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Reduction of threading dislocation density in Ge/Si using a heavily As-doped Ge seed layer

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High quality germanium (Ge) epitaxial film is grown directly on silicon (001) substrate with 6° off-cut using a heavily arsenic (As) doped Ge seed layer. The growth steps consists of (i) growth of a heavily As-doped Ge seed layer at low temperature (LT, at 400 °C), (ii) Ge growth with As gradually reduced to zero at high temperature (HT, at 650 °C), (iii) pure Ge growth at HT. This is followed by thermal cyclic annealing in hydrogen at temperature ranging from 600 to 850 °C. Analytical characterization have shown that the Ge epitaxial film with a thickness of ∼1.5 µm experiences thermally induced tensile strain of 0.20% with a threading dislocation density (TDD) of mid 10^6/cm^2 which is one order of magnitude lower than the control group without As doping and surface roughness of 0.37 nm. The reduction in TDD is due to the enhancement in velocity of dislocations in an As-doped Ge film.

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I. INTRODUCTION

The growth of germanium (Ge) epitaxial layer on silicon (Si) substrate has attracted great attention among researchers recently because of its potential applications in photonic and electronics devices.1–4 Most importantly, Ge is also a group IV material, making it compatible with Si and can be processed in a standard silicon manufacturing facility. Another important application is that the Ge-on-Si substrate (Ge/Si) can be used as a template for subsequent III-V compounds growth since Ge is lattice-matched with gallium arsenide (GaAs).5 The desired Ge epitaxial film must have low defect density (in term of threading dislocation density, TDD), smooth surface with thin buffer layers.

The main challenge for the growth of Ge on Si is the ~ 4% lattice mismatch between Si and Ge. This can result in a high defect density with rough surface. The well-known method to address this problem is through SiGe graded buffer with variable composition and smoothen the surface with chemical mechanical polishing (CMP) at a composition of Si_{0.5}Ge_{0.5}. Through this method, TDD of ~ 10^5/cm^2 can be achieved but it requires a 10 µm graded SiGe buffer layer.6,7 Such thickness is practical through typical high temperature CVD processes resulting in µm/min growth rates. However, it sometimes may be desirable to have thinner initial layers for some applications, e.g. laser, photovoltaic, etc.8,9

The two-step growth approach using various types of chemical vapour deposition (CVD) tools is also one of the well-known approaches.10–12 This approach consists of a low temperature
(330-400 °C) growth step that is followed by a high temperature (600-850 °C) Ge growth. The TDD can then be greatly reduced by post-growth annealing or thermal cyclic annealing. This method provides the Ge/Si with much higher TDD of $10^7$/cm$^2$.\textsuperscript{13-15}

Another approach to reduce the TDD is through annealing the germanium-on-insulator (GOI) which is fabricated through bonding and layer transfer a Ge epilayer that is grown using the two-step approach. Through this method, the etch-pit density (EPD) with $<10^6$/cm$^2$ is achievable.\textsuperscript{16,17}

In the 1960s and 1970s, several groups investigated the velocities of dislocations in undoped and doped Ge bulk crystals (grown by the Czochralski technique). They discovered that the velocity of dislocation is enhanced when the Ge crystal is doped with arsenic (As).\textsuperscript{18,19} This finding motivated us to investigate the possibility of using As doped Ge to reduce the TDD in Ge layer in this work. In this paper, Ge with an EPD of $<5 \times 10^6$/cm$^2$ has been demonstrated using an As-doped Ge seed layer and the details will be discussed in the following sections.

II. EXPERIMENTAL DETAILS

In this experiment, silicon (001) wafers (diameter = 200 mm, $p$-type, resistivity = 1-100 Ω-cm) with 6° off-cut toward [110] direction were cleaned using standard RCA solutions followed by dipping them into a diluted HF solution (HF : H$_2$O = 1 : 10 by volume). The 6° off-cut Si substrate was chosen because it can be used for subsequent III-V compound semiconductor materials growth in order to eliminate the formation of anti-phase domains. The cleaned wafers were loaded into the N$_2$-purged load-lock of the Aixtron MOCVD reactor in preparation for Ge growth.

To initiate the growth, the wafers were transferred to the growth chamber and baked in hydrogen (H$_2$) at 1050 °C for 10 min to desorb the thin surface oxide that is detrimental to the epitaxy process. After that, a thin Si layer was grown to condition the Si surface and to bury any surface contamination in order to provide a high quality surface for Ge growth. Subsequently, a three-step Ge growth was introduced to grow the Ge epilayer directly on a Si wafer. 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 with heavy As doping (concentration of the As dopants $\sim 10^{19}$/cm$^3$); (ii) high temperature Ge growth at 650 °C by gradually reducing the AsH$_3$ flow from maximum flow to zero, (iii) high temperature pure Ge growth at 650 °C to achieve the intended thickness with a reasonable growth rate. Thermal cyclic annealing 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. The thermal cycling was performed by H$_2$ annealing between 650 to 850 °C with a repetition of 5× and a 10 min hold time at 850 °C. For comparison, a control sample was grown, i.e. a Ge/Si substrate was grown under the same conditions but without As doping.

The properties of the Ge epitaxial film were characterized by various techniques. The transmission electron microscopy (TEM; Philips CM200) with an operating voltage of 200 kV was used to study the dislocations along the Ge/Si interface as well as the threading dislocations on the Ge surface. The strain and quality of the Ge film were measured by high resolution X-ray diffraction (HRXRD) using PANalytical X'Pert PRO. Rocking curves based on Si (004) were collected in the HRXRD measurements.

III. RESULTS AND DISCUSSION

The cross-sectional bright field transmission electron microscopy (X-TEM) image in Fig. 1 shows that the Ge epitaxial layer is grown as expected. The thickness of Ge epitaxial layer is 1.5 μm. The misfit dislocations are mostly confined along the Ge/Si re-growth interface as shown in the X-TEM image. In addition, most of the threading dislocations (TD) are confined within the first 700 nm Ge layer (above the Ge/Si interface) where the Ge epilayer is doped with As during growth steps (i) and (ii). Beyond this thickness, no visible TD is observed under X-TEM, indicating that a the surface of the Ge film has $< 10^8$ threading dislocations per cm$^2$ obtained during the high temperature pure Ge growth.
FIG. 1. Cross-sectional transmission electron microscopy (X-TEM) bright field image shows that the Ge on Si with 6° off-cut substrate. The threading dislocations are confined within the first 700 nm Ge epilayer. Beyond this thickness, minimum number of dislocations are observed which indicates a high quality Ge film.

The threading dislocations density (TDD) can be more accurately determined from the plan-view TEM by estimating the dislocations in a given area at a number of locations across the entire samples as shown in Fig. 2. Only one threading dislocation is found in Fig. 2(a), while no threading dislocation is found in most of the areas as shown in Fig. 2(b). The estimated TDD from Fig. 2(a) is $1.06 \pm 0.64 \times 10^7$/cm$^2$.

To quantify the TDD with lower magnification images, field emission scanning electron microscope (FESEM) was used with etch-pitting techniques. The samples were etched in an iodine solution for 1 sec. Since the dislocations are etched much faster in the etchant, etch pit can be delineated and observed. The etch pit density (EPD) value was estimated based on an average number of twenty plan-view FESEM images for better accuracy. The estimated EPD of the Ge epilayer with As-doped seed layer is $4.57 \pm 0.39 \times 10^6$/cm$^2$ as shown in Fig. 3(a). This is much lower as compared to the control sample (direct Ge grown on Si with 6° off-cut substrate without As doping) with EPD of $5.63 \pm 0.63 \times 10^7$/cm$^2$. It is clearly shown that the EPD is reduced by one-order of magnitude.

As previously reported, the velocity of dislocation is enhanced when the Ge bulk crystal is As-doped.\textsuperscript{18,19} This is due to the presence of shallow donor or acceptor levels at the dislocation or other defects such as kinks or anti-phase defects. The dislocation itself is thought to contain reconstructed bonds only, while there may be dangling bonds at its defects. These shallow levels could change to deep levels while the kink pair / kink reaches its saddle point of formation / movement, respectively. The saddle point structure has a highest occupied level displaced to about mid-gap. The difference in energy between these levels is spent for kink pair formation / kink

FIG. 2. Plan view TEM images showing the threading dislocations on the Ge surface. (a) One threading dislocation is observed on the area. (b) No threading dislocation is observed.
migration and so lowers the activation energy of the dislocation.\textsuperscript{20–22} Hence, the \textit{n}-type doped Ge is experiencing an enhancement in dislocation motion. Similar explanation can be applied in our case. Since the velocity of the dislocations of the As-doped Ge epitaxial film is improved, there is a higher probability that the dislocations Burgers vector with the opposite sign meet more readily and annihilate during the thermal cyclic annealing process. Thus, the TDD can be reduced to a greater degree than with no doping and lower dislocation velocity.

Since the strain state of the final Ge epilayer affects its electrical and optical properties, high resolution x-ray diffraction (HRXRD) study was performed to estimate the strain level of the Ge epilayer. Fig. 4 illustrates the HRXRD measurement on the off-cut substrate. The strain level of the Ge epilayer can be estimated using method in previous reports.\textsuperscript{14,15} The Ge epilayer with and without the As doping seed layer experience a tensile strain of 0.21\% and 0.16\%, respectively. 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.\textsuperscript{23} The position of Ge peak with As-doped is shifted to the right with reference to the control sample, indicating that the Ge with arsenic doping has slightly higher tensile strain. In addition, the full width half maximum (FWHM) of the Ge peak with arsenic
doping is about 171 arcsec, which is smaller than the control sample of 211 arcsec. The decrease in FWHM and the increase in intensity of Ge peak indicate that the Ge with As-doped seed layer provides a better crystallinity as a better crystal has more reflective planes.

Both the Ge peaks are asymmetric and show a clear shoulder at the side towards higher incidence angles. This is due to Ge/Si intermixing at the interface during thermal processing that perturbs the abrupt interface, which results in an intermediate Si$_{1-x}$Ge$_x$ layer. The Ge epilayer with As-doped seed layer has a broader shoulder as compared to the control which indicates that the composition of Si$_{1-x}$Ge$_x$ changes more gradually (in the case of As-doped) instead of an abrupt change (in the case of un-doped Ge seed layer). This behavior may contribute to TDD reduction. Recently, it was reported that Si-Ge interdiffusivity is enhanced by 10-20 times when the Ge is highly doped with phosphorus (P) due to much faster P transport towards the Ge seeding layer, which increases Si-Ge interdiffusion due to the Fermi level effect. This work suggests that heavy levels of arsenic doping may also increase interdiffusion by the same mechanism.

The RMS surface roughness of the sample is 0.37 nm as estimated from the AFM images shown in Fig. 5. In the previous results where the Ge epilayer was grown using the un-doped Ge seed layer, the RMS roughness is about 2 nm. In addition, a clear crosshatch pattern is seen on the 6° off-cut sample. The smooth surface is a result of dislocation motion occurring after the completion of epitaxial growth. In addition, the As dopants may also have helped to promote the migration of Ge atoms during the high temperature annealing which further improve the smoothness of Ge epilayer.

Another way to determine the quality of the Ge epilayer is through the intensity of photoluminescence (PL) emitted from a light emitting diode (LED) structure that is grown on the Ge/Si substrate. As the efficiency of an optoelectronic device is mainly depending on the lifetime of minority carriers, a higher TDD will reduce the lifetime of the minority carrier and leads to lower efficiency. For comparison, a red InGaP LED structure is grown on the GaAs bulk substrate (n-type with Si doping of $1 - 4 \times 10^{18}$/cm$^3$), Ge epilayer with and without As-doped seed layer under the same batch of growth. As shown in Fig. 6, the PL intensity of the InGaP LED grown on the Ge epilayer with As-doped is comparable to that on the GaAs substrate. On the other hand, the PL...
FIG. 6. Photoluminescence (PL) of the red InGaP LED structure that is grown on Ge/Si with and without As doped seed layer and GaAs substrate. The PL intensity of the Ge/Si with As-doped seed layer is comparable to the GaAs substrate.

intensity is the lowest for the control sample. The shift of PL peak location between the GaAs substrate and Ge epilayer with As-doped seed layer is due to the strain of the starting materials. For GaAs substrate, it is a strain-free material; whereas the Ge epilayer with As-doped has a tensile strain of 0.2%.

IV. CONCLUSION

In summary, the EPD of the Ge epitaxial films grown on Si substrate with 6° offcut is reduced by at least one order of magnitude to $< 5 \times 10^6$/cm² using Ge seed layer with arsenic doping. The FWHM of Ge peak in the HRXRD is also reduced by ~20%. In addition, the RMS roughness is of the lowest reported values of 0.37 nm. The high quality of Ge epilayers have been verified as it can be used for the growth of red InGaP LED structure with PL intensity comparable to GaAs substrate.

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