Journal of Applied Physics ARTICLE scitation.org/journal/jap

On the alloying and strain effects of divacancy energy level in *n*-type $Si_{1-x}Ge_x$

Cite as: J. Appl. Phys. **126**, 235707 (2019); doi: 10.1063/1.5126111
Submitted: 29 August 2019 · Accepted: 4 December 2019 ·
Published Online: 20 December 2019

View Online Export Citation CrossMark

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ABSTRACT

Deep level transient spectroscopy was used to investigate point defects introduced by room temperature He-ion irradiation in both fully strained and partially relaxed phosphorous doped *n*-type $Si_{1-x}Ge_x$ films epitaxially grown on the Si (001) substrate by chemical vapor deposition. Two major point defects are identified as the doubly negative charge state of the divacancy ($V_2^{=/-}$) and the V-P pair (*E*-center). The activation enthalpy (E_H) of $V_2^{=/-}$ was investigated upon strain and alloying effects in order to quantify their individual impact. The deduced variation of activation enthalpy associated with the sole strain effect in strained films is found to decrease linearly as a function of strain (tetragonal mismatch), corresponding to 56 meV/GPa regardless of the degree of strain relaxation for $0 \leq x \leq 0.1$. This result may suggest that while the strain and alloying have an additive effect on the variation of E_H, may however have different physical origins.

I. INTRODUCTION

The vacancy-donor-impurity atom (V-D labeled *E*-center), the vacancy-oxygen (V-O as the *A* centre), and the divacancy (V_2) are the most dominant defects induced in Si crystals by irradiation with high energy particles (electrons, proton, He ions, etc.). The structural and electronic properties of the V-D, V-O, and V_2 defects in Si are well understood.[1–5] The divacancy-related defects have a huge technological impact because they are usually introduced during the industrial fabrication process. The divacancy defect can also be introduced as a secondary defect resulting from the interaction of vacancies during their thermally activated migration. Such defects strongly participate in the diffusion process of doping impurities. Indeed, it has been established that a divacancy may have four charge states in silicon introducing three energy levels in the band gap, namely, $V_2^{0/+}$, corresponding to a donor level in the bandgap at 0.18 eV above the valence band (E_v), as well as $V_2^{=/-}$ and $V_2^{-/0}$, corresponding to two acceptor levels in the bandgap at 0.24 and 0.41 eV, respectively, below the conduction band bottom (E_c).[6] The development of the $Si_{1-x}Ge_x$ technology gave a new drive to the studies of electrically active defects, and V_2 in particular. Further, the $Si_{1-x}Ge_x$ layer allows divacancy-related defect engineering when the bandgap decreases with the increase of either Ge content or strain.[7,8] Previous studies related to the divacancy point defect were focused on either the fully strained[9,10] or fully relaxed[11] $Si_{1-x}Ge_x$ layer. The compositional dependence of the two acceptor levels of the divacancy has previously been studied in epitaxially grown fully relaxed *n*-type $Si_{1-x}Ge_x$ layers.[11] It is shown that for $x \leq 0.25$, both the single ($V_2^{-/0}$) and double negatively ($V_2^{=/-}$) charge state levels move gradually deeper into the bandgap of $Si_{1-x}Ge_x$ with increasing Ge content. Moreover, the activation enthalpy difference of the two levels $V_2^{-/0}$ and $V_2^{-/0}$ seems to remain constant (≈0.2 eV) for the Ge content of up to $x = 0.25$.[11] The effect of strain on the single acceptor level of the divacancy has also been studied in fully strained *n*-type $Si_{0.87}Ge_{0.13}$.[9,10] It has been found that the activation enthalpy of $V_2^{-/0}$ decreases with respect to pure Si. In fact, in the strained $Si_{1-x}Ge_x$ epilayer, both alloying

and strain coexist and much less is known about the effect of strain only on the position of energy levels of divacancies in the strained and partially relaxed $Si_{1-x}Ge_x$ layer. Actually, the bandgap of $Si_{1-x}Ge_x$ decreases with both alloying and strain, the latter being due to the relatively larger size of the Ge atom. It should be stressed that, in our previous work, the focus was on the effect of strain on the energy level of the *E*-center.[12] In this work, we report on the electronic properties of the He-ion bombardment induced double charge state ($V_2^{=/-}$) divacancy defect in the strained *n*-type $Si_{1-x}Ge_x$ ($0 \le x \le 0.10$) epilayer by using DLTS. More precisely, the quantitative variation of the activation enthalpy of $V_2^{=/-}$ in $Si_{1-x}Ge_x$ films upon the sole effect of strain is analyzed in detail.

II. EXPERIMENTAL DETAILS

n-Type (001) oriented $Si_{1-x}Ge_x$ epilayers (x = 0, 0.04, and 0.10) have been grown epitaxially by rapid thermal chemical vapor deposition (RTCVD) on a lightly doped (around 5×10^{16} cm^{-3}) Si buffer layer itself grown on an n^+-Si (001) substrate. The $Si_{1-x}Ge_x$ epilayers were uniformly doped by phosphorous to about 7×10^{16} cm^{-3}. The Ge content was determined by Rutherford backscattering spectrometry (RBS) and was found to be uniformly distributed within the $Si_{1-x}Ge_x$ epilayers. The $Si_{1-x}Ge_x$ epilayers were found to be fully strained for x = 0.04 and partially relaxed for x = 0.10. The average degree of strain relaxation (τ) for x = 0.10 was about 20%, as determined from high-resolution x-ray diffraction (HRXRD).[13] After chemical cleaning, the circular palladium (Pd) Schottky contacts, 0.77 mm in diameter and 2000-Å-thick, were resistively deposited on the $Si_{1-x}Ge_x$ epilayers through a metal contact mask. The fabricated samples were irradiated with 5.4 MeV He ions to a dose of 8.2×10^{11} cm^{-2} at a fluence rate of 7.1×10^6 cm^{-2}s^{-1} using an americium 214 (^{241}Am) source. For control purposes, Pd Schottky contacts were fabricated on substrates, which were chemically cleaned but not exposed to the He ions. Deep level transient spectroscopy (DLTS)[14] was used to study the defects present within the depletion region of the He-ion irradiated $Si_{1-x}Ge_x$ epilayers.

III. RESULTS AND DISCUSSION

Figure 1 depicts the DLTS spectra of He-ion irradiated Pd/*n*-$Si_{1-x}Ge_x$ (x = 0, 0.04, and 0.10) Schottky diodes under the same DLTS biasing conditions. The DLTS spectrum (not shown here) of the control "nonirradiated" sample indicated the absence of any defect in the limit of DLTS detection (defects concentration lower than 1×10^{12} cm^{-3}). After He-ion irradiation, two major peaks are observed in the DLTS spectra for x = 0, 0.04, and 0.10, which have been previously[12] associated with $V_2^{=/-}$ and V-P pair (*E*-center). The activation enthalpy (E_H) and apparent capture cross section (σ_{na}) of both $V_2^{=/-}$ and V-P pair defects were determined from the Arrhenius plot of $\ln(T^2/e)$ vs $1000/T$, where *e* is the emission rate at temperature *T*. The extracted E_H and σ_{na} of levels $V_2^{=/-}$ and V-P pair for our epitaxial silicon are in good agreement with previously reported results for silicon irradiated with high energy particles.[15] In fact, the accurate examination of Fig. 1 shows the existence of three peaks deduced from the multi-Gaussian function fitting of the DLTS curves for the three compositions. The low-temperature peak is indeed attributed to the double charge $V_2^{=/-}$, while the

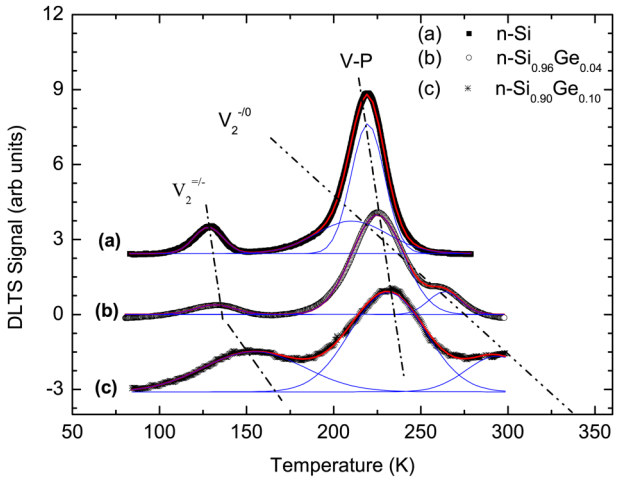

FIG. 1. DLTS spectra for the *n*-Si (a), fully strained *n*-$Si_{0.96}Ge_{0.04}$ (b), and partially relaxed *n*-$Si_{0.90}Ge_{0.10}$ (c) samples irradiated with 5.4 MeV He ions. All spectra were recorded at a lock-in amplifier frequency of 46 Hz, i.e., a decay time constant of 9.23 ms. The solid blue lines correspond to the multi-Gaussian fitting of the DLTS curves, while the red line is the sum (resultant) of the blue lines.

high-temperature peak (with the relatively highest DLTS signal) is deconvoluted into two peaks that are attributed to both V-P pair and single charge state ($V_2^{-/0}$) divacancy. The contribution from $V_2^{-/0}$ with respect to that of the V-P center is minor. This assignment is also supported by the fact that the phosphorous doping concentration in our *n*-Si and *n*-$Si_{1-x}Ge_x$ epilayers is relatively high ($\approx 7 \times 10^{16}$ cm^{-3}). Actually, it is assumed that both defects $V_2^{-/0}$ and $V_2^{=/-}$ have the same weight.[16] This is the case for the two compositions x = 0 and 0.10 (curves a and c). The amplitude of the single charge state of V_2 for x = 0.04 (curve b) is, however, slightly higher as compared to the double charge state of V_2. This might be associated with incomplete carriers filling of the double charge state level. Indeed, this amplitude difference of the two charge states of V_2 was previously explained in terms of local carriers compensation and its influence on the filling of the two levels; the doubly charged divacancy is not filled to the same extent as the single charge state when the material becomes stressed by increasing damage.[17] Moreover, the shift to higher temperature of the position of the so believed $V_2^{-/0}$ as the Ge content increases is coherent with the trend observed in previous work.[11]

In the following, we investigate the effect of both alloying and strain on the activation enthalpy E_H of $V_2^{=/-}$ only. Figure 2 shows the value of E_H for Si, fully strained $Si_{0.96}Ge_{0.04}$ and partially relaxed $Si_{0.90}Ge_{0.10}$ epilayers. The variation of E_H with alloying in fully relaxed $Si_{1-x}Ge_x$ reported by Skardi *et al.*[11] is also displayed in this figure for comparison purposes. In the fully relaxed $Si_{1-x}Ge_x$ ($0 \le x \le 0.15$) epilayer, E_H associated with $V_2^{=/-}$ increases linearly with increasing Ge content.[11] In our fully strained and partially relaxed $Si_{1-x}Ge_x$ epilayers, E_H of $V_2^{=/-}$ decreases when both Ge content and strain increase. In fact, the variation of E_H (ΔE_H) with respect to Si upon Ge content in our strained films includes

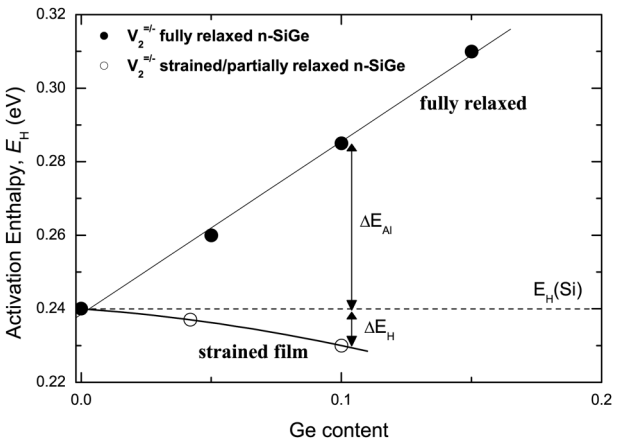

FIG. 2. The effect of composition on the activation enthalpy E_H for the $V_2^{=/-}$ level in strained and partially relaxed $Si_{1-x}Ge_x$ as compared to data for the E_H of the $V_2^{=/-}$ level in fully relaxed $Si_{1-x}Ge_x$.[11] Solid lines are linear and polynomial fits to data for fully relaxed and strained films, respectively. Note that our data for x = 0.04 correspond to fully strained and x = 0.10 to partially relaxed films.

both alloying ΔE_{Al} and strain effects ΔE_S, namely, $\Delta E_H = \Delta E_{Al} + \Delta E_S$ (where $\Delta E_{Al} > 0$ and $\Delta E_S < 0$). Considering the Ge content linear variation of E_H with respect to Si (ΔE_{Al}) in the fully relaxed $Si_{1-x}Ge_x$ epilayer,[11] one can deduce properly ΔE_S. The associated ΔE_S value of $V_2^{=/-}$ is 20 and 50 meV for the fully strained $Si_{0.96}Ge_{0.04}$ and the partially relaxed $Si_{0.90}Ge_{0.10}$ films, respectively. The calculated activation enthalpy ($E_H - \Delta E_{Al}$) associated with strain effect only (i.e., ΔE_S with respect to activation enthalpy of Si) vs HRXRD-deduced tetragonal mismatch is displayed in Fig. 3, showing a linear variation relationship. The decrease rate of strain driven activation enthalpy is found to be about 7.6 eV/unit of

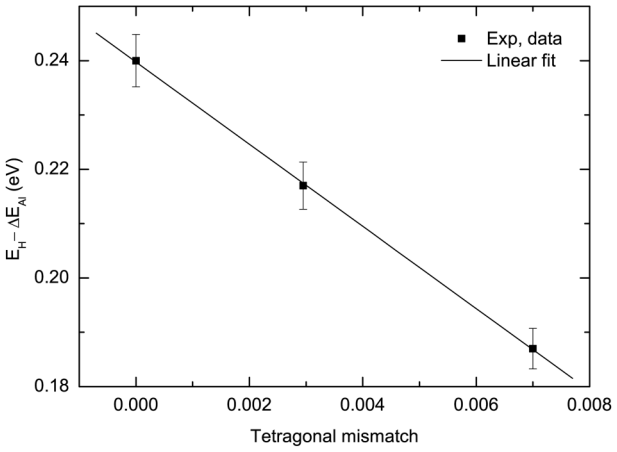

FIG. 3. The activation enthalpy E_H of $V_2^{=/-}$ from which the Ge alloying effect (ΔE_{Al}) has been subtracted ($E_H - \Delta E_{Al}$) vs HRXRD-deduced tetragonal mismatch in the strained $Si_{1-x}Ge_x$ epilayer.

tetragonal mismatch equivalent to 56 meV/GPa. This latter value is independent of the rate of strain (either fully or partially relaxed). This result is consistent with data obtained on the single charge state of the divacancy $V_2^{-/0}$ in the fully strained $Si_{0.87}Ge_{0.13}$ epilayer reported by Monakhov *et al.*[9,10] Indeed, it has been shown that the activation enthalpy of $V_2^{-/0}$ in fully strained $Si_{0.87}Ge_{0.13}$ decreases with respect to that of pure Si. Activation enthalpies of 0.44 and 0.42 eV were obtained for $V_2^{-/0}$ in Si and $Si_{0.87}Ge_{0.13}$, respectively, leading to a relative variation (with respect to Si) of 20 meV. It is evident that this latter variation of E_H for $V_2^{-/0}$ in fully strained $Si_{0.87}Ge_{0.13}$ is due to both alloying and strain effects. The activation enthalpy of $V_2^{-/0}$ in fully relaxed $Si_{0.87}Ge_{0.13}$ was extracted from the plot of Fig. 2 ($E_H \approx 0.47$ eV) in Ref. 11. In order to quantify the sole strain effect on the activation enthalpy of $V_2^{-/0}$, the alloying effect related enthalpy was first subtracted from E_H in fully strained $Si_{0.87}Ge_{0.13}$ giving $\Delta E_S \approx 50$ meV. A value of the strain of about 5.46×10^{-3} has been evaluated for the fully strained $Si_{0.87}Ge_{0.13}$ using Vegard's law. This value of strain is about 0.98 GPa equivalent hydrostatic pressure. The decrease rate of the strain driven activation enthalpy of $V_2^{-/0}$ is found to be about 51 meV/GPa. This result is in fair agreement with our results, confirming that the two charge states $V_2^{/0}$ and $V_2^{=/-}$ behave the same way as a function of the strain only. It is worth noting that, as the decrease rate (56 meV/GPa) of E_H of the $V_2^{=/-}$ level is independent of the degree of strain, we argue that the effect of strain and alloying on the activation enthalpy in the strained $Si_{1-x}Ge_x$ epilayer may have different physical origins.

IV. CONCLUSION

In this work, we have investigated the individual effect of alloying and strain on the activation enthalpy E_H of the double charge state of the divacancy $V_2^{=/-}$ in the strained $Si_{1-x}Ge_x$ epilayer. The compressive strain in the $Si_{1-x}Ge_x$ epilayer reduces considerably E_H of the acceptor level of the double charge state of divacancy ($V_2^{=/-}$). This strain effect on E_H is also found to be independent and opposite to the alloying effect in the strained $Si_{1-x}Ge_x$ epilayer. More precisely, the rate of the decrease of E_H due to the sole strain effect is about 56 meV/GPa regardless of the degree of strain relaxation in the strained $Si_{1-x}Ge_x$ epilayer for $x \leq 0.10$. This result may help engineering defects in $Si_{1-x}Ge_x$ films.

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