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Novel aspects of oxygen diffusion in silicon

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Normal diffusion of interstitial oxygen atoms (O_i) accounts for the rate of oxygen aggregation in silicon for $T > 500\,^\circ C$. There is evidence for the dissociation of SiO_2 precipitates (Ostwald ripening) and the formation of self-interstitials (I-atoms) to accommodate the local increase in volume. For $T < 500\,^\circ C$, measurements of the loss of oxygen atoms from solution indicate that O_2 dimer formation is the rate-limiting process, but dissociation of dimers must be taken into account when modelling this process. Large clusters of up to 10–20 O_i atoms, usually assigned to thermal donor (TD) defects cannot form unless dimer diffusion is much greater (by a factor of 10^4 to 10^7) than diffusion of O_i atoms and unless there is dissociation of clusters with the emission of dimers. Hydrogen impurities enhance O_i diffusion by a catalytic process and speed up donor formation. Infrared absorption measurements reveal H–O_i complexes and there is also partial passivation of TD defects to produce shallow thermal donors (STDs).

1. Introduction

Silicon crystals grown by the Czochralski (CZ) method from a melt contained in a silica crucible incorporate a supersaturated solution of oxygen impurity atoms in a concentration, $[O_i]$, close to $10^{18}\,cm^{-3}$. These atoms in their dispersed state occupy bonded off-axis interstitial sites with a mean position midway between nearest-neighbour silicon atoms (Fig. 1), and they are electrically neutral. The lack of electrical activity is fortunate as $[O_i]$ is typically orders of magnitude greater than the concentrations of donor or acceptor atoms introduced to fabricate the active region of integrated circuits.

The role of oxygen is nevertheless very significant. Its presence leads to a hardening of silicon so that plastic deformation is inhibited during device processing and the preaggregation of O_i atoms by diffusion leads to the formation of SiO_2 precipitates that act as diffusion sinks for unwanted fast-diffusing metallic contaminants. All the precipitates need to be located below the surface region of the wafer where the circuit is to be fabricated. In practice, a CZ wafer is first heated at a high temperature ($T > \sim 1100\,^\circ C$) to cause outdiffusion of O_i atoms so that $[O_i]$ is depleted in this surface region, called a denuded zone. A second treatment at a low temperature ($T < 800\,^\circ C$) leads to the nucleation and growth of small SiO_2 precipitate particles in the underlying silicon, again as a result of diffusion. In a third treatment at an intermediate temperature ($T > 900\,^\circ C$), some of these particles grow to form the required larger precipitates but others redissolve during dissociation. It is clear that detailed knowledge is required about the diffusion coefficient, D_{oxy}, of O_i atoms over a wide range of temperatures [1, 2].

In the lowest temperature range ($T \leqslant 500\,^\circ C$) anneals of as-grown CZ Si lead to the formation of small clusters of atoms that act as electrically active [3, 4] double donors [5], the so-called thermal donors. There is a family of these defects TD(N) with $1 \leqslant N \leqslant 16$ that evolves (increasing N) with increasing anneal time [6] but the structures of these donors are still unclear, although the presence of oxygen atoms has been confirmed by electron nuclear double resonance (ENDOR) measurements [7]. If these defects incorporate up to 16 or more O_i atoms, as is commonly assumed, we shall show that there is a major problem of understanding the mechanism of their formation; they cannot form by normal (O_i) oxygen diffusion because the process is too slow by many orders of magnitude.

It has been suggested that the TD(N) centres alternatively incorporate only a few O_i atoms (possibly a dimer), together with clustered self-interstitials (I atoms) [8] since these intrinsic defects have to be generated to accommodate the local increase in volume when O_i atoms cluster to form SiO_2 [9, 10]. This secondary process is well-documented in relation to high temperature anneals when one I atom is produced for every two O_i atoms that precipitate. There is strong evidence that the process also occurs in the range $500 \leqslant T \leqslant 650\,^\circ C$ because of the formation of ribbon-like defects observed by high resolution transmission electron microscopy (TEM) [11, 12]. However, the critical number of O_i atoms in a cluster required for the ejection of the first I atom during low temperature anneals ($T < 500\,^\circ C$) is unknown. *Ab initio* theory has implied that this process is endothermic for a dimer but has also led to the proposal that a single I atom, bonded to a pair of adjacent over

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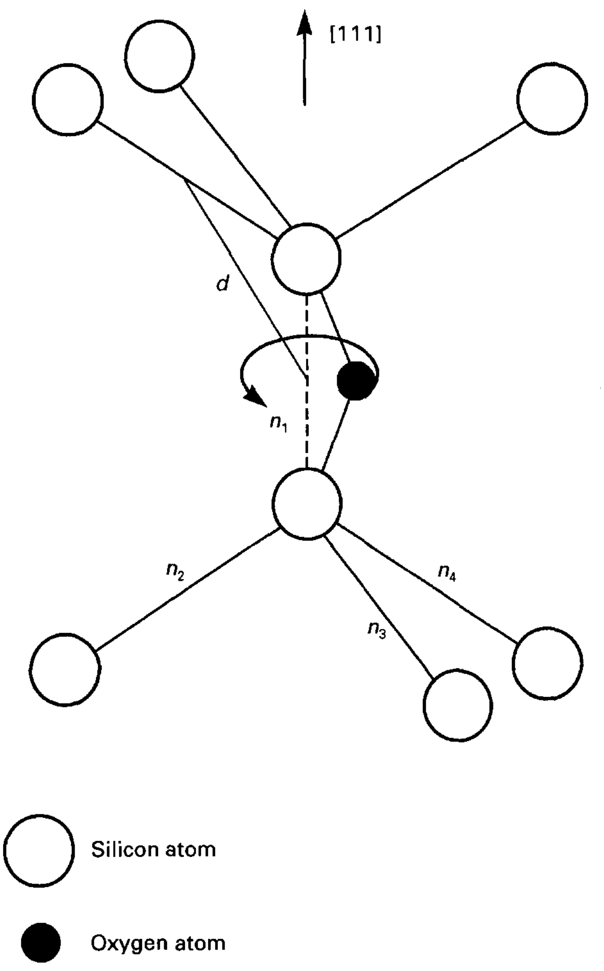

Figure 1 Geometry of a bonded interstitial oxygen impurity atom in silicon showing the off-axis site and the mean diffusion jump distance d. The bond populations, n_1 to n_4, are equal under equilibrium conditions but n_1 is reduced relative to $n_2 = n_3 = n_4$ when the Si is heated to $T \sim 400\,^{\circ}\mathrm{C}$ and a uniaxial stress is applied along the [1 1 1] axis [19].

co-ordinated O_i atoms, constitutes the core of a TD centre and that this I atom is responsible for the electrical activity [13].

Another early proposal was that D_{oxy} is enhanced significantly at low temperatures ($T \leqslant 500\,^{\circ}\mathrm{C}$), possibly due to interactions with I atoms [14], but we shall show that the rate of loss of O_i atoms from solution would then be orders of magnitude greater than measured. This conclusion has been verified experimentally by studies of silicon containing hydrogen impurity atoms [15]. These atoms may be introduced by heating Si in H_2 gas, or a hydrogen plasma; then there are correlated enhancements of the rate of O_i loss and TD formation [16].

This paper presents measurements and the results of modelling that lead to a resolution of the oxygen diffusion problem in high purity, undoped silicon when it is heated to low temperatures ($T < 500\,^{\circ}\mathrm{C}$). Two types of measurement are available that lead to unambiguous conclusions. The first allows D_{oxy} to be measured by the relaxation of stress-induced dichroism, involving single diffusion jumps of oxygen atoms [17]. The second relates to the loss of O_i atoms from solution due to the formation of oxygen clusters. Both types of measurement have been used to characterize the diffusion of oxygen either in as-grown or prehydrogenated Si [16]. To explain the formation of "large" oxygen clusters (10–20 atoms), we propose that oxygen dimers (O_2), once formed, diffuse more rapidly than isolated O_i atoms [16, 18] and that dissociation of larger clusters occurs with the emission of dimers. This paper is a short review of our work with our latest interpretations set against the current state of knowledge.

2. Normal oxygen diffusion

It is now well known from infrared vibrational absorption measurements that oxygen impurities in silicon occupy off-axis bond-centred interstitial sites (Fig. 1) [19]. A $\langle 1\,1\,1 \rangle$ symmetry axis was also implied in early work in which D_{oxy} was determined to be $0.21 \exp(-2.55\ \mathrm{eV}/kT)\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ by measurements of internal friction carried out in the temperature range ($1325 > T > 850\,^{\circ}\mathrm{C}$) [20, 21]. Damping of acoustic waves (100 or 300 kHz) did not occur if the associated stress axis was parallel to a $\langle 1\,0\,0 \rangle$ direction, demonstrating that the O_i atom had to be in a local configuration with a $\langle 1\,1\,1 \rangle$ axis. Values of D_{oxy} were subsequently determined by analysing concentration profiles of ^{18}O diffused at similarly high temperatures into floating zone (FZ) Si (essentially oxygen-free), using secondary ion mass spectrography (SIMS) [22]. These measurements were complemented by a range of other studies (Fig. 2) [19].

The value of D_{oxy} was also determined from the rate of relaxation of stress-induced dichroism of the 9 μm IR absorption band that is due to the antisymmetric vibrational mode of O_i impurities with displacements parallel to a $\langle 1\,1\,1 \rangle$ bond axis (Fig. 1). These measurements relate to single diffusion jumps of the O_i atom from one bond to the next [17]. The normally equal occupations of the four $\langle 1\,1\,1 \rangle$ bonds by O_i atoms are first modified by heating samples at $\sim 400\,^{\circ}\mathrm{C}$ for 30 min, while they are subjected to a uniaxial stress, then cooling them to 300 K with the stress still applied. When the stress is applied along a [1 1 1] axis, the occupation of the bonds parallel to this axis is reduced and there are increased occupations of the other three types of (1 1 1) bond. These non-equilibrium site occupations are lost exponentially during a subsequent isothermal anneal after removal of the stress. The time constant τ for this process is determined from measurements of the loss of dichroism of the 9 μm band by making IR absorption measurement with polarized light. These measurements yield values of $D_{oxy} = a_0^2/64\tau$ for the range $400 \geqslant T \geqslant 330\,^{\circ}\mathrm{C}$ with no adjustable parameters since $a_0 = 0.542$ nm is just the lattice spacing of the Si crystal [19].

A combination of the high and low temperature data leads to normal values of the oxygen diffusion coefficient given by $D_{oxy} = 0.13 \exp(-2.53\ \mathrm{eV}/kT)$ $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ (Fig. 2) [22]. There is a consensus that the diffusion mechanism does not involve lattice vacancies, I atoms or other impurities [19].

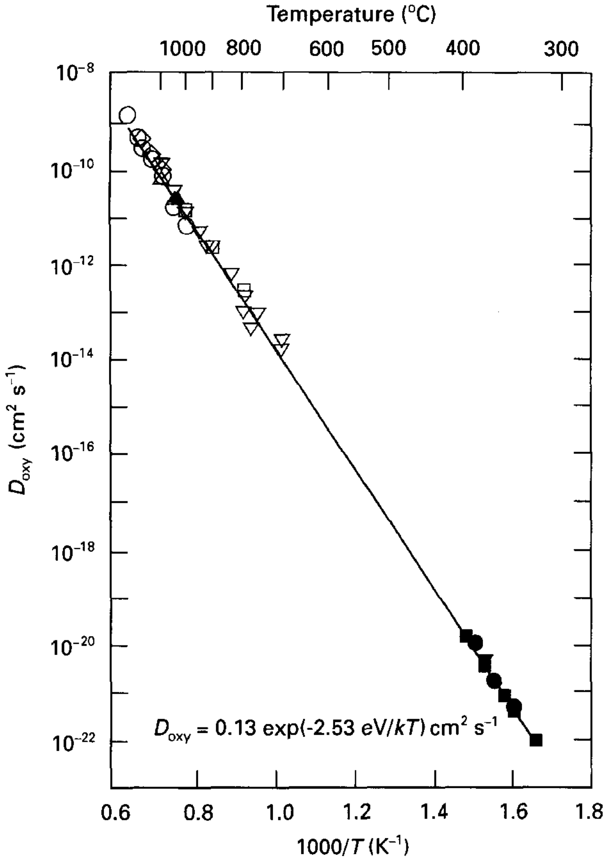

Figure 2 A compilation of measured values of D_{oxy} [19].

3. Aggregation of O_i atoms

3.1. High temperatures ($T \geqslant 650$ °C).

Heat treatments of CZ Si at high temperatures lead to the formation of precipitates of amorphous SiO_2 particles that are identified by TEM, small angle neutron scattering (SANS) [23] or by chemical etching. The measured sizes and number densities of these particles, together with the rate of loss of O_i atoms from solution, determined from reductions in the integrated absorption of the 9 μm IR band, demonstrate that normal O_i diffusion is the rate-limiting process for the precipitation [24]. I atom generation is detected by TEM using the presence of punched-out dissociation loops around precipitate particles or using the formation of stacking faults [1, 2]. It is important to note that, during extended anneals, small particles redissolve by dissociation and large particles become larger, a process known as Ostwald ripening [23]. Thus the SiO_2:Si system is in a state of dynamic equilibrium.

3.2. Intermediate temperatures (500 $\leqslant T \leqslant$ 600 °C)

In this temperature range, SiO_2 precipitate particles are too small to be detected by TEM or SANS, but if D_{oxy} is assumed to have its "normal" values, the number density and hence the average size of the particles can be estimated from the measured rate of O_i loss [25]. At 500 °C the particles are thereby estimated to incorporate only 10–20 O_i atoms. Ribbon-like defects detected by TEM are now attributed to the condensation of I atoms generated by O_i aggregation [11, 12].

In addition, it has been found from measurements of IR electronic absorption that there is annihilation of TD(N) defects formed in a prior anneal at $T < 500$ °C [26]. Isolated O_i atoms are regenerated during this process, as indicated by increases in the strength of the 9 μm IR band. Apart from TD1, "early" donors (TD2, TD3, etc.) are lost first, implying that they incorporate fewer oxygen atoms than donors with larger values of N. Estimates of the solubility of the O_i atoms imply that only a quasi-equilibrium is established, this is because the interface energy of the particles with the Si matrix plays an important role [19]. These results provide further evidence that the aggregates are very small in this temperature range. An extrapolation to lower temperatures of the number of O_i atoms in each SiO_2 precipitate particle measured for $T \geqslant 650$ °C implies that only dimers should be formed for anneals extending to ~100 h at $T < 450$ °C.

3.3. Low temperatures ($T \leqslant 500$ °C)

There is an obvious test of the conclusion that O_2 dimers are the predominant centres formed at low temperatures. The rate of loss of O_i atoms from solution (IR measurements of the 9 μm band) should be in accord with the value predicted by second-order kinetics, $d[O_i]/dt = -8\pi r_c D_{oxy}[O_i]^2$ leading to

$$[O_i]^{-1} - [O_i]_0^{-1} = 8\pi r_c D_{oxy} t \qquad (1)$$

where r_c is the capture radius at which the two atoms bind together. The numerical factor of 8 occurs rather than the usual value of 4 because both O_i atoms are diffusing to give an effective diffusion coefficient of $2D_{oxy}$. The assumption is that any diffusion sinks present in the crystal (defects or impurities other than O_i atoms) have much lower concentrations than the grown-in concentration of $[O_i] \sim 10^{18}\ cm^{-3}$. Thus, there are no adjustable parameters since r_c is expected to be ~0.5 nm. Measurements reported in our early work for $[O_i]_t$ versus time for anneals at 420 °C and 450 °C [27] led to values of D_{oxy} indistinguishable from normal values interpolated from the data shown in Fig. 2. But the value obtained for an anneal at 500 °C led to a value of D_{oxy} of only $1.0 \times 10^{18}\ cm^2\ s^{-1}$ that was too small by a factor of ~5. This discrepancy was attributed to dimer dissociation so that the number of pairs present after a given anneal time t was smaller than the number that should have been formed according to the simple model used.

The model of second-order kinetics can be extended to include the serial formation of trimers and larger clusters O_n by the sequential capture of further O_i atoms. Such computer modelling predicts the results shown in Fig. 3 for $T = 450$ °C [28]. For $t \sim 100$ h the concentrations of $[O_3]$, $[O_4]$, etc., are smaller by factors of ~10 for every extra O_i atom added to the dimer. Although these results support the view that dimer formation is the dominant process and although they vindicate the use of second-order kinetics with only a small error (~10%), they do lead to an apparent impasse because there is no obvious way of generating measurable concentrations of clusters incorporating 10 or more oxygen atoms. This is the

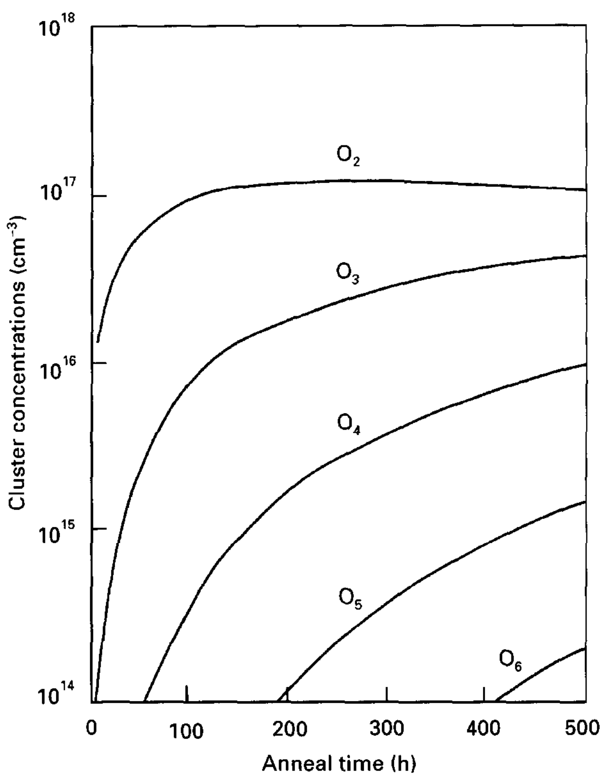

Figure 3 The evolution of oxygen aggregates O_2, O_3, O_4, etc., with increasing anneal time at 450 °C calculated for serial reactions in which only O_i atoms are mobile with the normal value of D_{oxy} [16, 28].

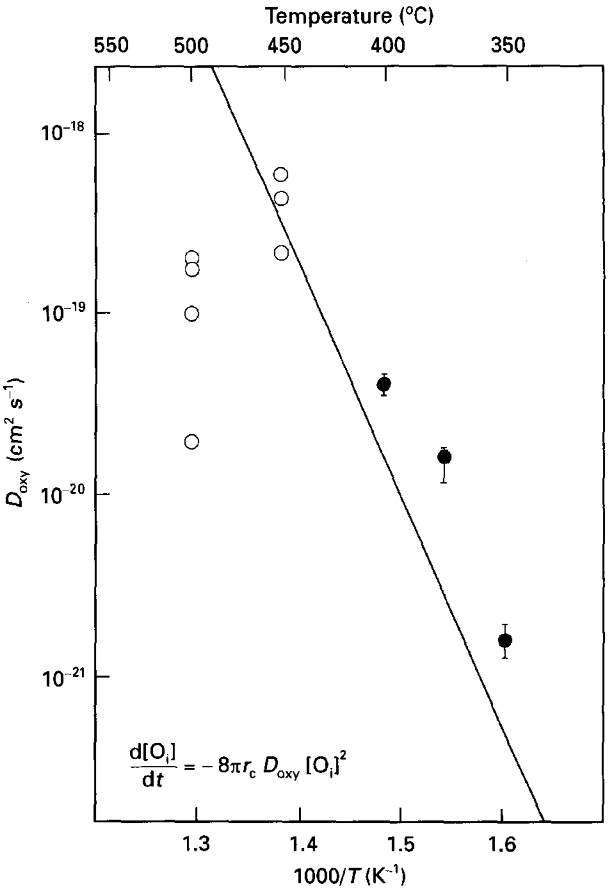

Figure 4 Values of D_{oxy} deduced from the rates of O_i loss using second-order kinetics for five CZ crystals with different values of $[O_i]_0$. D_{oxy} is independent of $[O_i]_0$ for $T \leqslant 400$ °C but larger than the "normal" values (the solid line) by a factor of 3–10. These relatively small increases may be due to the presence of a small concentration of grown-in hydrogen impurities or to the formation and dissociation of O_3 trimers (see Section 5). For $T > 450$ °C the apparent values of D_{oxy} decrease with decreasing values of $[O_i]$ due to dissociation of oxygen clusters [16].

central problem that has to be resolved. To overcome this difficulty, previous workers assumed that D_{oxy} is enhanced at low temperatures so that large clusters could form during the anneal [14]. But then there would be a discrepancy with the rate of loss of O_i atoms from solution; these measurements were not made in earlier work, so the discrepancy was not apparent.

We have now made extensive measurements on a range of samples with five different grown-in $[O_i]$ concentrations (15, 11.6, 11.0, 9.3 and 8.2×10^{17} cm^{-3}) following anneals at a temperature in the range 350–500 °C, with heating times up to 15000 h (~2 years) at 350 °C [16]. Values of D_{oxy}, determined from the rates of O_i loss and modelling by second-order kinetics (Equation 1) were independent of $[O_i]$ for $T \leqslant 400$ °C. However, the apparent value of D_{oxy} deduced by this procedure decreased as $[O_i]$ was decreased for anneals at $T = 450$ °C: the range of D_{oxy} extended over some two orders of magnitude for $T = 500$ °C and all the values were lower than the normal values (Fig. 4) of D_{oxy}. This interpretation of the data for anneals at 450 and 500 °C is clearly non-physical and indicates the importance of dissociation processes, as implied earlier. The rate of loss of O_i atoms from solution varied as $[O_i]^n$ for $T \leqslant 400$ °C with $n = 2$, but n then increased to 3.5 to 450 °C and 9 at 500 °C. This suggests that only aggregates of some 10 or more oxygen atoms (on average) were stable at the higher temperature.

Resistivity measurements (four-point probe) made on the same samples showed that there was formation of one TD centre for approximately every 10 O_i atoms lost, irrespective of the initial values of $[O_i]$, the anneal temperature or the period of the anneal up to the time when $\sum TD(N)$ reached its maximum value [16]. It is not clear why the correlation factor should be 10 or even why it should have a constant value if TD(N) transforms to TD($N + 1$) by the addition of an O_i atom. The rate of TD formation also varied as $[O_i]^n$ with the same values of n (for a given anneal temperature) as those found for O_i loss. These correlations would seem to imply that all the lost oxygen atoms are incorporated in TD centres.

4. Effects of hydrogenation

As the next step, we measured rates of oxygen loss and TD formation resulting from low temperature anneals of samples that had been pretreated in H_2 gas at a temperature in the range 900–1300 °C then quenched to room temperature. The concentrations of incorporated hydrogen atoms are then $\sim 10^{16}$ cm^{-3} and 10^{14} cm^{-1} for quenches from 1300 and 900 °C, respectively, as determined by secondary ion mass spectrometry (SIMS) (for deuterium) and independently by infrared measurements of the formation of boron–hydrogen pairs [29]. We had previously shown, from measurements of the relaxation of stress-induced dichroism, that the hydrogenation procedure led to increased rates of O_i diffusion with $D_{oxy}(H) = 3.2 \times 10^{-4} \exp(-1.96\,eV/kT)\,cm^2\,s^{-1}$ [16]. Because of the lower activation energy compared with that for normal O_i diffusion, the enhancement process is significant only for $T < 500\,°C$. *Ab initio* theory developed by two separate groups has indicated that hydrogen atoms present in either bond-centred sites [30] or antibonding sites [31] could interact catalytically with neighbouring O_i atoms and lower the energy of their saddlepoint configuration during a diffusion jump. Measurements of the rate of loss of O_i from solution show corresponding enhancements for long-range diffusion and correlated increases of the rate of TD formation. Enhancement factors are close to 5, 30 and 300 for $T = 450\,°C$, 400 °C and 350 °C, respectively. The number of O_i atoms lost per donor formed stays at the value of 10. Thus, the rate of oxygen dimerization controls the rate of thermal donor formation. It follows that arbitrarily invoking an increased value of D_{oxy} to explain the formation of large oxygen clusters in *as-grown* material (TD centres) does not provide a solution to the problem defined in Section 3.3 since there would be a corresponding increase in the rate of O_i loss from solution, contrary to the measurements that are now available.

Direct evidence for H–O interactions has been indicated by the observation of a vibrational absorption line at 1075.1 cm^{-1} (Fig. 5) in hydrogenated *n* or *p*-type CZ Si [32, 33]. This line shows a small shift to a higher frequency of 1076.6 cm^{-1} in deuterated Si and is likely to result from an O_i atom paired with an H atom occupying a neighbouring site. This absorption has not been observed in the oxygen-free float zone Si, nor has a high frequency hydrogen stretch mode been detected. Further work is required to determine the structure of the defect responsible.

5. Oxygen dimer diffusion

So far, it has been assumed that all oxygen clusters are immobile, and effects of dissociation have not been considered. It has been proposed that O_2 dimers may diffuse more rapidly than isolated O_i atoms, by a factor of up to 10^7 [18]. It could be argued that the presence of the second O_i atom lowers the saddlepoint energy for a diffusion jump of the first O_i atom, perhaps in a similar way to that for the H–O interaction [30]. Provided there is binding of the two O_i atoms in the dimer, as implied by the kinetic analysis and measurements discussed above, there will be correlated diffusion jumps of the two atoms but eventually the dimer will dissociate. It is important to consider the two possibilities for the dissociation time constant: (a) the time constant is greater than the time for the diffusing dimer to be trapped by another O_i atom to form an *immobile* trimer, and (b) the time constant is

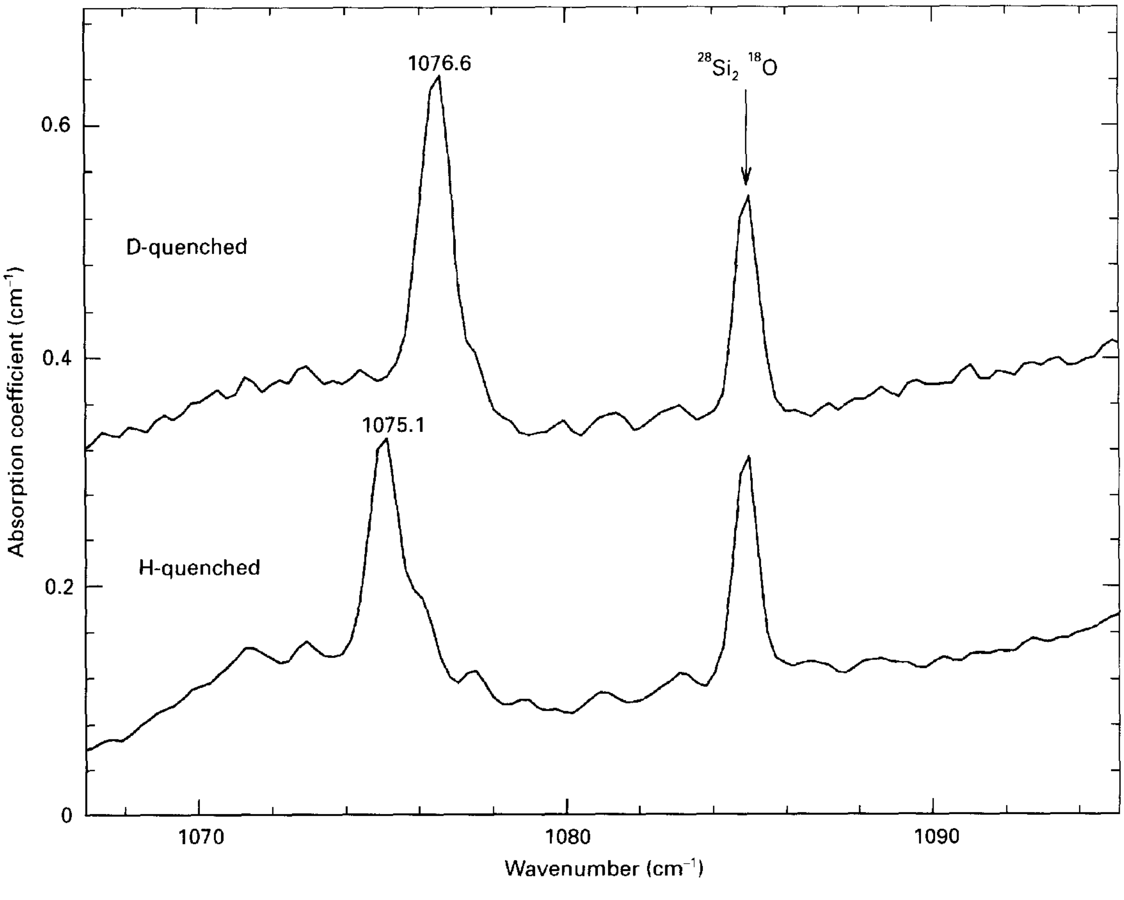

Figure 5 IR spectra (~ 10 K) showing vibrational modes attributed to H–O_i and D–O_i complexes in CZ samples heated at 1300 °C in H_2 or D_2 gas at atmospheric pressure and quenched into silicone oil [33]. The concentrations are estimated to be ~$3 \times 10^{15}\,cm^{-3}$ by comparing the strengths of the lines with that due to naturally occurring $^{18}O_i$ (0.20% abundant at 1085 cm^{-3}). These lines were first reported in Markevich *et al.* [32].

smaller [16]. In case (a) the rate of formation of the trimers would be very similar to the rate of formation of dimers (without rapid O_2 diffusion) and a very low equilibrium concentration of dimers would result. The trimer is unlikely to be stable, as it is also a very small cluster, so dimers and O_i atoms would be regenerated by dissociation, leading indirectly to an enhancement in the diffusion of O_i atoms at low temperatures (Fig. 4). It also follows that two dimers can combine to form O_4, whereas a dimer and a trimer can combine to form O_5. Modelling of dimer reorganization and regeneration [34, 35] appears to be consistent with the formation of clusters incorporating up to 10 or more O_i atoms. This agglomeration process can occur on the required time-scale only because of the assumed high rate of dimer diffusion. An essential result of this model is that the O_i loss is still predicted to occur as a second-order process because *dimer* formation is the rate-limiting process. If, however, diffusing dimers tend to dissociate (for $T \geqslant 450\,^\circ\mathrm{C}$) before being captured by an O_i atom, the rate of $3O_i$ atoms combining to form a trimer is still enhanced, but the kinetics will tend towards third-order instead of second-order. More generally, the order of the kinetics will be related to the size of the first "stable" cluster being produced, whereas the rate of the aggregation process will be reduced compared with the situation when diffusing dimers are captured before they dissociate. This is consistent with the data shown in Fig. 4 since the values of D_{oxy} calculated from measurements of O_i loss, without allowance for dissociation, are much too small for the samples containing the smallest grown-in oxygen concentrations.

6. Conclusions

It has been shown that O_i loss from solution in silicon occurs with second-order kinetics for $T \leqslant 400\,^\circ\mathrm{C}$ and it is implied that dimer formation is then the rate-limiting process. Rapid dimer diffusion and dissociation processes have been invoked to account for the presence of the relatively large oxygen clusters that are presumed to form at these temperatures. For the range $400 \leqslant T \leqslant 500\,^\circ\mathrm{C}$, dimer dissociation prior to dimer capture by an O_i atom becomes important, the order of the kinetics increases, and the rate decreases in agreement with previously unexplained data [28]. The proposed model of rapid dimer (O_2) diffusion could in principle be reformulated in terms of rapid diffusion of O_2I or O_2V complex, where V is a lattice vacancy formed by the ejection of an I atom. Generation of self-interstitials at some stage during oxygen agglomeration would be essential to support any proposal that placed an I atom at the core of a TD centre [13].

It has been demonstrated that the presence of hydrogen in Si leads to greatly enhanced O_i diffusion and correlated TD formation at $T \leqslant 450\,^\circ\mathrm{C}$. And remember that hydrogen may pair with various other impurities, particularly those that produce electrical activity so that this activity is then passivated. Partial passivation of double donors, such as sulphur in Si, to give single donors has also been demonstrated by IR measurements of electronic absorption [36]. It is implied that members of the TD(N) family might also be converted to corresponding members of the shallow thermal (single) donor STD(N) family [37] and recent evidence to support that proposal has now been obtained (Fig. 6) [38]. There also appears to be a link to

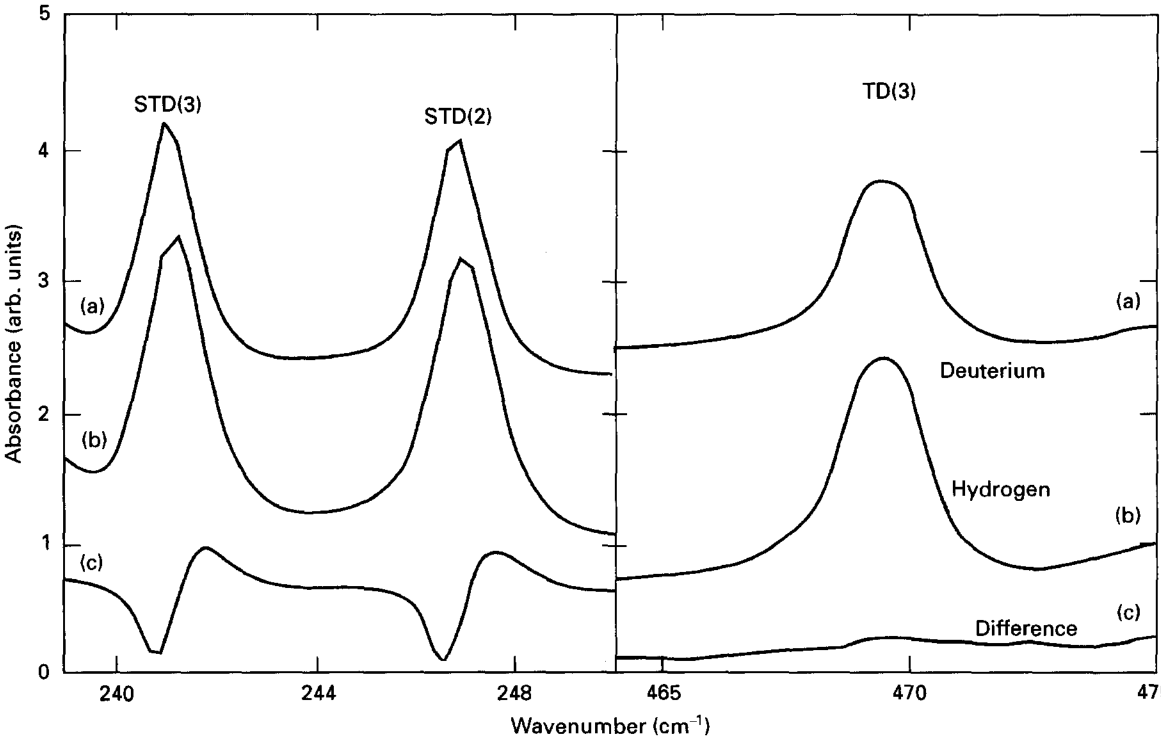

Figure 6 IR electronic absorption (~10 K) from two CZ samples following an anneal at 350 °C for 30 min. Sample (a) was preheated in H_2 gas at 1300 °C and sample (b) in D_2 gas (cf. Fig. 5). The energy (wavenumber) of the transition from the double thermal donor TD(3) near 470 cm^{-1} is the same in both samples as shown by the difference spectrum (c). However, the transitions of two shallow donors labelled STD(3) and STD(2) are shifted to lower energies in the deuterated sample compared with the hydrogenated sample [38]. This shows that an H atom is bound in the donor core and the shift results from the changed zero-point vibrational energy and anharmonic effects.

the well-known NL10 electron paramagnetic resonance (EPR) spectrum since recent measurements have revealed a proton or deuteron interaction in the core of these structures [39].

The problems discussed here extend back some 40 years but significant progress has been made in recent studies. The oxygen diffusion process is central to our understanding and the role of hydrogen in enhancing D_{oxy} appears to have come as a surprise. Although early publications [40, 41] implied this effect and pointed the way, inexplicably, they seem to have been ignored for some 30 years. Further work is still in progress, as illustrated by the results of Fig. 6. Understanding and being able to control the initial stages of oxygen aggregation are crucially important to producing effective gettering during device fabrication, particularly as the feature sizes become ever smaller.

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