Ge Self-Diffusion in Compressively Strained Ge Grown on Relaxed Si$_{0.2}$Ge$_{0.8}$

Yoko Kawamura$^1$, Masashi Uematsu$^1$, Kohei M. Itoh$^1$, Yusuke Hoshi$^2$, Kentaro Sawano$^2$, Yasuhiro Shiraki$^3$, Eugene E. Haller$^3$, and Maksym Myronov$^4$

$^1$Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan
$^2$Tokyo City University, 8-15-1 Todoroki, Setagaya-ku, Tokyo 158-0082, Japan
$^3$University of California at Berkeley, 1 Cyclotron Road, Berkeley, California 94720, USA
$^4$The University of Warwick, Coventry CV4 7AL, United Kingdom

1. Introduction

Recently, there has been an increased interest in the use of compressively strained germanium (s-Ge) in channel regions of p-type metal-oxide-semiconductor (MOS) field-effect transistors because of their ability to enhance hole mobility. Compressively s-Ge is fabricated on relaxed silicon germanium (SiGe), which has a smaller lattice constant than that of Ge, and strain is controlled by varying the Ge content in the relaxed SiGe. A thorough understanding of Ge self-diffusion in s-Ge leads to clarify the properties of point defects and their associated dopant diffusion mechanisms, which is crucial for the technical innovation of s-Ge channel MOS devices. In recent years, there have been several interesting reports on Si and Ge self-diffusion in s-Ge. It is difficult to observe and quantitatively evaluate diffusion in s-Ge because the strain is easily relaxed during annealing. In order to maintain the strain, s-Ge needs to be a thin layer, where dislocation density is low. In this work, we successfully fabricated relaxed Si$_{0.2}$Ge$_{0.8}$/compressively s-Ge isotope superlattice (SL)/relaxed Si$_{0.2}$Ge$_{0.8}$ heterostructures. Furthermore, we present the first measurements of Ge self-diffusion in compressively s-Ge.

2. Experiment

Figure 1 shows the schematic illustration of relaxed Si$_{0.2}$Ge$_{0.8}$(50nm)/s-Ge isotope SL(60nm)/relaxed Si$_{0.2}$Ge$_{0.8}$(50nm) heterostructures fabricated in this study. In order to smooth the sample surface and avoid contaminating the s-Ge layer, a 50-nm-thick Si$_{0.2}$Ge$_{0.8}$ buffer layer was grown by molecular beam epitaxy on Si$_{0.2}$Ge$_{0.8}$ virtual substrates, which in turn was grown by chemical vapor deposition. The GeSL, composed of alternating layers of isotopically enriched $^{70}$Ge and natural Ge ($^{64}$Ge), was grown on the buffer layer. Finally, a 50-nm-thick relaxed Si$_{0.2}$Ge$_{0.8}$ cap layer was grown on the top as a stressor. The GeSL was sandwiched by two $^{64}$Ge (10nm) layers which act as barrier layers for Si interdiffusion into GeSL (40nm). These samples were annealed at temperatures between 475 and 600 °C for 0.5 – 61 h in a resistively heated furnace under a flow of 99.999 % pure Ar. The strains in the s-Ge were measured by X-ray diffraction (XRD). The depth profiles of $^{74}$Ge in the heterostructures were measured by secondary ion mass spectroscopy (SIMS). Ge self-diffusivities in s-Ge were determined by using a partial differential equation solver ZOMBIE. By using cross-sectional transmission electron microscopy, we saw that the effects of strain relaxation due to the creation of dislocations are negligible.

3. Result and discussion

Figure 2 shows the intensity peaks of asymmetrical (224) reciprocal space mapping (RSM) before and after annealing at 550 °C for 6 h, where the Q$_s$ corresponds to horizontal lattice constant. The Q$_s$ of s-Ge agreed well with that of relaxed Si$_{0.2}$Ge$_{0.8}$, both before and after annealing. The strains in s-Ge calculated from these peak values were $-0.71\%$, which corresponds to an in-plane stress of $-0.96$ GPa, in the sample before annealing with the minus sign for compressive strain, and $-0.66\%$ after annealing. We obtained similar results of $-0.71\%$ after annealing at 550 °C for 1 h and $-0.66\%$ for 3 h, respectively. These results show that the compressive biaxial strain of approximately $-0.7\%$ was maintained during the annealing process. Figure 3 shows the depth profiles of $^{74}$Ge in the heterostructures measured by SIMS before and after annealing at 550 °C for 1 – 6 h and the simulation results. The SIMS depth profiles were fitted using a single value of Ge self-diffusivity for each temperature. We obtained a Ge self-diffusivity value of $6.40\times10^{-18}$ cm$^2$/s at 550 °C under compressive strain of approximately $-0.7\%$. Figure 4 compares the temperature dependencies of Ge self-diffusivities in the strained and relaxed Ge obtained in this work, and the diffusivities in relaxed Ge previously reported in [4]. The values for relaxed Ge show an agreement with the previously reported values. However, we found that the Ge self-diffusivities in s-Ge were about 3.5 times larger than those in relaxed Ge at a diffusion
temperature within the range of 475 – 600 °C. The activation enthalpies of Ge self-diffusion were estimated to be 3.07 eV in s-Ge and 3.11 eV in relaxed Ge. It is known that Ge diffuses by a vacancy in relaxed Ge [4]. The closeness of the values indicates that Ge self-diffusion in compressively s-Ge also proceeds by the vacancy mechanism. Furthermore, we discuss the increase of the diffusivities in s-Ge in terms of the activation volume ($V^{sd}$) of self-diffusion.

$$V^{sd} = -kT \left( \frac{\partial \ln D}{\partial p} \right)_{T},$$

(1)

where $k$ is Boltzmann constant, $T$ is absolute temperature and $D$ is self-diffusivity at constant temperature [4,5]. $V^{sd}$ can be either positive or negative, depending upon whether $D$ decreases or increases with $p$, respectively. The activation volume characterizes the effect of pressure on self-diffusivity and is an important property of the defects responsible for the diffusion. The activation enthalpy of self-diffusion under pressure changes by the work $pV^{sd}$ of the system. In the case of the vacancy mechanism, $V^{sd}$ is the volume change of the system upon the formation ($V^f$) and migration ($V^m$) of a vacancy, according to $V^{sd} = V^f + V^m$.

(2)

When a vacancy is created in crystalline Ge, one Ge atom leaves a lattice site and migrates to the surface. The volume of the crystal increases by one Ge atomic volume ($\Omega_{vac}$) at standard $T$ and $p$ at the surface. $V^f$, however, depends on the degree to which the atoms surrounding the vacancy relax into it. Specifically, $V^f$ is decreased by the relaxation

In conclusion, by means of Si$_2$Ge$_{0.8}$/GeSL/Si$_2$Ge$_{0.8}$ heterostructures, the first measurements of Ge self-diffusion under compressive biaxial strain were performed. We found that Ge self-diffusivities in compressively s-Ge are larger compared to those in relaxed Ge. Moreover, we obtained $V_{vac}^{sd} = -0.66 \pm 0.06 \Omega_{vac}$. This result is consistent with previous work stating that relaxation in Ge is strong [4].

4. Conclusion

Fig. 4 Temperature dependences of Ge self-diffusivities

$V^f$ which is negative and, as a result, less than $\Omega_{vac}$. Therefore, $V^{sd}$ is given by

$$V^{sd} = \Omega_{vac} + V^f + V^m$$

(3)

Here, $V^m$ 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 [4]. Moreover, Aziz et al. [5] have reported that, if we have biaxial stress ($\sigma_{22} = \sigma_{11}$), $V^f$ is dominated by the relaxation and migration terms because there is no force on the surface and the work to create a lattice site at the surface should be zero. According to these models, the activation volume ($V^{sd}_{act}$) of Ge self-diffusion under compressive biaxial stress should be negative. In this work, the decrease of the activation enthalpy of Ge self-diffusion in s-Ge compared to that of relaxed Ge by the magnitude of the work $|\sigma_{22}V^{sd}_{act}|$ results in the increase of self-diffusivities, which allows us to obtain $V_{vac}^{sd} = -0.66 \pm 0.06 \Omega_{vac}$. This result is consistent with previous work stating that relaxation in Ge is strong [4].

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