Kinetics Modeling of the Carbon Vacancy Thermal Equilibration in 4H-SiC

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Abstract. The carbon vacancy (V_C) is a major limiting-defect of minority carrier lifetime in n-type 4H-SiC epitaxial layers and it is readily formed during high temperature processing. In this study, a kinetics model is put forward to address the thermodynamic equilibration of V_C , elucidating the possible atomistic mechanisms that control the V_C equilibration under C-rich conditions. Frenkel pair generation, injection of carbon interstitials (C_i 's) from the C-rich surface, followed by recombination with V_C 's, and diffusion of V_C 's towards the surface appear to be the major mechanisms involved. The modelling results show a close agreement with experimental deep-level transient spectroscopy (DLTS) depth profiles of V_C after annealing at different temperatures.

Introduction

The carbon vacancy (V_C) is a prevailing point defect in 4H-SiC epitaxial layers. It is reported as a major limiting defect of the minority charge carrier lifetime in n-type layers [1,2], with deep states in the 4H-SiC bandgap leading to recombination/trapping of the charge carriers. In current state-of-the-art as-grown epi-layers, the $[V_C]$ (brackets denote concentration) is typically in the 10^{12} cm^{-3} range and it is strongly enhanced, by about 2 orders of magnitude, after high-temperature processing [3]. Technologically, heat treatment at $\geq 1800 \text{ }^\circ\text{C}$ is important to achieve an adequate electrical activation of high fluence Al implanted regions, in order to realize low-resistivity p-type layers in bipolar power devices [4]. A formation enthalpy of $\sim 4.8 \text{ eV}$ under C-rich ambient conditions has been observed for V_C , both theoretically and experimentally [3,5].

Two different methods have commonly been explored to reduce the $[V_C]$ in as-grown epi-layers: (i) thermal oxidation of the Si-terminated 4H-SiC surface [6], and (ii) ion implantation in the near surface region followed by high temperature annealing [7,8]. In addition, we have recently demonstrated that annealing at the moderate temperature of $1500 \text{ }^\circ\text{C}$, establishing thermodynamic equilibrium under C-rich surface conditions (carbon cap), also can reduce the $[V_C]$ to the low 10^{11} cm^{-3} range [9]. All these three approaches are based on the concept of injecting carbon interstitials (C_i 's) from the surface and subsequent recombination with V_C 's in the epi-layer 'bulk'. However, the atomistic mechanisms controlling the equilibration of V_C are still not fully known and this holds for their kinetics as well. In the present study, we put forward a kinetics model to elucidate the physical processes governing the equilibration process of V_C under C-rich ambient conditions.

Kinetics Model

In the kinetics model, the equilibrium concentration of V_C ($[V_C]_{\text{Eq}}$) during heat treatment under C-rich surface conditions is assumed to be determined by two competing processes: (i) thermal generation of Frenkel pairs (V_C 's and C_i 's) in the epi-layer 'bulk', and (ii) annihilation of V_C 's via interaction with thermally injected C_i 's from the C-cap. Accordingly, the following partial differential equations can be derived from the theory of diffusion-limited reactions [10] and then

numerically solved to obtain one-dimensional $[V_C]$ versus depth profiles during elevated heat treatments,

$$\frac{\partial[V_C]}{\partial t} = G_{V_C} + \frac{\partial}{\partial x} \left(D_{V_C} \frac{\partial[V_C]}{\partial x} \right) - 4\pi R(D_{C_i} + D_{V_C})[C_i][V_C] \quad (1)$$

$$\frac{\partial[C_i]}{\partial t} = G_{C_i} + \frac{\partial}{\partial x} \left(D_{C_i} \frac{\partial[C_i]}{\partial x} \right) - 4\pi R(D_{C_i} + D_{V_C})[C_i][V_C]. \quad (2)$$

Here, G_{V_C} and G_{C_i} are the thermal generation rates of V_C and C_i , respectively, and they were set equal in the model since V_C 's and C_i 's are assumed to be generated as Frenkel pairs in the epi-layer 'bulk' [3]. Furthermore, t refers to the annealing time, and x to the sample depth. D_{C_i} and D_{V_C} are the diffusion coefficients of C_i and V_C respectively, and R is the reaction capture radius between V_C and C_i . The last term on the right side of Eq. 1 and Eq. 2 represents the recombination rate between V_C and C_i . The $[V_C]_{Eq}$ will be reached at each temperature when the variation of $[V_C]$ with t approaches zero, yielding,

$$[V_C]_{Eq} = \frac{G_{V_C} + \frac{\partial}{\partial x} \left(D_{V_C} \frac{\partial[V_C]}{\partial x} \right)}{4\pi R(D_{C_i} + D_{V_C})[C_i]}. \quad (3)$$

G_{V_C} , D_{V_C} , D_{C_i} , and the injected $[C_i]_{x=0}$ are used in the model as the fitting parameters to reproduce the experimental data, and they are all expressed by an Arrhenius equation,

$$X = X_o \exp \left(\frac{-E_{aX}}{kT} \right). \quad (4)$$

Here X represents the fitting parameter (i.e G_{V_C} , D_{V_C} , D_{C_i} , or $[C_i]_{x=0}$), X_o is a pre-exponential factor, E_{aX} is the activation energy for the process X , k is the Boltzmann constant, and T is the absolute temperature. In addition, the following initial conditions are applied,

$$[C_i]_{t=0} = 0, \quad \text{for } x > 0 \quad (5)$$

$$[V_C]_{t=0} = [V_C]_0 \quad \text{for } x \leq 10 \mu m \quad (6)$$

$$[V_C]_{t=0} = 100 \times [V_C]_0 \quad \text{for } x > 10 \mu m. \quad (7)$$

Here, $[V_C]_0$ represents the initial $[V_C]$ at $t = 0$, which is expected to be a few orders of magnitude higher in the highly n-type substrate ($x > 10 \mu m$) relative to the lightly n-type epi-layer ($x \leq 10 \mu m$), and the substrate in this case is assumed to serve as a sink for the thermally generated and rapidly migrating C_i 's. The C-cap /epi-layer interface is treated as a reflective boundary for V_C , while the epi-layer/substrate interface is regarded as a reference plane with no influence on the flux of C_i 's and V_C 's.

Results and Discussion

Figure 1 shows simulated depth profiles of $[V_C]$ for a wide concentration range (10^{11} - 10^{14} cm⁻³). The profiles exhibit good agreement with experimental deep level transient spectroscopy (DLTS) depth profiles of V_C in epitaxial samples post-growth heat treated between 1500 and 1950 °C, illustrating the validity of the model. The simulation results emphasize the significance of both the competing processes (i) and (ii), mentioned above, for the equilibration of $[V_C]$. The profiles show that V_C formation dominates at high temperatures where the generated $[V_C]$ is much higher than the injected $[C_i]$. In this case, the annihilation of V_C 's appears to be limited to a restricted region in the vicinity of the surface, yielding a continuous diffusion of V_C from the epi-layer 'bulk' towards the

surface due to the concentration gradient. This explains the observed decrease of $[V_C]$ towards the surface in the samples treated at ≥ 1800 °C, implying that thermodynamic equilibrium does not truly hold at depths >2 μm , but rather steady-state conditions which are rapidly established at high temperatures. While the V_C profile becomes essentially flat in the samples annealed at ≤ 1600 °C for which the near surface trapping of injected C_i 's is less because of the lower $[V_C]$. At moderate temperatures (≤ 1600 °C), the injected C_i 's can diffuse deeper into the epi-layer bulk and the annihilation of V_C 's takes place in the entire layer (10 μm). Hence, the injection of C_i 's is the process controlling the equilibration kinetics at moderate temperatures.

The pre-exponential factors and activation energies of the fitting parameters used in the model, G_{V_C} , D_{V_C} , D_{C_i} and $[C_i]_{x=0}$, were extracted from the Arrhenius plots in Figs. 2(a) and 2(b). The deduced activation energy for the generation rate of V_C ($E_{G_{V_C}}$) is about 6.3 eV, which is ~ 1.5 eV higher than the V_C formation energy of 4.8 eV determined experimentally and theoretically for V_C in the neutral charge state [3,5,9]. This reflects that in the Frenkel pair, V_C and C_i , formation process, the C_i diffuses away and leaves behind the less mobile V_C . Accordingly, the deduced activation energy of the V_C (and C_i) generation rate is given by the sum of the V_C formation energy and the migration energy of C_i . Therefore, the C_i migration energy ($E_{M_{C_i}}$) becomes ~ 1.5 eV, and this value is further corroborated by the results in Ref. [11]. As a result, values of D_{C_i} can be assumed in the simulations and then also $[C_i]_{x=0}$ can be determined. Here, it should be mentioned that based on Eq. 3, the values of $[C_i]_{x=0}$ and D_{C_i} can be decoupled only if D_{C_i} is known, since identical $[V_C]$ versus depth profiles are obtained at a given temperature as long as the product ($D_{C_i} \times [C_i]_{x=0}$) remains constant. Knowing the contribution of D_{C_i} , we then arrive at a value of ~ 1.7 eV for the activation energy of C_i injection (E_{inj}) in a close agreement with the activation energy for the flux of injected C_i reported in Ref. [12]. The deduced activation energy for

Fig. 1. Simulated depth profiles of $[V_C]$ in comparison with experimental profiles measured by DLTS in samples subjected to equilibrating heat treatments at different temperatures between 1500 and 1950 °C [3,9].

Figure 2. (a) The extracted values of the V_C generation rate (G_{V_C}) (left Y-axis) and the injected $[C_i]$ at $x=0$ (right Y-axis) from the simulations as a function of the reciprocal absolute annealing temperature. (b) Simulated values of the C_i diffusion coefficient (D_{C_i}) (left Y-axis) and the V_C diffusion coefficient (D_{V_C}) (right Y-axis) versus the reciprocal absolute annealing temperature.

V_C migration (E_{MV_C}) is ~ 2.5 eV as shown in Fig. 2(b), and D_{C_i} is ~ 3 -4 orders of magnitude higher than D_{V_C} at temperatures above 1500 °C. Thus, D_{V_C} in the denominator of Eq. 3 has a negligible influence on $[V_C]_{Eq}$, although D_{V_C} plays a significant role at high temperatures (≥ 1800 °C) when the generation rate of $[V_C]$ is high and the trapping of injected C_i 's near the surface is strong.

Finally, the model provides a possibility to estimate the equilibration time at different processing temperatures and the influence of the initial concentration of V_C . At the moderate temperature of 1500 °C, at which the V_C annihilation is the governing process, it was experimentally reported that $[V_C]_{Eq}$ occurs after about 40 min for as-grown epi-layers ($[V_C]_{t=0} \sim 4 \times 10^{12} \text{ cm}^{-3}$) with a thickness of 10 μm [9]. Further, in a sample first treated at 1950 °C (followed by rapid cooling) yielding $[V_C] \approx 2 \times 10^{14} \text{ cm}^{-3}$ and then re-annealed at 1500 °C, a duration of 3 h was found to be sufficient to reach the 1500 °C equilibrium. The simulation results exhibit a good agreement with both of these experimental observations, predicting an equilibration time of ~ 40 min and ~ 4.5 h at 1500 °C when $[V_C]_{t=0}$ equals $4 \times 10^{12} \text{ cm}^{-3}$ and $2 \times 10^{14} \text{ cm}^{-3}$, respectively. The model shows that $[V_C]_{Eq}$ of $\sim 4 \times 10^{10} \text{ cm}^{-3}$ can be reached after 1400 °C annealing if the duration employed is sufficient. This estimation provides guidance on how to control the $[V_C]$ to enhance the charge carrier lifetime in thick n-type epi-layers for high voltage 4H-SiC bipolar devices.

Summary

A defect kinetics model has been proposed in order to elucidate the physical processes controlling the equilibration of V_C in 4H-SiC epi-layers. The model assumes thermal generation of V_C 's by a bulk (Frenkel pair) process, injection of C_i 's from the surface under C-rich conditions (C-cap) followed by recombination with V_C 's in the bulk, and diffusion of V_C 's towards the surface, as the major processes during the equilibration. The simulated depth profiles of $[V_C]$ exhibit good quantitative agreement with DLTS experimental results, corroborating the validity of the model. In the model, both C_i and V_C are assumed to be mobile and activation energies of ~ 1.5 and 2.5 eV for the migration of C_i and V_C are deduced, respectively, in a good agreement with theoretical values reported in the literature.

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