

Oxygen Aggregation Phenomena in Silicon

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ABSTRACT

CZ Si samples containing a range of grown-in oxygen concentrations have been annealed at $T \leq 500^\circ\text{C}$ and the rates of O_i loss from solution and TD-formation have been monitored. The measurements can be explained in terms of serial oxygen aggregation at a rate controlled by dimer formation but only if O_2 dimers diffuse more rapidly than O_i atoms and if the dimers and other small clusters dissociate readily at the higher temperatures. Comparisons of the deduced O_i diffusion coefficients (D_{oxy}) with those measured by the relaxation of stress-induced dichroism imply small enhancements by factors of 3-10 at 350°C . This may be due to the presence of some grown-in hydrogen, consistent with the much larger effect of a pre-anneal of samples in H_2 gas at 1300°C . Alternatively, D_{oxy} may be enhanced by the trapping and subsequent dissociation of fast diffusing dimers. The analysis leads to the possibility of associating thermal donors with oxygen clusters incorporating up to ~ 10 O_i atoms.

1. INTRODUCTION

As-grown Czochralski (Cz) silicon contains isolated interstitial oxygen atoms in a concentration $[\text{O}_i]_0 \sim 10^{18} \text{ cm}^{-3}$. This is a highly supersaturated solution but is stable because the impurities are not mobile at room temperature. Oxygen diffusion has been measured by internal friction, by secondary ion mass spectrometry (SIMS) relating to profiles, by the relaxation of stress-induced dichroism (see the later discussion) and by other methods for the temperature range $1280 \geq T \geq 300^\circ\text{C}$ [1]. Normal values, i.e. unenhanced diffusion not involving other impurities or intrinsic defects, are described

by $D_{\text{Oxy}} = 0.13 \exp(-2.53 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$. If the temperature of Cz Si is raised above $\sim 350^\circ\text{C}$, D_{Oxy} becomes sufficiently large for long-range diffusion to occur, leading to the formation of $(\text{O}_i)_n$ aggregates, and it is possible to detect the loss of O_i atoms from solution by measured reductions in the strength of the infrared (IR) absorption of the $9 \mu\text{m}$ oxygen vibrational band. Complexing of oxygen with other impurities, particularly carbon and nitrogen can also occur but the present discussion will be confined to $(\text{O}_i)_n$ formation. It will however be demonstrated that catalytic interactions of fast diffusing hydrogen atoms with O_i atoms enhance D_{Oxy} for $T \leq 500^\circ\text{C}$ [1,2].

We have presented reviews of the kinetics of the O_i clustering process previously [1,3] but nucleation was not discussed. It was assumed that this was a homogeneous process for $(T > 600^\circ\text{C})$ since the resulting number density of SiO_2 particles, measured by chemical etching, transmission electron microscopy (TEM) or small angle neutron scattering (SANS) [3,4], increased as the anneal temperature decreased from $\sim 1000^\circ\text{C}$ (figure 1). The rates of O_i loss were shown to be due to the diffusion of individual atoms to the particles with normal values of D_{Oxy} . This result is not self-evident since self-interstitials (I-atoms) have to be generated at the surfaces of the SiO_2 particles to accommodate the local increase in volume [5,6] and this could have been the rate limiting process. Observations by SANS of Ostwald ripening showed that precipitates formed at 750°C were in a state of dynamic equilibrium [4]. Thus, there was direct evidence that the smaller particles redissolved and larger particles continued to grow so that the average size increased but the number density decreased with increasing anneal time after the initial nucleation period.

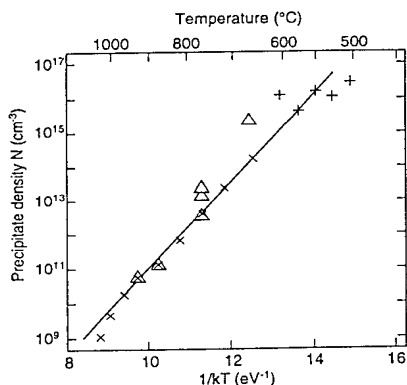


Figure 1. Arrhenius plot of the number density N of SiO_2 precipitates in samples cut from a crystal with $[\text{O}_i]_0 = 9 \pm 1 \times 10^{17} \text{ cm}^{-3}$ but not given a post-growth heat treatment [1].

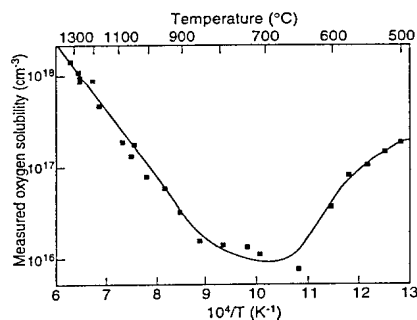


Figure 2. The measured solubility of O_i atoms in Si showing the flattening of the plot near 700°C and an upturn at lower T due to the presence of only very small particles[1].

Analysis of the O_i loss in the lower temperature range $500 \leq T \leq 600^\circ\text{C}$, with the assumption that D_{oxy} was normal, led to estimates of the number density of particles N (figure 1) that continued to increase with decreasing T , to yield $N \sim 10^{17} \text{ cm}^{-3}$ at 500°C . Each particle could on the average contain at most ~ 10 O_i atoms, depending upon the fraction of $[O_i]_0$ that had precipitated. The decrease in particle size is consistent with values of the oxygen solubility (figure 2) derived from a second independent parameter of the kinetic modelling. Thus, $[O_i]_s$ decreased initially with a heat of solution of 1.4 eV, as T decreased in the range $1050\text{-}700^\circ\text{C}$, but then passed through a minimum before rising again as T approached 500°C (figure 2). The interfacial energy between the particle and the matrix would become increasingly important and would enhance the probability of dissolution of particles formed in the nucleation stage. The linkage of these results ($500 \leq T \leq 600^\circ\text{C}$) to those at higher T provides strong evidence that D_{oxy} is indeed normal in this lower temperature range. In this context, we comment that ribbon-like defects (RLD) observed by TEM and originally attributed to coesite (SiO_2) are now thought to be defects nucleated by the condensation of I-atoms generated by the O_i precipitation (a full discussion is given in Ref. [2]). Their size would not therefore indicate the size of the $(O_i)_n$ clusters.

Studies of O_i loss have also been made for $T \leq 500^\circ\text{C}$. Irrespective of the details of proposed models, the first stage of O_i aggregation must be the diffusion of two O_i atoms to adjacent lattice sites [7] and the rate must be controlled by D_{oxy} . In early work it was assumed that $(O_i)_n$ clusters simply grew by the serial addition of O_i atoms to smaller clusters. These models led to claims that D_{oxy} was enhanced, by factors of $\geq 10^4$, by identifying members of the thermal donor series (TDN), formed in the same anneal, with $(O_i)_n$ clusters incorporating some speculated number $n \geq 4$ of O_i atoms (see [1] and [2]). The members of the TDN series, formed as a sequence with increasing N are easily distinguished by electronic IR absorption lines since the first donor ionization energy decreases from ~ 70 meV to 50 meV as N increases up to 16 [8]. However, neither the structure nor the number of O_i atoms in a TDN defect is known. More recently we have shown that the dependencies of $d\Sigma[\text{TDN}]/dt$ and $d[O_i]/dt$ on the power of $[O_i]_0$ are the same (figure 3). At $T \leq 400^\circ\text{C}$ there is a quadratic dependence, as expected for dimer formation, but at 450°C and 500°C the dependence varies as $[O_i]^{3.5}$

(approximately the fourth power [9]) and $[O_i]^9$ respectively. It is implied that particles containing up to 9 O_i atoms are formed at this highest temperature, consistent with other results discussed above. Nevertheless, reported slopes of Arrhenius plots for TD-formation [10] are smaller ($E_F \sim 1.7 - 2.0$ eV) than the activation energy for normal O_i diffusion ($E_D \sim 2.5$ eV), although the two processes have been shown to be linked with $\Delta[O_i]/\Delta\Sigma[\text{TDN}] \sim 10 \pm 2$ [2,3]. This apparent discrepancy and the question of whether or not D_{oxy} is

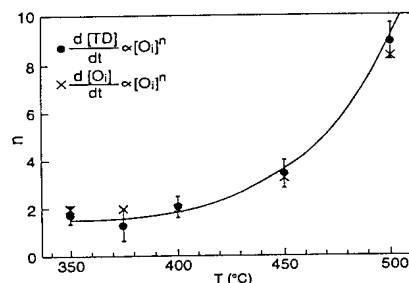


Figure 3. The power dependency n of $d[O_i]/dt$ and $d[\text{TD}]/dt$ on the value of the grown-in oxygen concentration [2].

enhanced clearly have to be resolved. Another long-standing problem is that the measured rates of O_i loss at 450°C for samples containing different grown-in oxygen concentrations $[O_i]_o$ imply a process with third order kinetics [11], rather than second order kinetics expected for a rate limitation due to dimer formation.

These problems are now addressed in relation to measurements of O_i loss during extended anneals at $T \leq 500^\circ\text{C}$ in a range of crystals containing different values of $[O_i]_o$. The measurements relate both to as-grown samples and to material following a hydrogenation pre-treatment at a high temperature (1300°C) prior to the anneals. Modelling of these extended data has led to the resolution of several problems but only if it is assumed that O_2 dimers diffuse more rapidly than O_i atoms [2, 12]. It is also implied that dimers must have high rates of dissociation for $T \geq 450^\circ\text{C}$. Indeed, understanding the dissociation processes for the various $(O_i)_n$ aggregates appears to be crucial to making further progress.

2. EXPERIMENTAL RESULTS FOR AS-GROWN SAMPLES

Samples were cut ($\sim 10 \times 10 \times 1.5 \text{ mm}^3$) from Cz crystals that had not received any post-growth heat treatment. The absorption coefficient α of the 9 μm IR band measured at 300K with a PE 983 double beam spectrometer, indicated that the concentrations of grown-in oxygen ($[O_i]_o$) were 15.0(A), 11.6(B), 11.0(C), 8.3(D), 9.3(E), 9.6(F) $\times 10^{17} \text{ cm}^{-3}$ respectively using the calibration of Baghdadi et al [13] and the usual ASTM procedure. Resistivity measurements were made with the 4-point probe technique and values of the total thermal donor concentration, $\Sigma[\text{TDN}]$, were deduced from a previous calibration [14]. These various samples were annealed isothermally in air at 350, 375, 400, 450 and 500°C and $[O_i]_{(t)}$ and the added donor concentrations were determined at each stage.

We have analysed the data for oxygen loss in terms of the expectations of second order kinetics, i.e. for $d[O_i]/dt = -8\pi r_c D_{oxy} [O_i]^2$, where r_c is the capture radius (taken to be 5Å) for dimer formation. Integration then yields $1/[O_i]_{(t)} = 1/[O_i]_o + 8\pi r_c D_{oxy} t$ so that a plot of the reciprocal of $[O_i]_{(t)}$ versus time should yield a line with a slope equal to $8\pi r_c D_{oxy}$, irrespective of the value of the constant $[O_i]_o$ for the particular crystal [7]. Measurements for the loss of the first 10% of O_i atoms for as-grown samples A-E are shown in figure 4 to illustrate the accuracy and their scope, involving anneals for up to 15,000 h at 350°C. The gradients (the tangent at $t = 0$) are independent of $[O_i]_o$ at 350, 375 and 400°C but systematic changes are evident for samples annealed at 450°C and particularly 500°C, as illustrated by the deduced values of D_{oxy} shown on an Arrhenius plot (figure 5) where the line corresponds to normal oxygen diffusion (see Section 1). Enhancements by a factor of 3, evident for the anneals at 350, 375 and 400°C are rather smaller than the factors of up to 10 found previously in other crystals [10]. The deduced values of D_{oxy} decrease with decreasing $[O_i]_o$ at 450°C and a similar but more pronounced effect is apparent for anneals at 500°C. It was found previously that much reduced values of D_{oxy} were obtained at 500°C, indicating the breakdown of second order kinetics [4].

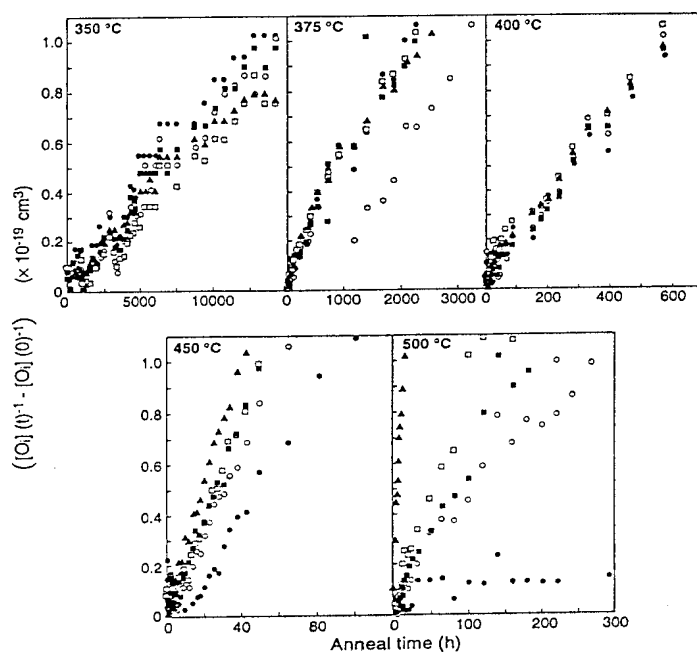


Figure 4. Loss of the first 10% of $[O_i]$ during anneals at various temperatures plotted according to second order kinetics for samples A(▲), B(□) C(■), D(○) and E(●) [2].

3. SAMPLES PRE-TREATED IN HYDROGEN GAS.

Samples from crystals A and F (see Section 2) were given heat treatments for 30 min at 1300°C in H_2 gas at atmospheric pressure in a silica tube and then rapidly quenched into silicone oil at room temperature. Such pre-treatments led to greatly enhanced rates of O_i diffusion jumps measured by the relaxation of stress-induced dichroism during anneals in the range $250\text{-}350^{\circ}\text{C}$. The corresponding values of $D_{\text{oxy}}(\text{enh}) = 2.0 \times 10^{-6} \exp(-1.68 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$ are shown in figure 6 (the dotted and dashed lines indicate the extent of likely errors). The presence of hydrogen in a concentration of $\sim 10^{16} \text{ atom cm}^{-3}$ was confirmed by SIMS measurements (deuterated samples) and by IR absorption from H-B pairs in boron (10^{17} cm^{-3}) doped silicon [15]. The rate of O_i loss during anneals at low temperatures due to O_i aggregation is also greatly enhanced (figure 7). Values of $D_{\text{oxy}}(\text{enh})$, again derived from second order kinetics, agree broadly with the dichroism data. However slightly higher values at the lower temperatures represent a discrepancy similar to that for the anneals of as-grown samples compared with normal values of D_{oxy} .

The rate of TD-formation in hydrogenated samples is also greatly enhanced for $T \leq 500^{\circ}\text{C}$ so that there is still a correlation with the loss of oxygen from solution, and the ratio $\Delta[O_i]/\Delta\Sigma[\text{TDN}]$ remains unchanged at a value close to 10. This behaviour is also

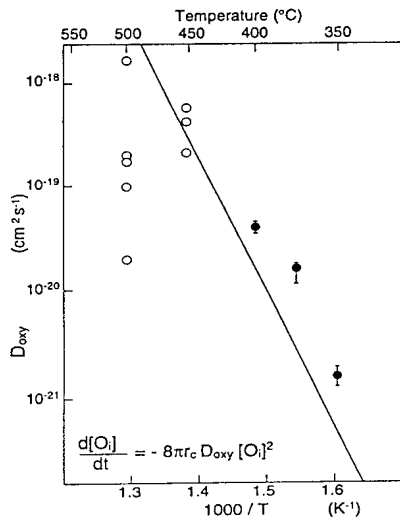


Figure 5. Average values of D_{oxy} for samples A-E annealed at $T < 400^\circ\text{C}$ (●) from second order kinetics, and apparent values for higher temperatures [2].

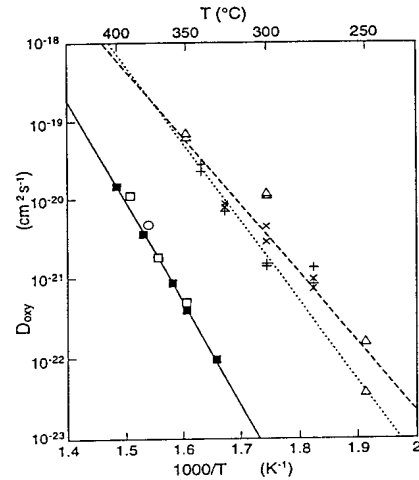


Figure 6. Values of D_{oxy} derived from the relaxation of stress-induced dichroism showing normal diffusion (□, ■, ○) and (Δ)(+)(x) enhancements due to the presence of hydrogen [2].

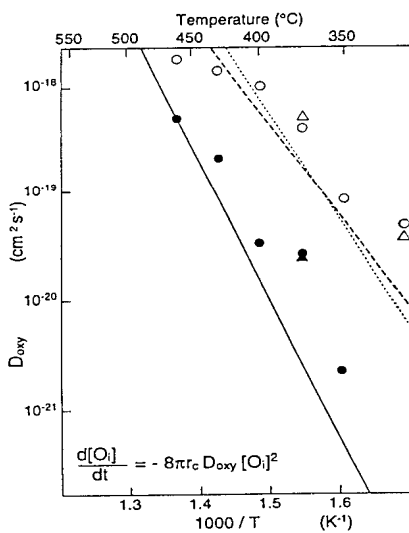


Figure 7. D_{oxy} derived from second order kinetics for crystals A (▲) and F (●) and corresponding data (Δ, ○) for samples hydrogenated at 1300°C [2].

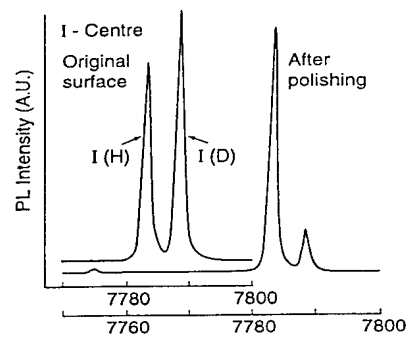


Figure 8. PL from the I-centre in Cz Si annealed at 450°C in argon containing D_2O vapour. The diffusion depth of D atoms is indicated by the reduction in I(D) after the removal of $25\mu\text{m}$ of Si from the surface [16].

apparent for T just greater than 500°C but the enhancements in both $d[\text{O}_i]/dt$ and $d\Sigma[\text{TDN}]/dt$ become negligible at slightly higher temperatures where there are anomalous changes in the kinetics as microscopic processes change to macroscopic precipitation [1].

Recently, photoluminescence (PL) measurements made on heat treated as-grown Si (450°C) have revealed the presence of defect complexes incorporating carbon and hydrogen leading to the view that most as-grown silicon may contain a small concentration of hydrogen. When deuterium was introduced into the samples by heating them at 450°C in D_2 gas or D_2O there was a relatively large shift in the energy of the PL transition (figure 8). D-atoms diffused only some $25\ \mu\text{m}$ into the surface whereas hydrogen appeared to be present throughout the thickness of the sample [16]. Other measurements of IR electronic absorption from oxygen clusters that act as *shallow* thermal donors have shown that hydrogen atoms are actually incorporated in some of these defects [17]. Thus the energies of the far IR electronic transitions are shifted when H atoms are replaced by D atoms due to a modified electron-phonon interaction (figure 9). These same defects may be responsible for the electron paramagnetic resonance (EPR) spectrum NL10, since associated electron nuclear double resonance (ENDOR) transitions from hydrogen have been detected [18]. There is no evidence that hydrogen is incorporated in normal thermal donors TDN revealed by IR spectra and the NL8 EPR spectrum. NL10 defects may therefore be TD centres passivated with one H-atom so that they are converted to single donors. Since NL10 defects are found in Si that has not been deliberately hydrogenated it follows that there is additional spectroscopic evidence that all as-grown CZ Si contains H impurities.

It could then be argued that the small enhancements in D_{oxy} deduced from the rate of oxygen agglomeration at low temperatures in as-received material are due to grown-in hydrogen, but it is not obvious that this argument can be applied to the deliberately hydrogenated samples. According to theory, the enhancement should depend on the concentration of mobile H-atoms present which is likely to be different for measurements of O_i loss and dichroism loss respectively because the latter measurements require an intermediate anneal of the sample (both for as-grown and hydrogenated material) at 400°C for 30 min under a uni-axial stress to induce the dichroism. Alternative possibilities are (a) that the capture radii for dimer formation could be as large as $10\text{-}15\text{\AA}$ [1], (b) that stress dichroism measurements under-estimate the value of D_{oxy} , for reasons that are presently unknown, or (c) that some other process occurs (see Section 4).

4. DISCUSSION

We now consider various models in an attempt to explain the observed O_i precipitation and to investigate the longer term possibility of assigning O_n aggregates of certain sizes to particular TDN defects. To start, we recall the model (a) of Tan et al [11] in which two O_i atoms diffuse to form an O_2 dimer that is stable and immobile. There is further diffusion of O_i atoms to convert O_2 to O_3 etc, to build up a sequence of clusters. The results of modelling are shown in figure 10 for heating times at 450°C up to 500 h,

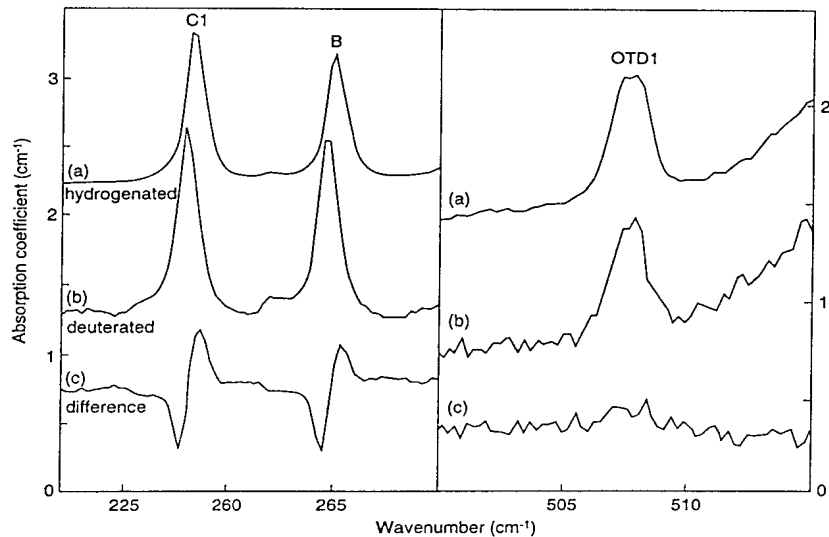


Figure 9. $1s \rightarrow 2p_{\pm}$ transitions of electrons bound to STDs (B and C1) (left) and TD1 (right) in the spectra of samples pre-heated in (a) H_2 and (b) D_2 , followed by an anneal at $350^\circ C$ for 30 min. The difference spectra (c) reveal shifts in the B and C(1) lines when H is replaced by D [16].

assuming a normal value of D_{oxy} . The concentrations of $[O_2] \sim 10^{17} \text{ cm}^{-3}$, $[O_3] \sim 10^{16} \text{ cm}^{-3}$, $[O_4] \sim 10^{15} \text{ cm}^{-3}$ (200h), etc rapidly decrease with increasing size and since $[O_2]$ is dominant, the use of simple second order kinetics is an excellent approximation, justifying our earlier assumptions. We see that $[O_2]$ is a factor of ~ 10 greater than $\Sigma[TDN] \sim 10^{16} \text{ cm}^{-3}$ and so it is not possible to make an assignment of O_2 defects to TD-centres. If allowance is made for dissociation of all O_n clusters ($n \geq 2$) at the same rate (model b), there is no change in the kinetics of O_i loss at short times because the concentrations of $[O_n]$ have to build up before they can dissociate. In addition, there is no explanation of the observed modified kinetics (a change to third order) at $450^\circ C$ and a higher order (depending on $[O_i]_0$) at $500^\circ C$ [11]. A radical modification is clearly required.

It has been proposed [12] that O_2 dimers diffuse more rapidly than O_i atoms and there is some support for this proposal from theory [see Ref. 1]. We therefore remodelled the kinetics of O_i loss with the assumption that $D(O_2) = 10^4 D_{oxy}$ (normal) (model (c)). The result is that once O_2 pairs are formed they diffuse rapidly and are trapped by an O_i atom, the defect present in the highest concentration, to give an O_3 cluster that is assumed to be immobile and stable. Thus, the rate, $d[O_i]/dt$, is increased by a factor of $3/2$, the concentration of $[O_3]$ reaches $\sim 10^{17} \text{ cm}^{-3}$ after 100 h, while $[O_4]$ reaches $\sim 2 \times 10^{15} \text{ cm}^{-3}$, and so on (figure 11a). This model cannot therefore offer an explanation for

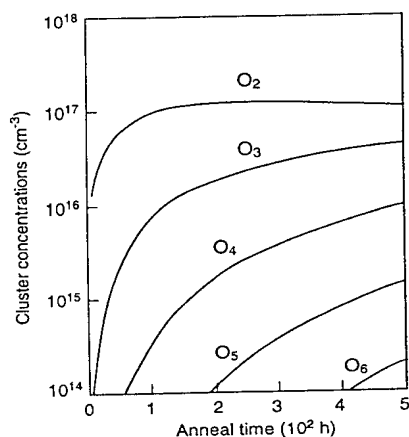


Figure 10. The serial growth of O_2 , O_3 , O_4 etc., clusters as a function of time with a normal value of D_{oxy} and without dissociation [11]

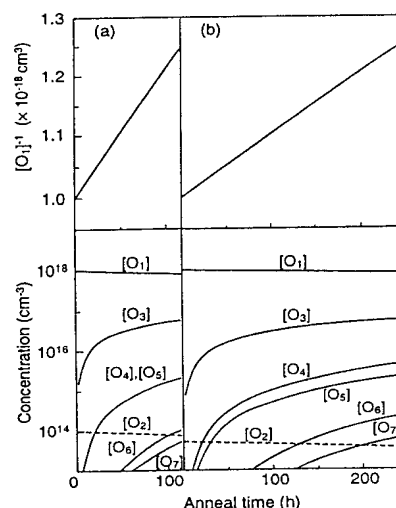


Figure 11. Variations of $[O_i]^{-1}$ of the simulated evolution of O_2 , O_3 etc, assuming $D_{O_2}/D_{oxy} = 10^4$ (a) when all clusters are stable and (b) when dimer dissociation occurs at a rate of $2 \times 10^{-3} \text{ s}^{-1}$.

the observed kinetics at $T \geq 450^\circ\text{C}$, nor can assignments be made to a family of TD defects if they are to be attributed to O_n clusters.

In Section 1 we presented evidence that dissociation of O_n clusters is important and so it is logical to suppose that O_2 dimers, the smallest cluster, would be the least stable. We therefore remodelled the O_i loss with rapid O_2 diffusion (as above) but also with rapid O_2 dissociation (model (d)). The lifetime is considered to be "long" in this model if it is greater than the time for O_2 to diffuse to and be trapped by an O_i atom. Otherwise, the lifetime is considered to be short. If dimers form and dissociate sequentially a few times during the formation of O_3 clusters, there is still an enhanced overall rate for the reaction but the kinetics tend to third order (figure 11b). If the lifetime of O_2 is long (at $T < 450^\circ\text{C}$) the kinetics are second order.

The likelihood of dissociation can be extended to larger clusters which could release an O_i atom, or alternatively an O_2 dimer. The time available for dissociation is relatively much longer than that for dimer dissociation since the clusters will have to survive extended anneals and not just the transit time for a dimer to be captured by an O_i atom or a larger oxygen cluster. The consequence is that the concentrations of a number of larger clusters can build up to values approaching $\sim 10^{16} \text{ cm}^{-3}$. This is obvious since $[O_2]$ reaches $\sim 10^{17} \text{ cm}^{-3}$ in model (a) but has a very low value (10^{14} cm^{-3}) in model (d). Thus

if a concentration of 10^{17} cm^{-3} dimers were re-organised into O_8 clusters, they would be present in a concentration $[\text{O}_8] \sim 2.5 \times 10^{16} \text{ cm}^{-3}$, etc : this number is clearly over-estimated, as dissociation of dimers would reduce the rates of cluster formation. Nevertheless, there appears to be a mechanism whereby larger clusters can be generated with a possibility of assignments to TD centres at some future stage.

5. CONCLUSIONS

We have shown that the loss of oxygen from solution for $T \leq 500^\circ\text{C}$ is rate limited by diffusion of 2 O_i atoms to form dimers. If D_{oxy} is enhanced by a hydrogenation treatment prior to the anneal, there is a corresponding increase in $d[\text{O}_i]/dt$ and a correlation with $d\Sigma[\text{TDN}]/dt$ so that the ratio $-\Delta[\text{O}_i]/\Delta\Sigma[\text{TDN}]$ remains close to 10. It is also apparent that dissociation is important at $T \geq 450^\circ\text{C}$ since there is a breakdown of second order kinetics. This has been modelled with the assumptions that O_2 dimers diffuse very rapidly and dissociate rapidly. The implication that mostly large O_n clusters form ($n \sim 10$) at 500°C is consistent with other measurements and analyses for oxygen loss at $T \geq 500^\circ\text{C}$. With these assumptions it is possible to generate clusters with a range of sizes and it may be possible to assign particular clusters to members of the TDN family. An Arrhenius plot of D_{oxy} or $\Sigma[\text{TDN}]$ will have lower values at high T than those expected from second order kinetics because of $(\text{O}_i)_n$ dissociation, and larger values at low T if there are small enhancements of D_{oxy} . The average slope will then be less than 2.5 eV, the activation energy for normal oxygen diffusion. This can explain the measured values of $\sim 2.0 \text{ eV}$, while the ratio of $\Delta[\text{O}_i]/\Delta\Sigma[\text{TDN}] \sim 10$ does not change.

It has already been stated that small enhancements of D_{oxy} at $(350\text{--}400^\circ\text{C})$ could occur due to the presence of grown-in hydrogen but it is then difficult to explain the extra enhancement found in the hydrogenated samples (figure 7) at the lowest temperatures. An alternative possibility is that the enhancements result from the capture and subsequent dissociation of dimers at isolated O_i atoms [19]. There is no suggestion that O_3 trimers are mobile but the transient interaction could lead to a change in the location of the O_i atom so that it would appear that a diffusion jump had occurred. The rate of this reaction would be given by $4\pi r_c[\text{O}_2]D(\text{O}_2)s^{-1}$ per O_i atom, leading to a jump distance of $\sim 2\text{\AA}$ between adjacent bond-centred sites. In that case, $D_{\text{oxy}}(\text{enh})$ would be equal to $2.4 \times 10^{-22} [\text{O}_2] D(\text{O}_2) \text{ cm}^2\text{s}^{-1}$, with r_c set equal to 5\AA . To observe an effect the value of the enhanced diffusion coefficient would have to be at least as great as $D_{\text{oxy}}(\text{normal})$ leading to $D(\text{O}_2)/D_{\text{oxy}} > 4 \times 10^{21} [\text{O}_2]^{-1}$. If $[\text{O}_2]$ were of the order of 10^{14} cm^{-3} (figure 11), the ratio $D(\text{O}_2)/D_{\text{oxy}}$ would have to be greater than $\sim 10^8$. These values are in general accord with the findings of Gösele and Tan[13] for $T = 450^\circ\text{C}$, although they deduced a larger value of $D(\text{O}_2)$ but a correspondingly smaller value of $[\text{O}_2] \sim 5 \times 10^{12} \text{ cm}^{-3}$. Enhancements would become more apparent at $T < 450^\circ\text{C}$ and may not be observed in experiments that detect only single O_i diffusion jumps, as in the relaxation of stress-induced dichroism. In the light of the present results, there could be an implication that $D(\text{O}_2)$ is enhanced as well as D_{oxy} when hydrogen is present. This would be necessary to explain the data in figure 7, where the estimates of D_{oxy} again lie above the line for enhanced O_i diffusions after hydrogenation. It would seem that the

enhancement factor of 10^4 chosen to construct figure 11 may be too small by several orders of magnitude [13].

Fast diffusing O_2 species could also be captured by substitutional carbon impurities that could be displaced into interstitial sites to produce stable defects such as the P-centre [20] (attributed to an O_2C_i complex) and perhaps the I-centre (figure 8). In that case, the dimers could not agglomerate to form large $(O_i)_n$ clusters that may be the TD-centres. This would explain the suppression of TD-formation in high carbon silicon [21]. There could likewise be interactions with boron or aluminium impurities, [7]. Thus the model outlined gives a straightforward explanation for all the major observations relating to the kinetics of TD-formation, although the reason for their electrical activity has not been considered. The role of I-atoms has not been discussed here but their involvement in TD formation is certainly not ruled out by the present work. Nevertheless it is necessary for further *ab initio* calculations to be made to test the validity of the proposed speculations, particularly that of rapid dimer diffusion.

Other new information may be obtained from studies of vibrational absorption that has been attributed to TD-centres [22]. The interpretation of the most recent results [23] appears to be complex. A rather definitive statement that the strength of the new vibrational absorption due to TD-centres corresponds to $\sim 10 O_i$ atoms per donor is not however justified. This is because the calibration factor for the $9\mu m$ O_i band (relating to the peak absorption coefficient, α) is used to estimate the number of O_i atoms involved but no account is taken of the smaller linewidths (Δ) of the "donor" lines of $\sim 4cm^{-1}$, compared with $\Delta \sim 35cm^{-1}$ for the $9\mu m$ band at 300K: concentrations have to be related to the integrated absorption ($\alpha\Delta$). Use of the O_i calibration therefore implies only about one O_i atom per TD, as pointed out previously [2]. This number may also be incorrect if clustered O_i atoms have different bonding configurations from the Si- O_i -Si structure [24]. Further work is required to establish the relevant calibration.

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REFERENCES

- [1] Newman R.C. and Jones R. : in Semiconductors and Semimetals, edited by F. Shimura (Academic, San Diego, 1994), Vol. 42 Chapt 8 pp-352.
- [2] McQuaid S.A., Binns M.J., Londos C.A., Tucker J.H., Brown A.R. and Newman R.C. : J. Appl. Phys. (1995), 77, 1427
- [3] Newman R.C. : in Defects in Silicon II, edited by W. M. Bullis, U. Gösele and F. Shimura, Electrochem Soc. (Pennington PA, 1991) Vol. 91-9, p271.
- [4] Newman R.C., Claybourn M., Kinder S.H., Messoloras S., Oates A.S. and Stewart R.J. : in Semiconductor Silicon edited by H. R. Huff, T. Abe and B. Kolbesen (Electrochem Soc. Pennington, NJ 1986), Vol 86-4, p766.
- [5] Bullough R. and Newman R.C. : Rep. Prog. in Phys. (1970), 33, 101.
- [6] Gösele U., : Mater. Res. Soc. Symp. Proc. (1986), 59, 419..
- [7] Newman R.C. : J. Phys. C. (1985), 18, L967.

- [8] Götz W., Pensl G. and Zulehner W. : Phys. Rev., (1992), B46, 4312.
- [9] Kaiser W., Frisch, H.L. and Reiss, H. : Phys. Rev. (1958), 112, 1546.
- [10] Newman R.C., Brown A.R., Murray R., Tipping A.K. and Tucker J.H. : in Semiconductor Silicon, edited by H. R. Huff, K. G. Barraclough and K. Chikawa (Electrochem Soc., Pennington NJ, 1990) Vol 90-7, p734.
- [11] Tan T.Y., Kleinhenz R. and Schneider C.P. : Mater. Res. Soc. Symp. Proc. (1986), 59, 195.
- [12] Gösele U. and Tan H.Y. : Appl. Phys. (1982), A28, 79.
- [13] Baghdadi A. Bullis W.M., Croarkin M.C., Y.-Z Li, Scace R.I., Series R.W., Stallhofer and Watanabe M. : J. Electrochem Soc. (1989), 36, 2015.
- [14] Claybourn M. and Newman R.C. : Appl. Phys. Lett. (1988), 52, 2139.
- [15] Binns M.J., McQuaid S.A., Newman R.C. and Lightowlers E.C. : Semicond. Sci. Technol. (1993), 8, 1908.
- [16] Lightowlers E.C., Newman R.C. and Tucker J.H. : Semicond. Sci. Technol. (1994), 9, 1370.
- [17] McQuaid S.A. , Newman R.C. and Lightowlers E.C. : Semicond. Sci. Technol., (1994), 9, 1736.
- [18] Martynov Yu.V., Gregorkiewicz T. and Ammerlaan C.A.J. : Phys. Rev. Lett. (1995), 74, 2030.
- [19] Snyder, L.C., Corbett, J.W., Deák, P. And Wu, R. : Mat. Res. Soc. Symp. Proc. (1988) 104, 179.
- [20] Kürner, W., Sauer, R. Dörnen A. and Thonke, K. : Phys. Rev. (1989), 39B, 13327.
- [21] Bean, A.R. and Newman, R.C. : J. Phys. Chem. Solids (1972) 33, 255.
- [22] Lindström, J.L. and Hallberg, T. : Phys. Rev. Lett. (1994), 72, 2729.
- [23] Lindström, J.L. and Hallberg, T. : J. Appl. Phys. (1995), 77, 2684.
- [24] Deák, P., Snyder, L.C. and Corbett, J.W., Phys. Rev. (1992), B45, 11612.