Aspects of the Defect Reactions Related to Carbon Impurity in Silicon

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Deep-level transient spectroscopy (DLTS) measurements are reported for the well-studied carbon (C) and oxygen (O) related centers with activation energy around $E_c = 0.36 \text{ eV}$ in irradiated p-Si. Comparisons of the concentrations of this defect state with those of the carbon interstitial (CI) defect state in pulled and float-zone material have been considered. The results yield some new insight concerning the CI involvement in reactions with primary defects and other impurities a) during and after low-temperature irradiation and b) after annealing around room temperature.

KEYWORDS: silicon, lattice, point defects, impurities, reactions, electron irradiation, DLTS (deep-level transient spectroscopy), C interstitial, C interstitial-C substitutional pair

§1. Introduction

The two primary defects produced in Si by 1.5 MeV electron irradiation at 80 K are the isolated lattice vacancies (V) and self-interstitials (Si). The V and the Si, which survive the recombination participate in various reactions forming secondary defects. In p-Si, V becomes mobile at $\sim 150 \text{ K}$ and combines with another V to form divacancies ($V_2$), with O to form (O + V) pairs, with acceptor impurities (A) (where A stands for B, Al, …) to form (A + V) associates. Si has so far eluded direct experimental detection. However, it is well known that in p-Si, Si is very mobile even at low temperatures and is selectively trapped by acceptor impurities with which it exchanges sites.\(^{3}\) This process, known as the Watkins replacement mechanism, is also valid between substitutional carbon atoms (C\(_i\)) and Si, leading to the formation of the bonded C\(_i\).\(^{3}\) The latter defect\(^{5-9}\) gives a donor level at $-E_c = 0.30 \text{ eV}$ and an acceptor level appearing only in n-Si at $-E_c = -0.12 \text{ eV}$. Interactions of Si with O and the production of divacancy defects with adjacent Si have also been proposed.\(^{6-8}\)

Near room temperature, C\(_i\) begins to migrate. Among a variety of reactions in which C\(_i\) participates the most dominant are with C\(_i\),\(^{7}\) O\(^{9}\) and (O + V)\(^{10}\) pairs. In this work, we have employed the unique performances of the DLTS technique to investigate possible interactions of C\(_i\) with other defects at low temperatures and at room temperature after annealing.

§2. Experimental

The Schottky diodes used in this study were fabricated by evaporation of aluminum on boron-doped, float-zone ($\rho = 6.4 - 7.4 \Omega \cdot \text{cm}$) and pulled ($\rho = 3 - 50 \Omega \cdot \text{cm}$) p-type Si wafers. The carbon concentration was $2.5 \times 10^{16}$ atoms/cm\(^3\) in both materials. Irradiations were performed in situ at 80 K with 1.5 MeV electrons from a Van der Graaf accelerator. The dosage was about $2 \times 10^{16} \text{e}^{-}/\text{cm}^2$. The measurements were carried out by a standard box-car spectrometer.\(^{11}\) They were performed at 5 V reverse bias and 5.7 V filling pulse amplitude to eliminate the built-in voltage of the junctions.

Activation energies reported here were determined from Arrhenius plots (log$_{10}$ $E_c / T^2$ versus $1 / T$) without allowing for the electric field effect or the temperature dependence of the capture cross sections on the thermal emission of the traps.

§3. Results and Discussion

Figure 1 (solid curve) shows the majority of the DLTS spectrum of the float-zone Si after annealing at 315 K for 5 hours. The dotted curve depicts the C\(_i\) peak immediately after the 80 K irradiation. Figure 2 is the corresponding diagram of Fig. 1 for the pulled material. Each peak is labelled with the letter H (for holes) and a number in brackets expressing the activation energy from the valence band.

Identification of the defect states was done on the basis of the energy positions in the gap, the introduction rates, the thermal stabilities and comparisons with previous assignments in the literature.\(^{1-5,10}\) Thus, peak H\(_1\) in both figures is possibly related to $V_2$. It is created during irradiation and increases its amplitude when V migrates. The level around $E_c = 0.23 \text{ eV}$ was correlated\(^{7}\) with the positive charge state of $V_2$ in p-type Si. However, the measured activation energy from our experiments was systematically smaller than the above value. This fact might be taken as an indication that $V_2$ created by irradiation at low temperatures presumably traps some self-interstitials which in turn change its electronic state. In that case, peak H\(_1\) may not arise from exactly the same defect structure in the two materials. This means that the measured equal activation energies in the float-zone and pulled Si may be accidental within the experimental errors. These ideas should also be considered when attempting to explain the observed differences in the line shape of the $V_2$ between the two materials.

Peak H\(_2\) in both figures represents C\(_i\). It appears immediately after irradiation and begins to anneal out at around room temperature. The decay of the C\(_i\) signal is accompanied by the concomitant growth of the H\(_3\)(0.34) peak in the float-zone and the H\(_3\)(0.37) peak in
Fig. 1. The DLTS spectrum of float-zone Si irradiated at 80 K after annealing at 315 K for 5 hours (solid curve). The dashed curve depicts the C1 peak evoked immediately after the irradiation (e− = 40 s−1).

Fig. 2. The DLTS spectrum of pulled Si irradiated at 80 K after annealing at 315 K for 5 hours (solid curve). The dashed curve depicts the C1 peak evoked immediately after the irradiation (e− = 40 s−1).

the pulled Si. Therefore, in a preliminary assignment we could tentatively correlate peak H1 in both materials with a C-related centre. The observed faster disappearance of the C1 signal in the pulled material spectrum is consistent with its larger O content which could provide an increased number of trapping sites for the migrating C1 in the Si network.13)

Comparing the peak amplitudes of H2 and H3, it is obvious that the concentration of the C-related center in the float-zone Si is smaller than the decrease of the concentration of the C1. In the pulled material, however, where the C1 signal completely disappears with the annealing, the
concentration of the H₂(0.37) peak is larger than that of the
H₂(0.28) peak. We shall discuss the two Si materials separately.

3.1 _C-interactions in float-zone Si_

In this case, since the emergence of H₂ is simultaneous with
the decay of H₂, we can assume that the C_i are not
totally converted to the C-related centre. In other words, it
is possible that part of the C_i's join some unknown defect\(^{11}\) which are presumably electrically neutral and
thus elude detection by DLTS. Our observations are also
consistent with IR studies which concluded\(^{12}\) that a small
fraction of the C_i defects must be lost at other traps.

Prior to any discussion of this matter, we shall focus
our attention on the observed decrease of the linewidth
of H₂ after annealing (Fig. 1). One may presume that two
defect states contribute to the creation of peak H₂, one of
which anneals out earlier than the other. However, such
a conclusion is not supported by the facts. A capture
cross-section analysis with the pulse-width variation
method\(^{13}\) gave only one branch in the plot of log (S_o - S)
vs \(t_p\) (S is the DLTS output for a pulse-width \(t_p\), and S_o
the saturated DLTS output for large pulse durations) indi-
cating that only one defect contributes to the creation of
H₂. Furthermore, the appearance of the transient from
peak H₂ in the screen of a very sensitive oscilloscope does not give the impression, as far as we
can say, of a nonexponential one. During preliminary
characterization of the samples prior to irradiation, the
DLTS spectra were almost ideal showing almost no
features, especially in the temperature region where the
C_i signal appears. Additionally, C_i is a well-known defect
and nowhere in the literature has any other defect been
reported under the same conditions of irradiation, giving
rise to a level in the same position in the gap.

Immediately after the irradiation a very strong peak ap-
pears in the spectra. This peak could be partially seen
even with the two fastest available rate windows of 1000
s\(^{-1}\) and 2500 s\(^{-1}\). The minimum temperature possible to
achieve with our equipment prevented the determination
of the energy level of the defect. The peak began to decay
from \(-160\) K onwards. The decrease in the amplitude
was accompanied by the increase of the amplitude of the
V₂-related peak and the emergence of other peaks at-
tributed to the (O+V) and the (B_i+V)\(^{14}\) pairs. We have
tentatively identified it as arising from the \(E_+ + 0.13\) eV
level of the vacancy. However, it has been shown\(^{15}\) that
the V is a negative-U system and the signal related to its
level is due to the simultaneous emission of two holes,
thus it is twice the normal amplitude. Therefore, its real
concentration is half the normally\(^{16}\) calculated concen-
tration. We found that this initial concentration of the V is
larger than the sum of the concentrations of the V-related
centers (V₂, O+V, B_i+V) created after its migra-
tion. Thus, some of the vacancies should be trapped
elsewhere. A possible candidate is carbon. Since C_i are
im- mobile at low temperatures, a carbon-vacancy pairing
would result from the migration of the V. Although this
process is expected to appear in the spectra as a certain
decrease of the amplitude of the C_i peak, such an effect
was not observed here. (C+V) pairs could also be
formed at high temperatures. The possibility of a mobile
C_i to combine with V₂ has been previously considered
and rejected on the grounds of Coulombic repulsion,

3.2 _C-interactions in pulled Si_

In this case, we have the seemingly contradictory
results that the final number of C_i atoms is larger than the
initial number measured prior to annealing. Thus, the
question of where these excess C_i's come from immedi-
ately arises. In the following, a number of possible
causes will be discussed in an attempt to interpret the ob-
erved phenomenon.

3.2.1 _C-related complexes_

According to this model, an electrically neutral car-
bon-related complex forming at low temperatures breaks
up at around room temperature and the liberated C_i con-
tribute to the formation of the H₂ peak. A reasonable can-
idate would again be the (C+V) pair. Previously we
had minimized the possibility of its formation from proc-
esses involving the migration of V or C_i. In the context of
the present interpretation, we consider the creation of a
different kind of (C+V) pair produced during radi-

It is worth noting the interesting suggestion that small
dislocation loops\(^{16}\) created by the irradiation could act as
sinks for the C_i. It is also possible that when the C_i-Si
bond is breaking up at around room temperature, a small
fraction of the liberated C_i is repositioned at the substitu-
tional sites. This idea has been tested by infrared absorp-
tion-spectroscopy with negative results\(^{16}\). From photolumines-
cence and absorption studies a conversion of the C_i-S_i
configuration to a C_i-S_i configuration during annealing
has also been postulated.\(^{16}\)

Another complex consistent with the discussed model
is the carbon-oxygen pair. Absorption bands observed at
922 and 932 cm\(^{-1}\) after low temperature irradiation were
ascribed to the vibrations of the (C+O) defect centers\(^\text{21}\) which are unstable at room temperature.

3.2.2 Si-related complexes

The formation of the short-lived, fast-diffusing metastable defect configurations in low-temperature irradiated Si was put forward previously.\(^\text{22}\) Based on this information, we believe that Si interstitials released by dissociation of some defects could interact with carbon atoms in normal lattice sites to provide the excess carbon interstitials. This idea has also been proposed previously to account for the increase in the strength of the C(1) band, attributed to C\(_i\), in n-type Si around 200 K. One possible defect is that comprising a silicon interstitial trapped by an interstitial oxygen atom.\(^\text{23}\) It is also known that mobile Si interstitials can be captured by vacancies which are formed by the direct radiation process when the energy of the incident electrons is in excess of some threshold value. It has been found that a fraction of these vacancy-Si interstitial complexes anneal below room temperature. A model invoking metastable vacancy-interstitial pairs\(^\text{24}\) has also been proposed and successfully used to explain the irradiation temperature dependence of some defects. However, preliminary annealing studies of the C\(_i\) at temperatures up to 260 K have not revealed any growth of the corresponding DLTS signal.

3.2.3 C\(_i\) at electrically neutral configuration

The \(E_c - 0.12\) eV level of the C\(_i\) in n-type Si is not observed after the low-temperature irradiation\(^\text{5}\) but at higher temperatures without complementary changes of the peaks in the DLTS spectrum to be detected. Growth stages for this level below room temperature have also been reported.\(^\text{7}\) Kimerling, based on the Jackson model,\(^\text{26}\) has postulated that a certain fraction of the C\(_i\) are locked in the silicon lattice in an electrically inactive configuration. Presumably, the associated defect state is pushed outside the energy gap. At higher temperatures these interstitials convert back to normal and the concentration of the C\(_i\) increases. Changes of the configuration of the C\(_i\) have also been proposed in another case to account for its annealing behaviour. Localized vibrational mode (LVM) spectroscopy studies\(^\text{27}\) show that a centre, labelled C(2) and tentatively attributed to the C\(_i\) in \(T_d\) symmetry, is produced immediately after the C(1) centre assigned to the normal interstitial in \(C_3\)\(_v\) symmetry starts to decay. Based on the above considerations, we would suggest that a small fraction of the C\(_i\) created by the irradiation forms an electrically neutral configuration which, at around room temperature, transforms to the normal one contributing to a further increase of the amplitude of the \(H_3\) peak. It should be remembered that infrared absorption studies\(^\text{28}\) on high-dose electron irradiated Si at room temperature have shown that the removal of carbon atoms from normal lattice sites is not exactly correlated with the formation of the other observed C-related defects. This then leads to the question of the destination of the carbon.

A capture cross-section analysis gave two branches, and consequently, two capture cross sections \((\sigma_c = 1.2 \times 10^{-16} \text{ cm}^2, \sigma_p = 5 \times 10^{-18} \text{ cm}^2)\) for the peak \(H_3(0.37)\) in the pulled material and one branch giving \((\sigma = 5 \times 10^{-18} \text{ cm}^2)\) for the peak \(H_3(0.34)\) in the float-zone Si. These results are consistent with the aforementioned models. Since \(C_3\) is the main trap for the mobile C\(_i\), we believe that the center with the capture cross section \(5 \times 10^{-18} \text{ cm}^2\), present in both Si materials, is the C\(_3\) pair. In the float-zone material, some of the C\(_3\)'s are lost to unknown traps. In the pulled material, there is a competition between oxygen and the unknown traps for capturing the C\(_3\) when oxygen prevails. Consequently, (C\(_3\) + O) or (C + O + V) complexes are formed giving the corresponding \(\alpha = 2 \times 10^{-16} \text{ cm}^2\) branch. We shall see in the next paragraph that the validity of these correlations has recently been in doubt.

3.2.4 One of the defects giving the \(E_c + 0.37\) eV level does not contain C

Lately, experiments performed on electron-irradiated n-Si\(^\text{29}\) have revealed that the C\(_3\)-C\(_i\) pair is a bistable defect with two configurations and two corresponding levels, \(E_c - 0.10\) eV and \(E_c - 0.17\) eV. In p-Si,\(^\text{30}\) only one configuration of the above defects has been seen by DLTS giving a donor level at \(E_c + 0.09\) eV, in agreement with previous assignments.\(^\text{31}\) Obviously, the correlation\(^\text{32}\) of the \(E_c + 0.33\) eV with the C\(_3\)-C\(_i\) pair is seriously challenged. Furthermore, recent measurements\(^\text{33}\) have concluded that the G15 electron paramagnetic resonance spectrum associated with the (C + O + V) center,\(^\text{33}\) the 0.97 eV photoluminescence line, the C(3) infrared absorption band and the DLTS level at \(E_c + 0.38\) eV have a common origin, the C\(_3\)-O\(_0\) pair. Thus, based on the above information, only the C\(_3\)-O\(_0\) defect could be considered to contribute to the DLTS peak \(H_3\) with \(E_c + 0.37\) eV energy. The nature of the second component of \(H_3\) is not certain. Nevertheless, H\(_3\) appears to grow in our spectra simultaneously with the C\(_i\) decay. It might be argued that C only indirectly helps the formation of the second component of the H\(_3\) peak by participating in some intermediate reactions but is not involved in its structure. A (partial) chemical identification would refer to the second component of H\(_3\) as an oxygen-related, carbon-dependent centre.

4. Conclusions

Irrespective of the fine detail and the operative mechanism which governs the movement of C atoms through the Si network, our data indicate that the interaction of the C impurity with other defects in the Si lattice might be much more complicated than previously thought. Carbon follows different and more intricate reaction patterns in the oxygen-rich Si material than in the oxygen-leak Si material. The complete understanding of the carbon interplay with other defects in Si requires further investigation with a combination of experimental techniques.

References

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