Effect of oxygen on the migration of the carbon interstitial defect in silicon

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The deep-level transient spectroscopy signal arising from the carbon interstitial [C(i)] defect in electron-irradiated silicon has been observed to anneal out more rapidly in the pulled than in the float-zone material. We tentatively attribute this behavior to the influence of the oxygen impurity which is always present in silicon. The latter could affect the diffusional migration of the C(i) atom by (a) causing a larger distortion in the pulled Si lattice; (b) providing more trapping sites for the mobile carbon interstitials; and (c) presumably transferring energy to the carbon atoms, helping their movement through the lattice. (d) The possible formation of short-lived, fast-diffusing transient species can also be invoked.

I. INTRODUCTION

No element can be totally purified. Impurities are always present. In the case of silicon, carbon and oxygen have been regarded as the two major unintentionally added impurities. Carbon occupies substitutional sites [C(s)], it is electrically inactive, and has a local phonon mode frequency at 607 cm^{-1}, as detected by infrared absorption measurements.[1] Oxygen, on the other hand, is interstitially [C(i)] incorporated in the silicon lattice occupying puckered, bond-centered positions between two nearest-neighbor silicon atoms.[2] Its presence is manifested by the absorption bands at 1205, 1106, and 515 cm^{-1}. The investigation of the last band has led Shimura *et al.*[3] to suggest that O(i) may be forming chainlike structures in the Si lattice. O(i) is electrically neutral.

There is no doubt that C(i) forms through the Watkins replacement mechanism[4] when a Si interstitial [Si(i)] created by the irradiation, is trapped by a C(s) atom which is knocked to an interstitial position. It forms a mixed dumbbell configuration, the ⟨100⟩ C—Si bond split interstitially where a silicon and a carbon atom partially share a single substitutional site.[5] C(i) introduces a well-known electronic level within the forbidden gap of p-type silicon, around 0.30 eV above the valence band.[6,7]

At about room temperature C(i) begins to migrate with an activation energy around 0.8($\pm$0.1) eV (Ref. 6) and a preexponential frequency around 10^{10} s^{-1}. The diffusion takes place by the interstitialcy process where the carbon atom moves to share the site of its neighbor.[5,8] As it is traveling through the lattice C(i) can be trapped either by another substitutional carbon atom forming a [C(i)+C(s)] pair,[7,9] recently corrected[10] as [C(s) + Si(i)−C(s)] or by an interstitial oxygen atom forming a [C(i)+O(i)] pair,[11,12] or by the (O+V) pair (V is a vacancy) forming the (C + O + V) complex.[13] From luminescence studies in Si the possibility that a C(i) may be captured by a [C(s)+O(i)] pair has also been invoked.[14]

The disappearance of the C(i) peak is always accompanied by the growth in the deep-level transient spectroscopy (DLTS) spectra of another peak with an activation energy calculated to be around 0.36 eV above the valence band. Its nature has been correlated either with the [C(i)+C(s)] pair,[7] or with the (C + O + V) complex[6,13] and recently with the [C(i)+O(i)] pair[15,16] or a combination between the aforementioned structures.[13,16]

II. EXPERIMENTAL

DLTS measurements were carried out on Schottky diodes of boron-doped, float-zone (resistivity ρ = 6.4–7.4 Ω cm) and pulled ρ = (3.5–5 Ω cm) silicon material. The defects were introduced at 80 K with 1.5 MeV electrons from a Van de Graaff accelerator. The measurements were performed *in situ* using a standard boxcar capacitance spectrometer.[17] Annealing studies have proved very fruitful in adding useful information concerning the nature and the properties of imperfections produced by radiation damage in semiconductors. To this end, the DLTS technique is a vital tool, second to none in studying the thermal stability of defects by monitoring their peak amplitudes in the spectrum against heat treatment.

In our Si material, although we have not determined their exact concentrations, oxygen atoms should be present on the order of 10^{16} cm^{-3} in the float zone and 10^{18} cm^{-3} in the pulled Si. Carbon content is probably on the order of 10^{16} cm^{-3} in both materials.

III. RESULTS AND DISCUSSION

The DLTS spectra obtained from boron-doped, float-zone, and pulled silicon specimens of the same resistivities and subjected to similar irradiation treatment at 80 K, have been reported previously.[18,19] The results of the present work are succinctly summarized as follows. As the temperature of the samples rises approaching room temperature, a peak with E_v + 0.28 eV energy assigned to C(i) has been observed to diminish more rapidly in the pulled than in the float-zone Si. More specifically the C(i) signal in the pulled Si disappears in a few hours at

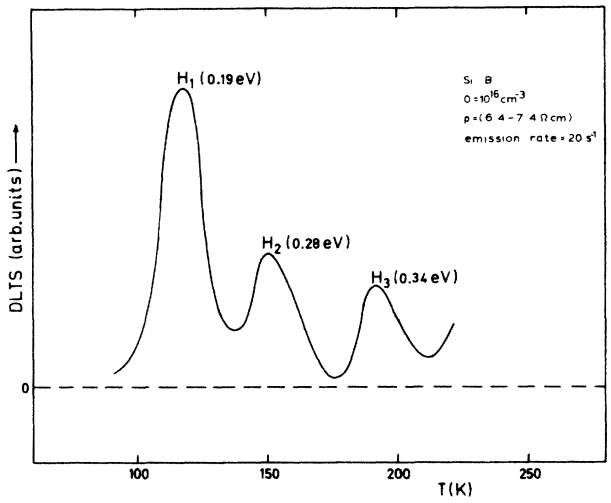

FIG. 1. The DLTS spectrum of float-zone electron-irradiated p-type Si, at 80 K, after annealing at 320 K for 5 h and a final anneal at 450 K for 90 min.

320 K but needs much more time to disappear in the float-zone Si. Figure 1 (for the float zone) and Fig. 2 (for the pulled) illustrate the results after an annealing of the samples at 450 K for 90 min. Prior to this annealing the specimens were held at 320 K for about 5 h which resulted in the extinction of the C(i) signal from the spectrum of the pulled Si but not of the float-zone one.

Peak H_1 in both materials is presumably the divacancy, which is not of interest in the present work. Peak H_2 in Fig. 1 is the C(i) signal after the thermal treatment above. As we see in Fig. 2, H_2 is not present, due to the 320-K anneal. Peak H_4 emerged after the 450-K annealing, as a faint signal assigned to the (B + O + V) complex.[13] Peak H_3 in both figures may be correlated either

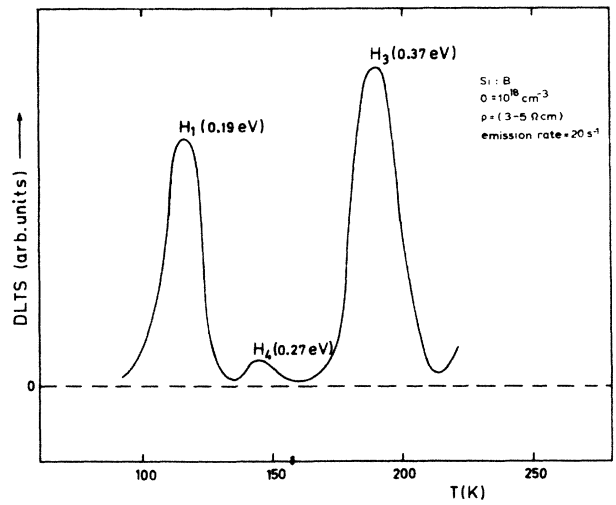

FIG. 2. The DLTS spectrum of pulled, electron-irradiated p-type Si, at 80 K, after annealing at 320 K for 5 h and a final anneal at 450 K for 90 min.

with the di-carbon center,[7] and/or the [C(i)+O(i)] pair designated the $C(3)$ center,[8] and/or the (C + O + V) complex usually reported as K center.[13]

The main purpose of this article is to emphasize the observed difference, not previously stressed, in the annealing behavior of the C(i) defect between high-oxygen and low-oxygen silicon material. In an attempt to interpret our observations we have invoked four possible causes, all of them necessarily connected to the oxygen presence.

A. Lattice distortion

Point defects in crystals inevitably distort the surrounding lattice. The host atoms near the defect are forced to move to new positions to minimize the total energy of the now imperfect crystal. In general we can say[20] that the defects break the periodicity of the perfect lattice, change the electronic charge distribution, and modify the local forces operating between atoms. Among the properties sensitive to distortion are obviously the formation and the migration energies and entropies of the defects. Thus the distortion can, in principle, affect atomic transport properties such as the migration and diffusion.

The interstitially incorporated oxygen in the Si lattice causes a local distortion to the unit cell. Its presence in an interstitial site off the ⟨111⟩ axis between two Si atoms produces a compression which tends to push them apart. Thus the lattice is expanded in some regions while it is obviously contracted elsewhere. Weigel *et al.*[21] showed that the potential energy of the interstitial oxygen in the diamond lattice is lower near the lattice atoms, indicating that the interstitial oxygen participates in substantial bonding with the lattice. Thus one would expect that these distortions cause some changes in the energy states of the C(i) atoms. More specifically, C(i) atoms near the distorted unit cell would be energetically less stable than near an undistorted unit cell. As a consequence of a general physical principle, C(i) have the tendency to move to the more stable positions. In other words, lattice distortion creates regions inside the crystal which contain energy density in excess of the average and regions with energy less than the average. This situation may give rise to dynamical processes which cannot otherwise occur in an undistorted lattice. Since the oxygen content is two orders of magnitude higher in the pulled than in the float-zone Si, the distorted regions would be proportionally more in the former material. This larger tendency of the carbon atoms to move in the high-oxygen Si lattice is consistent with the faster annealing rate observed for the C(i) defect.

The model suggested above is clearly strictly qualitative. Its basic idea, put in an alternative way, is that the binding energy of a carbon interstitial atom near a deformed unit cell is generally smaller than that near an undistorted one, which statistically implies that in the pulled Si material the average binding energy of the C(i) is smaller than that in the float-zone material. In any case, the migration of an interstitial atom through the lattice by successive jumps between neighboring positions presupposes that its energy exceeds the barrier energy

separating the well between the above two positions. In our line of argument, the previous conclusion that the average binding energy of the interstitial carbon atoms is smaller in the pulled Si is equivalent to the statement that the average barrier height for diffusion is smaller in the latter material. It is obviously very difficult to describe these ideas in macroscopic terms. However, we shall attempt to address the issue on a more mathematical basis.

The diffusion of a defect with successive jumps through the lattice is obviously a thermally activated process. The probability that it will jump from one equilibrium position to another across a barrier E caused by the host atom is

$$\nu=\nu_0\exp(-E/k_BT) ,$$

where, in the framework of the rate theory approximation,[22] ν_0 is a characteristic vibrational frequency given by $\nu_0=k_BT/h$, where k_B is the Boltzmann factor and h Planck's constant. The barrier height E accounts for the interaction of the defect with the surrounding atoms. Evidently, a smaller barrier height set by the surrounding lattice in the pulled material as compared with that in the float-zone material means a larger probability for the migration of the carbon atoms.

Nevertheless, some difficulties arise with this model if we think that oxygen is one per million atoms in the pulled and 10^{-2} per 10^6 atoms in the float-zone material. This poses the following question: Is the excess oxygen content in the former material adequate to cause a substantial drop of the barrier which could account for the phenomenon? Although the possible chainlike structure[3] of oxygen in the Si lattice and the fact that oxygen distribution in pulled Si is highly inhomogeneous[23] tend to reinforce the model, we have the feeling that the excess lattice distortion in the high-oxygen Si could not account by itself for the observed faster annealing rate. Firm statements, however, cannot be made without an exact mathematical analysis.

The following argument could be put forward to the contrary as well. Evidently, due to lattice distortions, carbon atoms have different surroundings inside the crystal. Due to electronic reorganization the energy of the bound electrons is changed. As a result the corresponding level of the C(i) in the gap should be broadend. Consequently, the observed DLTS peak would also be expected to be broadened due to nonexponential transients. Such a broadening of the C(i) peak in the pulled Si, as compared with that in the float-zone, has not been observed.

Although the available data do not seem to bear out this theory, this does not necessarily imply that it is incorrect. The resulting broadening of the peak, if it exists, may very well be below the limits of the DLTS resolution and thus cannot be detected.[24] Certainly, the above arguments feed some speculations concerning the adequacy of the model to explain the faster annealing rate of C(i) in the pulled Si. All these considerations bring us to the second point.

B. Provision of more trapping sites

The signal from the C(i) defect in the DLTS spectrum persists as the atoms diffuse (if time averaged over diffusion jumps) and begins to disappear only when a reaction takes place. Thus the rate of the diffusion process depends on the reactions which C(i) undergoes as it begins traveling through the Si lattice. We cite three of the more possible reactions in which C(i) may participate:

$$\mathrm{C}(i)+\mathrm{C}(s)\rightarrow[\mathrm{C}(i)+\mathrm{C}(s)] , \tag{1}$$

$$\mathrm{C}(i)+(\mathrm{O}+V)\rightarrow(\mathrm{C}+\mathrm{O}+V) , \tag{2}$$

$$\mathrm{C}(i)+\mathrm{O}(i)\rightarrow[\mathrm{C}(i)+\mathrm{O}(i)] . \tag{3}$$

Recalling that the rate of a particular process in its simplest case can be expressed as $R=A\exp(-E/k_BT)$ it is obvious that the rate of each of the above reactions would be characterized by its own activation energy E and its own prefactor A. We may write, correspondingly,

$$R_1=A_1\exp(-E_1/k_BT) , \tag{4}$$

$$R_2=A_2\exp(-E_2/k_BT) , \tag{5}$$

$$R_3=A_3\exp(-E_3/k_BT) . \tag{6}$$

The probability of a diffusing C(i) atom undergoing the above reactions depends on the concentrations of the C(s), (O+V), and O(i), respectively, and on the corresponding reaction cross sections. We suppose now that the possibilities of the above reactions occurring are statistically independent. This implies that the total rate for the reaction processes is the product of all the individual rates. By following the considerations of Schluter,[25] the total rate for the extrinsic reaction probability of the diffusion process may be written

$$R_{\mathrm{extr}}=A_{\mathrm{extr}}\exp(-E_{\mathrm{extr}}/k_BT) , \tag{7}$$

where

$$A_{\mathrm{extr}}=A_1A_2A_3 \tag{8}$$

and

$$E_{\mathrm{extr}}=E_1+E_2+E_3 . \tag{9}$$

Since the concentrations of O(i) and (O+V) are larger in the pulled Si we would expect A_{extr} to be different and more specifically larger in this material than in the float-zone one. This means that R_{extr} would also be larger in the pulled Si.

Due to the larger lattice distortion in the pulled Si, as already mentioned, the barrier height E_{intr} for jumps of the C(i) atoms between successive equilibrium positions is smaller in the pulled material than in the float-zone Si. Thus the intrinsic jump probability

$$R_{\mathrm{intr}}=A_{\mathrm{intr}}\exp(-E_{\mathrm{intr}}/k_BT) \tag{10}$$

would also be larger in the pulled Si. Considering now relations (7) and (10) and supposing again that the various possibilities of the two events occurring are statistically independent we may write the final formula for the diffusion process as

$$R = A \exp(-E/k_B T) , \quad (11)$$

where

$$A = A_{\text{intr}} A_{\text{extr}} \quad (12)$$

and

$$E = E_{\text{intr}} + E_{\text{extr}} . \quad (13)$$

It is clear that the provision by oxygen of more trapping sites for the mobile carbon atoms can enhance the annealing rate of the latter in the pulled Si. The above theory has a certain validity and we attach special significance to this on the grounds that it could provide a rationale for trying to reconcile our results with those of Watkins and Brower.[5] In their experiments they used carbon-rich Si (C: 10^{17} cm^{-3}). This may mean that in the competition between C(s), O(i), and (O+V) for capturing the C(i) atoms the reaction

$$C(i) + C(s) \rightarrow [C(i) + C(s)]$$

prevails; it is the main process, the primary reaction channel for the moving carbon atoms. In that case the provision by oxygen of more trapping sites for C(i) has no effect on the total rate R of the diffusion process. It should be worth noticing that recent measurements on an electronic transition at 856 meV assigned[26] to the C(i) center, show that the latter defect decays in pulled Si with a shorter time constant than in the float-zone Si having about the same carbon content (2×10^{17} cm^{-3}) as in Ref. 5. Woolley *et al.*[26] ascribed the phenomenon to the increased number of trapping sites for the C(i) in the pulled material.

C. Transferring energy to C(i)

As we have mentioned earlier, oxygen interrupts a Si—Si valence bond forming a nonlinear Si—O—Si molecule. There are six equivalent positions for the oxygen, for each nearest-neighbor Si pair. At elevated temperatures the oxygen jumps very easily from one orientation to another, behaving as an almost free rotator at room temperature.[27] Given the natural tendency of carbon and oxygen to combine, forming CO molecules, it is very likely[28] for the easily rotating oxygen atoms to come in contact with a C(i) atom. In that case energy may be transferred to the carbon atoms, helping them to displace more easily in the Si lattice. It is understood that this event has a greater possibility of occurring in the high-oxygen material.

Energy transfer can also occur in the following way. C(i) is an electrically active defect in silicon. We cannot rule out the possibility that a C(i) atom may exchange carriers, by a thermal-activated process, with another oxygen-dependent electrically active defect.[28] In that case, we may think of a carrier-assisted transport. It is well known[29] that the capture of carriers can release energy in the vicinity of a defect. Thus, broadly speaking, the mechanism for this enhanced migration is that part of the electronic energy released upon carrier capture could supply a portion of the necessary energy for the defect to make the diffusional jump. In other words, released electronic energy could be taken up as motional energy by the C(i) atoms, helping them to overcome the potential barrier between two neighboring sites.

D. Mediation of short-lived transient structures

In the approach we put forward the idea that C(i) may combine with an oxygen-related structure, giving rise to short-lived, fast-diffusion [at least faster than the C(i) alone] species which dominate at a certain temperature region and are then destroyed. These species dissociate at around room temperature, and act as diffusion vehicles for the carbon atoms, helping them to propel more rapidly in the Si lattice. A possible candidate may be the [O(i)+Si(i)] pair which, combined with the C(i) atom, could play a catalytic role in the migration of the latter. The formation of [C(i)+O(i)+Si(i)] complexes has been previously invoked[30] in a model for thermal donors in Si heated at 450 °C. There are also indications of structure analogies between C and O-related radiation effects and the 450–500 °C thermal defects.[31]

It has no meaning to speculate further on the process that might occur, on the basis of the limited experimental information available at present. However, we lean toward an explanation where some of the aforementioned processes may occur in parallel.

IV. CONCLUSIONS

Experimental data show that a high interstitial oxygen content in Si enhances the annealing rate of the carbon interstitial defects. In an attempt to interpret our observations that C(i) anneals out more rapidly in the pulled than in the float-zone Si we have put forward some theoretical models. Their main ingredient is the idea that the phenomenon is indissolubly linked to the oxygen content. We believe that annealing experiments on specimens with different oxygen and carbon concentrations, irradiated at different doses, would provide crucial information on the subject, particularly on the exact mechanism with which oxygen affects the carbon movement through the Si lattice.

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