

Effect of oxygen concentration on the kinetics of thermal donor formation in silicon at temperatures between 350 and 500 °C

C. A. Londos,^{a)} M. J. Binns,^{b)} A. R. Brown, S. A. McQuaid, and R. C. Newman
Interdisciplinary Research Centre for Semiconductor Materials, The Blackett Laboratory, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BZ, United Kingdom

(Received 7 October 1992; accepted for publication 3 January 1993)

Early measurements of the initial rate of thermal donor formation in Czochralski silicon at 450 °C revealed a dependency on the fourth power of the oxygen concentration. This result has led to the view that the core of the defects contained four oxygen atoms. We now show that this dependency is observed only for anneals close to 450 °C. Our results indicate that oxygen dimerization controls the thermal donor formation kinetics but that the dimers become increasingly unstable above 400 °C.

Thermal donors (TDs) are generated in oxygen-rich silicon crystals during heat treatments below ~500 °C. Despite almost 40 yr of research in this field, the atomic structure of these important defects remains unknown. Early in the history of this work,^{1,2} it was found that the initial rate of donor formation, $(d[\text{TD}]/dt)_0$, at 450 °C was proportional to the fourth power of the grown-in interstitial oxygen concentration, $[\text{O}_i]_0$. Using simple kinetic arguments, this result was considered to provide evidence that the core of TD defects contained four oxygen atoms. This observation has been generally accepted and widely quoted since its publication. However, only a single anneal temperature was investigated. In view of the significance which has been attached to this work, we have carried out similar measurements over a much wider range of temperatures (350 °C < T < 500 °C). Our results at 450 °C agree closely with the published data, but we observe a strong deviation from a fourth-power dependence at other anneal temperatures.

Samples were prepared from five different crystals, A–E all grown by the Czochralski (Cz) technique but not subjected to a postgrowth heat treatment. IR measurements of $[\text{O}_i]$ and $[\text{C}_s]$ were carried out according to the relevant ASTM procedures³ using a Perkin Elmer PE983 double-beam dispersive spectrometer. The calibration of the 9 μm IR band given in Ref. 4 was used to deduce values of $[\text{O}_i]$. The background boron-doping levels in crystals B–E were estimated by heating specimens to 650 °C for 30 min to annihilate TD centers introduced during growth, and then measuring the room temperature resistivity of the material. The properties of the crystals are summarized in Table I. Samples with dimensions 20 × 10 × 1 mm were cut from each of the crystals and the surfaces were mechanically polished. Room temperature resistivities, determined by the four-point probe method, and IR measurements of $[\text{O}_i]_0$ were obtained for each specimen. Since the samples cannot be considered semi-finite, the resistivity measurements were corrected to allow for the sample geometry.⁵

Sets of samples, one from each of the crystals (Table I) were annealed isothermally and $[\text{TD}]$ was deduced from resistivity measurements obtained at each stage of the anneal using a calibration which accounts for incomplete ionization of the deeper double donors at room temperature.⁶ The value of $[\text{TD}]$ was deduced after making allowance for the compensation due to the background boron doping in crystals B–D. Separate sets of samples were annealed at 350, 375, 400, 450, and 500 °C.

During the early stages of the anneals at the lower temperatures (< 400 °C), equivalent to the time required to form $[\text{TD}] \sim 5 \times 10^{15} \text{ cm}^{-3}$, the growth in $[\text{TD}]$ was linear with anneal time, t , allowing the initial rate of donor formation, $(d[\text{TD}]/dt)_0$ to be estimated. At the highest temperature of 500 °C, the growth of $[\text{TD}]$ tended to deviate from a straight line after the formation of a lower concentration of donors, which was $\sim 2 \times 10^{14} \text{ cm}^{-3}$ in the case of the sample with lowest oxygen content ($[\text{O}_i]_0 = 8.3 \times 10^{17} \text{ cm}^{-3}$). At a given anneal temperature, $(d[\text{TD}]/dt)_0$ increased as expected with increases in $[\text{O}_i]_0$ (Fig. 1). The variation was fitted to the power law dependency^{1,2}

$$(d[\text{TD}]/dt)_0 \propto [\text{O}_i]_0^n, \quad (1)$$

where the value of n was determined from the slope of a double logarithmic plot of $(d[\text{TD}]/dt)_0$ against $[\text{O}_i]_0$ (Fig. 1). During the time over which the $(d[\text{TD}]/dt)_0$ was determined, $[\text{O}_i]$ decreased by less than 10% so that it could be considered to be a constant, equal to the value measured before the crystals were annealed. For the isothermal anneal at 450 °C we determine a value of $n = 3.5$ which is close to the previously reported value of 4.^{1,2} However, at

TABLE I. Initial interstitial oxygen, substitutional carbon, and substitutional boron concentrations of the five crystals studied.

Crystal	$[\text{O}_i]$ ($\times 10^{18} \text{ cm}^{-3}$)	$[\text{C}_s]$ ($\times 10^{16} \text{ cm}^{-3}$)	$[\text{B}]$ ($\times 10^{14} \text{ cm}^{-3}$)	Supplier
A	1.50	3	Undoped	Wacker-Chemitronic
B	1.16	< 1	2	MEMC
C	1.10	< 1	4	MEMC
D	0.93	< 1	5	MEMC
E	0.83	< 1	< 1	MEMC

^{a)}Permanent address: Solid State Section, Physics Department, University of Athens, Panepistimiupolis, Zografos, Athens, Greece.

^{b)}Permanent address: Hüls (UK) Ltd., MEMC Division, Featherstone Road, Wolverton Mill South, Milton Keynes, Bucks MK12 5TB, United Kingdom.

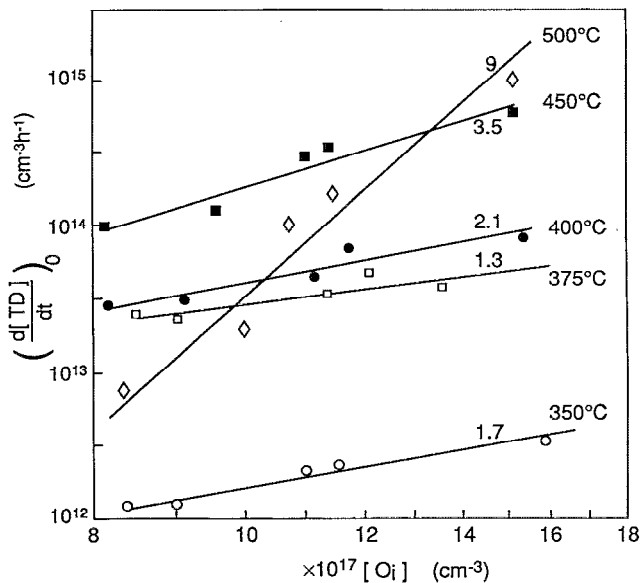


FIG. 1. A double logarithmic plot of the initial rate of thermal donor formation as a function of initial oxygen content in silicon grown by the Cz technique during isothermal anneals at (○) 350 °C, (□) 375 °C, (●) 400 °C, (■) 450 °C, and (◇) 500 °C. The gradient, n , of the variation is shown for each anneal temperature. The increase in $(d[TD]/dt)_0$ with anneal temperature is consistent with increases in oxygen diffusivity. The apparently anomalously small values measured at 500 °C, particularly for low values of $[O_i]$, are ascribed to a high O_2 dimer dissociation rate on the time scale of the measurement.

other anneal temperatures n was found to vary systematically (Fig. 2), reaching 9 at 500 °C and falling to ~ 2 at below 400 °C.

The mechanism which controls the formation of TD defects has been shown to be the same over the temperature range 400–500 °C.⁷ The rate limiting step in this process is presumably the agglomeration of a number, N , of oxygen atoms. At low temperatures, the agglomerate would be stable, and $(d[TD]/dt)_0$ would depend on the N th power of $[O_i]$. However, at higher temperatures ag-

glomerates would tend to dissociate on a similar time scale as that required to cause a measurable increase in $[TD]$. Under these conditions the growth of $[TD]$ would not be linear, particularly for material with low $[O_i]_0$, as found at 500 °C. The requirement to make measurements of $d[TD]/dt$ over a finite anneal time, would lead to a value of n greater than N . This would appear to be the case for anneals at temperatures above 400 °C since n has a constant value a lower temperatures. Since $n \sim 2$ under these conditions (Fig. 2), it is implied that $N=2$ and that the kinetics of TD formation are limited by the rate of O_2 dimer formation. It is inferred then that dissociation of O_2 dimers becomes increasingly significant above 400 °C. The temperature of 450 °C chosen for the early studies would appear not to have been low enough to ignore this process and the value of $n=4$ is an overestimate of N .

It is worth noting that the value of oxygen diffusivity would have to be about one order of magnitude larger than its normal value to account for the measured concentrations of TD centers at 450 °C if their core structure contains four oxygen atoms and the clusters form only by the diffusion of isolated O_i atoms.⁸ Although oxygen dimerization would appear to control the TD formation rate, it should not necessarily be assumed that the core of the defect contains only two oxygen atoms, since an O_3 structure would give a better kinetic fit if only O_i atoms are mobile.⁸ Alternatively, it has been suggested⁹ that O_2 may have a higher diffusivity than O_i so that O_2 might rapidly become O_3 or O_4 after its formation. The suppression of TD formation in material containing a high concentration of carbon, suggests that self-interstitials play an essential role in the formation of the defect.¹⁰ Consequently, even if dimer diffusivity is not higher than that of isolated oxygen, it is possible that the dimerization process limits the TD formation rate indirectly, by controlling the generation rate of self-interstitials in the crystal.

We thank N. Sarno (MEMC Electronic Materials SpA, Italy) and Wacker-Chemitronic for supplying the material used in this work. The Science and Engineering Research Council (UK) provided financial support of this project. A. R. B. acknowledges receipt of a research studentship.

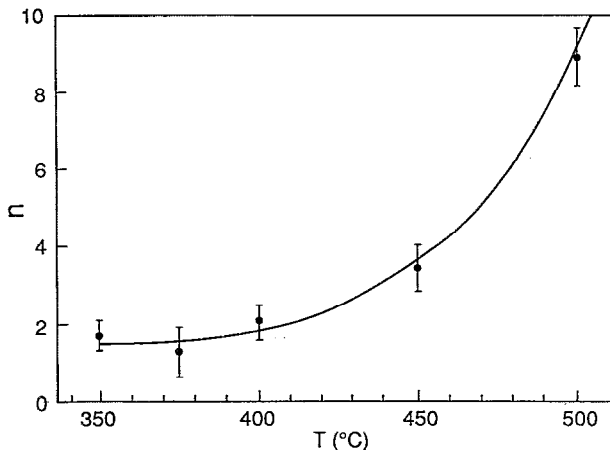


FIG. 2. The power dependency, n , of the initial rate of thermal donor formation on initial oxygen concentration in Cz silicon as a function of anneal temperature.

¹W. Kaiser, Phys. Rev. **105**, 1751 (1957).

²W. Kaiser, H. L. Frisch, and H. Reiss, Phys. Rev. **112**, 1546 (1958).

³ASTM Standard Test Method F121-83 and F123-83 for interstitial oxygen and substitutional carbon content of silicon by infrared absorption.

⁴A. Baghdadi, W. M. Bullis, M. C. Croarkin, Yue-Zhen Li, R. I. Scace, R. W. Series, W. Stallhofer, and M. Watanabe, J. Electrochem. Soc. **136**, 2015 (1989).

⁵A. Uhlir, Bell Syst. Tech. J. **34**, 105 (1955).

⁶M. Claybourn and R. C. Newman, Appl. Phys. Lett. **52**, 2139 (1988).

⁷M. Claybourn and R. C. Newman, Appl. Phys. Lett. **51**, 2197 (1987).

⁸T. Y. Tan, R. Kleinhenz, and C. P. Schneider, Mater. Res. Soc. Symp. Proc. **59**, 195 (1986).

⁹U. Gösele and T. Y. Tan, Appl. Phys. A **28**, 79 (1982).

¹⁰R. C. Newman, Mater. Res. Soc. Symp. Proc. **59**, 205 (1986).