I. INTRODUCTION

Compressively strained Ge (s-Ge) grown on a relaxed Si_{1-x}Ge_x virtual substrate (VS) is attracting much attention as a promising candidate for a next generation higher mobility p-type MOSFET.\(^1\)\(^-\)\(^3\) Knowledge of self-diffusion in compressively strained Ge, which is required to understand the kinetics of the dopant diffusion and activation, is essential for the development of the s-Ge based MOS technology. In addition, the investigation of self-diffusion is important, not only to design appropriate device processing schemes, but also from the physics point of view. Self-diffusion is the most fundamental process of atomic transport in a solid. A study of self-diffusion can provide valuable information on the properties of native point defects, which are responsible for the diffusion processes. In particular, Ge self-diffusion in Ge takes place by a simple vacancy-mediated mechanism. The s-Ge matrix is, therefore, an ideal system to study and to understand the effect of strain on self-diffusion in a solid.

Recently, Si and Ge self-diffusion in relaxed Si_{1-x}Ge_x has been widely investigated by probing the concentration profiles of stable or radio isotopes as tracers in relaxed Si_{1-x}Ge_x epitaxial layers (0 ≤ x ≤ 1).\(^4\)\(^-\)\(^8\) In this case, a decrease in the activation enthalpy with increasing Ge content, x, has been observed. The influence of compressive strain on the Si/Ge interdiffusion has been described in the literature by Cowern et al.\(^9\) In their case, enhanced Ge diffusion has been observed. On the contrary, the number of self-diffusion studies in strained materials is extremely limited. Zangenberg et al. have reported retardation (enhancement) of Ge self-diffusion in Si_{0.9}Ge_{0.1} under the tensile (compressive) strain of 0.21%.\(^4\) However, a theoretical description of the observed phenomena was not achieved because of the complication induced by the existence of two constituents, Si and Ge, and due to multi-diffusion mechanisms involving interstitials and vacancies. Aziz et al.\(^10\)\(^-\)\(^12\) have theoretically predicted the thermodynamic effects of hydrostatic pressure and biaxial strain on dopant- and self-diffusion mediated by the simple vacancy and interstitial mechanism in a crystalline solid based on a generalized activation volume model. They demonstrated the consistency of the prediction for antimony (Sb) diffusion in hydrostatically compressed Si and in biaxially strained Si (tensile) and SiGe (compressive). For self-diffusion, however, the theoretical finding has never been experimentally tested.

Here we report on an experimental study of self-diffusion in Ge under biaxial compressive strain. The experimental observation is quantitatively described in terms of the behavior of the vacancies in Ge by means of the activation volume with relevant previous experimental diffusion results.

II. EXPERIMENTAL

Figure 1 shows the schematic illustration of a heterostructure employed in this work. A 50-nm-thick natSi_{0.2}natGe_{0.8} buffer layer was grown by solid-source molecular beam epitaxy (MBE) on a natSi_{0.2}natGe_{0.8} VS grown by chemical vapor deposition.\(^13\) The MBE growth of the Ge isotope superlattice (SL) consisting of alternating layers of isotopically enriched 70Ge (70Ge: 96.3%, 72Ge: 2.1%, 73Ge: 0.1%, 75Ge: 1.2%, and 76Ge: 0.3%) and natGe (70Ge: 20.5%, 72Ge: 27.4%, 73Ge: 7.8%, 74Ge: 36.5%, and 76Ge: 7.8%) was performed on the natSi_{0.2}natGe_{0.8} buffer layer using the procedure described in Ref. 14. The thickness of each isotope layer was 8 nm. Finally, a 50-nm-thick relaxed natSi_{0.2}natGe_{0.8} cap layer was MBE-grown on the top as a stressor. Two natGe (10 nm) barrier layers sandwiching the Ge isotope SL were inserted to avoid interdiffused Si reaching the Ge isotope SL during diffusion annealing. The total thickness of the strained Ge layer was 60 nm including the Ge isotope SL and barrier layers. The sample was cut into a number of smaller pieces and they were annealed at various diffusion temperatures between 475 and 600°C for 0.5–61 h in a.
The compressive strains in s-Ge after the diffusion annealing are 0.71% for 1 h, 0.68% for 3 h, and 0.66% for 6 h, respectively. The compressive strain in s-Ge before annealing is 0.71%. These results confirm that the heterostructures remained pseudomorphic to the underlying VS throughout the diffusion annealing. The cross-sectional transmission electron microscopy with a JEM-2100 F operating at 200 kV allows us to assume that the simple vacancy mechanism is also responsible for Ge self-diffusion in Ge with a threading dislocation density of $10^6$ cm$^{-2}$. The latter set of values agrees with the simple Ge isotope SL grown on a (001)-oriented Ge substrate employed in our previous studies. The enhancement of the Ge self-diffusivity by a factor of $\sim 3.5$ due to the compressive biaxial strain of $\sim 0.71\%$ is experimentally established in the temperature range of 475 to 600 °C. Annealing at higher temperatures introduces the relaxation of s-Ge and at lower temperatures does not induce a large enough change in the $^{74}$Ge concentration profile for SIMS evaluation.

We now turn our attention to the origin of the enhancement by a factor of $\sim 3.5$. It is well-established that Ge self-diffusion in unstrained Ge is mediated by the simple vacancy mechanism. The similarity between the activation enthalpy of s-Ge and that of unstrained Ge, as shown in Fig. 4, allows us to assume that the simple vacancy mechanism is also responsible for Ge self-diffusion in Ge with a compressive strain resulting from the heterostructures.
Since the first term on the right-hand side of Eq. (3) represents a small correction well within a few percent of $V^{SD}$, the observed increase in $D^{SD}$ with $p$ is attributable to the activation volume term.$^{20,24,25}$ Therefore, $V^{SD}$ can be described by

$$V^{SD} = -k_BT \frac{\partial \ln D^{SD}}{\partial p}, \quad (4)$$

and becomes positive (negative) when $D^{SD}$ decreases (increases) with $p$. For the case of the vacancy mechanism, $V^{SD}$ is the sum of two components, $V^{SD} = V^F + V^M$, where the formation volume, $V^F$ is the volume change of the system upon formation of a vacancy in its standard state, and the migration volume, $V^M$ is the additional volume change when the vacancy reaches the saddle point in its migration path.$^{10–12}$ For a (001) thin-film geometry, the predominant source of vacancies is the free surface.$^{10–12}$ When a vacancy is created in crystalline Ge, one Ge atom leaves a lattice site and migrates to the surface. The resulting increase of the crystal volume corresponding to one Ge atomic volume ($\Omega_{Ge}$) is $2.26 \times 10^{-26}$ m$^3$/atom.$^{26}$ However, $V^F$ depends on the degree to which the atoms surrounding the vacancy relax toward the vacancy center. Thus, $V^{SD}$ is decreased by the relaxation volume ($V^R$) which takes a negative value. In addition, $V^M$ is also negative due to the fact that the diffusing atom via a vacancy is expanding a constriction at the saddle point in its migration path.$^{20}$ Then, the activation volume of the Ge self-diffusion under hydrostatic pressure is described as

$$V^{SD} = \Omega_{Ge} + V^R + V^M, \quad (5)$$

and is smaller than $+\Omega_{Ge}$. Ažić et al.$^{10–12}$ further generalized the activation volume for a non-hydrostatic stress state by defining an activation strain tensor. The formation strain tensor ($V^F$) is described as

$$V^F = \Omega_{Ge} \begin{bmatrix} 0 & 1 \\ 0 & 3 \end{bmatrix}, \quad (6)$$

The first term on the right-hand side of Eq. (6) shows the volume change corresponding to $\Omega_{Ge}$ at the free surface when a vacancy is created inside the crystal. The second term indicates that the relaxation volume propagates out elastically to surfaces and provides equal contributions in all directions.$^{11}$ In addition, the migration strain tensor ($V^M$) is defined as

$$V^M = \begin{bmatrix} V^M_{\perp} & V^M_{\perp} \\ V^M_{\perp} & V^M_{\perp} \end{bmatrix}, \quad (7)$$

where $V^M_{\perp}$ and $V^M_{\parallel}$ are the volume changes perpendicular and parallel to the direction of the net transport at the saddle point in its migration path. Under hydrostatic stress, the activation volume is the scalar activation volume conventionally defined in Eq. (5), which is the sum of the trace of Eq. (6), $\Omega_{Ge} + V^R$, and that of Eq. (7), $V^M$. In the presence of biaxial stress ($\sigma_{biax}$), the work needed to create a lattice site at the surface is zero because there is no normal force at the surface. Furthermore, the part of $V^R$ that propagates on the free surface and interacts with the zero normal stress does not contribute to the work performed against the stress field. Therefore, the contribution of the activation volume to self-
diffusion under biaxial stress via the vacancy mechanism, $V_{SD}$, can be described as

$$V_{SD} = \frac{2}{3} \omega R + \omega M - \omega ||$$,  \hspace{1cm} (8)

which is dominated by the relaxation and migration volume terms. Therefore, $V_{SD}$ is negative. According to the strain tensor model and activation volume described in Eq. (4), the contribution of the activation volume to self-diffusion under biaxial stress can be described as

$$V_{SD} = -kT \frac{\partial \ln D_{SD}}{\partial \sigma_{hiax}} \bigg| _T.$$  \hspace{1cm} (9)

Based on Eq. (9) and the Ge self-diffusivities obtained experimentally ($D_{SD}$) in this work, we find, $V_{SD} = (-0.65 \pm 0.21)\omega_{Ge}$. $V_{SD} \approx -\omega_{Ge}$ implies that upon the formation and migration of a vacancy, there exists a strong inward constriction of the lattice. The increase of Ge self-diffusivities in s-Ge results from the decrease of the activation enthalpy by the negative work performed against the stress field, $\sigma_{hiax}$. The compressive biaxial strain of 0.71% is expected to produce a small change of $-0.09 \pm 0.03$ eV in the activation enthalpy. From the fittings by the Arrhenius expression, the difference between the activation enthalpy of self-diffusion in compressively strained Ge, 3.07 eV (this work), and in unstrained Ge, 3.13 eV (Ref. 19), can be found to be $-0.06$ eV ($= 3.07 - 3.13$ eV). This value is within the accuracy of the value of $-0.09 \pm 0.03$ eV deduced from the generalized activation volume model. Furthermore, from the comparison between the biaxial and hydrostatic stress states [Eqs. (5) and (8)], the following relationship can be given:

$$V_{SD} - \frac{2}{3} V_{hiax} = \omega_{Ge} + \left(\omega_M - \omega || \right).$$  \hspace{1cm} (10)

If the anisotropy in $\omega$ is negligibly small, the right-hand side of Eq. (10) should become $+\omega_{Ge}$. Aziz et al.\textsuperscript{10-12} have described the contribution of the activation volume under biaxial stress, $V_{biax}$, to the diffusion as $-(\dot{Q}/Y)$, where the biaxial modulus, $Y$, is the ratio of Young’s modulus to one minus the Poisson ratio. For the Sb diffusion,\textsuperscript{11,12} they have demonstrated the consistency of the predicted relationship by the values of $\dot{Q}$ by Kringhøj et al.\textsuperscript{22} and an activation volume $V = +0.066\omega$ determined for hydrostatically compressed Si in their work. The results are $V + (3/2)(\dot{Q}/Y) = +1.20 \pm 0.33\omega$ for tensile Si and $V + (3/2)(\dot{Q}/Y) = +0.93 \pm 0.20\omega$ for the compressively strained Si$_{0.91}$Ge$_{0.09}$ alloy, which agrees with the prediction of $+1\omega$ ($\dot{Y} = 180.5$ GPa for these cases). Werner et al.\textsuperscript{20} reported positive values of the activation volume ($V_{SD}$) for Ge self-diffusion in Ge under hydrostatic pressure in the temperature range of 603 to 813°C. Inserting the $V_{hiax}$ deduced in this study and $V_{SD} = +0.24\omega_{Ge}$ at 603°C reported in Ref. 20 into Eq. (10), we find $V_{SD} - \frac{3}{2} V_{hiax} = (+1.22 \pm 0.21)\omega_{Ge}$, which is fully consistent with the $+1\omega_{Ge}$ prediction.

IV. CONCLUSIONS

In conclusion, we have designed and conducted an experiment to reliably obtain the Ge self-diffusivity in biaxially compressed Ge. The compressive strain enhances Ge self-diffusion. The degree of the enhancement is described quantitatively by the theoretical prediction of a generalized activation volume model of a simple vacancy mediated diffusion.\textsuperscript{10-12}

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