrared data shown in (a).

#### CONCLUSIONS

The kinetic model which we have presented is capable of predicting fairly detailed behavior of the observed thermal donor species and of reproducing the observed temperature- and oxygen- concentration dependences. The thermal donor kinetic fit indicated that only the first thermal donor had significant dissociation, at least in the 450° C temperature range and for short annealing times.

The KFR and OSB models argued for the assignment of a core based upon the numerical solutions to aggregation rate equations for specific oxygen clusters. We attempted a similar identification procedure using the rate constants as determined by our model and the number of oxygen atoms in the first thermal donor as a parameter. This study revealed that cores with three, four or five oxygen atoms are all ca-

pable of fitting the annealing curves, if minor adjustments in the overall calibration to absorption coefficients are made. We argue on the basis of this result that the identification of a thermal donor core cannot rest on the results of a best-fit kinetic scheme alone.

Finally we remark upon the thermal donor formation rate constants derived for this model. The capture radii for the donors is seen to be greatly enlarged over the expected levels of a few angstroms. Capture radii for the donors TD-2 - TD-5 are between 25 and 125 Å, and for TD-1 this value is several hundred angstroms! One possible mechanism for partially explaining the enormous capture radii is the existence of Coulombic attraction between diffusing oxygen atoms and ionized thermal donor cores [14]. Correlation effects [15] might play a part in the formation of donors close in size to the largest unstable species, since dissociation produces a spatial correlation between the donors and diffusing oxygen atoms. The thermal pre-history of the wafer is likely to exert strong influence on the donor formation rate [16]. This may be due to spatial correlations built up during pre-heat-treatments or the cooling of the wafer after crystal growth. Further experiments are needed in order to quantify more clearly the dependence of thermal donor formation upon the initial configuration of the oxygen atoms.

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