
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Author(s): Lee, Young Joo & von Boehm, J. & Nieminen, Risto M.
Title: Interstitial oxygen loss and the formation of thermal double donors in Si
Year: 2001
Version: Final published version

Please cite the original version:

Lee, Young Joo & von Boehm, J. & Nieminen, Risto M. 2001. Interstitial oxygen loss and the formation of thermal double donors in Si. Applied Physics Letters. Volume 79, Issue 10. 1453-1455. ISSN 0003-6951 (printed). DOI: 10.1063/1.1389505.

Rights: © 2001 AIP Publishing. This article may be downloaded for personal use only. Any other use requires prior permission of the authors and the American Institute of Physics. The following article appeared in Applied Physics Letters, Volume 79, Issue 10 and may be found at <http://scitation.aip.org/content/aip/journal/apl/79/10/10.1063/1.1389505>.

All material supplied via Aaltodoc is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Interstitial oxygen loss and the formation of thermal double donors in Si

Young Joo Lee, J. von Boehm, and R. M. Nieminen

Citation: *Applied Physics Letters* **79**, 1453 (2001); doi: 10.1063/1.1389505

View online: <http://dx.doi.org/10.1063/1.1389505>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/79/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Subband and transport calculations in double n-type \$\delta\$ -doped quantum wells in Si](#)

J. Appl. Phys. **99**, 033702 (2006); 10.1063/1.2168024

[Formation rates of iron-acceptor pairs in crystalline silicon](#)

J. Appl. Phys. **98**, 083509 (2005); 10.1063/1.2102071

[Hydrogen plasma-enhanced thermal donor formation in n-type oxygen-doped high-resistivity float-zone silicon](#)

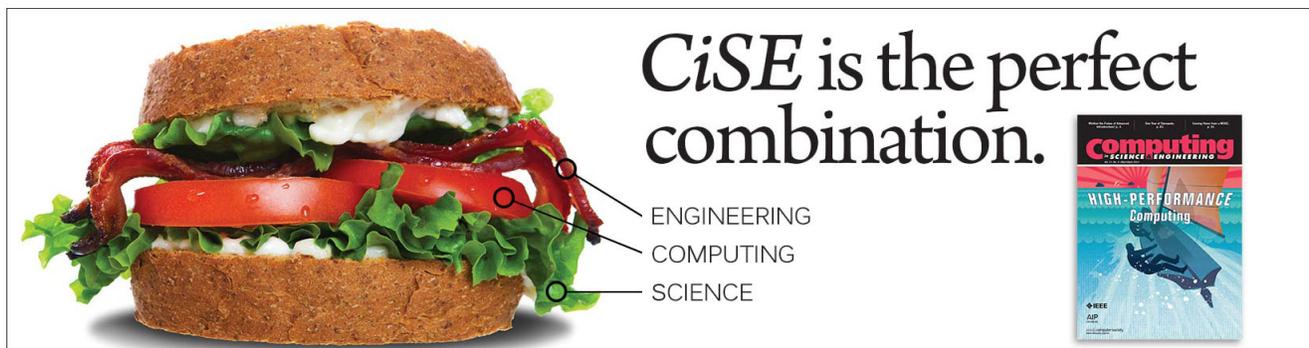
Appl. Phys. Lett. **81**, 1842 (2002); 10.1063/1.1504487

[Annihilation of thermal double donors in silicon](#)

J. Appl. Phys. **87**, 1681 (2000); 10.1063/1.372077

[Ultrashallow thermal donor formation in silicon by annealing in ambient oxygen](#)

J. Appl. Phys. **85**, 8054 (1999); 10.1063/1.370642

An advertisement for CiSE (Computing, Science, Engineering). On the left is a large sandwich with lettuce, tomato, and meat. On the right, the text 'CiSE is the perfect combination.' is written in a large, serif font. Below this text are three lines: 'ENGINEERING', 'COMPUTING', and 'SCIENCE', each with a line pointing to a corresponding ingredient in the sandwich. To the right of the text is a small image of a journal cover titled 'Computing SCIENCE ENGINEERING' with the subtitle 'HIGH-PERFORMANCE Computing' and an image of a person in a blue suit.

Interstitial oxygen loss and the formation of thermal double donors in Si

Young Joo Lee, J. von Boehm, and R. M. Nieminen^{a)}

COMP/Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02015 HUT, Finland

(Received 13 February 2001; accepted for publication 1 June 2001)

The combination of first-principles total energy calculations and a general kinetic model, which takes into account all processes of association, dissociation, and restructuring, is used to study the kinetics of thermal double donors (TDDs) in silicon over the temperature range of 300–650 °C. A strong correlation is found between the formation rate of TDDs and the loss rate of interstitial oxygen atoms. Also, a close agreement with experiments is obtained. It is found that TDDs grow via consecutive reactions where fast diffusing oxygen dimers and all TDDs capture interstitial oxygen atoms. © 2001 American Institute of Physics. [DOI: 10.1063/1.1389505]

Several kinetic models have been developed to describe the formation and annihilation of thermal double donors (TDDs) appearing in as-grown Czochralski silicon during annealing in the temperature range 350–550 °C.^{1–4} Usually, TDDs are assumed to have a common core onto which supersaturated oxygen is aggregated. One of the most important experimental results is the fast process of oxygen aggregation which takes place with a lower activation energy of 1.8 eV compared to the activation energy of 2.54 eV of the diffusion of interstitial oxygen (O_i).^{5,6} Most often, an oxygen dimer (O_{2i}) is assumed to be responsible for fast diffusion in the temperature range 350–550 °C,^{7–9} in which case the formation would proceed as O_{2i}+O_{2i}→TDD1, TDD1+O_{2i}→TDD2, and so on. The main problem here is the fact that a far too high O_{2i} diffusivity is required.⁸ On the other hand, it has been argued that a kinetic model without enhanced oxygen diffusion could give the formation and annihilation kinetics of TDDs at 550 °C.¹⁰ Thus, it is obvious that a satisfactory model which could give the kinetics of TDDs over the whole relevant temperature range of 300–650 °C is still lacking.

We have recently developed a general kinetic model which describes properly the early stages of the formation of TDDs in the low-temperature range 350–420 °C.¹¹ The aim of the present letter is to extend the previous calculations and to report the long-time annealing behavior for the whole relevant temperature range of 300–650 °C. Of specific interest is the role of O_i loss in the growth of the TDD series. We study the early formation rate of TDDs and the O_i loss rate, which are observed experimentally to attain their maxima at 450–500 °C,^{12–15} and to be proportional to the second and fourth power of the initial O_i concentration [O_i]₀ at 350–400 and 450 °C, respectively.^{13,16,17}

Our kinetic model—including all processes of association, dissociation, and restructuring between isomers of oxygen complexes—is described in more detail elsewhere.¹⁸ All energies used in the kinetic model are obtained by the density-functional total energy calculations.^{11,18–20} We find that the chain-like oxygen complexes are energetically most favorable and have the lowest migration energies.^{11,18,20} The oxygen chains are ring-type and systematically assigned to

TDD_n with increasing number of oxygen atoms up to O₁₄ as follows: O_i-O_{2r} (TDD0), O_{2i}-O_{2r} (TDD1), O_i-O_{2r}-O_i (TDD2), O_i-O_{3r}-O_i (TDD3), O_i-O_{4r}-O_i (TDD4),..., O_i-O_{12r}-O_i (TDD12).^{11,20}

In the kinetic model, the association of two migrating oxygen chains O_j (containing *j* O atoms) and O_k into an O_{j+k} complex occurs with the reaction rate $(1 + \delta_{jk})^{-1} 4\pi r_0 (D_j + D_k) [O_j][O_k]$, where *r*₀ is the capture radius, $D_j = D_{j0} \exp(-E_j^m/kT)$ is the diffusivity of the O_j chain (E_j^m is the migration energy).²¹ The dissociation of the O_{j+k} chain into the O_j and O_k chains occurs with the reaction rate $A r_0^{-2} (D_j + D_k) \exp(-E_{jk}^b/kT) [O_{j+k}]$, where *A* is a dimensionless factor and E_{jk}^b is the binding energy of the O_{j+k} chain against dissociation into the O_j and O_k chains. The restructuring of the complexes O_k into the other structures occurs with the rate $\nu \exp(-\Delta E/kT) [O_k]$ where ν is a frequency factor and ΔE is the activation energy for the restructuring process. The longest O chains considered consist of 14 O atoms.¹¹

The calculated early formation rate of TDDs, $d(\sum_n [\text{TDD}_n])/dt$, and the corresponding loss rate of O_i, $-d[O_i]/dt$, are shown as functions of annealing temperature in Fig. 1. The rates are determined by a linear fit in the range of 0–5 h for $T \leq 550$ °C and 0–2 h for $T > 550$ °C. The calculated formation rate of TDDs and the loss rate of O_i are strongly correlated to each other, both having a distinct maximum just above 500 °C. The O_i loss rate is always higher than the formation rate of TDDs because each TDD includes several oxygen atoms (about 6.5 on the average). Both calculated rates have a maximum at about 510 °C, which agrees reasonably well with the experimental value of 450–500 °C.^{12–15} The calculated reaction order *n* in the relation $d(\sum_j [\text{TDD}_j])/dt \propto [O_i]_0^n$ equals 2 at 350–400 °C and increases to 4 at 450 °C, in close agreement with experiments where *n* is found to equal 2 at 350–400 °C (Refs. 13 and 17) and to increase to 3.5–4 at 450 °C.^{13,16,17}

The activation energies of O_i loss and total TDD formation are determined from the Arrhenius plots, which are shown in Fig. 2. The kinetic simulations give the values of 1.0 and 1.9 eV for the temperature ranges of 300–400 and 400–530 °C, respectively, for both O_i loss and total TDD formation. This clearly shows again that the O_i loss and the total TDD formation are strongly correlated. The calculated

^{a)}Electronic mail: rni@hugo.hut.fi

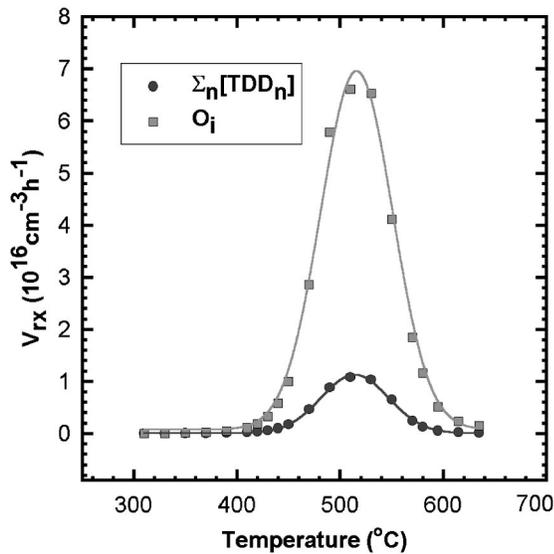


FIG. 1. Calculated formation rate of TDDs and the corresponding O_i loss rate in n -type Si with the electron chemical potential of $\mu_e = 0.38$ eV (the calculated band-gap energy is 0.56 eV). The initial oxygen concentration is $[O_i]_o = 1.0 \times 10^{18} \text{ cm}^{-3}$. V_{rx} denotes the reaction rate. The lines are Gaussian fits to the calculated values.

activation energies are in close agreement with the corresponding experimental values of 1.2 and 1.7–1.8 eV.^{6,22,23}

To compare the simulated O_i loss rates with the experiments by Newman and his co-workers,^{13–15} the effective diffusivity, D_{eff} , is determined from the calculated rates of O_i loss using the equation suggested by Newman and his co-workers:^{13–15}

$$D_{\text{eff}} = -\frac{1}{8\pi r_0} \frac{d[O_i]}{dt} [O_i]^{-2}. \quad (1)$$

The calculated values of D_{eff} are given for the two different initial concentrations of O_i in Fig. 3 together with experimental ones available.^{13–15} The calculated general be-

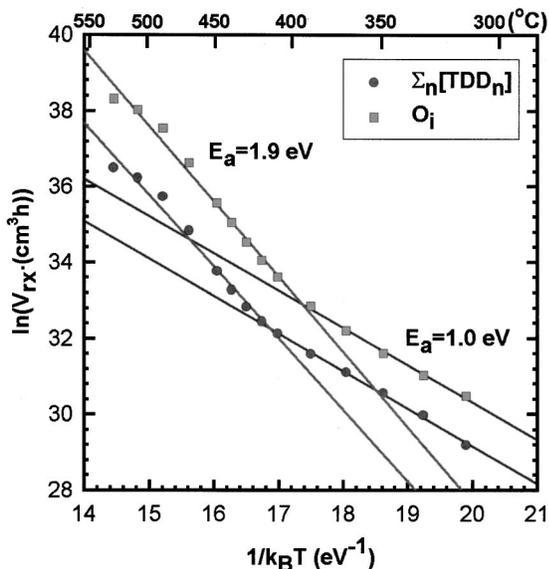


FIG. 2. Arrhenius plot for the calculated O_i loss rate and total TDD formation rate for the n -type silicon with the electron chemical potential of $\mu_e = 0.38$ eV. The initial oxygen concentration is $[O_i]_o = 1.0 \times 10^{18} \text{ cm}^{-3}$. V_{rx} denotes the reaction rate. The lines are linear fits to the calculated values. The TDD formation rate is from Ref. 11.

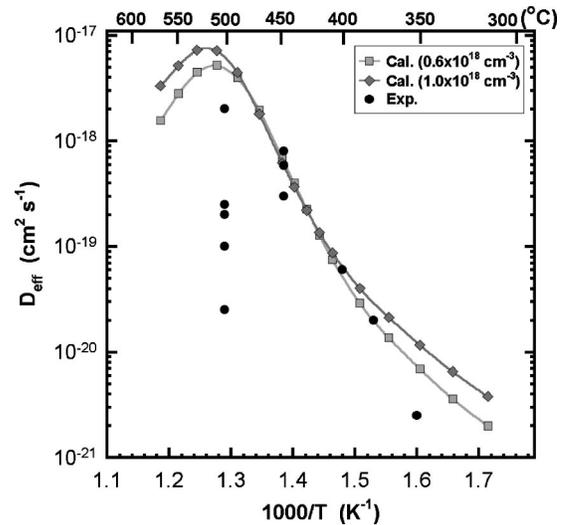


FIG. 3. Quantity D_{eff} determined from the O_i loss rate. The squares and diamonds represent the simulated values for the initial concentrations $[O_i]_o = 0.6 \times 10^{18}$ and $[O_i]_o = 1.0 \times 10^{18} \text{ cm}^{-3}$, respectively. The circles denote the experimental values from Refs. 13–15, deduced with $[O_i]_o = 0.825 - 1.5 \times 10^{18} \text{ cm}^{-3}$.

havior of D_{eff} agrees closely with that found experimentally,^{13–15} although the calculated D_{eff} exceeds the experimental one for $T > 450^\circ\text{C}$. This implies that also the calculated $-d[O_i]/dt$ agrees reasonably well with the experimentally determined loss rate.

Having established a reasonable agreement with experiments over the whole temperature range of $350\text{--}650^\circ\text{C}$, we briefly compare our kinetic model with earlier suggested models. While the other models usually consider TDDs as immobile targets onto which O_i s or alternatively fast diffusing O_{2i} s or other oxygen related fast diffusing species aggregate,^{5,9,10,13–16,24} our results reverse the situation. According to our kinetic simulations, the TDD growth is caused by the consecutive reactions where fast diffusing O_{2i} s and ring-type oxygen chains (including the TDDs) all capture less mobile O_i s.^{11,20} The calculated migration energies are 2.3 eV for O_i , 0.4–1.6 eV for $O_2\text{--}O_9$, and 1.6–2.1 eV for $O_{10}\text{--}O_{13}$, respectively.^{11,18} Each O_i capture gives rise to a formation of a new TDD: $\text{TDD}_n + O_i \rightarrow \text{TDD}(n+1)$. The main reason for this behavior is the fact that $[O_i]$ is several orders of magnitude larger than any other $[O_k]$, making the association terms $4\pi r_0(D_i + D_k)[O_i][O_k]$ much larger than the similar terms $(1 + \delta_{jk})^{-1} 4\pi r_0(D_j + D_k)[O_j][O_k]$, not including $[O_i]$ (although the diffusion constant D_i of O_i is significantly smaller than other diffusion constants, the sum $D_i + D_k$ is still of the same order of magnitude as any other sum $D_j + D_k$). For the same reason, it is natural that the formation rates for reactions $O_{2i} + O_n \rightarrow O_{n+2}$ not including an O_i capture turn out to be negligible.

Our kinetic model does not require any anomalously high O diffusivity and/or anomalously long annealing times, which are required by the models based solely on O_i diffusion.^{13–15} The simulated O_i loss—especially around $400\text{--}450^\circ\text{C}$ —remains reasonably close to the experimentally observed O_i loss, and at the same time measurable concentrations of long O chains with up to 14 O atoms (corresponding to TDD12) are formed within a short time of about 10 h. Any anomalously growing O_3 concentration^{9,14} is not

observed in the kinetic simulations because the O_3 chain is one of the FDS in the consecutive reactions.^{11,18,20}

The decrease of the calculated early formation rate of TDDs at $T > 500$ °C is due to the regeneration of O_i s via the dissociation reactions of oxygen chains. The dissociation reactions are found to be mainly of the type $TDD_n \rightarrow O_i + TDD_{(n-1)}$ (or more generally for the chains $O_n \rightarrow O_i + O_{n-1}$), where the less mobile O_i is “left behind.” This behavior is due to the fact that in the dissociation term $A r_0^{-2} (D_j + D_{n-j}) \exp(-E_{j,n-j}^b/k_B T) [O_n]$, the binding energy $E_{j,n-j}^b$ is smaller for O_i and O_{n-1} than for any other combination of O_j and O_{n-j} ($D_i + D_{n-1}$ is always of the same order of magnitude as $D_j + D_{n-j}$).

In conclusion, we have studied the complex kinetics of dissolved oxygen in silicon. Our results show that the detailed understanding of experimental characterization can be achieved through the combination of first-principles total energy calculations and kinetic modeling. The presented results give a realistic description—at least at the semiquantitative level—of the kinetics of TDDs over the whole relevant temperature range of 300–650 °C.

This work has been supported by the Academy of Finland through the Center of Excellence Program (2000–2005). The authors thank Professor M. J. Puska and Dr. M. Pesola for many valuable discussions. The authors acknowledge the generous computing resources of the Center for the Scientific Computing (CSC), Espoo, Finland. The authors would like to thank O. Jääskeläinen for his technical support in computing.

- ¹B. Pajot, H. Compain, J. Lerouille, and B. Clerjand, *Physica B & C* **117&118**, 110 (1983).
- ²P. Wagner and J. Hage, *Appl. Phys. A: Solids Surf.* **49**, 123 (1989).
- ³W. Götz, G. Pensl, and W. Zulehner, *Phys. Rev. B* **46**, 4312 (1992).
- ⁴*Early Stages of Oxygen Precipitation in Silicon*, edited by R. Jones (Kluwer Academic, Dordrecht, 1996).
- ⁵A. Ourmazd, W. Schröter, and A. Bourret, *J. Appl. Phys.* **56**, 1670 (1984).
- ⁶V. P. Markevich, L. F. Makarenko, and L. I. Murin, *Phys. Status Solidi A* **97**, K173 (1986).
- ⁷U. Gösele and T. Y. Tan, *Appl. Phys. A: Solids Surf.* **28**, 79 (1982).
- ⁸L. I. Murin and V. P. Markevich, in *Early Stages of Oxygen Precipitation in Silicon*, edited by R. Jones (Kluwer Academic, Dordrecht, 1996), p. 329.
- ⁹D. Åberg, B. G. Svensson, T. Hallberg, and J. L. Lindström, *Phys. Rev. B* **58**, 12944 (1998).
- ¹⁰W. Götz, G. Pensl, W. Zulehner, R. C. Newman, and S. A. McQuaid, *J. Appl. Phys.* **84**, 3561 (1998).
- ¹¹Y. J. Lee, J. von Boehm, M. Pesola, and R. M. Nieminen, *Phys. Rev. Lett.* **86**, 3060 (2001).
- ¹²V. Cazcarra and P. Zunino, *J. Appl. Phys.* **51**, 4206 (1980).
- ¹³S. A. McQuaid, M. J. Binns, C. A. Londos, J. H. Tucker, A. R. Brown, and R. C. Newman, *J. Appl. Phys.* **77**, 1427 (1995).
- ¹⁴R. C. Newman, in *Early Stages of Oxygen Precipitation in Silicon*, edited by R. Jones (Kluwer Academic, Dordrecht, 1996), p. 19.
- ¹⁵R. C. Newman, *Mater. Sci. Eng., B* **36**, 1 (1996).
- ¹⁶W. Kaiser, H. L. Frisch, and H. Reiss, *Phys. Rev.* **112**, 1546 (1958).
- ¹⁷C. A. Londos, M. J. Binns, A. R. Brown, S. A. McQuaid, and R. C. Newman, *Appl. Phys. Lett.* **62**, 1525 (1993).
- ¹⁸Y. J. Lee, J. von Boehm, M. Pesola, and R. M. Nieminen (unpublished).
- ¹⁹S. Pöykkö, M. J. Puska, and R. M. Nieminen, *Phys. Rev. B* **53**, 3813 (1996).
- ²⁰M. Pesola, Y. J. Lee, J. von Boehm, M. Kaukonen, and R. M. Nieminen, *Phys. Rev. Lett.* **84**, 5343 (2000).
- ²¹T. R. Waite, *Phys. Rev.* **107**, 463 (1957).
- ²²T. Hallberg and J. L. Lindström, *Mater. Sci. Eng., B* **36**, 13 (1996).
- ²³M. Claybourn and R. C. Newman, *Appl. Phys. Lett.* **51**, 2197 (1987).
- ²⁴S. A. McQuaid, R. C. Newman, and E. Munoz, *Mater. Sci. Eng., B* **36**, 171 (1996).