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# Growth and characterization of germanium epitaxial film on silicon (001) with germane precursor in metal organic chemical vapour deposition (MOCVD) chamber

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The quality of germanium (Ge) epitaxial film grown directly on a silicon (Si) (001) substrate with 6° off-cut using conventional germane precursor in a metal organic chemical vapour deposition (MOCVD) system is studied. The growth sequence consists of several steps at low temperature (LT) at 400 °C, intermediate temperature ramp (LT-HT) of ∼10 °C/min and high temperature (HT) at 600 °C. This is followed by post-growth annealing in hydrogen at temperature ranging from 650 to 825 °C. The Ge epitaxial film of thickness ∼ 1 $\mu$m experiences thermally induced tensile strain of 0.11 % with a treading dislocation density (TDD) of $\sim 10^7/\text{cm}^2$ and the root-mean-square (RMS) roughness of ∼ 0.75 nm. The benefit of growing Ge epitaxial film using MOCVD is that the subsequent III-V materials can be grown *in-situ* without the need of breaking the vacuum hence it is manufacturing worthy. © *2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License*. [http://dx.doi.org/10.1063/1.4822424]

## I. INTRODUCTION

As the fundamental scaling limits of the silicon (Si) complementary metal-oxide-semiconductor (CMOS) transistors are approached, a paradigm shift has taken place in the industry from dimensional scaling alone to materials innovations. III-V materials which show 20–70 times higher electron mobility and ∼20 times higher conductivity than that of Si has become a promising candidate. Recently, III-V materials has been proposed for future high speed and low power computation applications.[1–7] However, Si still cannot be replaced by III-V materials because the III-V substrates are expensive and smaller in size due to their brittleness (wafer diameters are typically less than 200 mm). Therefore, III-V materials have to be integrated onto the Si substrate in order to be compatible with the mainstream CMOS manufacturing. Recently, a number of research groups have investigated the III-V growth on Si for optoelectronic and microelectronics applications.[8,9] Direct growth of the III-V materials on Si is challenging due to the large lattice mismatch between these two materials (for example, the mismatch is 4.1% in the case of gallium arsenide (GaAs)). Hence, germanium (Ge) which has a lattice constant that perfectly matches with the GaAs is used to act as a buffer layer between the Si and GaAs.[10–13]

Direct growth of Ge on Si is usually achieved in ultra-high vacuum chemical vapour deposition (UHV-CVD)[14–16] or reduced pressure chemical vapour deposition (RPCVD).[17–19] The main disadvantage of using these two methods is the inability to deposit the subsequent III-V materials (which

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can be grown in MOCVD) without breaking the vacuum. If one can grow the Ge on Si substrate in the MOCVD chamber, *in-situ* growth of the subsequent III-V materials becomes possible. Based on the author knowledge, there is no reports on growing and characterizing the Ge epitaxy film directly on Si in a MOCVD reactor. In this work, we report the Ge growth directly on Si with 6° off-cut toward the [110] by a three-step approach in a MOCVD chamber and the characterization results. The Si with 6° off-cut toward the [110] is used to reduce the antiphase domains (APD) that occur during the subsequent III-V materials growth.[20–22] Germane ($GeH_4$) is used as the pre-cursor in the MOCVD chamber for Ge growth.

## II. EXPERIMENTAL DETAILS

The epitaxial Ge layer was grown on a (001)-oriented Si substrate (diameter = 150 mm, *p*-type, resistivity = 0.01-0.025 Ω-cm) with a 6° off-cut toward the [110] direction. The Si substrate was cleaned in piranha solution ($H_2SO_4$: $H_2O_2$ = 4:1) followed by dipping it into a diluted HF solution (HF : $H_2O$ = 1:20). The cleaned wafer was loaded into the $N_2$-purged load-lock of the Thomas Swan MOCVD reactor. To initiate the growth, the wafer was transferred to the growth chamber and a thin Si layer was grown. The thin Si layer growth consisted of two steps, Si initialization at 825 °C and Si re-growth at 650 °C. This step was used to condition the Si surface and to bury any surface contamination in order to provide a high quality surface for Ge growth. After that, the Ge layer was grown. The precursor for Ge is 15% germane ($GeH_4$) diluted in $H_2$ balance. A three-step Ge growth was introduced and the target thickness was 1 $\mu$m. The three steps in the growth sequence were: (i) low temperature growth at 400 °C to obtain a relatively smooth and continuous Ge seed layer; (ii) low to high temperature ramping from 400 to 600 °C at a rate of 10 °C/min; and (iii) high temperature growth at 600 °C to achieve the intended thickness with reasonable growth rate. Thermal cycling was introduced immediately after step (iii) to enhance the surface mobility of the Ge atoms in order to control the surface roughness and to reduce the TDD.[23,24] The thermal cycling was performed by $H_2$ annealing between 650 to 825 °C with a repetition of 8× with 10 min annealing at 825 °C. Both Si and Ge layers were grown in the MOCVD reactor chamber having a base pressure of 100 mbar.

The quality of Ge epitaxial film was characterized by various techniques. The Ge RMS roughness was determined by atomic force microscope (AFM) of Nanoscope IV in the tapping mode. Transmission electron microscopy (TEM) of JOEL 2010F with operating voltage of 200 kV was used to study the threading dislocation densities (TDD) of the Ge layer and dislocations along the Ge/Si interface. X-Ray Diffraction (XRD) (PANalytical X'Pert PRO) was used to determine the crystallinity and strain level of the Ge epilayer. The Si (004) reflection was used for the XRD rocking curves.

## III. RESULTS AND DISCUSSION

The cross-sectional bright field TEM images in Fig. 1 show that the Si re-growth and Ge epitaxial layers are deposited successfully. The thickness of Ge epitaxial film is 950 nm which is closely matched with the targeted value of 1 $\mu$m. The 475 nm thick Si re-growth film is defect-free as observed from Fig. 1(a). A white line is drawn as an eye guideline to differentiate the Si regrowth layer and Si substrate. In addition, the misfit dislocations are mostly confined along the Ge/Si re-growth interface as shown in Fig. 1(b). The Si re-growth layer is inserted as it can be used to replace the 1000 °C hydrogen ($H_2$) baking step which is conventionally used to desorb the thin surface oxide that is detrimental to the epitaxy process.

The treading dislocations density (TDD) can be determined from the plan-view TEM by estimating the dislocations in a given area at a number of locations across the samples as shown in Fig. 2. The estimated TDD is $4.83 \pm 1.03 \times 10^7$ /cm$^2$. The TDD value is estimated based on an average number of forty plan-view TEM images for better accuracy. The RMS surface roughness of the sample is 0.75 nm as estimated from the AFM images shown in Fig. 3. In addition, a clear cross-hatch pattern is seen on the 6° off-cut sample.

Since the strain state of the final Ge epilayer heavily affects its electrical and optical properties, XRD study is performed to estimate the strain level of the Ge epilayer. A schematic illustrates the

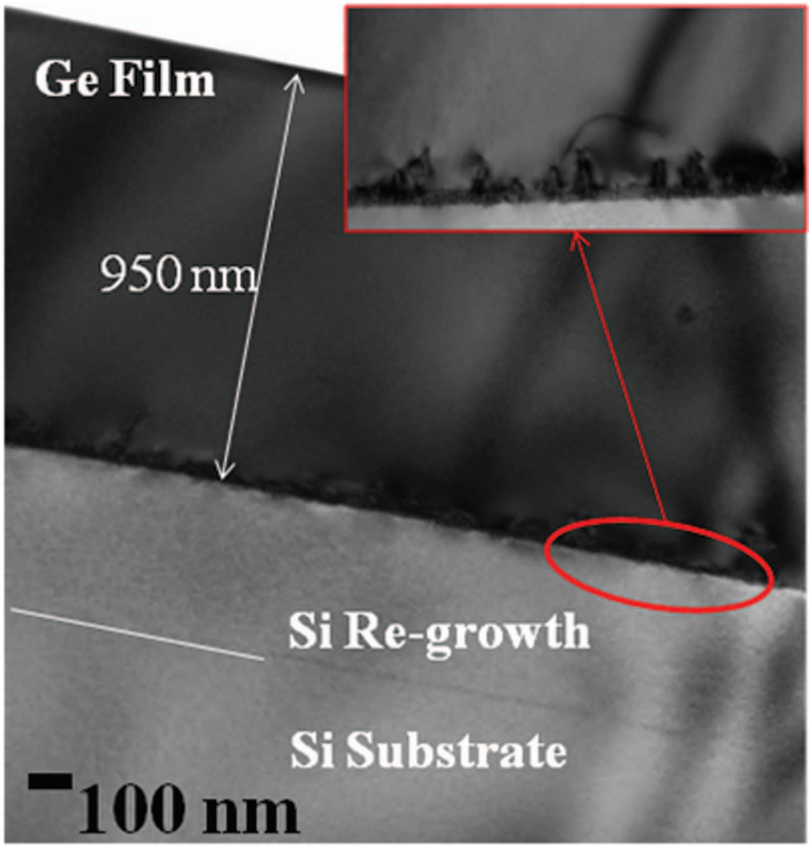

FIG. 1. Cross-sectional view TEM bright field images showing the Ge epitaxial film on the Si substrate. The subset image show the misfit dislocations are confined along the Ge/Si re-growth interface.

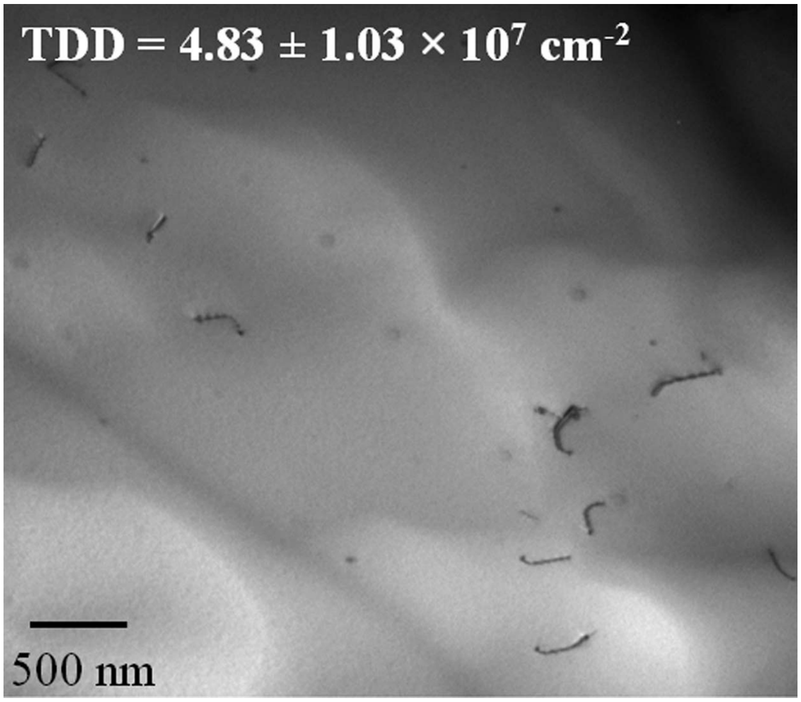

FIG. 2. Plan view TEM image shows the threading dislocations in the Ge film.

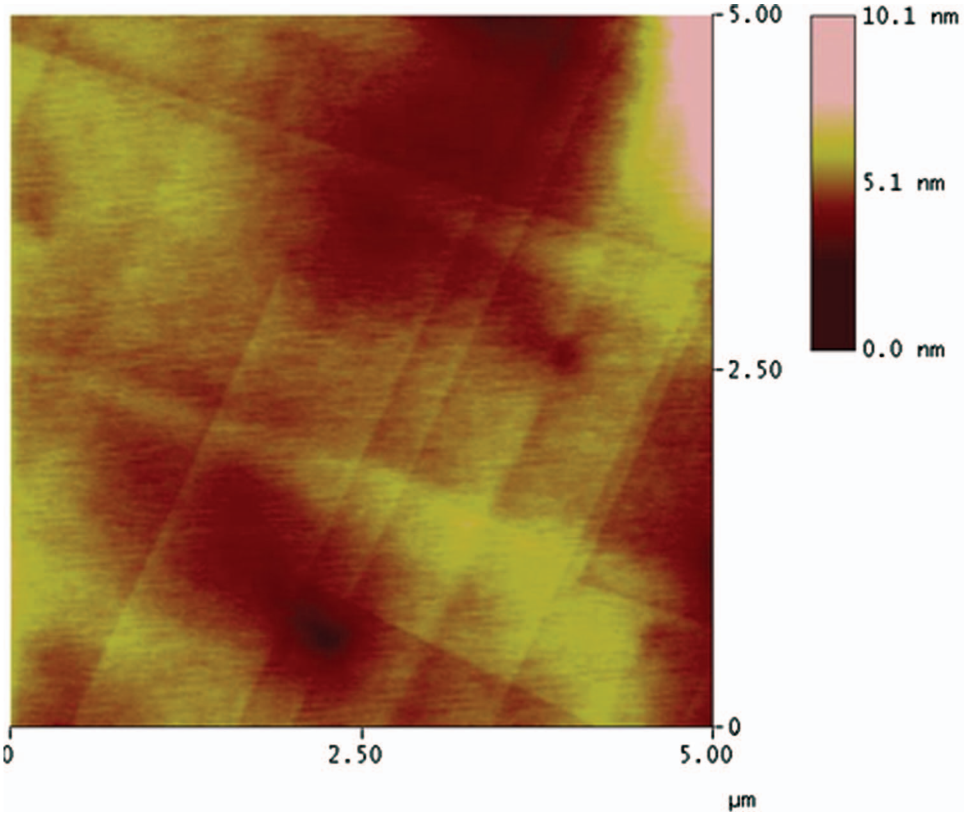

FIG. 3. Two dimensional (2-D) AFM scans (dimension: 5 $\mu$m × 5 $\mu$m) showing the RMS roughness of the as-grown Ge epilayer on Si substrate.

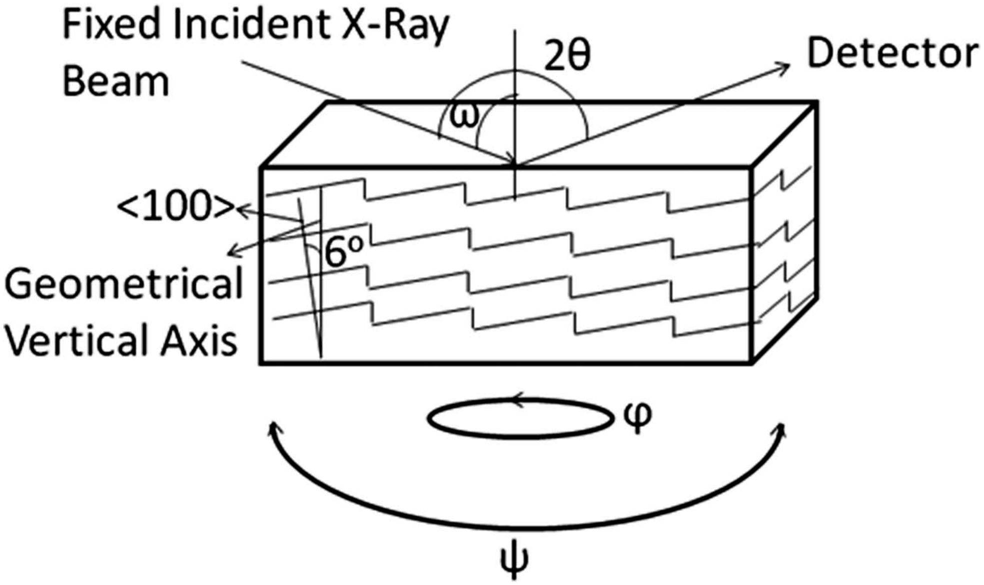

FIG. 4. A schematic illustrates the XRD measurement on the offcut substrate.

XRD measurement on the offcut substrate is shown in Fig. 4. The XRD analysis in Fig. 5 shows that the crystalline quality of the Ge epilayer. The Ge signal curve is asymmetric and shows a clear shoulder at the side towards higher incidence angles. This is due to the Ge/Si intermixing at the interface during thermal processing that perturbs the abrupt interface, which results in an intermediate

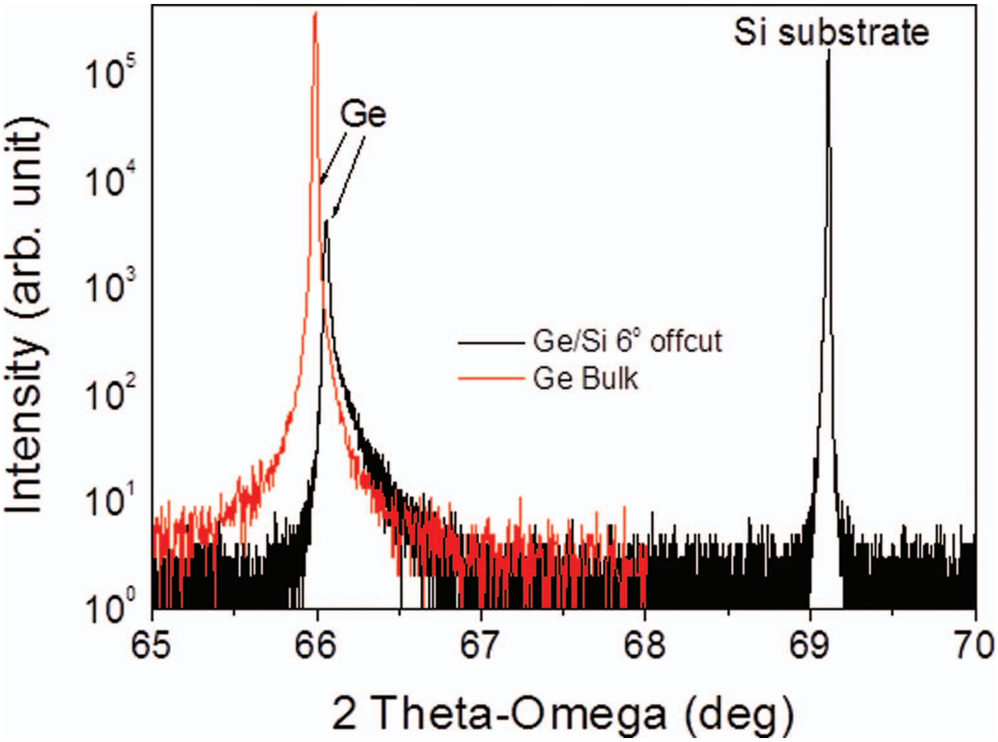

FIG. 5. High resolution x-ray diffraction (HRXRD) profile illustrates the crystallinity and the strain state of the Ge epitaxial film with reference to bulk Ge.

$Si_{1-x}Ge_x$ layer. The Ge peak is shifted to the right with reference to the Ge bulk substrate as a result of a tensile strain. The tensile strain is thermally induced in the Ge epilayer during cooling from high temperature processing steps to room temperature, as Ge has linear coefficient of thermal expansion (CTE) of 5.8 ppm/°C compare to Si of 2.6 ppm/°C.[14]

The angular separation between the epitaxial film and the substrate peak in the (004) rocking curve at an azimuth angle $\varphi$, is given by[25]

$$\begin{aligned} &\Delta\theta_{004}(\varphi) = \Delta\theta_{B004} + \Delta\varphi\cos(\varphi - \varphi_0) \\ &where \\ &\Delta\theta_{B004} = \Delta\theta_{B004,epitaxial} - \Delta\theta_{B004,substrate} \end{aligned} \tag{1}$$

$\Delta\theta_{B004}$ is the difference in Bragg angles between the epitaxial layer and the substrate. $\Delta\varphi$ is the crystallographic tilt between the [001] axes of the epitaxial layer and the substrate. $\varphi_0$ specifies the direction of this tilt.

The points (pairs of the Ge peak position and its respective $\varphi$) can be fitted by a linear equation with the intercept and slope of the straight line equal to the $\Delta\theta_{B004}$ and $\Delta\varphi$, respectively. The confidence level of the fitting is as high as 98.8 %. From the fitting, the $\Delta\theta_{B004} = 1.5203$ and $\Delta\varphi = 0.1658$. The out of plane lattice constant is then determined by the Bragg angle of the epitaxial layer:[25]

$$a^{\perp} = \frac{2\lambda}{\sin(\frac{\omega_{si}}{2} - \Delta\theta B_{004})} \tag{2}$$

where $\lambda$ is the incident wavelength of radiation (Cu $K_{\alpha 1}$ line, $\lambda = 1.5406$ Å) and $\omega_{Si}$ is the angular position of Si peak from the HRXRD of Si (004). Using the equation (2), $a^{\perp}$ of the Ge on Si with 6° off-cut can be estimated as 5.6534 Å. The in-plane lattice constant, $a^{\parallel}$ of Ge epilayer can be calculated using equation (3) by taking the elastic modulus of Ge, $\upsilon = 0.271$, and the unstrained Ge

TABLE I. A comparison of the quality of Ge epitaxial film on Si (001) 6° off-cut wafers that is grown by MOCVD and RPCVD.

| Characterization Methods | Ge grown by MOCVD [This work] | Ge grown by RPCVD[26] |
|---|---|---|
| Thickness | 950 nm | 969 nm |
| TDD | $4.83 \pm 1.03 \times 10^7$ /cm$^2$ | $6.53 \pm 0.93 \times 10^7$ /cm$^2$ |
| AFM | RMS roughness of 0.77 nm | RMS roughness of 1.92 nm |
| XRD | 0.11% of tensile strain | 0.21% of tensile strain |

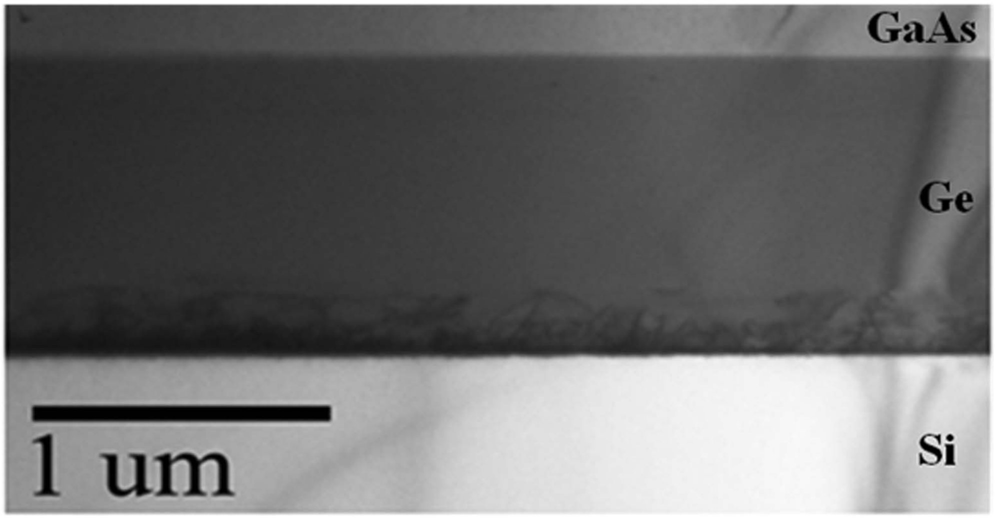

FIG. 6. Cross-sectional view TEM bright field image showing the GaAs epitaxial film on the Ge/Si substrate.

lattice constant, $a_{Ge} = 5.6576$ Å:

$$a^{\parallel} = \left(\frac{1+\upsilon}{2v}\right)\left[a_{Ge} - a^{\perp}\left(\frac{1-\upsilon}{1+v}\right)\right] \tag{3}$$

Therefore, the estimated $a^{\parallel}$ of Ge on Si with 6° off-cut is 5.6639 Å. The residual strain of the Ge epilayer can be calculated by equation (4):

$$\varepsilon = \frac{a^{\parallel}_{Ge} - a_{Ge}}{a_{Ge}} \tag{4}$$

The positive and negative value of $\varepsilon$ indicates either tensile or compressive strain. From the calculation, the Ge epilayer on Si 6° off-cut substrate experiences a tensile strain of 0.11%.

We have compared the properties and qualities of the Ge epitaxial film grown using MOCVD chamber with another sample that is grown by RPCVD.[26] In both samples, germane is used as the precursor. The comparison is summarized in Table I. The qualities of the Ge epitaxial film that is grown by two different deposition techniques are comparable. The main benefit of growing the Ge epitaxial film by MOCVD is that the subsequent III-V materials can be grown *in-situ* without the need of breaking up the vacuum. This can minimize the chance of particle contaminations and oxidation of the Ge film when the Ge/Si substrate is exposed to the ambient. In addition, investment in equipment and logistic can be lowered. Hence, direct III-V material on Si integration becomes possible in a single platform.

Lastly, we have also demonstrated the III-V materials (in this case, the GaAs) growth directly after the Ge growth as shown in Fig. 6. The details material and electrical characterization of the grown III-V materials will be discussed in the next paper.

## IV. CONCLUSION

In summary, a three-step epitaxial growth approach that consists of sequential steps, namely the LT, LT-HT ramp and HT growth followed by a post-growth thermal cycling is used to grow the Ge epitaxial film on Si substrate in a MOCVD chamber using conventional germane precursor. From the results obtained from the characterization methods as discussed, the Ge epitaxial film grown using this approach has good crystal quality with acceptable level of TDD ($\sim 10^7$ /cm$^2$) and RMS roughness (0.75 nm). The Ge film is under thermally induced tensile strain resulting from the growth approach (growth, annealing and cooling). The main benefit of growing the Ge epitaxial film in MOCVD is that the subsequent III–V materials can be grown *in-situ* without the need for breaking up the vacuum.

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