JOURNAL OF APPLIED PHYSICS **100**, 033523 (2006)

The $C_iC_s(Si_I)$ defect in silicon: An infrared spectroscopy study

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(Received 22 March 2006; accepted 23 May 2006; published online 9 August 2006)

Infrared (IR) spectroscopy was employed for a thorough study of the $C_iC_s(Si_I)$ defect formed in neutron-irradiated carbon-doped Czochralski silicon material. Its IR signals at 987 and 993 cm^{-1}, as well as the thermal evolution of the defect were examined and discussed. Based on a previously suggested structure model of this defect its local vibrational mode frequencies were calculated. The estimated values lie very close to the experimentally detected frequencies at 987 and 993 cm^{-1}, supporting their previous assignment to the $C_iC_s(Si_I)$ defect. The decay of the center in the spectra was found to be governed by a second order kinetics, with an activation energy around 1.27 eV.
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INTRODUCTION

The two main intrinsic defects in silicon are the vacancy (V) and the self-interstitials (Si_I) formed during growth and/or material processing; for instance, thermal treatments, implantations, irradiations, etc. Their presence has important consequences on the properties and generally the behavior of the material. They act as vehicles for various diffusion mechanisms and they interact with impurities and other defects in the crystal to form more complex defects which affect device operation.

The vacancy and most of the vacancy-related defects in Si have well-known electrical and/or optical signals which have been extensively studied so far. However, the picture concerning the Si_I's, the reactions they participate in, and their fate is much less clear.[1] Their high mobility, even at cryogenic temperatures, makes any direct experimental observation extremely difficult. However, they are selectively trapped by group III interstitial dopants in Si with which they exchange sites through the Watkins displacement mechanism. In a similar way they interact with carbon. With oxygen they form $O_i(Si_I)$ pairs. Si_I's can be therefore indirectly studied through the reactions they participate in and the formed complexes.

Carbon is a common contaminant in Si and its behavior affects a wide range of crystals subjected to various processes for electronic applications. Carbon and silicon are isoelectronic and therefore the investigation of the reaction they participate in, as well as the complexes they form, could shed some light on the elusive nature and behavior of of the Si_I's. Carbon is substitutionaly incorporated (C_s) in the crystal and acts[2,3] as selective trap of Si_I's being injected into bonded interstitial configuration C_i, ($C_s+Si_I \rightarrow C_i$). In fact, the formation[4] of the C_i defect is the first step of a multiple reaction leading to the formation of many carbon-related complexes. Actually, upon diffusion C_i reacts readily with C_s and O_i atoms forming[5,6] the C_iC_s and the C_iO_i defects, respectively. The C_i, C_iC_s, and C_iO_i defects can further trap Si_I's leading to the formation[4,7,8] of larger complexes as, for example, $C_i(Si_I)_n$, $C_iC_s(Si_I)_n$, and $C_iO_i(Si_I)_n$. In essence, carbon-related complexes are stores of Si_I's, thus controlling the amount of the Si_I's in the material. This is critical in preventing detrimental effects in microelectronic devices as those caused by the formation of larger clusters, such as the {113} extended defects.[9] The transient enhanced diffusion (TED) process,[10] which is responsible for anomalously high diffusion of boron, during anneals of boron-implanted material, could also be prevented by carbon. Obviously, in any defect kinetics modeling of reaction schemes, the formation of $C_i(Si_I)_n$, $C_iC_s(Si_I)_n$, and $C_iO_i(Si_I)_n$ $(n=1,2,\ldots)$ defects should be taken into account.[7,11] Thus the investigation of the properties and behavior of carbon-related silicon interstitial complexes is significant both for fundamental research and electronic applications.

As a continuation of a previous work,[12] this paper focuses on the study of the $C_iC_s(Si_I)$ defect in silicon. The local vibrational mode (LVM) frequencies of the defect structure are calculated and the thermal evolution of its signals in the IR spectra is carefully examined and discussed.

EXPERIMENT

Carbon-doped Czochralski silicon (Cz-Si) samples of 2 mm thickness were used. The initial oxygen and carbon contents of the material were $[O_i]_o=7.195\times10^{17}$ cm^{-3} and $[C_s]_o=9.35\times10^{16}$ cm^{-3}, respectively. The samples were then subjected to fast neutron irradiation at a fluence of $D=1\times10^{17}$ cm^{-3}. In comparison with electrons, neutrons cause much more damage in the materials. A much higher generation of primary defects is produced, which although to a large extent are annihilated by the reaction $V+Si_I\rightarrow\varnothing$, those surviving react between themselves as well as with other defects and impurities present in the lattice to form larger complexes. Therefore, it is more likely to observe self-interstitial related complexes in Si after neutron irradiation. 15 min isochronal anneals, in open furnace, were performed after the irradiation. The temperature step was $\sim$10 °C and the range of the anneals was from room temperature to 750 °C. IR spectra were taken after each annealing step by a Jasco-700 IR spectrometer.

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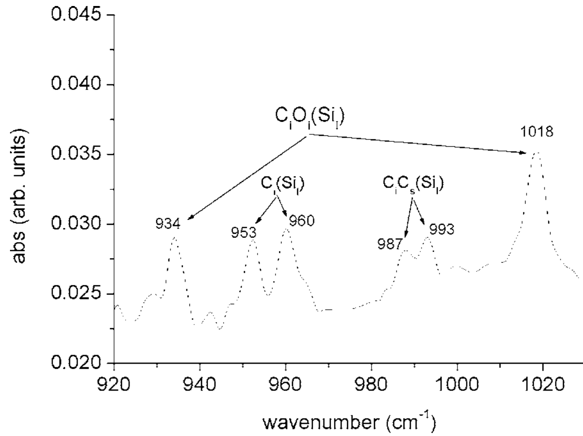

FIG. 1. Section of the infrared spectrum after neutron irradiation.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows a section of the absorption spectrum after the irradiation. The depicted pairs of peaks at (934, 1018 cm^{-1}), (953, 960 cm^{-1}), and (987, 993 cm^{-1}) have already been reported and discussed in the literature[12–14] and assigned to the $C_iO_i(Si_I)$,[14] $C_i(Si_I)$,[14] and $C_iC_s(Si_I)$ (Ref. 12) complexes, respectively. We shall concentrate on the $C_iC_s(Si_I)$ defect. Notice that the attribution of the (987, 993 cm^{-1}) pair to this defect was based on the following reasoning. In neutron irradiated material the $C_iO_i(Si_I)$, $C_i(Si_I)$, and $C_iC_s(Si_I)$ complexes are expected to form. The first two pairs had already been correlated[14] with certain bands in the spectra. It was therefore reasonable to consider that the remaining unassigned pair of bands at (987, 993 cm^{-1}) to be most possibly correlated with the $C_iC_s(Si_I)$ defect. Obviously, this allegation needs further verification, and one supporting element would be the theoretical calculation of the LVM frequencies of the structure.

The structure model of the $C_iC_s(Si_I)$ defect has been previously suggested[4,15] in the literature. The morphology of the defect corresponds to two Si–C dimers, where the carbon atom of the first dimer is bonded to the silicon atom of the second one (Fig. 2). The defect has a C_iC_i structure, where the two carbon interstitial atoms are attached to a silicon interstitial atom.

The following analysis is based on a previously reported procedure,[16] calculating the dipole-dipole interaction of the Si–C dipoles. The force constants of the two Si–C bonds are approximately the same and equal to K_{C_i}. K_{C_i} is given by the relation

$$K_{C_i} = m_C(\omega_{C_i})^2, \tag{1}$$

where m_C is the mass of the carbon defect and ω_{C_i} is the LVM frequencies of the interstitial carbon defect,[1] that is, $\omega_{C_i(1)}=922$ cm^{-1} and $\omega_{C_i(2)}=932$ cm^{-1}. By substituting the values of m_C and ω_{C_i} in Eq. (1) we get $K_{C_i(1)}=37.39$ eV/Å (Ref. 2) and $K_{C_i(2)}=38.2$ eV/Å,[2] correspondingly.

The two Si–C dimers operate as oscillating dipoles along the (010) and (001) directions, respectively. With the help of Fig. 2 the expressions of their dipole moments $\mathbf{p}_1$ and $\mathbf{p}_2$ are

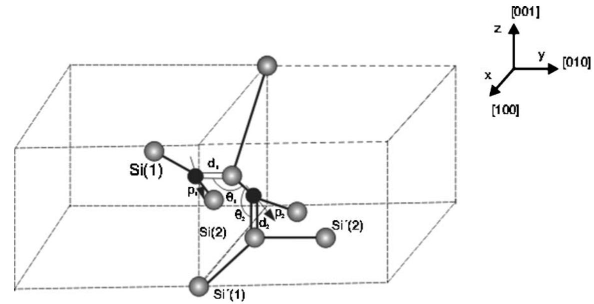

FIG. 2. Model for the $C_iC_s(Si_I)$ complex in Si. Bond lengths and angles have the values $d_1=1.766$ Å, $d_2=1.757$ Å, $\hat{\theta}_1=100.18°$, and $\hat{\theta}_2=117.19°$.

$$\mathbf{p}_1 = Z^*_{C_i}[r_1\hat{r}_1 + q_1\hat{y}], \quad \mathbf{p}_2 = Z^*_{C_i}[r_2\hat{r}_2 + q_2\hat{z}], \tag{2}$$

where $Z^*_{C_i}=3.2\,|e|$ is the effective charge[17] of the interstitial carbon atom, and r_1 and r_2 are the subtraction of the double bond lengths of the C_i atoms from the vertical distance from the straight line that connects the two pairs of substitutional Si atoms, numbered as Si (1), Si (2) and Si (1)′, Si (2)′, respectively (Fig. 2). All bond and angle values[15] used in the calculation procedure are sited in the caption of Fig. 2.

The effective Hamiltonian that describes the motion of the two interacting Si–C oscillating dimers is

$$H = \overset{\text{I}}{H_o} + \overset{\text{II}}{U_{\text{int}}} = \overbrace{\frac{p_1^2}{2m_C} + \frac{p_2^2}{2m_C} + \frac{1}{2}K_{\text{Si–C}}q_1^2 + \frac{1}{2}K_{\text{Si–C}}q_2^2}^{\text{I}} + \overbrace{\lambda_{C_iC_i}q_1q_2}^{\text{II}}, \tag{3}$$

where U_{int} is the potential energy of the two dipoles, given[18] by the formula

$$U_{\text{int}} = \frac{\mathbf{p}_1\cdot\mathbf{p}_2 - 3(\hat{n}\cdot\mathbf{p}_1)(\hat{n}\cdot\mathbf{p}_2)}{d^3}, \tag{4}$$

where $\hat{n}$ is the unit vector along the direction that connects the two dipoles and $d=2.964$ Å is the distance between them. The unit vector along the C–C direction is

$$\hat{n} = \frac{0.12\hat{x} - 1.32\hat{y} + 2.65\hat{z}}{2.964}. \tag{5}$$

The q-dependent part, $\lambda_{C_iC_i}$, of the dipole-dipole interaction is found, by combining Eqs. (2)–(4) to be equal to

$$\lambda_{C_iC_i} = 10.5(Z^*_{C_i})^2/d^3 = 6.8\ \text{eV/Å}^2. \tag{6}$$

The well-known Hamiltonian of Eq. (3) has two normal modes, with frequencies

$$\omega_1 = \sqrt{\frac{K_{\text{Si–C}} - \lambda_{C_iC_i}}{m_C}} \tag{7}$$

and

$$\omega_2 = \sqrt{\frac{K_{\text{Si–C}} + \lambda_{C_iC_i}}{m_C}}. \tag{8}$$

For $K_{C_i(1)}$ we get

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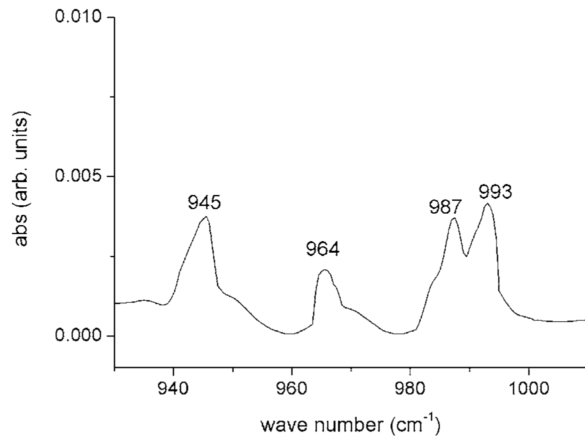

FIG. 3. The thermal evolution of the (987, 993 cm^{-1}) and the (945, 964 cm^{-1}) pairs of bands.

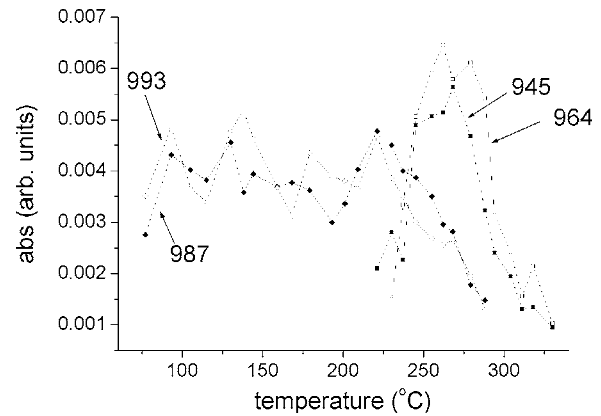

FIG. 4. Section of the IR spectrum after the irradiation and the isochronal anneal sequence.

$$\omega_{1C_iC_i(1)} = 833 \text{ cm}^{-1} \text{ and } \omega_{2C_iC_i(1)} = 1001 \text{ cm}^{-1} \tag{9}$$

and for $K_{C_i(2)}$ we get

$$\omega_{1C_iC_i(2)} = 843 \text{ cm}^{-1} \text{ and } \omega_{2C_iC_i(2)} = 1010 \text{ cm}^{-1}. \tag{10}$$

The two higher frequencies at 1001 and 1010 cm^{-1} of the two antisymmetric modes of the defect are close to the 987 and 993 cm^{-1} lines correspondingly, observed in our IR spectra. We attribute them to the $C_iC_s(Si_I)$ defect. The two lower frequency LVM bands of the symmetric modes of the defect are not detected in our IR spectra. These two weak signals may be masked by the two stronger signals of the *V*O and the C_iO_i defects occurring in the same spectral region, that is, at 830 and 860 cm^{-1}, respectively.

The decay of the (987, 993 cm^{-1}) pair of bands is accompanied in the spectra by the emergence of two other bands at 945 and 964 cm^{-1}. Figure 3 shows a section of the absorption spectrum after the irradiation and the isochronal annealing sequence. Figure 4 shows the thermal evolution of the (987, 993 cm^{-1}) and the (945, 964 cm^{-1}) pairs of bands.

The thermal evolution and the destruction of defects are generally complex issues due to the various mechanisms involved, as, for example, dissociation, migration and annihilation to sinks, or pairing with other defects to generate complexes. In our case, we shall reasonably consider, as seen below, that the $C_iC_s(Si_I)$ defect responsible for the (987, 993 cm^{-1}) pair reacts with another defect to produce a complex that gives rise to the (945, 964 cm^{-1}) pair. The atomic-scale mechanisms and processes that underline this observation are worth studying. Although it is difficult to address this issue a good point to start is by finding the order of the reaction kinetics that governs the phenomenon. To this end, some basic elements from the chemical reaction theory would be used together with some consideration about the possible structure that give rise to the (945, 964 cm^{-1}) pair of bands. Finding the reaction that describes the conversion of the (987, 993 cm^{-1}) center to the (945, 964 cm^{-1}) center is a key issue in understanding the phenomenon.

The interaction of two defects *A* and *B* to produce a more complex defect *AB* is described by a chemical reaction $A+B \rightarrow AB$. When the concentrations of two defects are approximately the same, second order kinetics describes their interaction. If *A* denotes the $C_iC_s(Si_I)$ defect, admittedly a pairing with itself is not considered as a possible reaction. One possibility is that the $C_iC_s(Si_I)$ defect captures Si_I's (denoted as the defect *B*), released from large clusters,[19] to form higher order members of the $C_iC_s(Si_I)_n$ family. Reasonably, a strong candidate would be the second member of the family, that is, the $C_iC_s(Si_I)_2$ structure. Assuming that the concentrations of the Si_I's and the $C_iC_s(Si_I)$ are about the same, a strong candidate for the identity of the defect *AB* is the $C_iC_s(Si_I)_2$ center, the formation of which has already been predicted in the literature.[20] Consequently, the pair of bands (945, 964 cm^{-1}) is attributed to this defect and the following reaction occurs:

$$C_iC_s(Si_I) + Si_I \rightarrow C_iC_s(Si_I)_2.$$

The corresponding rate equation is

$$\frac{d[N_2]}{dt} = k_1[N_1]^2. \tag{11}$$

By integrating one gets

$$k_1\tau = \left(\frac{1}{[N_1]'} - \frac{1}{[N_1]_o}\right)\frac{[N_2]' - [N_2]_o}{[N_1]_o - [N_1]'}, \tag{12}$$

where k_1 is the reaction constant, $[N_1]_o$ the initial concentration of the defect *A*, $[N_1]'$ the concentration of the defect *A* after the annealing for time τ at temperature *T*, $[N_2]_o$ the initial concentration of the defect *AB*, and $[N_2]'$ the concentration of the defect *AB* after the annealing for time τ at temperature *T*.

By plotting $\ln(k_1\tau)$ vs $1/T$ (Fig. 5) it is seen that $k_1\tau$ exhibits an Arrhenius behavior, that is, $k_1 \propto \exp(-E_1/kT)$, *E* being the activation energy of the process and *k* the Boltzmann factor. An activation energy of $E_1 = (1.25 \pm 0.05)$ eV is deduced. This value has been calculated by considering the decay of the 993 cm^{-1} band and the growth of the 964 cm^{-1} band. Similar values are derived by combining the decay of the 993 cm^{-1} with the growth of 945 cm^{-1}, the decay of 987 cm^{-1} with the growth of 964 cm^{-1}, and the decay of 987 cm^{-1} with the growth of 945 cm^{-1}.

On the other hand, the rate equation that describes the decay of the (987, 993 cm^{-1}) pair is

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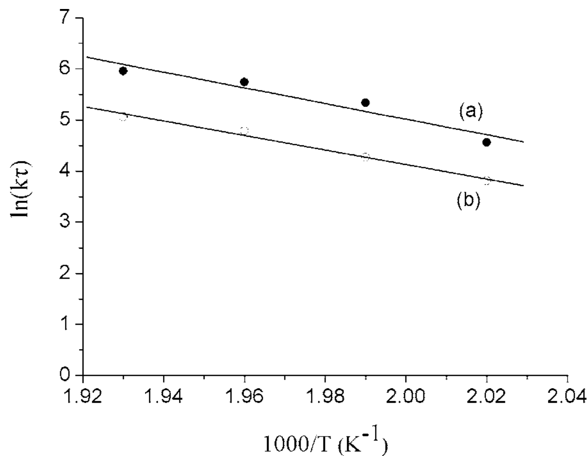

FIG. 5. (a) Plot of $\ln(k_1\tau)$ vs the inverse of the absolute temperature. Combined data are taken for the decay of the 987 cm^{-1} and the growth of the 945 cm^{-1} band. (b) Plot of $\ln(k_2\tau)$ vs the inverse of the absolute temperature. Data are taken for the decay of the 987 cm^{-1} band.

$$\frac{d[N_1]}{dt} = -k_2[N_1]^2. \tag{13}$$

The solution of this equation is

$$[N_1]_t = \frac{[N_1]_o}{1+[N_1]_o k_2 t} \text{ and } k_2\tau = \frac{1}{[N_1]'} - \frac{1}{[N_1]_o}, \tag{14}$$

where k_2 is the reaction constant, $[N_1]_o$ the initial concentration of the center, $[N_1]'$ the concentration of the center after the annealing for time τ at temperature T, and $[N_1]_t$ the concentration of the center at any time during the isochronal anneal at temperature T.

By plotting $\ln(k_2\tau)$ vs $1/T$ (Fig. 5) it is seen that $k_2\tau$ exhibits an Arrhenius behavior, that is, $k_2 \propto \exp(-E_2/kT)$, E_2 being the activation energy of the process and k the Boltzmann factor. The average activation energy deduced from the decay of the 987 and the 993 cm^{-1} signals is $E_2 = (1.29 \pm 0.05)$ eV.

On the basis of the above experimental results and analysis, it seems reasonably to suggest that the (945, 964 cm^{-1}) pair of bands originates from the $C_iC_s(Si_I)_2$ center. The activation energy that describes the formation of the $C_iC_s(Si_I)_2$ center through the reaction $C_iC_s(Si_I)+Si_I \rightarrow C_iC_s(Si_I)_2$ has an average value $(E_1+E_2)/2 = (1.27 \pm 0.05)$ eV.

In an early work,[21] reporting annealing studies of the 0.97 photoluminescence PL line of the basic C_iC_s center in neutron irradiated Si, an activation energy of 1.25 eV was quoted. This value is very close to that reported in this work for the $C_iC_s(Si_I)$ complex. It would appear that they were observing[21] the emission of Si_I's, as in the present work.

Noticeably, irrespective of the mechanism that is operative, the understanding of the production, of the association with other defects, and of the destruction of complexes containing Si_I's, as the $C_iC_s(Si_I)$, could provide information towards comprehending the role of Si_I's in Si material. In the present work the occurrence of the reaction channel $C_iC_s \xrightarrow{Si_I} C_iC_s(Si_I) \xrightarrow{Si_I} C_iC_s(Si_I)_2$ previously reported in the literature[14] is verified. It should be noted that the stability[22] of the basic C_iC_s center is 1.9 eV, making possible the reaction channel to occur, since without the basic center being stable, the higher order centers could not easily form.

CONCLUSIONS

We have studied the $C_iC_s(Si_I)$ defect in neutron-irradiated carbon-rich Si material. Our previous assignment of two bands (987, 993 cm^{-1}) to that defect has been corroborated by semiempirical calculations of the vibrational frequencies of the structure. The $C_iC_s(Si_I)$ defect is stable up to 250 °C. Its disappearance is accompanied in the spectra by the emergence of another pair of bands (945, 964 cm^{-1}). The decay of the former pair and the growth of the latter are described closely to be a second order kinetics with an average activation energy of 1.27 eV. Acceptably, the reaction $C_iC_s(Si_I)+Si_I \rightarrow C_iC_s(Si_I)_2$ is very likely to take place and therefore we suggest that the (945, 964 cm^{-1}) pair of bands is most possibly associated with the $C_iC_s(Si_I)_2$ complex. This assignment is consistent with reaction models postulating the successive aggregation of Si_I's on the initial C_iC_s defects formed by irradiation.

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