

## The effect of impurity-induced lattice strain and Fermi level position on low temperature oxygen diffusion in silicon

Zhidan Zeng,<sup>1,2</sup> J. D. Murphy,<sup>1,a)</sup> R. J. Falster,<sup>3,1</sup> Xiangyang Ma,<sup>2</sup> Deren Yang,<sup>2</sup> and P. R. Wilshaw<sup>1</sup>

<sup>1</sup>*Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, United Kingdom*

<sup>2</sup>*State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China*

<sup>3</sup>*MEMC Electronic Materials, viale Gherzi 31, 28100 Novara, Italy*

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Oxygen diffusion in silicon is known to be affected by high concentrations of impurities, although the mechanism underpinning this is poorly understood. We have studied oxygen transport in Czochralski silicon by analyzing data on the locking of dislocations by oxygen as a function of time and temperature. In this paper, we present new data from crystals grown to contain high levels of germanium and arsenic. We analyze these new data, together with our previous data for silicon with a high boron concentration, to further the understanding of the mechanism by which high impurity concentrations affect oxygen transport at temperatures at which the oxygen dimer dominates transport (up to 550 °C). Our results show that a high level of boron doping ( $\sim 3 \times 10^{18} \text{cm}^{-3}$ ) enhances the effective diffusivity of oxygen by a factor of  $\sim 8$  to  $\sim 25$  relative to low doped material with the same oxygen concentration. High levels of germanium doping ( $\sim 8 \times 10^{19} \text{cm}^{-3}$ ) and arsenic doping ( $\sim 2 \times 10^{19} \text{cm}^{-3}$ ) can both have a slight retardation effect on oxygen transport. The magnitude of the reduction measured is less than a factor of  $\sim 4$  in the heavily germanium doped specimens and less than a factor of  $\sim 5$  in the heavily arsenic doped specimens, and in most cases is significantly less than this. Germanium doping introduces considerable strain into the silicon lattice without affecting the Fermi level position, so data from these samples show that lattice strain affects oxygen dimer transport. The arsenic and boron doping levels in the materials studied give rise to lattice strain with a smaller magnitude and opposite sign to that in the germanium doped samples. It is therefore suggested that the Fermi level position also affects the transport of oxygen dimers. © 2011 American Institute of Physics. [doi:10.1063/1.3555625]

### I. INTRODUCTION

Silicon grown by the Czochralski method (Cz-Si) typically has an interstitial oxygen concentration of order  $10^{18} \text{cm}^{-3}$ , which is a consequence of the dissolution of the walls of the silica crucible which contains the melt. Oxygen in Cz-Si can give rise to both beneficial and detrimental effects. Oxygen precipitates produced by carefully controlled heat treatments can act as preferential nucleation sites for precipitates of harmful metallic impurities,<sup>1</sup> so by controlling the location of oxygen precipitates it is possible to confine metallic impurities to regions of wafers far from active devices in a process known as internal gettering (see<sup>2</sup>). Oxygen can also improve the mechanical strength of Cz-Si by precipitation in the bulk<sup>3,4</sup> and by atomic decoration of dislocations.<sup>5-7</sup> Oxygen-related defects can act as recombination centers, including thermal donor defects formed upon annealing at low temperatures,<sup>8</sup> boron-oxygen complexes formed upon illumination<sup>9</sup> and oxide precipitates.<sup>10,11</sup>

Studying the properties of silicon with high dopant concentrations has recently become of interest as device manufacturers are increasingly using material with very high ( $10^{18} \text{cm}^{-3}$  and above) concentrations of shallow dopants for power devices. Additionally, doping Cz-Si with high

concentrations of germanium has been shown to provide substantial benefits, including improved internal gettering,<sup>12</sup> a retardation in thermal donor formation,<sup>13,14</sup> a reduction in the formation of boron-oxygen defects<sup>15</sup> and improved mechanical properties.<sup>16</sup> In order to maximize the benefits and minimize the detrimental effects of oxygen in silicon, it is vital to understand how the presence of such high concentrations of dopants affects its transport properties.

The transport of oxygen in Cz-Si with standard shallow dopant concentrations ( $< 10^{16} \text{cm}^{-3}$ ) is well understood for temperatures between 700 and 1200 °C. The diffusivity of oxygen,  $D$ , in this temperature range is given by<sup>17</sup>

$$D = 0.13 \exp\left(-\frac{2.53 \text{ eV}}{kT}\right) \text{cm}^2 \text{s}^{-1}. \quad (1)$$

In the low temperature range (350 to 600 °C) oxygen transport has been found to be higher than would be expected from extrapolation of the high temperature data using Eq. 1.<sup>18-20</sup> The difference in oxygen transport between the two temperature ranges is attributed to the different species that are thought to dominate transport in these ranges. At high temperatures the oxygen monomer is responsible for transport; at low temperatures the oxygen dimer<sup>21</sup> is thought to be principally responsible and experimental evidence for this has been provided by a dislocation locking technique.<sup>20,22</sup>

<sup>a)</sup>Electronic mail: john.murphy@materials.ox.ac.uk.

As two different species are mainly responsible for the transport of oxygen in silicon, it is often necessary to describe oxygen transport in terms of an effective diffusivity,  $D_{eff}$ . This is defined as the constant of proportionality linking the flux of atoms,  $J$ , and the negative of the concentration gradient,  $dC/dx$ , according to

$$J = -D_{eff} \frac{dC}{dx}. \quad (2)$$

The effective diffusivity can be expressed in terms of the component concentrations and diffusivities according to<sup>20</sup>

$$D_{eff} = \frac{C_O D_O + 2C_{O_2} D_{O_2}}{C_O + 2C_{O_2}}, \quad (3)$$

where  $C_O$  and  $C_{O_2}$  are the concentrations of the oxygen monomer and dimer, respectively, and  $D_O$  and  $D_{O_2}$  are the diffusivities of the oxygen monomer and dimer, respectively. Since  $C_O \gg C_{O_2}$ , Eq. 3 can be approximated as

$$D_{eff} \approx D_O + 2 \frac{C_{O_2}}{C_O} D_{O_2}. \quad (4)$$

At low temperatures the oxygen dimer is believed to dominate transport so  $D_{O_2} \gg D_O$ . If it is then assumed that oxygen monomers and dimers exist in thermodynamic equilibrium then Eq. 4 can be simplified to:

$$D_{eff} \approx 2C_O D_{O_2} \exp\left(\frac{\Delta G_{binding}}{kT}\right), \quad (5)$$

where  $\Delta G_{binding}$  is the binding energy of the oxygen dimer. The diffusivity of the oxygen dimer,  $D_{O_2}$ , can be expressed in Arrhenius form as

$$D_{O_2} = D_{O_2} \exp\left(-\frac{E_{O_2}}{kT}\right), \quad (6)$$

where  $D_{O_2}$  is the oxygen dimer diffusivity prefactor and  $E_{O_2}$  is the activation energy for oxygen dimer diffusion. Combining Eqs. 5 and 6 gives the following expression for low temperature oxygen transport in silicon:

$$D_{eff} \approx 2C_O D_{O_2} \exp\left(\frac{\Delta G_{binding} - E_{O_2}}{kT}\right). \quad (7)$$

It is therefore important to realize that when total oxygen transport is measured at low temperatures, the activation energy for transport is not merely that for diffusion of the oxygen dimer, but also includes a component relating to the binding energy of the dimer. The results of the dislocation locking experiments show a kink in a plot of effective diffusivity as a function of temperature at  $\sim 700^\circ\text{C}$ .<sup>20,22</sup> Below this temperature, the dimer-dominated effective diffusivity was found to be oxygen concentration-dependent (as expected from Eq. 7) with an activation energy of  $\sim 1.5\text{ eV}$ .<sup>20,22</sup> Taking a value of the binding energy of the dimer as  $\sim 0.3\text{ eV}$ ,<sup>23</sup> suggests an activation energy for oxygen dimer diffusion of  $\sim 1.8\text{ eV}$ .

High concentrations of impurity atoms can affect the transport of oxygen in silicon. The results of studies of oxygen diffusion in silicon doped with high levels of boron (Group III), germanium (Group IV), arsenic (Group V) and antimony (Group V) are summarized in Table I. When comparing the results it is important to take into account that the different techniques used are sensitive to different transport processes. Secondary ion mass spectrometry (SIMS) out-diffusion and dislocation locking are sensitive to overall oxygen transport (to a surface or to a dislocation, respectively), so will essentially be determined by monomer diffusion at high temperatures and dimer diffusion at lower temperatures. Stress-induced dichroism is sensitive to single atomic jumps,<sup>24</sup> so consequently the study of Khirunenko *et al.*<sup>25</sup> can only measure the diffusion of oxygen monomers, even though their experiments were performed at temperatures at which oxygen dimers would dominate overall oxygen transport.

We first discuss the monomer-dominated results from the studies in Table I (those which include high temperature data<sup>26–29</sup> and the stress-induced dichroism study<sup>25</sup>). The data in these studies give rise to some contradictory results. The investigations show that at high temperatures high concentrations of boron either have no effect or slow down monomer diffusion,<sup>27,28</sup> that very high concentrations of germanium enhance<sup>29</sup> or reduce<sup>25</sup> monomer diffusion, that high concentrations of arsenic have no effect or slow monomer diffusion<sup>27</sup>

TABLE I. Reported effects of high concentrations of various dopants on the transport of oxygen in Cz-Si.

Dopant	Group	Concentration [ $\text{cm}^{-3}$ ]	Technique	Temperature	Effect on oxygen transport	Reference
B	III	$8 \times 10^{18}$ to $1.2 \times 10^{19}$	SIMS out-diffusion	$1050^\circ\text{C}$	None	[27]
B	III	$8 \times 10^{18}$ to $1.2 \times 10^{19}$	SIMS out-diffusion	$800^\circ\text{C}$	Slows (factor of $\sim 5$ )	[27]
B	III	$4.4 \times 10^{18}$	SIMS out-diffusion	$500$ and $800^\circ\text{C}$	None	[28]
B	III	$4.4 \times 10^{18}$	SIMS out-diffusion	$600$ to $700^\circ\text{C}$	Slows (factor of $\sim 2$ to $3$ )	[28]
B	III	$2.7 \times 10^{18}$ to $8.0 \times 10^{18}$	Dislocation locking	$350$ to $550^\circ\text{C}$	Enhances (factor of $\sim 40$ )	[31]
Ge	IV	$1 \times 10^{16}$ to $1 \times 10^{20}$	SIMS out-diffusion	$1050$ to $1200^\circ\text{C}$	Enhances	[29]
Ge	IV	$5 \times 10^{20}$ to $2.7 \times 10^{21}$	Stress-induced dichroism	$375^\circ\text{C}$	Slows (more with increasing [Ge])	[25]
As	V	$1.1 \times 10^{19}$	SIMS out-diffusion	$1050^\circ\text{C}$	None	[27]
As	V	$1.1 \times 10^{19}$	SIMS out-diffusion	$800^\circ\text{C}$	Slows (factor of $\sim 2.5$ )	[27]
As	V	$4 \times 10^{18}$ to $1.3 \times 10^{19}$	SIMS out-diffusion	$500$ to $800^\circ\text{C}$	Slows ( $E_A$ increased by $0.64$ to $0.68\text{ eV}$ )	[28]
Sb	V	$0.23$ to $2.1 \times 10^{18}$	SIMS out-diffusion	$950$ to $1100^\circ\text{C}$	None	[26]
Sb	V	$5 \times 10^{17}$	SIMS out-diffusion	$800$ to $1050^\circ\text{C}$	None	[27]
Sb	V	$1.3 \times 10^{18}$	SIMS out-diffusion	$600$ to $800^\circ\text{C}$	Slows ( $E_A$ increased by $1.40\text{ eV}$ )	[28]
Sb	V	$8 \times 10^{17}$	Dislocation locking	$450$ to $550^\circ\text{C}$	None	[31]

and that high concentrations of antimony have no effect on monomer diffusion.<sup>26,27</sup> An additional study by Sueoka *et al.* found oxygen precipitation, which is often controlled by oxygen diffusion, to be enhanced in heavily boron doped silicon.<sup>30</sup> If increased oxygen diffusion is responsible for the enhanced precipitation then this would contradict the results of the diffusion studies.<sup>27,28</sup>

Second, we discuss the dimer-dominated studies in Table I.<sup>28,31</sup> For high levels of boron-doping, the results of Takeno *et al.* at low temperatures<sup>28</sup> and Murphy *et al.*<sup>31</sup> are contradictory and suggest either a reduction or enhancement of oxygen diffusion, respectively. The one study which includes low temperature oxygen transport in highly-arsenic doped material shows a reduction in oxygen transport,<sup>28</sup> and this same study shows that oxygen dimer transport is reduced in highly-antimony doped material. While the study of Murphy *et al.* appears to suggest that lower, but still similar, concentrations of antimony have no significant effect on oxygen diffusion,<sup>31</sup> the fact that the antimony concentration in that work is lower than that of Takeno *et al.*<sup>28</sup> suggests it is possible that no effect would be detectable for this lower concentration. An additional study into the formation of thermal donors in Cz-Si containing a high concentration of tin (Group IV) infers that the oxygen diffusion is enhanced in the 500 to 570 °C temperature range.<sup>32</sup>

The results in Table I show that the effect on oxygen diffusion in silicon of high concentrations of dopants is not well understood, with some studies contradicting one another. Partly as a consequence of this, the mechanism by which the oxygen transport is affected is also not clear. In the case of material with high concentrations of shallow dopants, it is possible that a shift in the Fermi level position could explain the change in diffusion observed. A theoretical study by Adey *et al.* suggests the high boron doping will lower the activation energy for oxygen dimer diffusion to 0.86 eV from 1.33 eV in lightly boron doped silicon.<sup>33</sup> While this can qualitatively explain the enhancement of oxygen diffusion observed by Murphy *et al.*, the predicted change in activation energy is much too large to be consistent with the experimental measurements.<sup>31</sup> Furthermore, the fact that high levels of germanium doping have also been found to affect oxygen diffusion<sup>25,29</sup> suggests that lattice strain may play a role in the change in oxygen transport observed.

Dislocations in materials can be pinned by oxygen atoms and the stress required to unpin a dislocation is proportional to the amount of atomic oxygen segregated to the dislocation core.<sup>7,20,22,31</sup> From studying this unlocking stress as a function of annealing time and temperature it is possible to deduce information on impurity transport and impurity-dislocation interactions.<sup>7,20,22,31</sup> In this work, we apply the dislocation locking technique to Cz-Si doped with high concentrations of germanium and arsenic, and we compare the results to those previously published for Cz-Si doped with a high concentration of boron.<sup>31</sup> With these specimens we therefore have oxygen transport data measured by the same technique in material containing a high concentration of a p-type dopant, an n-type dopant, and an electrically inactive dopant. This will allow us to further the understanding of the effects of Fermi level and lattice strain on oxygen dimer diffusion in highly-doped silicon.

## II. EXPERIMENTAL METHODS

### A. Specimens

Experiments were conducted on Cz-Si grown with high concentrations of germanium (Ge<sup>+</sup>) and arsenic (As<sup>+</sup>). Control samples with a low concentration of phosphorus (control) were processed under identical conditions as the Ge<sup>+</sup> and As<sup>+</sup> specimens. Further data are included in this paper for Cz-Si doped with high a concentration of boron (B<sup>+</sup>).<sup>31</sup> The properties of all the samples considered are given in Table II.

The oxygen concentrations stated in Table II were measured by SIMS and the concentrations are stated to the DIN 50438/I (1995) standard. Fourier transform infrared spectroscopy (FTIR), with a calibration coefficient of  $3.14 \times 10^{17}/\text{cm}^2$ , was used to check the oxygen concentrations in the Ge<sup>+</sup> and the control samples. The values were in agreement with the SIMS data to within 6% for the Ge<sup>+</sup> samples and to within 2% for the control samples. Such a double check was not possible for the As<sup>+</sup> and B<sup>+</sup> samples due to free carrier absorption in these samples containing high concentrations of shallow dopants. The oxygen concentration in the B<sup>+</sup> wafer has been previously measured by gas fusion analysis to be  $7.5 \times 10^{17} \text{ cm}^{-3}$ ,<sup>31</sup> but the value from SIMS of  $8.7 \times 10^{17} \text{ cm}^{-3}$  is regarded as more accurate and so is used in the analysis in this paper instead of the previous value. It is also noted that two different As<sup>+</sup> wafers were used for the experiments. The oxygen concentration in the first As<sup>+</sup> wafer (used for annealing temperatures from 400 to 650 °C) was not particularly uniform. SIMS was performed from specimens selected from near the center and at 5mm from the edge of this wafer, and the oxygen concentrations measured were  $9.2 \times 10^{17} \text{ cm}^{-3}$  and  $7.0 \times 10^{17} \text{ cm}^{-3}$ , respectively. The average of these values was used in the analysis, with a larger error assigned to this specimen's oxygen concentration. The oxygen concentration in the second As<sup>+</sup> wafer (used for the anneals at 700 °C) was measured in the center of the wafer by SIMS to be  $7.2 \times 10^{17} \text{ cm}^{-3}$ . The concentrations of dopants other than oxygen stated in Table II were measured by SIMS for the Ge<sup>+</sup> and As<sup>+</sup> samples. A four-point probe was used to determine the resistivities of the B<sup>+</sup> and the control samples from which the dopant concentrations were deduced.

### B. Dislocation locking experiments

The dislocation locking experiments performed are described in detail in our previous papers,<sup>7,20,22,31,34</sup> so only

TABLE II. Properties of the different specimens used in this study. Oxygen concentrations were measured by SIMS and are stated to the DIN 50438/I (1995) standard.

Specimens	Dopant(s)	Group	Dopant concentration(s) [cm <sup>-3</sup> ]	Oxygen concentration [cm <sup>-3</sup> ]
B <sup>+</sup>	B	III	$3 \times 10^{18}$	$8.7 \times 10^{17}$
Ge <sup>+</sup>	Ge	IV	$8 \times 10^{19}$	$8.3 \times 10^{17}$
	B	III	$\sim 10^{15}$	
As <sup>+</sup>	As	V	$2 \times 10^{19}$	$(8.1 \pm 1.1) \times 10^{17}$
Control	P	V	$\sim 10^{15}$	$10.1 \times 10^{17}$

an overview is given here. Rectangular beams were cut or cleaved from the (100)-orientation wafers to have widths of  $\sim 4$  mm and lengths of  $\sim 30$  mm. The surfaces and edges of the beams were mechanically polished to a  $1 \mu\text{m}$  finish. Each beam was then subjected to a planar etch comprising HF (40%),  $\text{HNO}_3$  (69%), and  $\text{CH}_3\text{COOH}$  (glacial) in the volume ratio 8:75:17. This etch smoothed off any damage remaining after the mechanical polishing. For the  $\text{As}^+$  specimens the etch was performed for 30 mins, for the  $\text{Ge}^+$  and control specimens the etch was performed for 4 mins, and for the  $\text{B}^+$  specimens the etch was performed for approximately 2 mins.

A Vickers diamond tip was then used to make indents with a 0.1 N load and a 5 s dwell time at  $250 \mu\text{m}$  intervals along the long axis of each specimen. The specimens were then subjected to a four-point loading to produce a set of dislocation half-loops with diameter of  $\sim 200 \mu\text{m}$ . The temperature of the four-point loading was  $600^\circ\text{C}$  for the  $\text{Ge}^+$ ,  $\text{B}^+$ , and the control specimens. The  $\text{B}^+$  specimens were cooled to below  $400^\circ\text{C}$  with the load still applied to prevent excessive dislocation locking occurring prior to specimen removal from the rig. Due to the considerably higher dislocation velocity in highly-arsenic doped material,<sup>35</sup> the four-point loading for the  $\text{As}^+$  specimens was performed at  $550^\circ\text{C}$ .

The dislocation-containing specimens were then annealed in argon atmosphere at a constant temperature from  $400$  to  $700^\circ\text{C}$  for different times, allowing oxygen to diffuse to and lock the dislocations. The control,  $\text{Ge}^+$  and  $\text{As}^+$  specimens were annealed simultaneously in the same furnace to ensure they experienced exactly the same thermal treatments. The  $\text{B}^+$  specimens were annealed separately. Samples were then given a planar etch with the same composition as before, to remove  $30 \mu\text{m}$  from the surface of each sample. This removed damage associated with the indent and any material from which oxygen may have out-diffused during the annealing process. Each sample was then subjected to a three-point bend at  $550^\circ\text{C}$  to unlock the dislocations from the oxygen impurities. Points of intersection of the dislocation half-loops with the surface were then revealed by preferential etching. A Secco etch comprising  $\text{K}_2\text{Cr}_2\text{O}_7$  (0.15 M) and HF (40%) mixed in the volume ratio 1:2 was used for the  $\text{Ge}^+$  and the control specimens and an etch comprising HF (40%),  $\text{HNO}_3$  (69%), and  $\text{CH}_3\text{COOH}$  (glacial) mixed in the volume ratio 1:3:10 was used for the  $\text{B}^+$  specimens. Secco etching did not reveal dislocations in the  $\text{As}^+$  specimens, so a etchant comprising HF (40%),  $\text{HNO}_3$  (69%), and  $\text{H}_2\text{O}$  in the volume ratio 11:4:7 was used instead. By assuming a linear stress distribution from the outer contact to the center of the long-axis of the beam, the unlocking stress was determined by finding the minimum stress required to move a set of dislocation half-loops.

### III. RESULTS AND DISCUSSION

#### A. Experimental data

Fig. 1 shows the unlocking stress of the dislocations as a function of annealing time at  $400$ ,  $450$ ,  $500$ , and  $550^\circ\text{C}$  for all the specimens investigated, the details of which are given in Table I. In all cases, the unlocking stress initially increases approximately linearly with increasing annealing time over the range of annealing times studied. The rate of this increase

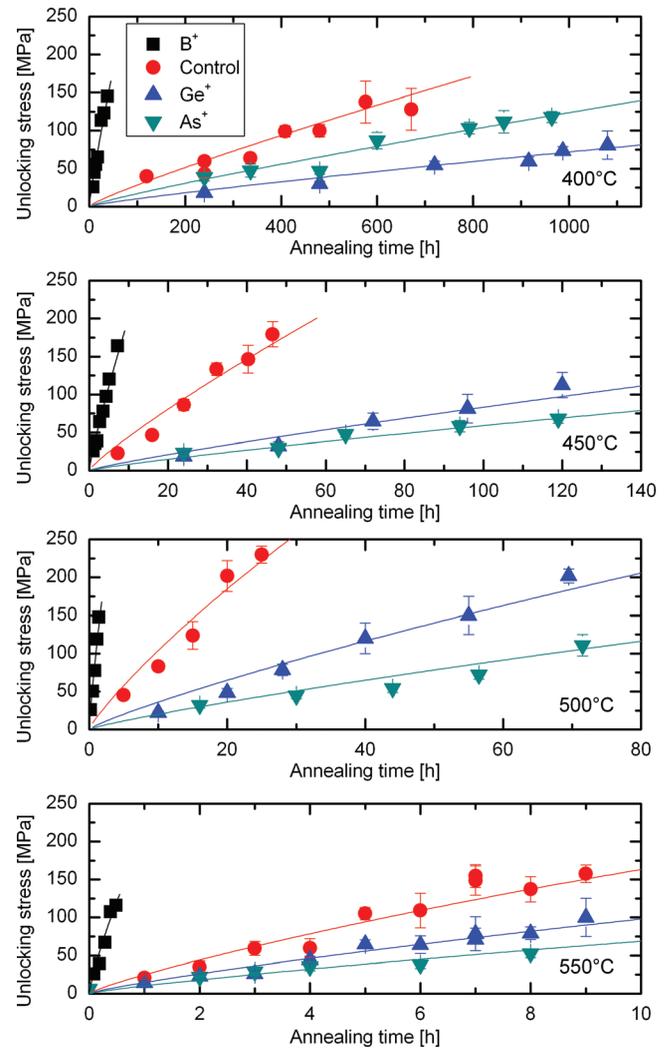


FIG. 1. (Color online) The dislocation unlocking stress as a function of annealing time at  $400$  to  $550^\circ\text{C}$ , temperatures at which the oxygen dimer dominates transport. The properties of the samples are given in Table II. The curves are from a numerical simulation of diffusion to a dislocation, as described in Sec. IV.

is considerably higher in the  $\text{B}^+$  specimens than in any of the other specimens considered. The rate of increase for the control specimens is always higher than that for the  $\text{Ge}^+$  and  $\text{As}^+$  specimens. At all temperatures considered except  $400^\circ\text{C}$ , the rate of increase in unlocking stress is higher in the  $\text{Ge}^+$  specimens than in the  $\text{As}^+$  specimens.

Figure 2 shows the unlocking stress of the dislocations as function of annealing time at  $650^\circ\text{C}$  for the  $\text{As}^+$  specimens and  $700^\circ\text{C}$  for the control,  $\text{Ge}^+$  and  $\text{As}^+$  specimens. For the relatively short annealing times investigated, the unlocking stress initially increases approximately linearly in the  $\text{As}^+$  specimens annealed at  $650^\circ\text{C}$ . At  $700^\circ\text{C}$ , the unlocking stress initially increases and then reaches a plateau. The value of unlocking stress at which the plateau occurs is highest in the control specimens, lower in the  $\text{Ge}^+$  specimens and then lower still in the  $\text{As}^+$  specimens.

#### B. Discussion

Our previous work on dislocation locking by oxygen in silicon with a low concentration of dopants has shown that

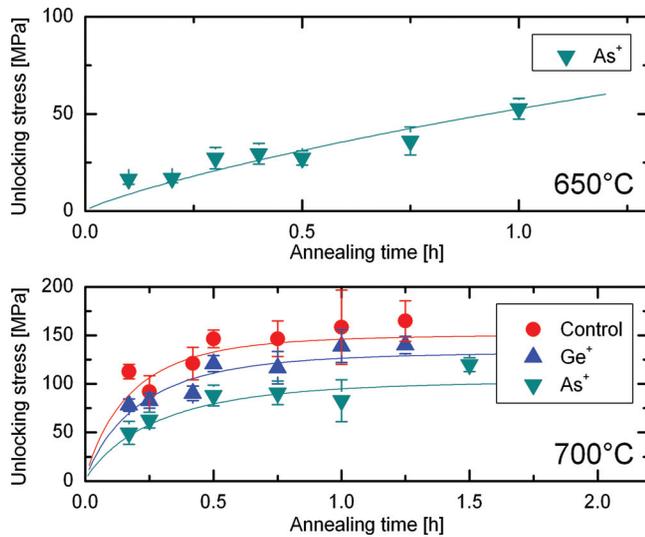


FIG. 2. (Color online) The dislocation unlocking stress as a function of annealing time at 650 to 700 °C for some of the samples listed in Table II. The curves are from a numerical simulation of diffusion to a dislocation, as described in Sec. IV.

the unlocking stress exhibits several regimes as a function of annealing time.<sup>7,20,22</sup> In the first regime, the unlocking stress initially increases approximately linearly, as oxygen is transported to the dislocations. In the second regime, the unlocking stress forms a plateau, as a local equilibrium is established between oxygen at the dislocation and oxygen in the bulk surrounding the dislocation. The rate of initial rise, and the duration and value of the plateau, are dependent on the annealing temperature and the bulk oxygen concentration.

The data presented in Figs. 1 and 2 show the same behavior in silicon containing a high concentration of dopants. Figure 1 shows that, for the annealing times considered, the gradient of the initial rise in unlocking stress is approximately linear. For the higher annealing temperatures shown in Fig. 1, such as at 550 °C, the rate of increase in unlocking stress reduces slightly for longer annealing times as the local equilibrium begins to form. In Fig. 2 it is shown that the unlocking stress reaches a plateau for the annealing times used at 700 °C. The value of the unlocking stress in this second regime,  $\tau_{plateau}$  varies according to<sup>7,20,22</sup>

$$\tau_{plateau} \propto C_O \exp\left(\frac{\Delta G_{dislocation}}{kT}\right) \quad (8)$$

where  $\Delta G_{dislocation}$  is the binding energy of the oxygen to the dislocation. According to this relationship, the value of the

steady-state unlocking stress in regime 2 depends linearly on the oxygen concentration in the sample. If we take the longest two anneals for each specimen type in Fig. 2, we find  $\tau_{plateau}$  to be approximately 162 MPa for the control specimens, 140 MPa for the Ge<sup>+</sup> specimens and 101 MPa for the As<sup>+</sup> specimens. If we normalize these stresses by the oxygen concentrations in the samples then we obtain  $1.6 \times 10^{-10}$  Pa cm<sup>-3</sup> for the control specimens,  $1.7 \times 10^{-10}$  Pa cm<sup>-3</sup> for the Ge<sup>+</sup> specimens and  $1.4 \times 10^{-10}$  Pa cm<sup>-3</sup> for the As<sup>+</sup> specimens. From a series of reproducibility measurements not presented here we know that the potential error in dislocation locking measurements is  $\sim 25\%$ , so, within experimental error, the regime 2 unlocking stress value scales with oxygen concentration in the same way that it does for the low doped material investigated previously.<sup>7,20,22</sup>

#### IV. ANALYSIS OF DISLOCATION LOCKING DATA IN TERMS OF OXYGEN TRANSPORT

##### A. Modeling

The dislocation locking data presented in Figs. 1 and 2 can be used to determine the effective diffusion coefficient of oxygen in silicon,  $D_{eff}$ . The unlocking stress is assumed to be directly proportional to the amount of oxygen at the dislocations. By performing a numerical simulation of oxygen accumulation at the dislocation core it is therefore possible to extract  $D_{eff}$  as a fit parameter. The details of the numerical simulation are given in our previous papers.<sup>7,20,22</sup> The fitting parameters used here are the same as those used previously and so are  $7.6 \times 10^{-5}$  eV K<sup>-1</sup> for entropy,  $5 \times 10^{22}$  cm<sup>-3</sup> for the number of available states at the dislocation core, 0.74 eV for the binding energy of oxygen to the dislocation,<sup>7,20,22</sup> 5 Å for the dislocation core radius<sup>36</sup> and the experimentally-measured oxygen concentrations in the wafers studied (see Table II). The unlocking stress per unit concentration of oxygen atoms at the dislocation has been experimentally-determined to be 7 Pa cm.<sup>7</sup>

The results of the numerical simulation are shown as continuous curves alongside the experimental data in Figs. 1 and 2. The values of  $D_{eff}$  used to give the simulated curves are stated in Table III, together with a value for the B<sup>+</sup> specimens at 350 °C for which the experimental data has been published previously.<sup>31</sup> These values are plotted in Fig. 3 alongside data from the literature obtained by a variety of other techniques.<sup>17</sup> The literature values relate to oxygen monomer diffusion and include high temperature measurements together with stress-induced dichroism measurements at low temperatures.

TABLE III. Values of the effective diffusion coefficient,  $D_{eff}$ , at different temperatures.

Specimens	Oxygen concentration [cm <sup>-3</sup> ]	$D_{eff}$ [10 <sup>-18</sup> cm <sup>2</sup> s <sup>-1</sup> ]						
		350 °C	400 °C	450 °C	500 °C	550 °C	650 °C	700 °C
B <sup>+</sup>	$8.7 \times 10^{17}$	8.0	62	360	1,700	4,400	—	—
Ge <sup>+</sup>	$8.3 \times 10^{17}$	—	1.0	13	47	170	—	9,000
As <sup>+</sup>	$(8.1 \pm 1.1) \times 10^{17}$	—	2.2	9.5	27	120	950	7,000
Control	$10.1 \times 10^{17}$	—	2.9	51	140	260	—	11,000

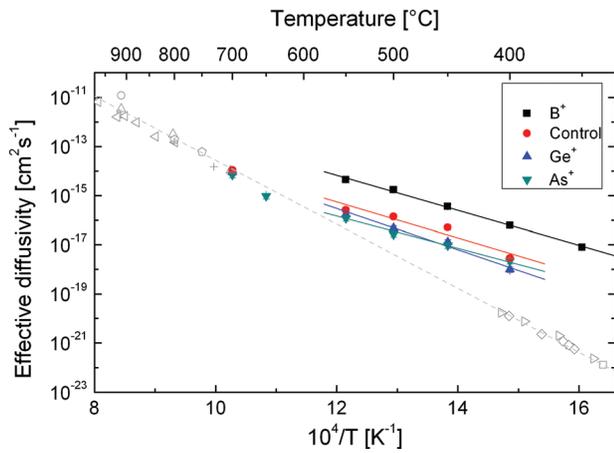


FIG. 3. (Color online) The effective diffusivity of oxygen in silicon as a function of temperature. Data from the dislocation locking experiments described in this paper are denoted by filled symbols. Best fit lines are plotted through these data at low temperatures with  $E_A$  and  $D_{0O_2}$  allowed to vary independently. The other symbols represent data from the literature for oxygen transport in Cz-Si with a low concentration of shallow dopants.<sup>17</sup> The dotted best-fit line to these other data is described by Eq. 1.

## B. Analysis in terms of oxygen transport

As discussed in Sec. I, analysis of the oxygen transport data is complicated by the fact that different oxygen species dominate transport at different temperatures. At low temperatures, including those for which data are plotted in Fig. 1, the oxygen dimer dominates transport.<sup>20,22</sup> Equation 7 shows that the effective diffusivity of the oxygen dimer depends linearly upon the bulk oxygen concentration. The specimens used in the current work have different concentrations of oxygen (see Table II), so consequently to isolate the effects of dopants, it is necessary to normalize  $D_{eff}$  by oxygen concentration. Fig. 4 shows  $D_{eff}$  normalized by the oxygen concentration at temperatures up to 550 °C and Table IV gives the values of  $D_{eff}$  normalized by oxygen concentration relative

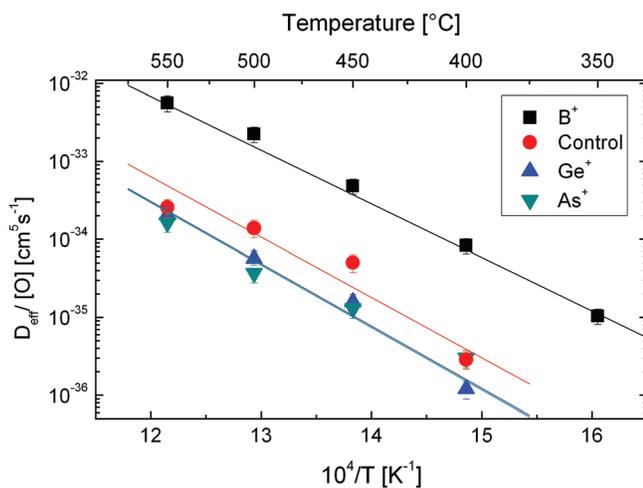


FIG. 4. (Color online) Effective diffusivity normalized by oxygen concentration in the temperature range in which the oxygen dimer is believed to dominate transport. In accordance with Eq. 7, this allows the data for the different samples to be compared directly in spite of the different oxygen concentrations in the samples. To produce the fit lines shown,  $D_{0O_2}$  has been fixed at  $0.03 \text{ cm}^2 \text{ s}^{-1}$  and  $E_A$  has been allowed to vary to provide a good fit to the data.

TABLE IV.  $D_{eff}$  normalized by bulk oxygen concentration in the highly-doped specimens relative to that in the low doped control specimens.

Specimens	$D_{eff}/[O]$ relative to control				Average
	400 °C	450 °C	500 °C	550 °C	
B <sup>+</sup>	24.8	8.2	14.1	19.6	16.7
Ge <sup>+</sup>	0.4	0.3	0.4	0.8	0.5
As <sup>+</sup>	0.9	0.2	0.2	0.6	0.5
Control	1.0	1.0	1.0	1.0	1.0

to those in the low doped-control samples. It can be seen that normalized oxygen transport to the dislocations is always considerably faster in the B<sup>+</sup> specimens than in the control specimens, being increased by a factor of  $\sim 8$  to  $\sim 25$  in the 400 to 550 °C temperature range. Oxygen transport to the dislocations in the Ge<sup>+</sup> and As<sup>+</sup> specimens is always slower than in the control specimens. In the 400 to 550 °C temperature range, the normalized oxygen transport in the Ge<sup>+</sup> specimens is  $\sim 0.3$  to  $\sim 0.8$  of that measured in the controls, whereas in the As<sup>+</sup> specimens the normalized oxygen transport is  $\sim 0.2$  to  $\sim 0.9$  of that measured in the controls.

Are the changes in  $D_{eff}$  measured, particularly the small changes in the Ge<sup>+</sup> and As<sup>+</sup> specimens, larger than the error in the measurement? Major errors in determining  $D_{eff}$  from the dislocation locking technique arise from determining the unlocking stress, fitting the simulation to the experimental data and maintaining constant temperature (particularly during the annealing stage). The potential error in determining the unlocking stress and fitting the simulation to the experimental data is believed to be  $\sim 25\%$ . Consideration of a thermally activation process with activation energy of  $\sim 1.5 \text{ eV}$  shows that just a 5 °C error (increase) in temperature can lead to an error of  $\sim 14\%$  at 550 °C and  $\sim 21\%$  at 400 °C. Thus, the error of determining  $D_{eff}$  from a single set of measurements in isolation, such as in the B<sup>+</sup> specimens considered here, is estimated at 40–50%. However, when comparing the relative normalized values of  $D_{eff}$  in the Ge<sup>+</sup>, As<sup>+</sup> and control specimens at specified temperatures, as in Table IV, the uncertainty is less than this, as these specimens were annealed simultaneously in the same furnace, so any error in temperature is minimal. Therefore, when comparing the values in Table IV, we estimate a  $\sim 50\%$  error in the B<sup>+</sup> values and a  $\sim 25\%$  error in the control and Ge<sup>+</sup> values. The lack of homogeneity in the oxygen concentration in the As<sup>+</sup> wafer contributes an additional error for these samples. Equation 7 shows that  $D_{eff}$  is linearly dependent on oxygen concentration, so the error due to the possible variation in oxygen concentration is less than 15%. We therefore expect an overall error of  $\sim 40\%$  in the As<sup>+</sup> specimens.

The change in oxygen transport in the B<sup>+</sup> specimens is much larger than the error, so the enhancement in oxygen transport in this material is unambiguous. In the Ge<sup>+</sup> and As<sup>+</sup> specimens, the retardation in oxygen transport is generally larger than the error in the measurement, although in two cases (550 °C for Ge<sup>+</sup> and 400 °C for As<sup>+</sup>) the normalized oxygen transport value measured in the control specimen lies within the error bar of that associated with the highly doped specimen. However, it remains the case that all

normalized  $D_{eff}$  measurements in the  $Ge^+$  and  $As^+$  specimens are below those in the control. We therefore conclude that our results are consistent with high levels of germanium and arsenic doping providing a slight retardation effect on oxygen transport in the temperature range considered. The magnitude of the retardation is at most no more than a factor of  $\sim 4$  in the  $Ge^+$  samples and no more than a factor of  $\sim 5$  in the  $As^+$  samples. Any effect due to the lack of homogeneity of oxygen in the  $As^+$  specimens is much smaller than the difference in  $D_{eff}$  we have measured in these specimens.

Dislocation locking data obtained at the higher annealing temperatures of  $650^\circ C$  and  $700^\circ C$  are presented in Fig. 2. Fig. 3 shows the effective diffusivity at these temperatures lies in the intermediate region, between the low temperatures where transport measured by dislocation locking is clearly dimer-dominated and the high temperatures where transport is clearly monomer-dominated. There are insufficient data to draw any conclusions as to the effects of high concentrations of arsenic and germanium on the transport of oxygen at these higher temperatures.

### C. Fitting of low temperature data

In principle, the individual values of  $D_{eff}$  derived from the dislocation locking data could be used to give an expression for the effective diffusivity of oxygen in the temperature range investigated. Equation 7 shows that  $D_{eff}$  at such temperatures is dependent on the bulk oxygen concentration. The low temperature effective diffusivity determined from the dislocation locking data will have the following form

$$D_{eff} \approx 2C_O D_{O_2} \exp\left(-\frac{E_A}{kT}\right), \quad (9)$$

where  $E_A$  is the activation energy for oxygen transport to the dislocations and other variables have the same definitions as in Eq. 7. The activation energy measured experimentally corresponds to  $E_A = -(\Delta G_{binding} - E_{O_2})$ , although it is noted that it is not possible to separate  $E_A$  into its components using data from dislocation locking experiments alone.

It is possible to fit the  $D_{eff}$  values obtained in a particular type of specimen to Eq. 9 in several different ways. Firstly,  $D_{O_2}$  and  $E_A$  can be determined independently from an Arrhenius plot. However, we do not believe our data are sufficiently accurate for this to be reliable. This is because just a small change in  $E_A$  arising from the errors in the values of  $D_{eff}$  would give rise to a very large change in  $D_{O_2}$ . Additionally, the temperature range over which  $D_{eff}$  was determined was just  $150^\circ C$  in most cases, which means  $D_{eff}$  varies only by two orders of magnitude. Another method of fitting the data to Eq. 9 is to fix either  $D_{O_2}$  or  $E_A$  and to allow the other parameter to vary. For instance, if we fix  $D_{O_2}$  to be  $0.03 \text{ cm}^2 \text{ s}^{-1}$  (the average value of  $D_{O_2}$  from the independent fits to the data in Fig. 3) and allow  $E_A$  to vary, we can produce the fits to the data shown in Fig. 4. The fit shown requires  $E_A \sim 1.4 \text{ eV}$  for the  $B^+$  specimens,  $\sim 1.5 \text{ eV}$  for the control specimens and  $\sim 1.6 \text{ eV}$  for the  $Ge^+$  and  $As^+$  specimens. Alternatively we can fix  $E_A$  at  $1.4 \text{ eV}$  and allow  $D_{O_2}$  to vary. The resulting fit is extremely similar to that shown in Fig. 4.

In this case  $D_{O_2}$  is  $0.05 \text{ cm}^2 \text{ s}^{-1}$  for the  $B^+$  specimens,  $0.004 \text{ cm}^2 \text{ s}^{-1}$  for the control specimens and  $0.002 \text{ cm}^2 \text{ s}^{-1}$  for the  $Ge^+$  and  $As^+$  specimens.

In practice, it is therefore not possible for us to state categorically an expression for the effective diffusivity of oxygen over the temperature range we have investigated. It is possible that a change in prefactor, activation energy or both can explain the experimental range of data obtained. We return to this discussion later.

## V. DISCUSSION

### A. Mechanical properties

The data presented in Figs. 1 and 2 show that in Cz-Si grown to contain high levels of boron, germanium and arsenic, considerable stresses are required to unlock dislocations from pinning oxygen impurities at  $550^\circ C$ . The dislocation locking behavior observed in these highly doped specimens was broadly the same as we have previously observed in low doped Cz-Si.<sup>7,20,22</sup> That is, we find an initial rise in unlocking stress with increasing annealing time (regime 1) followed by a plateau (regime 2), with the value of the unlocking stress in regime 2 being linearly dependent on the oxygen concentration. We have found no evidence to suggest that high levels of doping affects the mechanism of oxygen interaction with the dislocations under the conditions investigated.

### B. Oxygen transport at low temperatures

The main motivation of this study was to understand the effect of high levels of dopants on oxygen transport in silicon at low temperatures (up to  $\sim 550^\circ C$ ). Fig. 3 shows that the effective diffusivity in all the samples considered was considerably higher at these temperatures than would be expected from standard monomer diffusion. For instance, at  $400^\circ C$ , the lowest effective diffusion coefficient measured by dislocation locking is approximately two orders of magnitude larger than that measured for monomer diffusion by stress-induced dichroism.<sup>17,24</sup> Our previous work has shown this enhancement is due to oxygen dimer transport to the dislocations in low doped material.<sup>20,22</sup> The magnitude of the effective diffusion coefficients and the approximate values of the activation energies for the highly-doped silicon are broadly similar to those in the low doped material. This strongly suggests that the oxygen dimer is responsible for transport at low temperatures in the highly-doped specimens.

With different oxygen concentrations accounted for, compared to low doped Cz-Si control samples, we find that low temperature oxygen transport is strongly enhanced in Cz-Si specimens doped with  $3 \times 10^{18} \text{ cm}^{-3}$  of boron, whereas it is slightly retarded in samples doped with  $8 \times 10^{19} \text{ cm}^{-3}$  of germanium and  $2 \times 10^{19} \text{ cm}^{-3}$  of arsenic. The magnitude of the enhancement in the boron doped case (a factor of  $\sim 17$  on average) is much larger than the magnitude of the retardation in the germanium and arsenic doped cases (a factor of  $\sim 2$  on average). We discuss possible mechanisms for this later.

The effective diffusivity of oxygen in silicon at low temperatures is given by Eq. 9, which includes a prefactor

( $D_{0O_2}$ ) and an activation energy ( $E_A$ ). The prefactor generally relates to the attempt frequency for migration of the diffusing species.<sup>37</sup> The activation energy is controlled by the activation energy for dimer diffusion and the dimer binding energy, as shown in Eq. 7. While the results of the dislocation locking experiments show that oxygen transport is affected by the presence of high concentrations of dopants, it is not possible to isolate which of the two parameters (prefactor or activation energy) changes as consequence of the high doping level. This is because our data are not sufficiently accurate. However, it is possible to put upper limits on the change in each of these parameters that would be consistent with our data. Compared to  $E_A = 1.5$  eV in the controls, high levels of boron doping could reduce  $E_A$  by 0.1–0.2 eV at most, whereas high levels of germanium or arsenic doping could increase the activation energy by up to 0.1 eV at most. Compared to  $D_{0O_2} = 0.004$  cm<sup>2</sup>s<sup>-1</sup> in the controls, high levels of boron doping could increase  $D_{0O_2}$  by a factor of 10–20 at most, whereas high levels of germanium or arsenic doping could decrease the prefactor by a factor of 2–3 at most. While we cannot rule out a change in prefactor, it seems unlikely that the attempt frequency for oxygen dimer migration would be affected by high concentrations of dopants, so we suggest it is most likely that the change in oxygen transport measured empirically is due to a change in activation energy.

The activation energy measured by dislocation locking at low temperatures is given by  $E_A = -(\Delta G_{binding} - E_{O_2})$ , but it is not possible to separate the energy measured into the two separate terms from the dislocation locking data alone. In their recent paper, Yu *et al.* reported a reduction in the formation of the boron-oxygen related defect in highly germanium doped silicon.<sup>15</sup> Their explanation was that the oxygen dimer concentration was reduced significantly by a combination of two effects. These are firstly that the lattice strain induced by the germanium increases the energy for dimer formation and secondly their FTIR data suggest the formation of germanium-oxygen complexes which hence reduces the amount of oxygen available to form dimers. A reduction in the oxygen dimer concentration would linearly reduce oxygen transport to the dislocations in the 400 to 550 °C temperature range we have studied. When we account for differences in bulk oxygen concentrations, we have measured a very small reduction in oxygen transport in Ge<sup>+</sup> material by factors of just 2.4 at 400 °C, 3.2 at 450 °C, 2.5 at 500 °C and 1.3 at 550 °C relative to the control samples. If this is due to a change in  $E_A$ , rather than  $D_{0O_2}$ , then our results can be explained by a change in  $E_A$  of less than 0.1 eV. Yu *et al.* suggest that the oxygen dimer binding energy is changed by high levels of germanium doping.<sup>15</sup> Our experiments show that if  $E_{O_2}$  and  $\Delta G_{binding}$  vary as a consequence of high levels of germanium doping then they do so in such a way that the difference between them is less than 0.1 eV.

The study of Takeno *et al.*<sup>28</sup> measures a similar physical process to our dislocation locking work. Oxygen transport at 500 °C will be dominated by oxygen dimer diffusion, and at this temperature Takeno *et al.* measure the effective diffusivity to be  $3.1 \times 10^{-14}$  cm<sup>2</sup>s<sup>-1</sup> in low doped control specimens,

$4.1 \times 10^{-14}$  cm<sup>2</sup>s<sup>-1</sup> in specimens doped with  $4.4 \times 10^{18}$  cm<sup>-3</sup> of boron and  $1.7 \times 10^{-15}$  cm<sup>2</sup>s<sup>-1</sup> in specimens doped with  $4.0 \times 10^{18}$  cm<sup>-3</sup> of arsenic.<sup>28</sup> We can account for the difference in oxygen concentrations in their samples according to Eq. 7 and this re-analysis of their data reveals a small enhancement of oxygen transport in their heavily boron doped specimens by a factor of  $\sim 1.5$  and a reduction in oxygen transport in their heavily arsenic doped specimens by a factor of  $\sim 20$  relative to their controls. Our two studies could therefore be in qualitative agreement.

### C. Effect of strain and Fermi level position

We now turn our attention to possible mechanisms by which high concentrations of dopants could affect oxygen transport. Two possible mechanisms are considered. Firstly, heavy doping can introduce strain into the silicon lattice and may therefore change the energy required for impurities to migrate from one site to the next. Secondly, a suitably high concentration of electrically-active dopants will mean the material remains extrinsic at the temperature at which oxygen transport takes place. The Fermi level would therefore remain close to one of the band edges and could have the effect of altering the charge state of the oxygen dimer, so changing the way it diffuses through the lattice.

The doping levels in the B<sup>+</sup> and As<sup>+</sup> specimens (see Table II) are sufficiently high for the material to remain extrinsic, even at the highest annealing temperature used. Thus, the Fermi level lies just above the valence band in the B<sup>+</sup> specimens and just below the conduction band in the As<sup>+</sup> specimens. The Ge<sup>+</sup> samples have a low shallow dopant concentration and so, like the control samples, are intrinsic at all the annealing temperatures used.

The effect of a high dopant concentration on the lattice strain can be estimated by calculating the change of lattice parameter relative to that of low doped samples at room temperature. High levels of boron doping reduce the average lattice parameter<sup>38</sup> and hence put the lattice into compression overall. From the work of Kucytowski and Wokulska, we estimate that the change in lattice constant relative to the lattice constant in low doped material is  $\frac{\Delta a}{a} = -8 \times 10^{-6}$  for our B<sup>+</sup> specimens.<sup>38</sup> The average lattice constant in samples doped with high levels of arsenic is also reduced, with the lattice being put into compression overall,<sup>39</sup> even though the arsenic-silicon bond is found to be longer than the silicon-silicon bond.<sup>39–41</sup> Application of Vegard's law<sup>42</sup> to the data of Cargill *et al.* gives an estimate for our As<sup>+</sup> specimen of  $\frac{\Delta a}{a} = -7 \times 10^{-7}$ . High levels of germanium doping increase the average lattice constant<sup>43,44</sup> and hence put the lattice into tension overall. Application of Vegard's law<sup>42</sup> using the data of Dismukes *et al.*,<sup>44</sup> suggests a relative change in lattice parameter of  $\frac{\Delta a}{a} = +7 \times 10^{-5}$  in our Ge<sup>+</sup> samples. In summary, we estimate that on average there is a compressive strain in the B<sup>+</sup> specimens, a much smaller compressive strain in the As<sup>+</sup> specimens and a large tensile strain in the Ge<sup>+</sup> specimens.

The high level of germanium doping gives rise to a large increase in lattice parameter and, as in the control specimens, the material is intrinsic at temperatures of interest. This

suggests that the small retardation effect observed in the Ge<sup>+</sup> specimens is due to the strain in the lattice. As a tensile strain overall appears to reduce oxygen transport in the Ge<sup>+</sup> material, then it seems reasonable to expect that oxygen transport would be enhanced in material in which there is a compressive strain overall. However, this is not what is found in the As<sup>+</sup> specimens. The overall compressive strain in the As<sup>+</sup> specimens is likely to be very small, so any enhancement in oxygen transport it might give rise to may also be very small. It is suggested that the slight reduction in oxygen transport measured is due to a Fermi level-related effect arising from the fact that the As<sup>+</sup> material remains extrinsic over the range of annealing temperatures used. A much larger change in oxygen transport is measured in the B<sup>+</sup> specimens. In these specimens, the high level of boron doping puts the lattice into compression overall. However, the magnitude of the strain is likely to be significantly smaller than that of the strain of opposite sign in the Ge<sup>+</sup> specimens, in which the effect on oxygen diffusion was much smaller. It therefore seems unlikely that the lattice strain alone can explain the magnitude of oxygen transport enhancement in the B<sup>+</sup> specimens. As the B<sup>+</sup> material remains extrinsic at the temperatures investigated, it is suggested that the Fermi level position affects the transport of oxygen at low temperatures.

The effect of Fermi level position on oxygen diffusion has been considered by Adey *et al.*<sup>33</sup> They developed a theoretical model which suggests that the activation energy for oxygen dimer diffusion will be lower in highly doped p-type material than in p-type Cz-Si with a low concentration of shallow dopants. They suggested that the oxygen dimer in highly doped p-type Cz-Si exists in a double positive charge state, which diffuses by alternating between square and staggered forms with an activation energy of 0.86 eV. However, in material with a low concentration of shallow dopants their model suggests that the uncharged oxygen dimer is most stable and that it diffuses with an activation energy of 1.33 eV. The values of activation energy found by dislocation locking experiments are for oxygen transport and not dimer diffusion, as Eq. 7 shows. If the binding energy of the oxygen dimer is known, then the activation energy for oxygen dimer diffusion is the sum of the values found for transport and the binding energy. The binding energy of the oxygen dimer in low doped Cz-Si has been measured to be approximately 0.3 eV by Murin *et al.*<sup>23</sup> but has not been measured in highly doped Cz-Si. Thus, using the value of Murin *et al.* for low doped Cz-Si and the lowest possible activation energy in the B<sup>+</sup> material of ~1.4eV puts the oxygen dimer diffusion activation energy at approximately 1.7 eV. Thus, even if the dimer binding energy in highly doped Cz-Si is significantly smaller than 0.3 eV, the results presented in this paper are not consistent with a 0.47 eV reduction in the activation energy for diffusion between the highly doped and low doped p-type Cz-Si proposed by Adey *et al.*

The magnitudes of the impurity-induced lattice strains are not believed to be sufficiently large to have the effect on attempt frequency necessary to account for the effective diffusivities measured in the B<sup>+</sup> and As<sup>+</sup> specimens. We therefore conclude that the activation energy for oxygen dimer transport is affected by a Fermi level effect, which is larger

when the Fermi level is close to the valence band than when it is close to the conduction band. We are unable to isolate whether the Fermi level effect observed affects the binding energy of the dimer, the activation energy for dimer diffusion or a combination of both of these.

## VI. CONCLUSIONS

Dislocation locking experiments have been conducted in Cz-Si with high concentrations of boron, germanium and arsenic. The presence of high concentrations of these dopants did not appear to affect the mechanism of oxygen interaction with the dislocations for the conditions studied. Analysis of the dislocation locking data as a function of annealing time and temperature has allowed the effective diffusivity of oxygen to be measured. At low temperatures, at which oxygen dimers are responsible for transport, these dopants give rise to a change in oxygen transport compared to low-doped control specimens. In heavily boron doped material, with differences in oxygen concentrations accounted for, the effective diffusivity of oxygen is found to be enhanced by a factor of ~8 to ~25. High levels of germanium and arsenic doping were found to slightly retard the transport of oxygen. The magnitude of the retardation is measured to be less than a factor of ~4 in the heavily germanium doped specimens or a factor of ~5 in the heavily arsenic doped specimens, and in most cases is significantly less than this. It seems likely that high levels of doping gives rise to a change in the activation energy for oxygen dimer transport. Heavy germanium doping gives rise to a substantial increase in average lattice parameter and it is suggested that this is responsible for the slight retardation effect. Heavy arsenic doping provides only a very small decrease in lattice parameter and it is suggested that the retardation in this case is a Fermi level-related effect. Heavy boron doping leads to a fairly large decrease in lattice parameter, but the magnitude of the enhancement is consistent with this also being a Fermi level effect. Oxygen dimer transport is affected more strongly when the Fermi level is closer to the valence band than the conduction band.

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