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

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ABSTRACT

We have measured thermal donor and interstitial oxygen concentrations during isothermal anneals in samples containing different initial concentrations of interstitial oxygen. The rate of donor formation is a strong function of oxygen concentration at all temperatures and depends on [O2]3.5 at 450°C, similar to that found in previous studies. However the donor introduction rate tends asymptotically to a dependency on [O2]2 at lower temperatures. At these same temperatures, the loss of interstitial oxygen from solution is described by a model of stable O2 dimer formation. These results show that O2 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.

1. INTRODUCTION

The electrical properties of Czochralski (Cz) silicon are significantly altered during heat treatments at 300°C ≤ T ≤ 500°C due to the formation of thermal donor (TD) defects [1]. As-grown material contains oxygen impurities predominantly in the form of isolated interstitial atoms, Oi, in concentrations ~1018 cm−3. Early work by Kaiser [2] showed that the formation rate of TD defects, d[TD]/dt, during anneals at 450°C was proportional to the fourth power of the initial Oi concentration, [Oi](0). This result established that TD formation was due to the clustering of Oi atoms. This clustering was assumed to follow a sequential reaction in which the forward rates were controlled by Oi-atom diffusion. The dependence of d[TD]/dt on [Oi]4 was then taken to imply that most TD centres contained four Oi atoms [3]. Furthermore, the fact that more than one type of TD centre was formed [4] could be explained if O2 and O3 clusters also acted as donors. However, since that time, it has been demonstrated that the thermal donor series consists of as many as sixteen different centres [5]. It has also become apparent that to account for the formation of clusters containing four or more oxygen atoms at rates equivalent to d[TD]/dt would require that
the value of the oxygen diffusion coefficient, $D_{oxy}$, was enhanced by more than an order of magnitude [6]. On the other hand, the rate of loss of $[O_3]$ from solution at $-450^\circ C$ could be explained using normal values of $D_{oxy}$ provided mainly $O_2$ dimers were formed [7]. However, fitting second order kinetics to measurements at $450^\circ C$ led to values of $D_{oxy}$ which appeared to depend on $[O_3](0)$ [8] demonstrating a shortcoming of the simple dimer formation model used.

In order to explain some of these apparent inconsistencies, we measured $[O_3]$ and $[TD]$ in samples with different values of $[O_3](0)$ during isothermal anneals at temperatures over the wide range of temperatures $350^\circ C$ to $500^\circ C$. We shall show that $d[TD]/dt$ tends asymptotically to a dependence on $[O_3]^2$ at anneal temperatures below $450^\circ C$ (see also ref. 9). These observations are now correlated with measurements of the rate of oxygen loss from solution in the same sets of samples. At the temperatures at which $d[TD]/dt \propto [O_3]^2$, oxygen loss is shown to follow second order kinetics since the derived values of $D_{oxy}$ are independent of $[O_3](0)$. These results demonstrate that the rate limiting step in both $O_3$ loss and TD formation is $O_2$ dimer formation.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$[O_3]$ ($10^{17}$ cm$^{-3}$)</th>
<th>$[C_3]$ ($10^{16}$ cm$^{-3}$)</th>
<th>$[B]$ ($10^{15}$ cm$^{-3}$)</th>
<th>Supplier</th>
</tr>
</thead>
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<td>3</td>
<td>Undoped</td>
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<td>2</td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>MEMC</td>
</tr>
</tbody>
</table>

2. EXPERIMENT

Sets of samples cut from a range of as-grown Cz boules (Table 1), were isothermally annealed in air at temperatures in the range $350^\circ C \leq T \leq 500^\circ C$. Values of $[O_3]$ were determined by infrared localized vibrational mode spectroscopy in accordance with the ASTM procedure [10] and using the calibration of Baghdadi et al. [11]. Total concentrations of TD centres, $[TD]$, were deduced from resistivity measurements, applying correction factors to account for the finite sample thicknesses [12] and using the previously reported calibration [13].

2. RESULTS

$[O_3]$ decreased progressively with anneal time while $[TD]$ increased during the early stages and reached a maximum before subsequently decreasing. The initial rate of increase, $d[TD]/dt$, was measured for each sample, yielding values which increased with increasing $[O_3](0)$ at all anneal temperatures. The power dependence, $n$, where $d[TD]/dt \propto [O_3]^n$, was deduced from double logarithmic plots (figure 1). A value of 3.5 was determined at $450^\circ C$ (figure 2), in good agreement with previous studies at this temperature [2,14], but the present results demonstrate that $n$ is a
function of anneal temperature and tends asymptotically to a value of $\sim 2$ at lower temperatures ($T \leq 400^\circ C$). There is therefore an implication that the rate of oxygen clustering responsible for TD formation must be controlled by $O_2$ dimer formation:

$$O_1 + O_1 \rightarrow O_2.$$  \hspace{1cm} (1)

If the back dissociation reaction is insignificant compared with the forward reaction, the rate of loss of $[O_1]$ is given by:

$$\frac{d[O_1]}{dt} = -2k_r[O_1]^2,$$  \hspace{1cm} (2)

where $k_r$ is the forward reaction rate constant. By integrating equation 2 it is easy to show that values of $k_r$ can be obtained from the gradients of plots of $1/[O_1]$ versus anneal time. The values obtained in this way for all the different samples are shown in figure 3.

3. DISCUSSION

If dimer formation is controlled by the interaction and subsequent binding of diffusing $O_1$ atoms then $k_r = 4\pi r_c^2 D_{oxy}$, where $r_c$ is the corresponding capture radius. According to this model, $k_r$ should be independent of $[O_1](0)$. For measurements at low temperatures ($T \leq 400^\circ C$) (figure 3) there is agreement with this condition. At these temperatures it is possible to deduce values of $D_{oxy}$ assuming a value of $r_c = 5\AA$ (figure 4). The values obtained in this way are larger by
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Figure 4. Average values of $D_{\text{oxy}}$ deduced from the rates of oxygen loss in samples annealed at $T \leq 400^\circ\text{C}$. The line represents normal oxygen diffusion.

Figure 5. Decrease in interstitial oxygen concentration as a function of increasing TD concentration in a sample cut from crystal D annealed at 400$^\circ\text{C}$.

A factor of $\sim 4$ than those expected for normal oxygen diffusion. It would appear that $D_{\text{oxy}}$ is enhanced by the same factor, but there is no evidence for enhancements of more than an order of magnitude. At these temperatures, the rate of TD formation is directly proportional to the rate of formation of dimers and it is of interest to investigate the constant of proportionality ($1/N$).

Since O$_2$ dimer formation is the rate limiting step in the creation of TDs we may write:

$$\frac{d[\text{TD}]}{dt} = \left(1/N\right)\frac{d[\text{O}_2]}{dt}$$

(3)

where $N$ is the average number of oxygen atoms lost from solution per donor formed. In other words, decreases in $[\text{O}_2]$, $\Delta[\text{O}_2]$, during the heat treatment can be related directly to increases in $[\text{TD}]$, $\Delta[\text{TD}]$, and it is implied that the value of $N$ is independent of anneal time up to that at which $[\text{TD}]$ tends to saturate (figure 5). Within the errors of the measurement, the value of $\Delta[\text{O}_2]/\Delta[\text{TD}] \sim 10$ does not change despite the increasing relative concentrations of the higher order TD centres after longer anneal times. There is therefore no evidence that these donors contain more O-atoms than the lower order centres. No systematic variation is observed in the value of $\Delta[\text{O}_2]/\Delta[\text{TD}]$ with variations of $[\text{O}_2](0)$ or with the anneal temperature (figure 6), even at 450$^\circ\text{C}$. Values of $N$ could not be determined at 500$^\circ\text{C}$ and 350$^\circ\text{C}$ because the changes $\Delta[\text{O}_2]$ and $\Delta[\text{TD}]$ respectively were too small for accurate

Figure 6. The number of interstitial oxygen atoms lost from solution per TD formed in samples from crystals A (+), B (x), C (a), D (o) and E (■) as a function of anneal temperature.
measurements to be made.

The fact that the apparent value of $k_f$ depends on $[O_2]_0$ at 450°C (figure 3) implies that a process in addition to that described by equation 2 becomes significant at the higher temperatures, leading to a release of $O_2$ back into solution. Since this process would not appear to be significant at lower temperatures, the corresponding activation energy must be larger than that characteristic of the forward reaction rate, i.e., oxygen diffusion ($\sim 2.53$eV). This is reasonable since the energy required to remove an $O_2$ atom from a cluster would be the sum of the binding energy of the $O_2$ atom to the rest of the complex and the barrier to diffusion of the atom away from the cluster ($\sim 2.53$eV). The reverse reaction leads directly to correspondingly reduced donor formation rates so that equation 3 remains valid and N is unaffected at 450°C (figure 6) indicating that it is reasonable to assume that $O_2$ dissociation is responsible.

Since $N$ is much larger than 2, TD centres cannot be identified with $O_2$ 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 $\sim 10$ $O_2$ 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 $O_2$ atoms. This possibility has already been proposed [15] and theoretical calculations have offered some support [16].

4. CONCLUSIONS

The kinetics of thermal donor formation and oxygen loss have been measured for samples with different oxygen concentrations annealed at various temperatures. The kinetics have been explained self-consistently for the first time in terms of $O_2$ dimer formation. It has been shown that on average $\sim 10$ oxygen atoms are lost from solution for each thermal donor formed even after long anneal times and at high temperatures at which $O_2$ dimers appear to have significant rates of dissociation. If TD defects contain more than two oxygen atoms, the present observations imply that $O_2$ dimers diffuse more rapidly than $O_2$ atoms.

ACKNOWLEDGEMENTS

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REFERENCES

10) ASTM Standard Method F121-83, Annual Book of ASTM Standards 10.05, 1987,