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Impacts of doping on epitaxial germanium thin film quality and Si-Ge interdiffusion

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Abstract: Ge-on-Si structures with three different dopants (P, As and B) and those without intentional doping were grown, annealed and characterized by several different material characterization methods. All samples have a smooth surface (roughness < 1.5 nm), and the Ge films are almost entirely relaxed. B doped Ge films have threading dislocations above $1 \times 10^8$ cm$^{-2}$, while P and As doping can reduce the threading dislocation density to be less than $10^6$ cm$^{-2}$ without annealing. The interdiffusion of Si and Ge of different films have been investigated experimentally and theoretically. A quantitative model of Si-Ge interdiffusion under extrinsic conditions across the full $x_{Ge}$ range was established including the dislocation-mediated diffusion. The Kirkendall effect has been observed. The results are of technical significance for the structure, doping, and process design of Ge-on-Si based devices, especially for photonic applications.

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1. Introduction

Germanium (Ge), as the most silicon (Si) compatible semiconductor, are playing an increasingly important role in large-scale dense Si photonic integration, such as in light sensing and modulation [1, 2]. In the past few decades, researchers all over the world have invested extensive efforts in finding solutions to a Si-compatible lasing material system [3–9]. Among all of the candidates, III-V quantum dot (QD) lasers grown on Ge-on-Si substrates and Ge-on-Si lasers [10–12] have been demonstrated to be among the most promising on-chip light sources [13]. Besides laser applications, there are other Ge-on-Si structure-based devices, such as SiGe modulators, Ge photodiodes and GaAs-based devices on Ge/Si substrates, where different types of dopants can be involved.

It is important to consider the Ge film functions and quality requirements for different optoelectronic devices with Ge-on-Si structures. This lattice mismatch between Ge and Si causes two serious issues: high surface roughness resulting from the Stranski–Krastanov growth, and a high density of threading dislocations (TDs) in Ge epitaxial layers. Both severely affect the performance of Ge photodiodes and lasers due to more recombination centers introduced [1].

It is also very critical to minimize Si-Ge interdiffusion in Ge-on-Si based optoelectronic devices as interdiffusion changes Ge profiles and all properties related to Ge concentration such as the bandgap, effective mass, carrier mobility, carrier lifetime etc. According to the Ge laser simulations work of Li et al. [14] and Ke et al. [15], Si-Ge interdiffusion is one of the key reasons for the low efficiency and high threshold current density. The thickness of the Ge layer is on the order of 102 nm [12], which is thin enough to be susceptible to Si-Ge interdiffusion.

So far, there has been very limited studies on the doping impact on Ge-on-Si film quality. Lee et al. studied the impact of high concentration arsenic (As) on Ge epitaxial film grown on Si (001) with 6° off-cut. He concluded that the TDs density had been reduced by at least one order of magnitude to < 5 × 10^6 /cm^2 and attributed that to the enhancement in the velocity of the dislocation motion in an As-doped Ge film [16].

There have been a handful of studies on Si-Ge interdiffusion with/without doping. Xia et al. studied a few impacting factors of interdiffusion including temperature, tensile strain, compressive strain, Ge concentration, and oxidation [17–19]. Dong et al. [20] established a benchmarking model for Si-Ge interdiffusivity over the full Ge fraction range, which agrees with the vast majority of the experimental data in the area. Takeuchi and Ranade et al [21, 22], studied the Ge-Si interdiffusion in a polycrystalline Ge/Si structure under As doping. They reported that the interdiffusion was enhanced by about five times when the As doping level was 1 × 10^{21} cm^{-3}. Gavelle et al. [23] reported that interdiffusion is retarded when the Ge layer is doped with boron (B). On the other hand, Ranade et al. [21] reported that Si-Ge interdiffusion had been enhanced with boron. Cai et al. recently showed that high phosphorus (P) doping greatly accelerates Si-Ge interdiffusion due to the Fermi-level effect [24, 25], and successfully established a quantitative model. However, only one dopant (P) was involved and the Ge fraction was limited to 0.75 < x_{Ge} < 1. More data were needed for the full Ge range. Especially, interdiffusion with other dopants had not been well studied systematically, which was addressed in this work.

Ge-on-Si layers form Ge/Si interdiffusion couples. Another task that motivated this study was to observe the Kirkendall effect, which is the basis of the interdiffusivity extraction
method from interdiffused profiles. Historically, to observe the Kirkendall effect, inert marker layers were used. However, Ge/Si systems for device applications studied here are in nanometer scale and with high quality. The addition of marker layers should not degrade the Ge quality requirements or device performance, which is hard to achieve. Also, the amount of interdiffusion studied has not been significant to show that effect. Therefore, although interdiffusion can be easily measured, the Kirkendall effect had not been observed previously before this work.

2. Impacts of doping on Ge film quality

2.1. Structure design, growth and defect annealing

12 Ge-on-Si samples with 5 doping configurations (Fig. 1) and 3 annealing conditions (no annealing, 5 thermal cycles, and merged annealing) were designed. Sample U, A, P, B stand for undoped Ge/Si, As doped Ge/Si, P doped Ge/Si, and B doped Ge/Si respectively. Furthermore, we designed two different B concentrations to study B doping level and the Fermi level effect for B doped Ge/Si. One is with higher boron concentration (HB), and the other one is with a lower concentration (LB). The B concentration in Sample LB is lower than the intrinsic carrier density of Ge ($n_{i,Ge}$) except for the Ge/Si interface as seen in Fig. 6(b) in Section 3.1. Dopants concentration in Sample P, A and HB are higher than $n_{i,Ge}$. P and As doping levels were chosen as the highest concentration achievable in the epitaxial growth tool.

![Fig. 1. Schematic diagrams of the structures in this work. X stands for As/HB/LB/P or undoped.](image)

All samples were grown on 8-inches (100) Czochralski (CZ) Si wafers in a metal-organic chemical vapor deposition (MOCVD) tool, and the model isCrius CCS from Aixtron. The undoped, P and As doped wafers are 6° off-cut towards the [110] direction. As B-doped Ge is too rough for the subsequent materials growth, we used the on-axis Si wafers for the Ge growth except for the sample LB-5TC as a control sample. The wafer orientation information is listed in Table 1. Before a Si layer was deposited, the Si substrate was treated at 1050 ± 10 °C for 10 minutes under H₂ ambient at 400 mbar. Then, a 600 nm Si layer was deposited at 950 ± 10 °C under H₂ ambient at 100 mbar. To improve the Ge film quality and reduce the threading dislocations caused by the Ge-Si lattice difference, a 100 nm Ge seeding layer was deposited at 400 ± 10 °C under H₂ ambient at 100 mbar (low-temperature Ge growth) on top of the Si layer. Finally, a Ge film about 600 nm was deposited at 650 ± 10 °C under H₂ ambient at 100 mbar (high-temperature Ge growth). We denote these layers as “the top Ge layers” in the discussion below to differentiate from the Ge seeding layers. All the dopants quoted were in situ doped.

Immediately after the growth procedure, half of the samples were annealed inside the growth tool while another half were left unannealed (NA) for comparison. Post-deposition thermal cycling was performed by repeating a H₂ annealing cycle between low temperature (LT) and high temperature (HT) ranging from 600 °C to 850 °C for 5 times (5TC). Each
annealing step at HT was 10 minutes, at LT was 5 minutes to improve the quality of the Ge epitaxial film. The ramping up and down rates were around 1°C/s. Besides, for Sample LB and Sample A, we performed the merged high temperature (MHT), namely, with 850°C for 50 minutes anneal with no LT steps to check the difference between HT/LT thermal cycling and merged HT annealing. The temperatures quoted above were the nominal setting temperatures of the MOCVD reactor. After we obtained the Secondary Ion Mass Spectrometry (SIMS) data and compared with well-established interdiffusion model by Dong et al. [20], we found that 890 °C is the best fitting temperature using Dong et al.’s model for Sample U/P/LB/HB. Thus, we consider that as a calibrated experimental annealing temperature. For the sample A, since the surface temperature measured was about 20 °C lower than others, we consider the calibrated annealing temperature was 870 °C for Sample A.

2.2 Roughness characterization

Atomic Force Microscope (AFM) measurements were performed to obtain the surface roughness. The scanning area size was 1 μm × 1 μm. Several areas of each sample were measured. The roughness of the samples are around 0.3 - 1.5 nm (Table 1), which depends on the area selected and calculation methods. Different dopant configurations or annealing procedures have no significant effect on the surface roughness. The smooth surface is suitable for the transition layer application between GaAs and Si.

Table 1. Wafer offcut information and the average and root mean square (RMS) surface roughness of the samples.

| Wafer offcut | Average roughness (nm) | RMS roughness (nm) |
|--------------|------------------------|--------------------|
| U-NA 6°      | 0.65 ± 0.15            | 0.91 ± 0.26        |
| U-5TC 6°     | 0.59 ± 0.20            | 0.80 ± 0.29        |
| P-NA 6°      | 0.42 ± 0.08            | 0.57 ± 0.14        |
| P-5TC 6°     | 1.05 ± 0.35            | 1.49 ± 0.48        |
| A-NA 6°      | 0.34 ± 0.05            | 0.32 ± 0.03        |
| A-5TC 6°     | 0.28 ± 0.01            | 0.35 ± 0.01        |
| A-MHT 6°     | 0.82 ± 0.29            | 1.43 ± 0.69        |
| LB-NA 0°     | 0.27 ± 0.04            | 0.34 ± 0.05        |
| LB-5TC 6°    | 0.28 ± 0.03            | 0.36 ± 0.03        |
| LB-MHT 0°    | 0.31 ± 0.03            | 0.39 ± 0.04        |
| HB-NA 0°     | 0.52 ± 0.17            | 0.78 ± 0.35        |
| HB-5TC 0°    | 0.66 ± 0.25            | 0.97 ± 0.45        |

2.3 X-ray diffraction

High resolution X-ray diffraction (HRXRD) measurements were performed to measure the Ge strain levels using a PANalytical X’Pert PRO MRD with a triple axis configuration. Strain values of the Ge layers are extracted by fitting with the PANalytical Epitaxy software package.

The (0 0 4) Ω–20 scan results are shown in Fig. 2. The positions of the Ge peaks of all samples are under biaxial tensile strain in comparison with fully relaxed Ge peaks. For the unannealed samples, the associated degrees of relaxation R calculated by combining Eq. (3) and (4) from Ref [26], are within the range 103.9% - 105%. This means that the Ge layers are in a slightly tensile strained configuration (~0.16%), which is in agreement with literature results [26–28]. The tensile strain is thermally induced to the Ge epilayer during cooling from high-temperature growth or thermal annealing steps to room temperature. In the temperature
range of 20 °C to 650 °C, Ge has a coefficient of thermal expansion (CTE) of 5.8 – 8.1 ppm/°C larger than that Si, which is 2.6 – 4.1 ppm/°C [29].

Compared with the samples before annealing, the Ge peaks of those after annealing are much more asymmetric broadening towards the high incidence angle side. This is due to SiGe interdiffusion, which formed SiGe alloy regions with a graded Ge concentration, consistent with SIMS results discussed in Section 3. Sample P-5TC and A-5TC have larger interdiffusion than other samples, making their Ge peaks more broadened. The interdiffusion also shifts the “Ge” peaks towards the Si side, as the “Ge” bulk layers are no longer uniform Ge layers with 100% Ge. For example, according to the SIMS data, at the surface of P-5TC, $x_{Ge} = 0.98$, and $x_{Ge}$ decreases with the depth. From the XRD “Ge” peak, the relaxation of this layer can be calculated as 105.9% considering it as Ge$_{0.98}$Si$_{0.02}$. Considering the fact that $x_{Ge}$ decreases with the depth, the relaxation of all other regions is even less than 105.9%. Thus, we can conclude that for P-5TC, the Ge layer became a SiGe alloy region, which is still almost entirely relaxed. The same argument can be applied to A-5TC. The bottom line is that in the annealed samples, the top layer is a Ge rich layer with similar slight tensile strain, which is not going to influence the interdiffusion significantly [17].

2.4 Dislocation characterization

Conventionally, three methods are used to determine the threading dislocation density (TDD) in semiconductor materials: plan-view transmission electron microscopy (PVTEM), cross-section transmission electron microscopy (XTEM) and etch-pit-density (EPD) observation. EPD observation is suitable when TDD is less than $10^7$ cm$^{-2}$, and PVTEM observation is suitable when the TDD is higher than $10^8$ cm$^{-2}$ [30, 31]. Both experiments have been applied to characterize TDD in different samples. Besides, XTEM has been conducted to observe the defects at the Ge/Si interfaces in 2 typical samples.

2.4.1. EPD

Firstly, EPD measurements were performed to obtain the TDD of samples. Each sample was etched with iodine (I$_2$) solution. The I$_2$ solution is a mixture of CH$_3$COOH (100ml), HNO$_3$ (40ml), HF (10ml), I$_2$ (30mg) [32, 33]. Optical microscope and scanning electron microscope (SEM) imaging were used to observe and count the etch pits. The etch rate is approximately 40-80 nm/s depending on the dopants and doping level. After etching roughly half of the top Ge layer (about 300 nm), 4 to 6 different positions on the surface were imaged for TDD determination. Fig. 3(a) and (b) show the EPD results of Sample U-NA and LB-5TC respectively.
Table 2. TDD value of the 12 samples measured by EPD.

| Sample | TDD value (cm$^{-2}$) | Sample | TDD value (cm$^{-2}$) |
|--------|-----------------------|--------|-----------------------|
| U-NA   | $9.5 \pm 3 \times 10^5$ | A-MHT  | $1.2 \pm 0.5 \times 10^5$ |
| U-5TC  | $< 1 \times 10^5$      | LB-NA  | $> 2 \times 10^4$      |
| P-NA   | $3 \pm 1 \times 10^5$  | LB-5TC | $1.2 \pm 0.5 \times 10^8$ |
| P-5TC  | $1.75 \pm 1 \times 10^5$ | LB-MHT | $1.1 \pm 0.5 \times 10^8$ |
| A-NA   | $5 \pm 3 \times 10^5$  | HB-NA  | $> 2 \times 10^6$      |
| A-5TC  | $1.2 \pm 0.5 \times 10^5$ | HB-5TC | $> 2 \times 10^6$      |

Table 2 lists TDD values in the Ge films of the 12 samples measured by EPD. We can see that the B doped samples have the highest values ($> 10^8$ cm$^{-2}$). A Ge layer with such dense dislocations is not suitable as a transition layer between GaAs and Si, as the subsequent GaAs growth will be affected. The merged annealing and the 6 degree offcut don't have any impact on the TDD value compared with the corresponding 5TC annealing as seen in LB-5TC (6° offcut) and LB-MHT (0° offcut).

For As and P doped samples without annealing, TDDs in sample A-NA and P-NA are in the $10^5$ to $10^6$ cm$^{-2}$ range, one order of magnitude lower than that in U-NA. This TDD level is already low enough for electronic or photonic applications, and there is no need to have an extra defect annealing step for A-NA and P-NA.

On the other hand, TDDs in A-5TC and P-5TC are higher than that in U-5TC. This can be interpreted by the following pictures: (1) Dislocations move faster in As-doped Ge and slower in Ga-doped than in undoped Ge [34] due to the presence of shallow donor or acceptor levels at the dislocation or other defects such as kinks or antiphase defects. A similar explanation can be applied to P/B. We expect a suppression of dislocation generation in As/P doped Ge and prompting in B doped Ge. Thus, P/A-NA has a lower TDD value, and LB/HB-NA has a higher value than U-NA. (2) In Ge/Si, it is accepted that the dislocation core is a perfect sink for impurity atoms that arrive there [35, 36]. Impurities are known to be effectively gettered by dislocations [37]. Dislocations can be immobilized due to the formation of impurity complexes or clusters at dislocation sites through their accumulation [34]. Thus, P/A-5TC has a higher TDD than U-5TC.

In conclusion, B doping significantly impairs the Ge film quality, while As and P can reduce the TDD level without annealing. This provides a new method to fabricate high-quality Ge-on-Si films without defect annealing procedure, which can avoid undesired Si-Ge interdiffusion.
2.4.2 PVTEM

The specimens for PVTEM analysis of samples were prepared by using the chemical wet etching technique to thin Si substrates. XTEM specimen were prepared with FIB system of model Helios 450 from Thermo Fisher Scientific. The analysis of both PVTEM as well as XTEM specimens was performed in a microscope of model Titan 80-300 ST also from Therm Fisher Scientific. The microscope was operated at the accelerating voltage of 300 kV during the analysis. PVTEM specimens were tilted to 2beam diffraction condition before the recording of their images at different magnifications. For XTEM, high-angle annular dark-field (HAADF) scanning TEM (STEM) configuration was utilized to simultaneously enhance contrast from TDs and to suppress diffraction contrast Si lattice.

Figure 4 shows PVTEM images of Sample LB-NA and LB-5TC. Some of TDs are indicated by arrows in Fig. 4(a). The TDD values of Sample LB-NA, LB-5TC, LB-MHT, HB-NA and HB-5TC are $4.5 \pm 1.5 \times 10^8$, $1.5 \pm 0.5 \times 10^8$, $1.6 \pm 0.5 \times 10^8$, $8 \pm 2 \times 10^8$ and $1.7 \pm 0.5 \times 10^8$ cm$^{-2}$ respectively. The TDD measured by PVTEM are consistent with EPD results.

![Fig. 4. Images of PVTEM show different shapes and densities of threading dislocations in (a) LB-NA and; (b) LB-5TC.](image)

2.4.3 XTEM

![Fig. 5. Cross section TEM images in bright mode of Sample (a) U-5TC and; (b) LB-5TC. The TDD levels in regions close to the Ge seeding layer of both samples are estimated to over $1 \times 10^8$ cm$^{-2}$.](image)
As PVTEM can’t characterize the depth distribution of defects, XTEM has been performed to characterize defects throughout the top Ge layer depth range and down to Ge/Si interfaces. Sample U-5TC and LB-5TC represent the samples with low and high TDD in the Ge layers and were characterized by XTEM (Fig. 5). We can see that the TDs mainly exist in the Ge seeding layer (~100 nm thickness).

Despite the fact that U-5TC has a much lower TDD than LB-5TC in the top Ge layers measured by EPD at half of the top Ge layer thickness, both samples have a much higher density of TDs in the Ge seeding layers. We were able to estimate the TDD in the regions close to the top of the Ge seeding layers, which are about 1 to $2 \times 10^8$ cm$^{-2}$. Defect density increases even more when it gets closer to the bottom of the seeding layers (Ge/Si interfaces) as seen in Fig. 5. The possible TDs are encircled in the pictures. The TDs which transformed into loops and partials appear as dots, while those going upward along direction show as small lines. Other lines lying along the in-plane direction represent misfit dislocations (MDs). These massive MDs were generated on the Ge/Si interfaces during growth to relax lattice-mismatch strain, as shown in HRXRD results in Section 2.3. Boron doping doesn’t have much impact on the TDD in the Ge seeding layer according to the comparison between the two samples. Considering the fact that U-5TC has the lowest TDD and LB-5TC has a much higher TDD in the top Ge layers, it is reasonable to assume that the TDDs of P-5TC and A-5TC in Ge seeding layer should also be between that of the U-5TC and LB-5TC, which is similar in this case. Thus, we conclude that all dopants had little impact on the TDD level in the Ge seeding layer, where the Si-Ge interdiffusion mainly happened.

3. Impacts of doping on Si-Ge interdiffusion

3.1 Ge and dopants profiling

SIMS measurements were performed by Evans Analytical Group to obtain the Ge profiles in the samples. The samples were sputtered with 1 KeV Cs+ primary ion beam obliquely incident on the samples at 60° off the sample surface normal. The sputter rate was calibrated using stylus profilometer measurements. The measurement uncertainty of $x_{Ge}$ is ± 1%.

Figure 6(a) and 6(b) show the Ge and dopants SIMS profiles respectively. As Sample LB-5TC (6° offcut) has the same profiles as Sample LB-MHT (0° offcut), only Sample LB-5TC is shown. Ge and dopant profiles for Sample A-5TC (6° offcut) and Sample A-MHT (6° offcut) are also overlapping. According to diffusion theories, diffusivity is isotropic in cubic lattices. Therefore, the 6 degree offcut makes no difference in diffusion or interdiffusion. The overlapping profiles of A-5TC and A-MHT show that the merged annealing is equivalent to the 5TC annealing. It is worth mentioning that the profiles from different samples have been shifted laterally. As Ge sublimation happened during the annealing and reduced the Ge thicknesses of the annealed samples, one cannot use the absolute depth of the SIMS profiles...
due to the thickness difference. To compare the amount of interdiffusion, we use the slope of the Ge profiles as the evaluation criteria.

According to Fig. 6(a), all samples have very similar sharp Ge profiles at the Ge/Si interfaces before annealing. The Ge profiles almost overlap with each other. All the dopants have the highest concentration at the interface of Ge/Si, which is due to the segregation induced by a high density of defects at the interfaces. Sample U and sample LB have the least interdiffusion while sample P has the largest. Sample A has the second largest interdiffusion. While for sample HB, it has no significant difference over sample LB in $x_{Ge} < 0.7$ part, but it distinguishes itself from LB and U in $x_{Ge} > 0.7$ part. The interdiffusion profiles show a strong $x_{Ge}$ dependence, where much more diffusion happens in high Ge regions than in low Ge regions.

3.2 Effective interdiffusivity extraction

Boltzmann–Matano analysis was used to extract the time-averaged effective interdiffusivity ($\tilde{D}_{Si-Ge}$) as a function of $x_{Ge}$ from the concentration profiles. Theoretically, for Ge-Si interdiffusion couples, the condition for Boltzmann-Matano analysis is such that the interdiffusivity is only a function of the Ge molar fraction. It is not fully satisfied for extrinsic doping cases in P, As and highly B doped samples as interdiffusivity depends on doping levels. On top of that, dopants diffuse and segregate during annealing while Si-Ge interdiffusion happens. Nevertheless, we can still use this method to estimate the interdiffusivities $\tilde{D}_{Si-Ge}$.

The extracted $\tilde{D}_{Si-Ge}$ was illustrated in Fig. 7. In the full $x_{Ge}$ range, the interdiffusivity of Sample P ($\tilde{D}_P$) is 1.5 to 3 times higher than that of sample A ($\tilde{D}_A$), and $\tilde{D}_A$ is 1.5 to 2 times higher than that of Sample U ($\tilde{D}_U$). Both As and P enhances the interdiffusivity, which agrees with the previous studies [24, 25].

![Fig. 7. The time-averaged interdiffusivity as a function of Ge molar fraction using the Boltzmann-Matano method extracted from Sample U/P/A/HB/LB.](image)

For P and As in Ge, as their diffusivities are much faster than Si-Ge interdiffusion, we can approximate that major dopant motion happens much faster than the major Si-Ge motion, which enables us to use the final dopant profiles as stable dopant distributions for Si-Ge interdiffusion. This treatment is not valid for Ge with high B doping, as B diffusion in Ge ($1.5 \times 10^{-16}$ cm$^2$/s) [38] is comparable with Si-Ge interdiffusivity. In that case, the extraction of the time-averaged effective interdiffusivity ignores the B doping effect.
On the other hand, Sample LB, Sample HB, and Sample U do not exhibit much difference, especially in the $x_{\text{Ge}} < 0.6$ part. In the $x_{\text{Ge}} > 0.6$ range, their interdiffusivities do have some differences, and it shows that $\tilde{D}_{\text{LB}} > \tilde{D}_{\text{U}} > \tilde{D}_{\text{LB}}$. However, we should also keep in mind that we shouldn’t over-interpret the difference. Due to the SIMS broadening effect and the data resolution limit, we estimate the error bar of our interdiffusivity extraction is $\pm 50\%$.

To conclude, n-type doping (As and P) can enhance the Si-Ge interdiffusivity significantly while boron’s effect on that is small if any.

### 3.3 A Mechanisms of interdiffusion enhancement

From the experimental results above, we can see that as long as high P/As doping exists, the Si–Ge interdiffusivity will increase significantly. We need to discuss a few possible mechanisms:

1) Defect density. The possibility that this enhancement is due to a defect density difference is quite unlikely as the TDD values of Sample U and LB are close in the Ge seeding layers.

2) Strain. From our XRD results, all samples with different doping have similar strain levels, and the enhanced interdiffusion cannot be a result of strain difference.

3) Fermi-level effect [39]. The intrinsic carrier density of Si and Ge at $T = 890\, ^\circ\text{C}$ are $3.18 \times 10^{19}$ cm$^{-3}$ and $1.37 \times 10^{19}$ cm$^{-3}$ respectively, which are below the As/P doping concentration. This indicates that the Fermi-level effect existed during the annealing.

Cai et al. has investigated Si-Ge interdiffusion with a high P doping level in the range of $0.75 < x_{\text{Ge}} < 1$ [25]. The doping dependence was modeled successfully by a Fermi-enhancement factor (FF), which is defined as the ratio between extrinsic and intrinsic diffusion coefficient mediated by point defects. It can be expressed by the following formula:

$$
\frac{D(n)}{D(n)} = \frac{1 + \sum_{r=1}^{2} \frac{n_{r}^{m}}{n_{i}^{m}} \exp\left(\frac{rE_{r} - \sum_{n=r}^{m} E_{n}}{kT}\right)}{1 + \sum_{r=1}^{2} \frac{n_{r}^{m}}{n_{i}^{m}} \exp\left(\frac{rE_{r} - \sum_{n=r}^{m} E_{n}}{kT}\right)} = FF \quad (m = 1, m \geq 20).
$$

$E_{r}$ is the intrinsic Fermi level; $E_{r}$ and $E_{r}$ are energy levels of single negatively charged point defects ($V^{-}$) and doubly negatively charged point defects ($V^{2-}$) respectively, $(m = 1, m \geq 20)$ shows that interdiffusion is mainly dominated by $V^{2-}$ point defects. $E_{r}, (x_{\text{Ge}})$, and $E_{r}, (x_{\text{Ge}})$ were linearly interpolated between the value in Si and Ge [39, 40]. However, it will be inaccurate to use the same formula as our $x_{\text{Ge}}$ is from 0 to 1 instead of 0.75 to 1 in Cai et al.’s work. Interdiffusion can be mediated both by threading dislocations and by point defects in the lattice as seen in Eq. (2). The Fermi-enhancement factor shall only enhance $\tilde{D}_{\text{lattice}}$.

$$
\tilde{D}_{\text{total}} = \tilde{D}_{\text{dislocation}} + \tilde{D}_{\text{lattice}}
$$

The $\tilde{D}_{\text{dislocation}}$ will dominate when $x_{\text{Ge}} < 0.5$, while $\tilde{D}_{\text{lattice}}$ will dominate when $x_{\text{Ge}} > 0.7$ [23, 41, 42]. In Cai et al.’s study, $\tilde{D}_{\text{dislocation}}$ was neglected as $x_{\text{Ge}} > 0.75$. In our case, we should modify $\tilde{D}_{\text{total}}$ as shown in the following equation:
\[ \tilde{D}_{\text{total}} = \tilde{D}_{\text{dislocation}} + \tilde{D}_{\text{lattice}} \times FF, \]  

(3)

where

\[
FF = \frac{1 + \sum_{i=1}^{2} \left( \frac{n_i}{n} \right)^{m_i} \exp(-\frac{E_i - \sum_{r=1}^{\text{all}} E_r}{kT})}{1 + \sum_{i=1}^{2} \left( \frac{n_i}{n} \right)^{m_i} \exp(-\frac{E_i}{kT})}.
\]

(4)

The \( \tilde{D}_{\text{lattice}} \) term can be calculated according to Ref [20]. The \( \tilde{D}_{\text{dislocation}} \) term can be calculated as

\[ \tilde{D}_{\text{dislocation}} = \tilde{D}(n_i) - \tilde{D}_{\text{lattice}}, \]

(5)

where \( \tilde{D}(n_i) \) is extracted from Sample U.

The electron density \( n_i \), can be calculated using the same method in Ref. [25]. The last parameter is the calculation of \( n_i(x_{Ge}) \). Due to the limited data of \( n_i(x_{Ge}) \), Cai et al. used linear interpolation between \( n_{i,Ge} \) and \( n_{i,Sl} \) in his original code as Eq. (6). This approximation is good enough over the range 0.75 < \( x_{Ge} < 1 \). However, our work covers 0 < \( x_{Ge} < 1 \) range. Since at \( x_{Ge} < 0.85 \), \( Si_{1-x}Ge_x \) alloys have always been considered as a “Si-like” material due to its band structure and electronic properties [43, 44]. We also tried exponential interpolation between \( n_{i,Ge} \) and \( n_{i,Sl} \) as shown in Eq. (7).

\[ n_i(x_{Ge}) = n_{i,Ge}x_{Ge} + n_{i,Sl}(1-x_{Ge}) \]

(6)

\[ n_i(x_{Ge}) = n_{i,Sl} \exp(\ln(n_{i,Ge}x_{Ge}) \times n_{i,Sl}) \]

(7)

The simulation results with both approximation methods will be discussed in Section 3.4, and the later one turned out to be more accurate.

**3.4 Simulation of Ge profiles after annealing**

As B has little impact on Si-Ge interdiffusion. We will focus our simulation work on sample A-5TC and P-5TC. Ideally, it is best to simulate dopant diffusion, dopant segregation, and Si-Ge interdiffusion simultaneously. However, the diffusion and segregation of dopant involve many unknown coefficients such as the P/As diffusion segregation coefficients as a function of \( x_{Ge} \) and defect density. P and As diffusivity in Ge are over 20 times larger than \( \tilde{D}_{Sl-Ge} \) [20, 45]. Therefore, we consider that most of the P and As motion happen in the early stage of the annealing process, and reach a distribution close to the final distribution. For Si-Ge interdiffusion, as it is much slower and further away from the equilibrium, we expect that the interdiffusion motion happens throughout the annealing. Most of the interdiffusion motion happens after P and As reach a relative stable state, and we can approximate that the interdiffusion happens with a fixed P and As distribution same as the final profiles.

The simulation was done by Matlab™ to calculate \( \tilde{D}(n) \) in Eq. (3) and to simulate interdiffusion profiles using Fick’s second law:

\[ \frac{\partial C_{Ge}}{\partial t} = \frac{\partial}{\partial z} \left( \tilde{D}(n) \frac{\partial C_{Ge}}{\partial z} \right) \]

(9)
To solve the diffusion equation numerically, we used finite difference time domain (FDTD) method. The experimental data of A-NA and P-NA were used as the initial profiles of the simulation.

Fig. 8. Simulation results (lines) with different parameters in comparison with SIMS data (symbols). (a) Sample P-5TC; (b) sample A-5TC.

As discussed earlier, the calibrated annealing temperature are 890 °C and 870 °C for Sample P-5TC and A-5TC respectively. We also calculated simulation at T = 850 °C for Sample P-5TC and at T = 830 °C for Sample A-5TC to show the temperature sensitivity (Fig. 8). Another critical parameter in simulation is $n_i(x_{Ge})$. Both the exponential and the linear model were used for comparison.

As illustrated in Fig. 8, using T = 890/870 °C and $n_i(x_{Ge})$ exponential model can give the best Ge profile fitting results for sample P-5TC/A-5TC respectively. According to Fig. 8, although the linear interpolation of $n_i(x_{Ge})$ has a better fitting curve with P-5TC in $x_{Ge} > 0.6$ part compared with the exponential interpolation, it has a plateau in $0.4 < x_{Ge} < 0.6$. This plateau is not real, but a result due to the underestimation of interdiffusion enhancement in $x_{Ge} > 0.6$ region. Using the exponential interpolation of $n_i(x_{Ge})$ can solve this problem. Thus, we conclude that $n_i(x_{Ge})$ with an exponential dependence on $x_{Ge}$ is a better model than the linear model. As expected, the extracted temperatures (890/870 °C) worked better than the nominal reading temperature (850/830 °C) for Sample P-5TC/A-5TC.

At $x_{Ge} > 0.5$ part, P simulation results and P-5TC Ge SIMS profiles do not match as good. That inconsistency should be due to the over simplified treatment of P profile above. According to the Kirkendall effect, as Si diffuses much faster in Ge than Ge in Si, more lattice sites move to the Ge side due to the unbalanced vacancy flux associated with the interdiffusion. These creation and annihilation of lattice sites result in the movement of P profile towards the Si side during annealing. In our simulations, we assumed that the P profile didn’t change and used the final P profile as the P distribution during interdiffusion. This is not the case when the Kirkendall effect is significant; the true P profile is on the left side of the final P profile, which means that we underestimated the Fermi-enhancement effect at the Ge side. For sample A-5TC, we didn’t observe a similar problem, which is likely due to the lower concentration of As and lower annealing temperature, making the Kirkendall effect less significant.

3.5 Observation of the Kirkendall effect

To observe the Kirkendall effect, we annealed the P doped sample at T = 870 °C for 50 minutes and 200 minutes respectively in nitrogen gas. To prevent the Ge sublimation, a 120
nm thick SiO₂ was deposited on Ge using plasma enhanced CVD at 300 °C before the annealing.

Fig. 9. Ge and P profiles of P doped samples with no annealing, with 50 minutes annealing and 200 minutes annealing respectively. The annealing was at T = 870 °C. The SIMS profiles have not been shifted as there is no Ge sublimation during annealing.

According Fig. 9, before annealing, P has a sharp segregation peak at the Ge/Si interface. Compared to the unannealed sample P-NA, the lateral movement of P peak after 200 min annealing is about 70 nm towards the Si side. This is larger than the possible depth error of ±45 nm from the combination of the cross-wafer non-uniformity in epitaxial growth and the SIMS depth error. Therefore, we can confirm the observation of the Kirkendall effect, which leads to the lateral shifting of P during the annealing.

For doped Ge/Si structures, with only 3 elements such as P, Ge and Si, during thermal annealing, dopant diffusion, segregation, defect annealing, Si-Ge interdiffusion and exchange of lattice sites on both sides all happen simultaneously, making this a much more complicated physical picture than one expects.

4. Summary

To summarize, this work studied Ge-on-Si growth and Si-Ge interdiffusion with different doping conditions by experiments and theoretical modeling.

We found that different types of doping had no significant impact on the surface roughness and strain levels. All samples have a smooth surface (roughness < 1.5 nm). The Ge films are almost entirely relaxed with a small tensile strain from thermal expansion mismatch. On the other hand, even a low B doping level introduces lots of extra TDs (TDD > 1 × 10⁸ cm⁻²) in the top Ge layers compared to the undoped samples. P and As doping can reduce the TDD values of Ge films to be less than 10⁶ cm⁻² without annealing. This offers a new method to fabricate high-quality Ge-on-Si films without defect annealing procedure, which avoids undesired interdiffusion associated with defect annealing and is one of the major findings of this work. The two different annealing procedures (5TC and MHT) and wafer offcut orientations (0° and 6°) have a negligible impact on Ge film quality and interdiffusion. Photoluminescence studies of these samples and similar Ge films on (100) Si substrates are in process, and will be published separately.

Based on the interdiffusion data obtained from the experiments, theoretically, it is the first time that Ge-Si interdiffusion with n-type doping that has been successfully modelled and simulated across the whole xₑₑₑ range. Si-Ge interdiffusion is greatly enhanced in P and As doped samples, while B doping had little impact on that. We attributed this phenomenon to Fermi-level effect. We used the extrinsic n-doped Si-Ge interdiffusion model with the Fermi-enhance factor to describe the impact of the Fermi-level effect. The validity of the model was
proved by the comparisons between the simulations and the SIMS data from experiments with different anneal temperatures in $0 < x_{Ge} < 1$ range. We also reported the first observation of the Kirkendall effect in Ge-Si systems.

The results of this study are relevant to the design of optical and electronic devices with Ge-on-Si structures, including III-V lasers on Ge/Si, Ge-on-Si lasers, Ge modulators, and Ge photodetectors. For Ge-on-Si lasers, we recommend in situ high P or As doping by MOCVD without defect annealing instead of delta doping plus annealing as seen in the MIT’s work in Ref [12]. For undoped Ge-on-Si devices such as p-i-n photodetectors where the n-doped region is normally on top of the intrinsic and p-doped Ge, defect annealing is needed. For other applications, for example, Ge as a transition layer in InAs/GaAs quantum dot lasers on GaAs/Ge/Si, n-type doping is helpful to reduce TDD. In that case, if the bottom electrodes are on a p-doped GaAs layer, the Ge seeding layer and the bottom portion of the Ge can be n-doped to reduce the TDD in Ge and thus in GaAs and layers above.

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