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Modeling defect reactions processes to study the impact of carbon on the production and conversion of A-centers in silicon

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Abstract The vacancy-oxygen (*V*O or A-center) defect is one of the most significant defects in Czochralski-grown silicon (Cz-Si). Here we investigate the effect of carbon on the formation of *V*O defect and its conversion upon annealing to the VO_2 defect. Cz-Si samples with various carbon concentrations were irradiated by 2 MeV electrons. The formation of *V*O pair, its thermal stability and evolution and its conversion to the VO_2 defect were previously monitored and studied by means of infrared (IR) spectroscopy. Modeling of the formation process showed that the *V*O concentration has a square root dependency on the carbon substitutional (C_s) concentration. The conversion of the *V*O to the VO_2 defect decreases with the increase of the C_s concentration. The results are in agreement with the experimental observed dependency of the conversion ratio on the C_s concentration, since [*V*O] increases when [C_s] increases.

1 Introduction

Si is widely used for microelectronic, photovoltaic, and sensor devices, however, numerous defect-dopant interactions influencing its properties are not well established [1–5]. Crystal growth of Si by the Czochralski technique introduces significant concentrations of oxygen, which is an important impurity [6]. Oxygen is accommodated in the lattice at interstitial sites and the oxygen interstitials (O_i) are electrically inactive. O_i can be characterized by IR spectroscopy giving rise to a number of local vibrational modes (LVMs), the stronger among of which is a broad band at 1106 cm^{-1} (at room temperature) [7, 8]. This band is used for the calculation of the oxygen concentration in Czochralski-grown silicon (Cz-Si). O_i can bind to vacancies (*V*) forming *V*O pairs (via $V + O_i \rightarrow VO$) [9, 10]. The A-center is an important recombination [11] center and its electrical, optical and electronic properties have been investigated extensively [12–15]. In particular, the *V*O is electrically active with an acceptor level at $E_c-0.17$ eV [4, 11]. It is optically active with an LVM band at 830 cm^{-1} arising from its neutral charge state [13–15]. At around 300 °C the *V*O defect becomes mobile and can readily associate with an oxygen atom leading to the formation of the VO_2 defect. This is an important defect for the formation of larger clusters (for example, VO_n with $n > 2$) [13–15] and is a possible nucleation path for the formation of oxide precipitates [16–18]. Using IR spectroscopy the conversion of the *V*O to the VO_2 defect can be monitored by the decrease of the 830 cm^{-1} band of the *V*O and the simultaneous growth of the 885 cm^{-1} band of the VO_2.

Carbon has a smaller covalent radius than Si and shows a strong tendency for trapping self-interstitials. In this process, the C_s atoms are converted to carbon interstitials (C_i), which are readily captured by C_s and O_i impurities to form C_iC_s and C_iO_i defects respectively. Carbon gives rise to an LVM band at 605 cm^{-1}, at room temperature, which is used for the calculation of the carbon concentration in Cz-Si. Previous studies, [19–24] highlight the impact of

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carbon-related defects indicating its significance in the various defect processes in Si. The presence of carbon impacts the balance between vacancies and self-interstitials produced after irradiation and escaped annihilation. Therefore, the formation of secondary defects, involving the participation of intrinsic defects for instance the vacancy-oxygen defects is expected to be affected. As a continuation of previous experimental work, [23] in the present study we aim to understand the impact of the carbon impurity on the production of *V*O defect and its conversion to VO_2 by modeling the related defect reactions and how carbon affects their contribution in the above two processes.

2 Modeling of the *V*O production process

The main event during irradiation is the production of vacancies (*V*) and self-interstitials (I). Most of them are immediately annihilated $V + \mathrm{I} \rightarrow \emptyset$. Vacancies that survive annihilation are readily captured by oxygen impurities to produce *V*O centers. At the same time some of the produced *V*O are destroyed by the recombination with I. Thus, the two main reactions that govern the production of *V*O defect are:

$$V + \mathrm{O_i} \rightarrow V\mathrm{O}$$

$$V\mathrm{O} + \mathrm{I} \rightarrow \mathrm{O_i}$$

When C_s is present in the material, most of the I produced by the irradiation and survive annihilation are captured by carbon impurities, which are converted to C_i, ($C_s + I \rightarrow C_i$), leading to the formation of the C_iO_i and C_iC_s defects.

Calling G the production rate of the I ($G = \frac{d[I]}{dt}$), this is also the production rate of the *V* and also of the *V*O centers. Indeed, when the oxygen concentration is much larger than the concentrations of other competing traps for capturing vacancies, then all the vacancies are captured by oxygen. Therefore

$$G = \frac{d[I]}{dt} = \frac{d[V]}{dt} = \frac{d[VO]}{dt}$$

The balance of the radiation-produced I at a rate G and their loss at a rate $a_{Cs}[I]\,[C_s]$ due to trapping by carbon plus $a_{VO}[I]\,[VO]$ due to trapping by *V*O center leads to the expression:

$$G = a_{Cs}[I]\,[C_s] + a_{VO}[I]\,[VO]$$

where a_{Cs} and a_{VO} are the corresponding kinetic coefficients for the annihilation reactions $C_s + I \rightarrow C_i$ and $VO + I \rightarrow O_i$. This means that the quasi-steady-state concentration of I is:

$$[I] = \frac{G}{a_{C_s}[C_s] + a_{VO}[VO]} \tag{1}$$

As we mentioned above the *V*O centers are produced at a rate G and at the same time are destroyed by I at a rate $a_{VO}[I]\,[VO]$. The kinetic equation describing the whole process is therefore

$$\frac{d[VO]}{dt} = \mathrm{G} - a_{VO}[\mathrm{I}][\mathrm{VO}] \tag{2}$$

Upon substituting [I] from expression (1) in Eq (2) we receive:

$$\frac{d[VO]}{dt} = \frac{Ga_{Cs}[C_s]}{a_{Cs}[C_s] + a_{VO}[VO]} \tag{3}$$

At moderate carbon concentrations the $a_{VO}[VO]$ term can be larger than the $a_{Cs}[C_s]$ term, of course exerting very short time when [*V*O] is low. Then the kinetic equation is reduced in the expression

$$\frac{d[VO]}{dt} = \frac{Ga_{Cs}[C_s]}{a_{VO}[VO]}$$

Thus

$$\int [VO]d[VO] = \int G(\frac{a_{Cs}}{a_{VO}})[C_s]dt$$

or

$$\frac{[VO]^2}{2} = G(\frac{a_{Cs}}{a_{VO}})[C_s]t$$

that is

$$[VO] = \left(2\frac{a_{Cs}}{a_{VO}}\right)^{1/2}(G \cdot t)^{1/2} \cdot [C_s]^{1/2} \tag{4}$$

But G·t is the amount of the *V*O centers produced by the irradiation, which is proportional [25] to the fluence. In other words expression (4) implies that the *V*O concentration is proportional to the square root of the fluence, as well as to the square root of the carbon concentration. It means that for a certain fluence, [*V*O] is proportional to $[C_s]^{1/2}$.

To test the validity of the above conclusion we model the experimental results reported in our previous work [23]. Reasonably we shall use data from Table I of Ref. [23], and in particular those with fluence of $5 \times 10^{17}\ e^- \ cm^{-2}$ for which we have the most available data. Besides the three samples S_{12}, S_{13} and S_{14} (S_{11} was excluded as the initial C concentration is undetermined) we shall make use of an additional sample labeled S_{15} irradiated at the same fluence with $[C_s]_o = 75 \times 10^{16}\ cm^{-3}$ and $[O_i]_o = 6.73 \times 10^{16}\ cm^{-3}$.

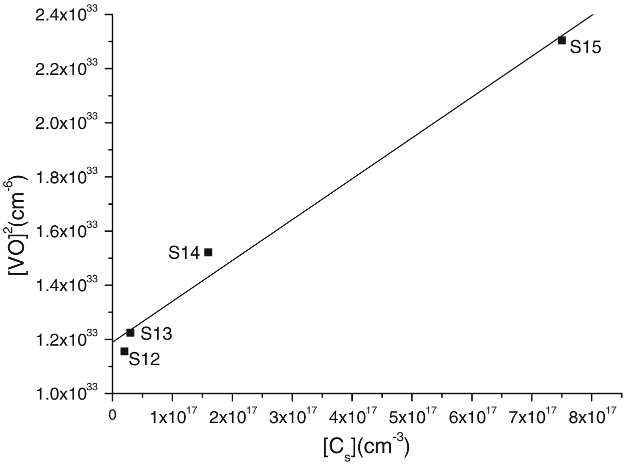

Fig. 1 The dependence of $[VO]^2$ with respect to $[C_s]$

For this sample it has been found that $[VO] = 4.8 \times 10^{16}$ cm^{-3} and $a_{VO2}/a_{VO} = 0.28$. Figure 1 shows a linear dependency of $[VO]^2$ versus $[C_s]$ in full agreement with the outcome expressed by relation (4).

Notably, the proportionality of $[VO]$ to the square root of the fluence is clearly seen in Fig. 6 of Ref. [26]. Physically, the observed enhancement of VO defect formation when $[C_s]$ increases can be understood as follows: In carbon containing Cz-Si material, the capture of self-interstitials by carbon atoms, in the course of irradiation, apparently increases the availability of vacancies and therefore the formation of VO defects is expected to be affected. More specifically, the formation of VO defects is expected to be enhanced in carbon-rich Si, since the disposition of vacancies for pairing with oxygen is increased. Notably, the phenomenon has been investigated in the past, but conflicted reports have been cited in the literature. It has been reported [27] for instance, that the variation of the carbon concentration in the silicon material does not affect the production rate of the A centers, although other works reported [28, 29] that the production of A centers is increased by the presence of carbon. Our results certainly verify the latter case and the suggested model provides a detailed explanation of the basic features of this phenomenon.

3 Modeling of the VO to VO_2 conversion process

There are numerous studies investigating the annealing of the VO defect in silicon. It is generally accepted that the loss of VO is governed [9, 30, 31] mainly by two reactions, one of 1-st order and one of 2-nd order. The first reaction is related with the capture of the migrating VO pair by an O_i atom leading to the formation of the VO_2 defect: $VO + O_i \rightarrow VO_2$. The second is related with the annihilation of VO by self-interstitials. There are two cases. Firstly, one may consider a direct annihilation by I, that is $VO + I \rightarrow O_i$. Sources of I are large self-interstitial clusters [9]. Generally, the order of this reaction is hard to be established. It is neither a 1-st order nor a 2-nd order. In fact, it is a linear reduction of VO. Secondly, one may consider an indirect annihilation of VO. The following reaction channel may be envisaged (V. V. Voronkov, private communication). At first, VO dissociates reversibly into $V + O_i$ then the liberated V is trapped by VO and it is the produced V_2O that is annihilated by I, giving back one VO while two VO were spend on production of one V_2O:

$$VO \rightarrow V + O_i$$

$$V + VO \rightarrow V_2O$$

$$V_2O + I \rightarrow VO.$$

Thus the VO annihilation is a 2-nd order reaction.

The kinetic equation describing the VO loss by two reactions one 1-st order ($VO + O_i \rightarrow VO_2$) and one 2-nd order (indirect annihilation of VO through V_2O) is:

$$\frac{d[VO]}{dt} = -A[VO]^2 - B[VO] \tag{5}$$

although the formation of VO_2 is described by the equation

$$\frac{d[VO_2]}{dt} = B[VO] \tag{6}$$

where A and B are the corresponding rate coefficients.By combining Eqs. (5) and (6), one receives

$$\frac{d[VO_2]}{d[VO]} = \frac{B[VO]}{-A[VO]^2 - B[VO]} = -\frac{1}{g[VO]+1},$$

where we put $g = {}^{A}\!/_{B}$

Thus

$$\mathrm{d}[VO_2] = \frac{-d[VO]}{g[VO]+1} = -\frac{1}{g}\frac{d[g[VO]+1]}{[g[VO]+1]}$$

then

$$\int_{0}^{[VO_2]_{final}} d[VO_2] = -\frac{1}{R}\int_{[VO]_{initial}}^{0} \frac{d[g[[VO]+1]}{[g[VO]+1]},$$

from which we receive

$$[VO_2]_{\mathrm{final}} = \frac{1}{g}\ln[g[VO]_{initial}+1]$$

Hereafter, for the sake of simplicity we shall use $[VO]$ and $[VO_2]$ instead of $[VO]_{\mathrm{initial}}$ and $[VO_2]_{\mathrm{final}}$. Finally we receive

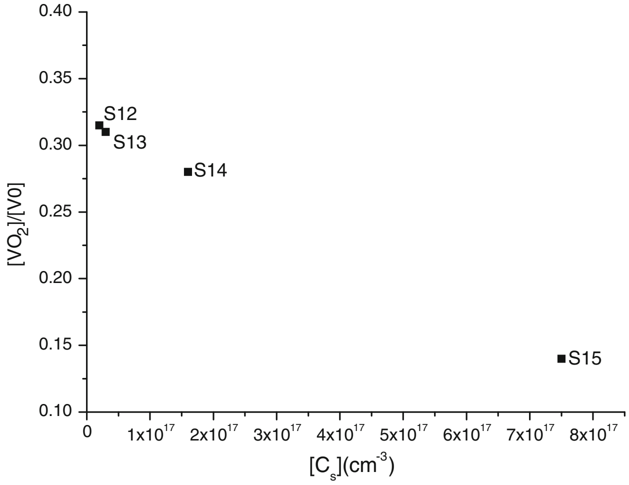

Fig. 2 The variation of $[VO_2]/[VO]$ as a function of $[C_s]$

$$\frac{[VO_2]}{[VO]} = \frac{1}{g}\frac{\ln[g[VO]+1]}{[VO]} \cong \frac{\ln[g[VO]]}{g[VO]}$$

Taking into account Eq. 4 it follows that

$$\frac{[VO_2]}{[VO]} \propto \frac{\ln[g\sqrt{[C_s]}]}{g\sqrt{[C_s]}} \tag{7}$$

Apparently, $[VO_2]/VO$ is a decreasing function of C_s. Figure 2 confirms this behaviour for the samples irradiated with fluence of 5×10^{17} e^- cm^{-2}. In reference with Table I of Ref. [23] in order to calculate the concentrations of the VO and VO_2 defects we used [29, 32] calibration coefficients 6.25×10^{16} cm^{-2} and 3.12×10^{16} cm^{-2} respectively. Physically, the observed reduction of the conversion ratio $[VO_2]/[VO]$ when the C_s concentration increases can be understood as follows: At above 300 °C when VO_2 begins to form, C_s can only trap momentarily the available self-interstitials which then are released in Si. In their turn these self-interstitials react with the present VO ($VO + I \rightarrow O_i$) and the formed VO_2 ($VO_2 + I \rightarrow VO$) defects. This in essence leads to a reduction of the formed VO_2 defects and to a final reduction of the conversion ratio VO_2/VO.

4 Summary

In the present study we modeled previous experimental results to investigate the impact of carbon on the production of VO and its subsequent conversion to the VO_2 defect in electron-irradiated Si. Modeling of the VO formation process results in a square root dependency on the C_s concentration, in agreement with the experimental results. Furthermore, our results showed that the VO_2/VO ratio decreases when the carbon content of the samples increases. Furthermore, the VO to the VO_2 conversion process indicates a decreasing dependency on the C_s concentration, also in agreement with the experimental results.

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