Dependence of Dicarbon Annealing Temperature in n-Si on Oxygen Concentration in the Crystal

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Abstract—The role of oxygen in the mechanism of dissociation of the dicarbon complex in n-Si into components is considered. It is assumed that released interstitial carbon atoms C\textsubscript{i} migrate through the crystal and react with both substitutional carbon C\textsubscript{s} and interstitial oxygen with the resulting formation of complexes C\textsubscript{i}C\textsubscript{s} and C\textsubscript{i}O\textsubscript{i}, respectively. The solution of a system of equations describing the formation of interstitial carbon atoms in the course of annealing of dicarbon show that the rate constant for the reaction of annealing of the C\textsubscript{i}C\textsubscript{s} complex (the G center) depends on the oxygen concentration. This dependence is treated as the dependence of the activation energy for annealing of a C\textsubscript{i}C\textsubscript{s} complex and, consequently, the dissociation energy of this complex on oxygen concentration. A more accurate value of dissociation energy for the G center was determined as 1.08 ± 0.03 eV. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Experiments with annealing of C\textsubscript{i}C\textsubscript{s} (dicarbon) complexes, or G centers, in n-Si (see, for example, [1, 2]) showed that the temperature of annealing of this center depends on the oxygen concentration in the crystal. The aforementioned G centers are annealed out at lower temperatures in silicon grown by the Czochralski method (Cz-Si) than in silicon grown by the floating-zone method (FZ-Si).

The dissociation energy for a C\textsubscript{i}C\textsubscript{s} complex ($E_{\text{C}_i\text{C}_s} = 1.10 ± 0.05$ eV) reported by Boyarkina et al. [3] was determined from comparison of the calculated kinetics of annealing for this complex with experimental data [1, 4] on the isochronous heat treatment of irradiated n-Si. It was assumed in the calculations that the reaction of annealing of a C\textsubscript{i}C\textsubscript{s} complex proceeds via the scheme of decomposition of this center into its constituent components with the subsequent migration of the released interstitial carbon atom C\textsubscript{i} through the crystal. The involvement of oxygen in this reaction was not taken into account.

The aim of this study is to calculate the annealing kinetics for a C\textsubscript{i}C\textsubscript{s} complex taking into account the effect of oxygen on the rate constant for the reaction of decomposition of the center under consideration.

2. INVOLVEMENT OF OXYGEN IN THE REACTION OF DECOMPOSITION OF A C\textsubscript{i}C\textsubscript{s} COMPLEX (THE G CENTER)

Interstitial carbon atoms released as a result of decomposition of G centers migrate and can be trapped by interstitial oxygen O\textsubscript{i} with the resulting formation of C\textsubscript{i}O\textsubscript{i} centers [6] or be retrapped by carbon at the Si lattice sites (substitutional carbon C\textsubscript{s}) with the resulting formation of C\textsubscript{i}C\textsubscript{s} complexes [5]. The trapping of C\textsubscript{i} atoms by atoms of substitutional carbon C\textsubscript{s} with the formation of new C\textsubscript{i}C\textsubscript{s} complexes leads to an increase in the characteristic time of decomposition of these complexes [2], which is equivalent to an increase in the activation energy for annealing out of these centers.

We write a system of equations that describe the variation in the concentrations of atoms of interstitial carbon C\textsubscript{i} and the G centers in the course of heat treatment as

\[ \begin{align*}
\frac{dN_G}{dt} &= -v_G N_G + k_{G,C_s} N_C N_C, \\
\frac{dN_C}{dt} &= v_G N_G - k_{C,O} N_C N_C - k_{C_s} N_C N_O,
\end{align*} \]

where $N_G$, $N_C$, and $N_O$ are the concentrations of G centers, interstitial carbon atoms C\textsubscript{i}, substitutional carbon atoms C\textsubscript{s}, and interstitial oxygen atoms O\textsubscript{i}; $v_G$ is the rate constant for the reaction of decomposition of a G center; and $k_{C,O}$ and $k_{C_s}$ are the probabilities of trapping of interstitial carbon atoms by atoms of substitutional carbon and interstitial oxygen, respectively.

Experiments with isochronous annealing of interstitial carbon atoms and C\textsubscript{i}C\textsubscript{s} complexes in n-Si irradiated with $^{60}$Co gamma-ray photons [1] showed that the con-
centrion of interstitial carbon atoms became negligible (≤ 10^{12} \text{cm}^{-3}) even at temperatures that were lower than the temperatures corresponding to annealing out of the C\text{C}_i, complex (310 K for Cz-Si and 380 K for FZ-Si). Therefore, we assume that the concentration of interstitial carbon atoms remains unchanged in the course of annealing the G centers; i.e., we have

\[ \frac{dN_{C_i}}{dt} = 0. \]  \hspace{1cm} (2)

By solving the system of Eqs. (1), we obtain

\[ N_{C_i} = \frac{v_G N_G}{k_{C,C_i} N_{C_i} + k_{C,C_i} N_{O}}. \]  \hspace{1cm} (3)

\[ \frac{dN_G}{dt} = -v_G N_G \frac{3N_{O}/N_{C_i}}{1 + 3N_{O}/N_{C_i}}. \]  \hspace{1cm} (4)

It was ascertained previously [5] that the probability that an interstitial carbon atom will be trapped by an oxygen atom exceeds the probability of its being trapped by substitutional carbon by approximately a factor of 3; i.e.,

\[ \frac{k_{C,O}}{k_{C,C_i}} \approx 3. \]  \hspace{1cm} (5)

As a result, we derive the following equation that describes the annealing out of the G centers:

\[ \frac{dN_G}{dt} = -v_G N_G \frac{3N_{O}/N_{C_i}}{1 + 3N_{O}/N_{C_i}}. \]  \hspace{1cm} (6)

It can be seen that the effective rate constant for the reaction of decomposition of the G center depends on the oxygen concentration; i.e.,

\[ v_G^{eff} = v_G \frac{3N_{O}/N_{C_i}}{1 + 3N_{O}/N_{C_i}}. \]  \hspace{1cm} (7)

3. DISCUSSION OF THE RESULTS OF CALCULATION

The concentration of substitutional carbon atoms \( N_{C_i} = (1-3) \times 10^{16} \text{cm}^{-3}\) both in FZ- and Cz-Si. In Cz-Si, the concentration of interstitial oxygen \( N_{O_i(Cz)} \leq 10^{18} \text{cm}^{-3}\), i.e., the ratio \( N_{O_i(Cz)}/N_{C_i} \gg 1\). The concentration of interstitial carbon atoms is defined as

\[ N_{C_i(Cz)} = \frac{v_G N_G}{k_{C,O_i} N_{O_i(Cz)}}. \]  \hspace{1cm} (8)

For FZ-Si, the corresponding relations are written as

\[ N_{O,(FZ)} = (1-3) \times 10^{16} \text{cm}^{-3}, \quad N_{O_i(FZ)}/N_{C} \approx 1, \]

\[ N_{C_i(FZ)} = \frac{v_G N_G}{k_{C,C_i} N_{C_i}}. \]  \hspace{1cm} (9)

The ratio between the concentration of interstitial carbon atoms in FZ-Si and that in Cz-Si is given by

\[ \frac{N_{C_i(Cz)}}{N_{C_i(FZ)}} \approx \frac{k_{C,C_i} N_{C_i}}{k_{C,O_i} N_{O_i(Cz)}} \ll 1. \]  \hspace{1cm} (10)

In the Cz-Si crystals, the concentration of interstitial carbon atoms is low; as a result, almost all these atoms are involved in the formation of the C\text{O}_i complexes, taking into account that there is a sufficient amount of oxygen in the crystals. At the same time, the concentration of interstitial carbon in FZ-Si is much higher and is sufficient for the formation of both C\text{O}_i complexes and new G centers, which entails an increase in the decomposition time for these centers. As a result, the activation energy for annealing out of G centers \( E_{ag} \) is higher in FZ-Si than in Cz-Si.

The activation energy for annealing out of a G center (by decomposition into its components) \( E_{ag} \) is the sum of the G-center dissociation energy \( E_{C,C_i} \), the energy of rearrangement of the electronic subsystem of the crystal \( W_{C,C_i}^{el} \), and the migration energy for the released interstitial carbon atom \( W_{C_i} \) [3]:

\[ E_{ag} = E_{C,C_i} + W_{C,C_i}^{el} + W_{C_i}. \]  \hspace{1cm} (11)

A variation in the rate constant for the reaction of decomposition of the C\text{C}_i, complex (the G center), which is described by formula (7), can be treated as a variation in the activation energy of this process by the quantity \( \delta E_{ag} \); i.e.,

\[ v_G^{eff} = v_G \exp \left( \frac{-\delta E_{ag}}{kT} \right). \]  \hspace{1cm} (12)

Comparing (7) and (12), we obtain

\[ \exp \left( \frac{-\delta E_{ag}}{kT} \right) = \frac{3N_{O}/N_{C_i}}{1 + 3N_{O}/N_{C_i}}; \]  \hspace{1cm} (13)

therefore,

\[ \delta E_{ag} = kT \ln \frac{1 + 3N_{O}/N_{C_i}}{3N_{O}/N_{C_i}} = kT \ln \left( 1 + \frac{N_{C_i}}{3N_{O_i}} \right). \]  \hspace{1cm} (14)