

## THE KINETICS OF OXYGEN LOSS AND THERMAL DONOR FORMATION IN SILICON AT TEMPERATURES BETWEEN 350°C AND 500°C

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### ABSTRACT

Thermal donor and interstitial oxygen concentrations in a range of samples have been measured during isothermal anneals. The rate of donor formation is a strong function of the initial oxygen concentration at all temperatures and depends on  $[O_i]^2$  at low temperatures ( $T \leq 400^\circ\text{C}$ ). At these same temperatures, the loss of interstitial oxygen from solution is described by a model of stable  $O_2$  dimer formation. These results show that  $O_2$  dimer formation is the rate limiting step in both oxygen loss and donor formation. If thermal donor defects contain more than two oxygen atoms then it is implied that oxygen dimers diffuse more rapidly than isolated oxygen atoms. Oxygen diffusion appears to be enhanced in as-grown material and the effect can be increased by heating material in hydrogen gas prior to the anneals.

### INTRODUCTION

Early work showed that heat treatment at  $450^\circ\text{C}$  of Czochralski (Cz) silicon led to the formation of thermal donor (TD) defects [1] and the rate of formation,  $d[\text{TD}]/dt$ , was proportional to the fourth power of the initial interstitial oxygen concentration,  $[O_i](0)$ . This result has been taken to imply that the predominant TD defect was formed by the diffusion and sequential aggregation of four oxygen atoms, although it is now known that this process could only occur on the observed time scale if the normal diffusivity of  $O_i$  atoms,  $D_{\text{oxy}} = 0.13 \exp(-2.53\text{eV}/kT) \text{cm}^2\text{s}^{-1}$ , were enhanced by an order of magnitude [2]. The presence of oxygen in the centres has been confirmed by ENDOR measurements [3] but self-interstitials may also be involved [4,5]. Infrared (IR) measurements of the electronic absorption from TD centres have revealed sixteen different centres [6] but the number of  $O_i$  atoms incorporated in the defects is unknown and the overall structure is still a matter of debate and speculation.

The loss of  $O_i$  atoms from solution during TD formation can be monitored as a function of anneal time,  $t$ , from measurements of the strength of the  $9\mu\text{m}$  IR band [7]. The first stage of aggregation must be the formation of  $O_2$  dimers but since these defects have not been detected directly, it is not possible to make a complete kinetic analysis. Nevertheless, the initial rate of dimer formation should be described by the equation  $d[O_i]/dt = -8\pi r_c D_{\text{oxy}} [O_i]^2$ , where  $r_c$  is the capture radius for dimer formation and  $D_{\text{oxy}}$  is the diffusivity of  $O_i$  atoms. Since  $r_c$  is expected to have a small value  $\sim 5\text{\AA}$ , values of  $D_{\text{oxy}}$  can be deduced from measurements of  $[O_i]$ -loss. Values obtained in this way were close to normal for anneals  $\sim 450^\circ\text{C}$  [7], but those obtained from measurements at other

temperatures yielded a slope of less than 2.53eV on an Arrhenius plot. At higher (500°C) and lower (~350°C) temperatures, the implied values of  $D_{\text{oxy}}$  were less and greater than normal respectively. While these discrepancies could be explained by dimer dissociation at higher temperatures and enhanced oxygen diffusion at lower temperatures, the deduced values of  $D_{\text{oxy}}$  at 450°C appeared to increase with increasing  $[O_i](0)$  [2], a result which is not physically reasonable. We now address these problems by measuring initial values of  $d[\text{TD}]/dt$  and  $d[O_i]/dt$  for samples with different values of  $[O_i](0)$  during isothermal anneals over a wide range of temperatures. The results demonstrate that the rate limiting step in TD formation, as well as oxygen loss, is due to  $O_2$  dimer formation and that  $D_{\text{oxy}}$  appears to be enhanced by a factor of ~4 in as-grown material. We then show that much larger enhancements can be produced in samples subjected to a prior heat treatment in hydrogen gas.

Table 1. Initial interstitial oxygen, substitutional carbon and boron concentrations in the crystals used in this study.

Crystal	$[O_i]$ ( $\times 10^{17} \text{ cm}^{-3}$ )	$[C_s]$ ( $\times 10^{16} \text{ cm}^{-3}$ )	$[B]$ ( $\times 10^{14} \text{ cm}^{-3}$ )	Supplier
A	15.0	3	Undoped	Wacker Chemitronic
B	11.6	<1	2	MEMC
C	11.0	<1	4	MEMC
D	9.33	<1	5	MEMC
E	8.25	<1	<1	MEMC
F	9.60	<1	1	Philips

## EXPERIMENT

Sets of samples cut from various as-grown Cz boules (A-E Table 1), were isothermally annealed in air at temperatures in the range  $350^\circ\text{C} \geq T \geq 500^\circ\text{C}$ . Separate anneals were carried out for samples cut from crystals A or F which had been heated in  $\text{H}_2(\text{g})$  at  $1300^\circ\text{C}$  for 30min in the manner described previously [8] together with as-grown control samples. Values of  $[O_i]$  were determined by IR spectroscopy ( $9\mu\text{m}$  band) using the ASTM procedure [9] and the latest calibration [10]. Total concentrations of TD centres,  $[\text{TD}]$ , were deduced from resistivity measurements [11] using the previously reported calibration [12].

## RESULTS

For all anneal temperatures, *initial* values of  $d[\text{TD}]/dt$  increased with increasing  $[O_i](0)$  in

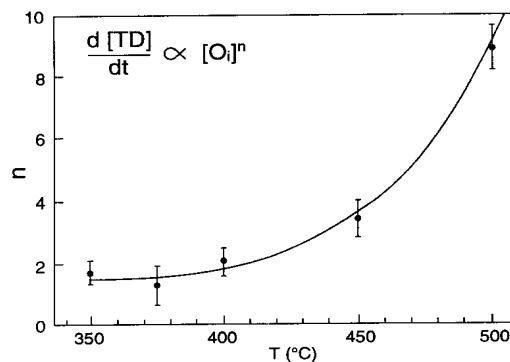


Figure 1. The power dependency of TD formation rate on initial  $[O_i]$  as a function of anneal temperature.

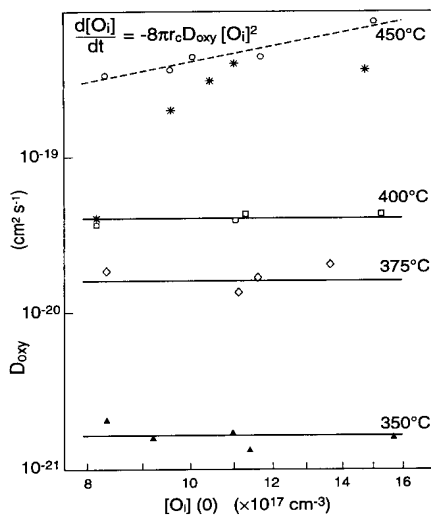


Figure 2. Values of  $D_{\text{oxy}}$  deduced from plots of  $([O_i](t))^{-1}$  as a function of  $[O_i](0)$  in as-grown samples annealed at 350 ( $\blacktriangle$ ), 375 ( $\diamond$ ), 400 ( $\square$ ), 450 ( $\circ$ ) and 500°C ( $*$ ).

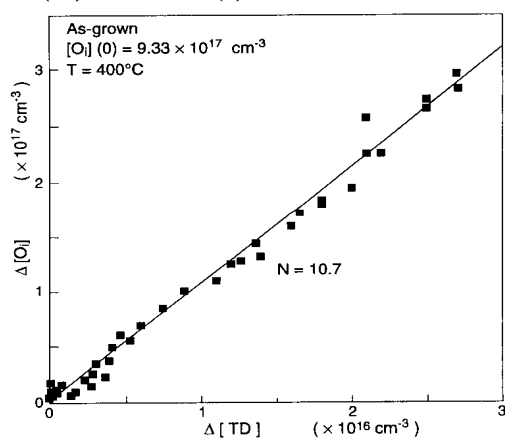


Figure 3. Decrease in  $[O_i]$  as a function of increasing  $[TD]$  in an as-grown sample cut from crystal D annealed at 400°C.

for material hydrogenated in this way and the corresponding rates were greatly increased relative to as-grown control samples. The ratio  $\Delta[O_i]/\Delta[TD]$  was unchanged (figure 4) demonstrating that the mechanism of oxygen loss was unaffected by the hydrogenation treatment. The values of  $D_{\text{oxy}}$  derived from the rates of  $[O_i]$ -loss in as-grown controls were in excellent agreement with the results for as-grown material already discussed (figure 5). However, the corresponding values for hydrogenated material were much larger (figure 5) and close to an extrapolation of the measurements of enhanced  $D_{\text{oxy}}$  [8]. The enhancements at 320°C measured in samples with

the different as-grown samples [13]. The power dependency,  $n$  (so that  $d[TD]/dt \propto [O_i]^n$ ) tended asymptotically to a value of  $\sim 2$  with decreasing anneal temperature ( $T \leq 400^\circ\text{C}$ ) (figure 1). These results demonstrate for the first time that the effective value of  $n$  increases with increasing temperature above 400°C and the value of  $\sim 3.5$  obtained at 450°C is in agreement with earlier work [1, 14]. According to the arguments of Kaiser et. al., the results imply that, at least at low temperatures, the rate limiting step in TD formation is due to  $O_2$  dimerization:  $O_i + O_i \rightarrow O_2$ . If the back dissociation reaction is insignificant compared with the forward reaction, values of  $8\pi r_c D_{\text{oxy}}$  can be obtained from the gradients of plots of  $1/[O_i]$  versus anneal time. Assuming  $r_c = 5\text{\AA}$ , estimates of  $D_{\text{oxy}}$  were obtained from the measurements (figure 2) and the value obtained was independent of  $[O_i](0)$ , as expected, at the low temperatures at which  $d[TD]/dt \propto [O_i]^2$ . The rate limiting step in both  $[O_i]$ -loss and TD formation is therefore shown to be  $O_2$  dimerization. Strong support for this conclusion is obtained from the ratio of oxygen loss,  $\Delta[O_i]$ , versus TDs created,  $\Delta[TD]$ , which is a constant ( $\sim 10$ ) independent of anneal time (figure 3). The ratio did not change with  $[O_i](0)$  in the different samples nor with anneal temperature (figure 4). The average values of  $D_{\text{oxy}}$  deduced from measurements ( $T \leq 400^\circ\text{C}$ ) are shown in figure 5 and are larger by a factor of  $\sim 4$  than normal. Since a value of  $r_c \sim 20\text{\AA}$  is unreasonably large for the interaction between two neutral  $O_i$  atoms,  $D_{\text{oxy}}$  must have been enhanced by a factor of  $\sim 4$  in as-grown material, independent of the value of  $[O_i](0)$ .

Previously we have shown that pretreatments of silicon in hydrogen gas led to enhancements of  $D_{\text{oxy}}$  measured by the relaxation of stress-induced dichroism [8]. Measurements of  $[O_i]$ -loss and TD-formation have now been made

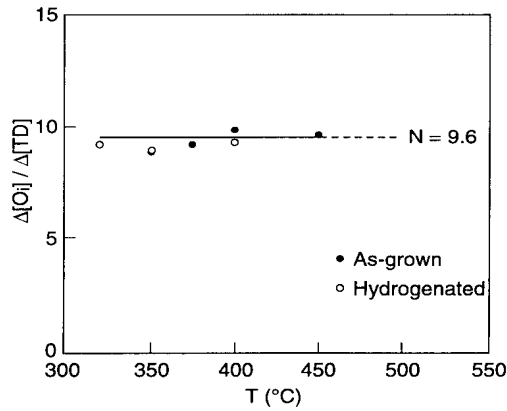


Figure 4. The number of  $O_i$  atoms lost per TD formed in as-grown (●) and hydrogenated (○) material as a function of anneal temperature.

dissociating clusters must either be TD centres themselves or an oxygen aggregate which is a necessary precursor to TD formation (most likely an  $O_2$  dimer). Since this process would not appear to be significant at lower temperatures, the corresponding activation energy must be larger than that for dimer formation ( $\sim 2.5\text{eV}$ ). This is reasonable since the energy required to remove an  $O_i$  atom from a cluster would be the sum of the binding energy of the  $O_i$  atom to the rest of the complex and the barrier to diffusion of the atom away from the cluster.

Since on average, five dimers are produced per TD formed, TD centres cannot be identified with bare  $O_2$  dimers. It is implied either that another defect diffuses to a minority of the dimers to form a TD centre or that dimers, once formed, diffuse rapidly to form clusters containing on average up to  $\sim 10 O_i$  atoms and that these clusters act as donors. It is interesting to note that if TD defects contain more than two oxygen atoms, their rapid introduction following dimer formation requires that  $O_2$  dimers diffuse more rapidly than  $O_i$  atoms. This possibility has already been proposed [15] and theoretical calculations have offered some support [16].

**CONCLUSIONS**

The kinetics of TD formation and oxygen loss have been measured for samples with different

different values of  $[O_i](0)$  were the same. These results demonstrate that the small enhancements of  $D_{oxy}$  which appear to occur in as-grown material may be explained by the mechanism responsible for the much larger effects in hydrogenated material.

Values of  $D_{oxy}$  derived from the rates  $[O_i]$ -loss at higher temperatures ( $T \geq 450^\circ\text{C}$ ) tended to increase with  $[O_i](0)$ . At the highest temperature, measurements for samples with low  $[O_i](0)$  led to values of  $D_{oxy}$  which were smaller than those for corresponding samples heated at lower temperatures (Figures 2 and 5). It is implied that oxygen clusters dissociate at rates comparable to the rate of  $[O_i]$ -loss as the temperature is increased above  $400^\circ\text{C}$ . The fact that this process leads directly to reduced rates of TD formation so that  $\Delta[O_i]/\Delta[TD]$  is unchanged (figure 4) indicates that the tendency to higher effective values of  $n$  (figure 1) can be explained in this way. The

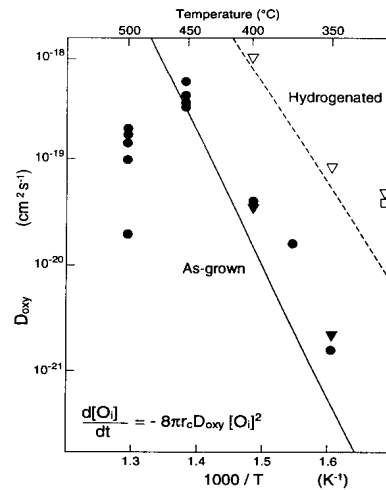


Figure 5. Arrhenius plot of  $D_{oxy}$  deduced from measurements of  $[O_i]$ -loss in as-grown samples from crystals A-E (●), as-grown control samples from crystals A (■) and F (▼) and hydrogenated samples from crystals A (□) and F (▽).

oxygen concentrations annealed at various temperatures and have been explained self-consistently for the first time in terms of O<sub>2</sub> dimer formation. On average ~10 oxygen atoms are lost from solution for each TD formed even after long anneal times and at high temperatures at which a back reaction leads to reduced rates of [O<sub>i</sub>]-loss and TD-formation. The rate limiting step in TD formation is due to O<sub>2</sub> dimerization so that if the defects contain more than two oxygen atoms it is implied that O<sub>2</sub> dimers diffuse more rapidly than O<sub>i</sub> atoms. Absolute values of D<sub>oxy</sub> in as-grown material are larger than normal and larger enhancements have been measured in hydrogenated material. The results provide indirect evidence for the presence of hydrogen in as-grown material.

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