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On the kinetics of thermal donor formation in silicon

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A model for the kinetic growth of oxygen-related thermal donors in Czochralski silicon at about 450 °C is presented. The model, which is based on the work of Suezawa and Sumino, derives forward reaction rates for the electrically active species by comparing analytic expressions for the early-time annealing kinetics with the infrared electronic absorption data. The analytic expressions, which are independent of the chemical structure of each species, result from three assumptions: (1) the donor defects beyond the first donor species (TD-1) are chemically stable at the donor formation temperature, (2) the reactions for the TD-1 and those electrically inactive clusters smaller than TD-1 are in equilibrium, and (3) the oxygen interstitial concentration remains constant for short annealing times. The parametrized values of the rate constants indicate that the forward rates of reaction vary widely between species, with a sharp peak at the reaction which takes the first electrically active species to the second. If the rate constants are taken to be of the form $K = 4\pi RD$, where R is the capture radius for the given forward reaction and D represents the effective diffusion coefficient, then the variation between reaction constants may be associated with differences in capture radii between species, with the diffusion coefficient assumed to be the value determined by Stavola *et al.* [Appl. Phys. Lett. **42**, 73 (1983)] for "as-provided" material, which has an activation energy of 1.95 eV. The model is successfully applied to the two available sets of infrared absorption data (the Oeder-Wagner and Suezawa-Sumino data) when differences in the annealing temperatures and initial oxygen concentrations are taken into account. The best-fit parameters found by fitting the analytic expressions are then applied to a set of chemical reaction equations which characterize the formation rates of specific oxygen aggregates. The use of such a set of coupled, nonlinear differential equations, which must be solved numerically, introduces free parameters for the oxygen clusters smaller than the first thermal donor. It is shown that the assignments of a thermal donor core containing two, three, four, or five oxygen atoms are all capable of fitting the experimental data. This result indicates that a best fit to the kinetic data cannot be used to argue for a specific thermal donor core. Finally, the authors discuss possible mechanisms for the enhanced values of the capture radii.

1. INTRODUCTION

Since the discovery of oxygen-related donor states in Czochralski silicon annealed at 400°–500°C,¹ concentrated efforts have been made to model the formation kinetics of these defects. The early model of Kaiser, Frisch, and Reiss (KFR),² based upon available resistivity data,³ successfully explained many of the salient features of the formation kinetics, including the power dependences of the initial donor introduction rate and the maximum concentration on the interstitial oxygen concentration. The KFR model assumed that three electrically active species comprised the thermal donors; complexes consisting of two, three, and four oxygen atoms, with the four-oxygen cluster representing the dominant donor species. The KFR model suffered

from the fact that the parametrized diffusion coefficient of interstitial oxygen differed greatly from the now-known value for dispersed material.⁴

Recent infrared absorption studies^{5–10} have indicated that the thermal donors comprise a hierarchy of at least nine divalent defects with successively shallower ground state energy levels. The IR measurements have furnished detailed information regarding the formation rates of each distinct species. Therefore, it has become necessary to provide more sophisticated kinetic models which are capable of explaining the formation rates of each distinct species.

The kinetic and structural model proposed by Ourmazd, Schröter, and Bourret (OSB)¹¹ has taken into account the multiplicity of defects observed by infrared studies, and has provided a reasonably good fit to the

kinetic data of Oeder and Wagner.⁸ Like the KFR model, their study concluded that in order to reproduce the absolute concentrations of thermal donors observed by electrical measurements, it was necessary to increase the forward reaction rates for the formation of the donor series. The OSB model proposed the existence of a fast-moving oxygen-silicon interstitial complex, which was at once capable of producing the high thermal donor introduction rates and explaining the discrepancy between the fast mechanism and the standard diffusion coefficient of oxygen as measured by dichroic recovery.^{4,12}

The OSB model associated the electrical activity of the thermal donors to the presence of a silicon interstitial in the core, and argued from a best-fit procedure to the infrared data that the first active donor complex contains five oxygen atoms. The model assumed that each thermal donor complex is capable of dissociating, and therefore associated a chemical binding energy with each species. The parameters used in the best-fit procedure thus include the binding energy for each complex and the effective diffusion coefficient for the aggregating oxygen atoms.

A different approach to the problem of thermal donor aggregation was suggested by Suezawa and Sumino (S + S) in 1984, when they attempted to fit their infrared spectroscopic data to a simple model based on the concept of successively equilibrating agglomerating species. The following three assumptions were proposed by S + S regarding the oxygen-related aggregates:

- (1) The oxygen interstitial concentration remains constant for short annealing times.
- (2) There exists an oxygen-related cluster beyond which all larger complexes are chemically stable.
- (3) The reactions for aggregates smaller than this first stable species are in equilibrium.

These assumptions were used to derive approximate solutions for the oxygen clusters, and S + S were able to show a good correlation to their annealing curves for the absorption coefficients of the various thermal donors. S + S argued that, based upon the parameters obtained from this model, the thermal donor core (TD-1) is an aggregate containing three oxygen atoms.

In this paper we introduce a kinetic model based upon the approximate scheme proposed by S + S, and successfully apply it to the IR data of both Oeder and Wagner⁸ and S + S. 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 free parameters in our model are determined by comparing the annealing curves to the analytic solutions found by applying the aforementioned approximations. 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,¹³ 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 th reaction and D is the diffusion coefficient. Since the difference in annealing temperature between the Oeder-Wagner and S + S studies is only 11 °C, the temperature dependence of the formation reactions cannot be accurately determined, but we show that the temperature variation can be reproduced using, as the diffusion coefficient for all the reactions, the value for "as-provided" material measured by Stavola *et al.*¹² Differences in the forward reaction rates between donor species are thus attributed to variations in the capture radii.

II. 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. The ground-state level becomes shallower due to the repulsion between the agglomerating oxygen atom and the shallow electrons.¹⁴⁻¹⁶ The aggregation proceeds as follows:

At some size the oxygen clusters become electrically active, and this complex corresponds to the first thermal donor (TD-1). Since the nature of the core of the thermal donor has not been settled upon at this time, kinetic models must treat the number of oxygen atoms in the first thermal donor as a parameter.

Rate equations characterizing the reactions (2) can be expressed as

$$\begin{aligned} \frac{dO_i}{dt} = & k_{i-1} O_1 O_{i-1} - k_i O_1 O_i \\ & + k_{-(i+1)} O_{i+1} - k_{-i} O_i, \end{aligned} \quad (3)$$

where the k_i are the forward rate constants, the k_{-i} represent dissociation constants, and O_i is the concentration of the species containing (i) oxygen atoms.

The kinetic fitting procedure for this type of treatment is to write down a set of equations similar to (3), one corresponding to each cluster of (i) oxygen atoms. The forward and reverse rate constants are treated as parameters and the set of coupled differential equations is solved numerically. The parameters are varied in a trial-and-error manner, and the best fit is assumed to be reached when the calculation produces a consecutive ladder of clusters with similar growth kinetics to the thermal donors observed by infrared spectroscopy.

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The forward reaction rates are treated as parameters because the predictions of kinetic models such as KFR and OSB cannot reproduce the observed kinetics when the experimentally determined diffusion coefficient is used in (1). Since there is no experimental evidence regarding the reverse rate constants, these are freely varied. The number of oxygen atoms in the first electrically active species may be treated as a parameter to be determined by the correspondence between the calculated and experimentally observed kinetic curves, or may be treated as predetermined by identification from a structural model of the core.¹⁷⁻²²

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. No additional information is presumed by such a kinetic theory, so the number of unknown parameters is not actually reduced. But the latter approach allows free parameters to be derived directly from the saturation time and concentration of each thermal donor species rather than to be chosen by a trial-and-error fitting. This approach also eliminates the necessity of identifying a specific oxygen cluster with the thermal donor core, and we argue that such an identification cannot be made on the basis of a best fit to kinetic curves alone.

This type of approach was proposed by S + S, 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 Suezawa and Sumino and Oeder and Wagner,⁸ but first we note a modification in interpretation of the infrared spectra that is necessary²³ to bring the S + S experimental results in line with those of Oeder and Wagner and Pajot *et al.*⁷

The ladders of increasingly shallower ground states seen by Oeder and Wagner, Pajot *et al.*, and S + S are nearly identical, as can be seen in Table I. The only striking difference between the three studies is the presence of the second electrically active species (TD-2) in the S + S measurements. As Table I indicates, 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 for the thermal donor hierarchy in silicon.¹⁴⁻¹⁶ The ground-state energies predicted by the perturbation calculations can reproduce the S + S IR data to within the limits of experimental error, but only if their TD-2 is removed.

The question arises as to what is the so-called TD-2 in the S + S spectra? We think it is unlikely to be a misidentified excited state of one of the other donors for two reasons: (1) Its kinetic growth as monitored by the neutral-donor transitions $1s - 2p_{\pm}$ is different from the

TABLE I. Neutral donor binding energy differences (in meV) from the deepest thermal donor ground state observed in the hierarchy. If the first level (TD-2) in the S + S ladder is removed, close agreement between the three ground state ladders is obtained.

Oeder-Wagner	Pajot <i>et al.</i>	Suezawa-Sumino
2.4	2.4	0.9
4.6	4.7	2.5
7.0	7.0	4.8
9.1	9.0	7.2
		9.4

other donors, and (2) The excited state spectral lines attributed to it by S + S corresponds exactly to the energies predicted by effective-mass theory²⁴⁻²⁶ and observed experimentally for other shallow donors.²⁷ Therefore TD-2 is most likely a donor defect chemically related to the thermal donors, but distinct from the TD series.

With this assumption, the thermal donors seen by S + S can be re-labeled 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 proposed by S + S, which were discussed earlier. In the present work we will use this set of assumptions as a starting point, but will modify many of the resulting features of the model. We must, of course, alter their formulation in order to remove TD-2, which is chemically different from the other defects and therefore does not fit into the aggregation scheme. In addition, we show that the analytic solutions presented by S + S are not derived correctly, and give the correct series of expression to be fit to the data.

FIG. 1. Modified kinetic curves for the growth of thermal donors as a function of annealing time at 471.3 °C as measured by S + S. Initial oxygen concentration = $7.85 \times 10^{17} \text{ cm}^{-3}$.

Application of the S + S assumptions to a set of expressions similar to (3) leads to the following simplifications:

$$\frac{dO_i}{dt} = 0 \quad (4)$$

for all clusters smaller than the first stable species. The expression for the equilibrium concentration of an equilibrated species O_m , where $m = 1 \rightarrow n$ and n represents the last unstable species, is

$$O_m = K O_1^m, \quad (5)$$

where

$$K = \frac{k_{(m-1)} k_{(m-2)} k_{(m-3)} \cdots k_1}{k_{-(m-1)} k_{-(m-2)} k_{-(m-3)} \cdots k_{-1}}. \quad (6)$$

The time derivative of the concentration of the first chemically stable species (hence the first species not assumed to be in equilibrium) is written:

$$\frac{dO_{n+1}}{dt} = k_n O_1 O_n - k_{n+1} O_1 O_{n+1}. \quad (7)$$

The expression for the concentration O_{n+1} is thus

$$O_{n+1} = (k_n O_n / k_{n+1}) [1 - \exp(-k_{n+1} O_1 t)]. \quad (8)$$

The concentration of each species larger than O_{n+1} has a time derivative identical to (7), and thus the solutions for the concentrations of these higher-order species must be found by inserting the expression for the concentration of the preceding aggregate. These differential equations are seen to be exact, and upon application of the proper integrating factors the expressions for their concentrations may be found:

$$O_{n+2} = (k_n O_n / k_{n+2}) G_2, \quad (9)$$

where

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

and $W = k_{n+2} - k_{n+1}$;

$$O_{n+3} = (k_n O_n / k_{n+3}) G_3, \quad (10)$$

with

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

where

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

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

and

$$Z_3 = (k_{n+3} - k_{n+1})(k_{n+3} - k_{n+2});$$

$$O_{n+4} = (k_n O_n / k_{n+4}) G_4, \quad (11)$$

where

$$G_4 = 1 - (k_{n+2} k_{n+3} k_{n+4} / X_1) \exp[-k_{n+1} O_1 t] + (k_{n+1} k_{n+3} k_{n+4} / X_2) \exp[-k_{n+2} O_1 t] - (k_{n+1} k_{n+2} k_{n+4} / X_3) \exp[-k_{n+3} O_1 t] + (k_{n+1} k_{n+2} k_{n+3} / X_4) \exp[-k_{n+4} O_1 t],$$

and

$$X_1 = (k_{n+2} - k_{n+1})(k_{n+3} - k_{n+1}) \times (k_{n+4} - k_{n+1}),$$

$$X_2 = (k_{n+2} - k_{n+1})(k_{n+3} - k_{n+2}) \times (k_{n+4} - k_{n+2}),$$

$$X_3 = (k_{n+3} - k_{n+1})(k_{n+3} - k_{n+2}) \times (k_{n+4} - k_{n+3}),$$

$$X_4 = (k_{n+4} - k_{n+2})(k_{n+4} - k_{n+1}) \times (k_{n+4} - k_{n+3}).$$

The values of the k_i 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 (4.3), 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 parameter has an impact on the physical implications of the model because it determines where the onset of chemical stability occurs: from the first of the approximations of the model it follows that only O_n and the electrically inactive complexes below it have a significant dissociation rate at the donor formation temperature.

We attempted to model the thermal donor spectrum as measured by S + S using three different choices

FIG. 2. Best fit to experimental data for the thermal donor spectrum as measured by S + S using three different choices for the id

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FIG. 2. Best fit (solid lines) to the S + S annealing curves shown in Fig. 1 (dashed lines).

for the identity of O_n :

- (1) O_n corresponding to the largest inactive complex, or $O_{n+1} \rightarrow \text{TD-1}$,
- (2) $O_n \rightarrow \text{TD-1}$,
- (3) $O_n \rightarrow \text{TD-2}$.

The results for correspondence (2) were very close to experimental observations. The fitting which resulted from this approximation is shown in Fig. 2, with the appropriate rate constants appearing in Fig. 3.

The best fit obtained by this model is superior to one in which all the forward reaction rates are set equal and the reverse rate constants are treated as parameters.^{11,28} This is evident in the initial rise of the donor annealing curves and in the concentration of TD-1 relative to the other species. The analytic solutions clearly predict that the concentrations of the electrically active species will remain constant once they saturate; this is due to the approximation that the oxygen interstitial concentration remains constant as well as to the assumption of chemical stability.

III. GENERALIZATION TO OTHER ANNEALING STUDIES

The forward rate constants, whether they take on the simple form (1) or not, will be temperature-dependent, so that their form must be known before the kinetic model is extended to other infrared studies. We choose to assume that the form of the rate constants is given by (1), where the temperature dependence is only in the diffusion coefficient. The variation in reaction constants between species is thus attributed to varying capture radii; later we will speculate as to the possible origins of this effect. We choose to take as the diffusion coefficient which characterizes thermal donor formation the value determined by Stavola *et al.*¹² for "as-provided" material; this coefficient is nearly two orders

FIG. 3. Forward rate constants k_i ($\text{cm}^3 \text{s}^{-1}$) for thermal donor species TD-1 (index n) through TD-5 (index $n+4$).

of magnitude higher than the well-established value found for dispersed material.⁴ The capture radii which result from this assignment are given in Table II.

The model can then be modified by adjusting the initial oxygen concentration and the temperature-dependent diffusion coefficient:

$$D = 4.00 \times 10^{-4} \exp(-1.95/kT) \text{ (cm}^2/\text{s)}. \quad (12)$$

TABLE II. Capture radii (in Å) for the thermal donor series as determined by the analytic model presented in the text. The capture radius for TD-1, for example, is the value which controls the reaction which takes TD-1 to TD-2.

Thermal donor	Capture radius (Å)
TD-1	825
TD-2	111
TD-3	30
TD-4	28
TD-5	80

FIG. 4. (a) Kinetic curves for the growth of thermal donors as a function of annealing time at 460 °C as measured by Oeder and Wagner. Initial oxygen concentration = 10^{18} cm^{-3} . (b) Best fit (solid lines) to the annealing curves in (a) (dashed lines).

The capture radii found by the parametrization to the Suezawa-Sumino data can then be used in any further kinetic fit. Figure 4 illustrates the results of such an adjustment applied to the data of Oeder and Wagner.⁸ 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.

The effect of a change in the calibration of the absorption coefficient at the 9μ band to the oxygen interstitial concentration²⁹ will have no effect on the predictions of the model for an annealing study at one given temperature. It is clear from the form of Eqs. (6)–(11) that a change in the oxygen interstitial concentration will merely necessitate a scaling of the parameterized rate constants. An additional overall scaling will occur as a result of the adjustment of (3). Such an adjustment will, of course, have an impact on the extension of the

model to data at other temperatures, since the relative contributions of the capture radius and the diffusion coefficient to a given thermal donor rate constant will have been changed.

Changes in the relative calibrations of the thermal donor electronic absorption lines will have a large impact upon the predictions of the model. The simplest approximation for these relative calibrations is to assume that the oscillator strengths for all transitions are the same.¹⁰ This follows from the fact that the binding energies of the thermal donor series are nearly the same, and hence the wavefunctions should be similar. However, a recent study³⁰ has indicated that the oscillator strengths may vary, although the values determined for the dominant species in early-time annealing are not seen to vary strongly.

IV. CONNECTION WITH AGGREGATION SCHEMES

The formulation we have presented can be associated with models for aggregation kinetics, such as OSB, which involve chemical reaction rate equations for specific oxygen clusters. In this manner we may probe whether the number of oxygen atoms in each donor defect has an influence upon the predictions of the model. The rate constants we have obtained earlier may be inserted in equations of the form (3), and a series of such coupled differential equations may be solved numerically, in a manner similar to the OSB study. As in the OSB treatment, the thermal donors are assumed to be formed by the successive addition of a single oxygen atom.

Identification of the thermal donor core corresponds to the assignment of (n), the number of oxygen atoms in TD-1, in (7); in the best-fit procedure this is treated as a parameter. Additionally, free parameters for the forward and reverse rate constants for the electrically inactive species containing fewer oxygen atoms than TD-1 will be introduced. These parameters have the single constraint that the reactions for the inactive species reach equilibrium within the same time scale as does TD-1.

A best-fit procedure using the rate constants as determined by our model and the number of oxygen atoms in the first thermal donor as a parameter revealed that suitable adjustments of the parameters for inactive species enable models with cores containing two, three, four, or five oxygen atoms to fit the annealing curves of S + S. The predictions of the model for these choices of the core are shown in Figs. 5(a)–5(d), with the rate constants for the reaction hierarchy listed in Table III. Note that the reaction rates as determined by the analytic treatment of Sec. II are simply shifted to correspond to the thermal donor hierarchy for each choice of TD-1.

One possible way to determine the number of oxygen atoms in the thermal donor core is to calculate the

FIG. 5. Best-fit model curves for thermal donor growth.

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TABLE
oxygen
 $O_1 + C$

FIG. 5. Best fit to the annealing curves of S + S (Fig. 1) using the aggregation scheme described in the text, for the following choices of a thermal donor core: (a) O_2 , (b) O_3 , (c) O_4 , and (d) O_5 .

dependence of the initial total donor introduction rate upon the oxygen concentration for each choice of a core, and to compare the predictions with the experimentally determined oxygen-concentration dependence.^{31,32} This analysis has been carried out for the four thermal

donor core models, and the calculated initial growth rates plotted versus oxygen-interstitial concentration in Fig. 6. As can be seen in the figure, this analysis failed to provide kinetic evidence for the donor core, since three of the four core models yielded initial introduction rates

TABLE III. Capture radii, R (Å) and reverse rate constants, B (sec⁻¹) for the series of oxygen clusters assuming cores of two, three, four, or five oxygen atoms in TD-1, for the annealing temperature 471.3°C. The capture radius corresponding to O_n is the value for the reaction $O_1 + O_n \rightarrow O_{n+1}$. The reverse rate constant B associated with O_n is the value for the dissociation: $O_n \rightarrow O_1 + O_{n-1}$.

	O_2 core		O_3 core		O_4 core		O_5 core	
	R	B	R	B	R	B	R	B
O_1	0.25	...	5	...	5	...	5	...
O_2	825	10^{-3}	5	2.5×10^{-4}	25	10^{-3}	25	10^{-3}
O_3	111	0	825	2.5×10^{-4}	250	2.5×10^{-4}	250	2.5×10^{-4}
O_4	30	0	111	0	825	1×10^{-4}	500	10^{-4}
O_5	28	0	30	0	111	0	825	10^{-4}
O_6	80	0	28	0	30	0	111	0
O_7			80	0	28	0	30	0
O_8					80	0	28	0
O_9							80	0

FIG. 6. Plot of the total thermal donor introduction rate ($\text{cm}^{-3} \text{s}^{-1}$) during the first 3 h as a function of the initial oxygen concentration (cm^{-3}). The four lines correspond to the total donor introduction rates as calculated by the kinetic model described in the text for the four choices of a thermal donor core. The slopes of these lines all fall within, or near to, the experimentally determined value as determined by Cazcarra and Zunino.³⁴

within the error bars of Ref. 32, which found that at 450 °C:

$$\frac{d[\text{TD}]}{dt} = k_f O_i^{3.5 \pm 1.0} \quad (t < 3 \text{ h}). \quad (13)$$

Evidence for the oxygen-concentration dependence of the maximum thermal donor concentration also exists,³³ but a comparison between this model and the experimental value could not be made since rate constants for donors above TD-5 have not been determined, and these species will contribute significantly in extended annealing periods. Thus the connection between the present model and chemical reaction schemes has not been capable of providing information about the number of oxygen atoms in the thermal donor core. Although physical arguments regarding the growth rate parameters for the precursor clusters, as well as experimentally determined oxygen-concentration dependences of specific thermal donors,^{10,30} may provide evidence for a particular choice of a core, we argue on the basis of these results that the identification of a thermal donor core cannot rest on the results of a best-fit kinetic scheme alone.

V. ENHANCEMENT OF CAPTURE RADII

The present model has shown that the thermal donor annealing kinetics of S + S and Oeder-Wagner may be explained provided that certain forward reaction rates are enlarged greatly over the values expected using the known diffusion coefficient of oxygen in silicon in Eq. (1). If the anomalous diffusion coefficient for oxygen in "as-provided" material¹² is employed in (1), the capture radii (R_i) for the donors above TD-1 are required to be enlarged by about one order of magnitude over the expected levels of a few Å, while R_i for TD-1 is seen to be raised by two orders of magnitude. If the standard diffusion coefficient for oxygen in well-dispersed material is assumed, the parameterized values of the forward rate constants will demand that all the capture radii must be raised by an additional two orders of magnitude for the kinetics to be explained. It is possible, considering the fact that the existing data have not provided a stringent test of the temperature dependence of the donor growth rates, that the effective diffusion coefficient for thermal donor formation is higher than the value measured in Ref. 12, thus allowing the capture radii to take on expected values. For instance, if the effective diffusion coefficient of oxygen takes on the value proposed by OSB,¹¹ then all capture radii will be in the range of a few angstroms. One way to determine whether the enhancement is occurring in the capture radii or in the diffusion coefficient is to study the temperature dependence of TD formation. We are presently carrying out such investigations.

Before discussing possible mechanisms for enhancement of capture radii, we note that the present model does not predict an enhancement in the capture radius of the oxygen interstitial. As is shown in Table III, the forward reaction rate for dimerization as determined by our model will depend upon the choice of core species. If the diffusion coefficient is assumed to be the value found for "as-provided" material,¹² then the capture radius for the monomer (oxygen interstitial) is predicted to take on its expected value of about 5 Å^2 for all choices of a core except TD-1 $\leftrightarrow$ O₂. For this case, the predicted capture radius is actually a factor of 20 below the expected value. If the diffusion coefficient is chosen as the standard value predicted for dispersed material,⁴ then the monomer capture radius must be enhanced by a factor of 20 for all choices of a core except TD-1 $\leftrightarrow$ O₂. In this case the capture radius would take on its expected value. Recent measurements of the loss of oxygen interstitials as a function of annealing time at 450 °C^{34,35} indicate that the forward reaction for dimerization proceeds at the rate predicted by Eq. (1) using a capture radius of 5 Å and the oxygen diffusion coefficient measured for dispersed material,⁴ a finding which is in agreement with our model only for the choice of a thermal donor core TD-1 $\leftrightarrow$ O₂.

One possible mechanism for partially explaining the enhancement of capture radii for the thermal donors involves enlargement by Coulombic effects. Cluster calculations of oxygen in silicon³⁶ indicate that the high electronegativity of oxygen will cause the diffusing oxygen interstitials to attract on the order of one additional electron charge even in the saddle point of their motion. Thus they will be attracted to the positively charged thermal donor cores. Using the standard model for attractive potentials in aggregation kinetics,³⁷ one finds that the capture radii for the donor defects is approximately 40 Å for an ionic interaction. Since the oxygen interstitial-thermal donor interaction is more likely that of a charge and a dipole, the effective radius would be smaller. Therefore this effect may only partially explain the enhancement in forward reaction rates, and cannot explain the wide variation in the rate constants between various species.

Classical nucleation phenomena^{38,39} may also play a role in the high rate constants, since the nucleation rate will depend upon the geometry of the growing clusters. Thermal donors are believed to grow in a chain-like structure rather than spherically, so it is conceivable that wide variations in the forward rate coefficients could result. Correlation effects⁴⁰⁻⁴³ might have a strong influence in the formation of donors close in size to the largest unstable species (TD-1), since the back reaction produces a spatial correlation between the donors and diffusing oxygen atoms. The influence of correlation upon the annealing kinetics is suggested by the high value of the capture radius for TD-1 relative to all other complexes, since this is the only species with significant back reactions. This strong enhancement in the capture radius for TD-1 suggests another possibility: that TD-1 is in fact mobile. While this suggestion should be investigated, it is beyond the scope of the present work, since it involves the thermal donor structure.

The thermal pre-history of the wafer apparently exerts a strong influence on the donor formation rate. Oehrlein *et al.*⁴⁴ have shown that the pre-heat-treatment history has large effects on the initial thermal donor growth rate. This may be due to spatial correlations built up during the pre-heating process or even during the cooling of the wafer after crystal growth. The availability of nucleation embryos is also expected to be a determining factor in the growth rates.

VI. CONCLUSIONS

The kinetic model which we have presented is capable of predicting in fair detail the observed behavior of the various thermal donor species, and of reproducing the observed temperature- and oxygen-concentration dependences. We have shown that this model can accurately reproduce the kinetic growth rates of the thermal

donor hierarchy observed by both S + S and Oeder-Wagner. Confidence in a simple theory such as this is justifiable in the sense that the unknown parameters are tied directly to experimentally observed quantities: from the saturation concentrations and times one can essentially derive all the parameters needed to complete the theory. The presence of the rate constant in the exponential factor in (8)-(11) links the saturation time of a given species with the growth rate of the next-higher-order species. This interdependence of the parameters exists for the entire series of equations.

The one parameter not tied directly to the experimental data is the specific thermal donor which corresponds to the onset of chemical stability. This value can only be found by a trial-and-error fitting procedure, as we have done, since we have no reliable information regarding the stability or chemical nature of any of the thermal donor species.

The temperature dependence of thermal donor formation cannot be determined by this model because the two IR studies used to determine reaction rates for the donor hierarchy are very similar in annealing temperature.^{8,10} The temperature dependence of the diffusion coefficient for nondispersed silicon as given by Stavola *et al.*¹² is sufficient to account for the differences between the two sets of data. This assignment results in capture radii for some of the thermal donors which are greatly enhanced over the expected values.²

The kinetic model we have presented differs from both the KFR and OSB models in that it does not propose a structure for the thermal donor core. We have carried out calculations similar to those found in the OSB model, in order to determine whether the parameters found in our model can be used to determine the number of oxygen atoms in the thermal donor core. We found that cores with two, three, four, or five oxygen atoms are all allowed by the model, since the use of rate equations similar to (3) introduces free parameters for the small electrically inactive clusters which precede thermal donor formation. These parameters may be varied so that different cores can all be accommodated by the kinetic model. We note, however, that physical arguments regarding the growth rate parameters for the precursor clusters may provide evidence for a particular choice of a core.

Finally possible reasons for the relative variation of the capture radii, as well as their overall enhancement above the expected value of a few angstroms, were discussed. Coulombic effects, as well as phenomena relating to classical nucleation theory, may play a role in the formation kinetics of thermal donors. Because the temperature dependence of the donor growth rates has not been clearly determined by the IR studies, it is possible that the effective diffusion coefficient for oxygen aggregation is significantly higher than the value chosen

here.^{11,18} Correlation effects may be the major force in enhancing thermal donor formation, and further experiments will be 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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