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Growth of Single Crystalline Germanium Thin Film on (100) Silicon Substrate

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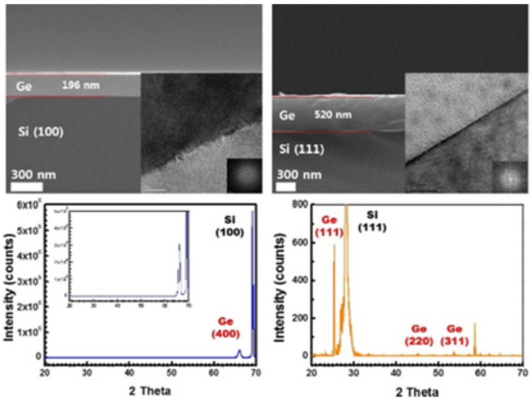
Epitaxial growth of germanium thin films (GeTFs) on Si (111) and Si (100) substrates was investigated, and the prepared films were compared with the films grown on SiO_2 substrates. Ge films were prepared in three steps. Initially, a Ge interlayer film with thickness of ~ 10 nm was deposited on the substrate followed by annealing and recrystallization of the film. A Ge film with a thickness of 500 nm was then deposited. A single crystalline Ge film was grown on Si (100) whereas polycrystalline films were grown on the other substrates. The growth rate of the films depends on the type of the substrates used, which in turn determines the crystallinity of the films. Highly crystalline films were obtained with slow growth rates. The single crystalline epitaxial layer of GeTFs formed on Si (100) exhibited a lower threading dislocation density as compared with those grown on Si (111) and SiO_2.

Keywords: single crystal, GeTF, Si (100), growth rate, three step growth



1. INTRODUCTION

Over the last two decades, the growth of III-V and other compound semiconductors on Si substrates has attracted considerable attention owing to their potential in the fabrication of monolithic circuit of III-V devices with Si. For example, optoelectronic and photonic devices can be fabricated when integrated circuits based on III-V semiconductors are grown on Si substrates.[1-5] However, the high lattice mismatch (4.18%) between Si and III-V compounds results in high dislocation densities, thereby significantly degrading the properties of the devices.

Germanium (Ge) has been considered as an interesting substrate for III-V semiconductor growth owing to the small lattice mismatch (less than 1%) between Ge and III-V compounds, making it possible to prepare compound films exhibiting a low dislocation density and a high crystallinity.[6-9] However, bulk Ge substrates are expensive and difficult to prepare. Therefore, the growth of high quality Ge films has been investigated on various substrates such as Si and SiO_2.[10,11] Furthermore, the performance of the prepared III-V circuits can be greatly improved owing to the greater hole mobility in the Ge layer and since the growth of high quality III-V semiconductor films can be achieved.[12] The growth of high quality Ge films on Si is difficult since several parameters in the growth process should be carefully controlled. The type of substrates used (Si (111), Si (100), or SiO_2 in this case) is a crucial factor in the production high quality Ge films since the growth of Ge strongly depends on it.[13-18]

In this study, we investigate the growth of Ge films on Si (111), Si (100), and SiO_2 substrates using a three-step growth technique, consisting of the deposition of a Ge interlayer at a

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low temperature, annealing, and deposition of a Ge layer at a high temperature. High quality-, single crystalline Ge films could be grown on Si (100), and polycrystalline films are grown on the other substrates. Thus, the substrate plays a critical role (in the formation of flatter interlayer surfaces with lower defects densities) in the growth of Ge films, and high quality single crystalline Ge films can be grown by selecting suitable Si substrates.

2. EXPERIMENTAL PROCEDURE

Ge films were grown using an ultra-high vacuum-chemical vapor deposition (UHV-CVD) method using GeH_4 as the precursor. The background pressure was maintained at $\sim 5 \times 10^{-7}$ Torr. Si (111), Si (100), and SiO_2/Si substrates were pre-cleaned using acetone and ethanol in an ultrasonic cleaner before deposition. The substrate was then transferred into a chamber followed by subjecting to thermal annealing at 400 °C for 10 min. After cleaning, a three-step growth was performed, which involved the low-temperature growth of the thin Ge layer, annealing, and high-temperature growth of the thick Ge layer. In the first step, a Ge film having a thickness less than 10 nm was grown at 400 °C for 20 min. On SiO_2, the growth rate was estimated to be around 0.5 nm/min. Thermal annealing was then performed at 500 °C for 30 min. The top Ge layer was then grown at 500 °C for 30 min. The obtained Ge films were characterized using X-Ray diffraction (XRD, PANalytical X'Pert PRO high resolution XRD system), high resolution transmission electron microscopy (HRTEM, FEI Titan working at 300 kV), and scanning electron microscopy (SEM, JEOL working at 15 kV). The threshold dislocation density of the films was estimated with a selective etching method using the etchants composed of acetic acid (CH_3COOH), nitric acid (HNO_3), hydrogen fluoride (HF), and iodine (I_2) with a ratio of 5:3:3:1/10.

3. RESULTS AND DISCUSSION

Figure 1(a), (b), and (c) show the cross section SEM images of Ge films grown on SiO_2, Si (111), and Si (100), respectively. Uniform Ge films are formed regardless of the type of the substrates used. The thickness and the growth rate of the film grown on SiO_2 are 327 nm and ~11 nm/min, respectively (Fig. 1(a)). With Si (111) and Si (100), GeTFs with a thickness of 520 nm and 196 nm are formed with a growth rate of 17 nm/min and 6.5 nm/min, respectively (Fig. 1(b) and (c)).

XRD patterns shown in Figs. 1(d), (e), and (f) provide details about the crystallinity of GeTFs fabricated on SiO_2, Si (111), and Si (100), respectively. Several peaks corresponding to (111), (220), and (311) reflections of Ge are observed in the range of 20 °-70 ° (2Θ). The Ge film grown on SiO_2 is poly-crystalline in nature, and the strong peak observed at 66 ° with the lowest full width at half maximum (FWHM) corresponds to the main crystalline orientation of Ge. The

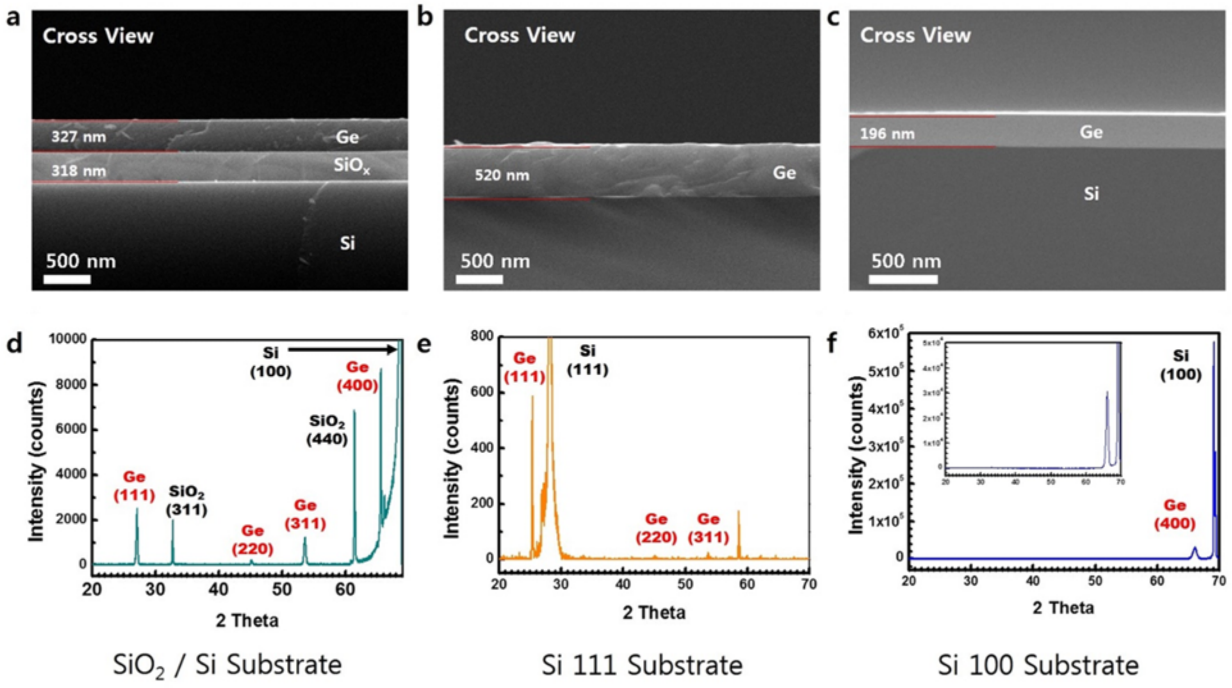

Fig. 1. Cross-SEM images of GeTFs formed on (a) SiO_2, (b) Si (111), and (c) Si (100). XRD patterns of GeTFs grown on (d) SiO_2, (e) Si (111), and (f) Si (100).

preferential crystallization of the GeTF formed on Si (111) proceeds along the [111] direction. The presence of highly intense and narrow diffraction peaks of Ge indicates the formation of highly crystalline products. GeTF formed on Si(111) exhibits small peaks corresponding to (220) and (311) reflections, indicating the presence of poly-crystalline Ge resulting from a non-epitaxial growth. A dominant (100) peak of Ge can be clearly seen in Fig. 1(f). The peak observed at $2\Theta = 69°$ corresponds to (400) reflection originating from Si (100). The XRD pattern indicates that a single crystalline Ge film with a preferred orientation along [100] is eventually formed on Si (100).

Figure 2 shows the cross-sectional TEM image, high-resolution image, and selected area electron diffraction (SAED) patterns of GeTFs grown on SiO_2, Si (111), Si (100). High-quality single crystalline GeTFs are grown on Si (100) whereas low-quality crystalline GeTFs are grown on Si (111) and SiO_2. The polycrystalline rings indicating the preferred growth orientations of GeTF (Fig. 2(a) and (b)) are related to the substrate orientation. The (111) polycrystalline ring observed for the sample on the Si (111) could be attributed to the secondary twinning on the inclined {111} planes of Ge.[14]

The quality of Ge films, their morphology, and crystalline states depend on the substrates used. The growth rate varies depending on the substrate, and a slow growth rate results in the formation of high quality single crystalline Ge films. The lattice mismatch between Ge and Si is 4.18%. The lattice mismatch can be compensated by the biaxial strain occurring during the early stages of film formation, resulting in the Stranski-Krastanow growth mode in the case of Ge deposition on Si substrates.[12]

In case of (111) Ge films grown on Si (111), two different kinds of (111) surface terminations exist such that a single dangling bond per surface atom and a single coordination atop site with three dangling bonds per surface atom are

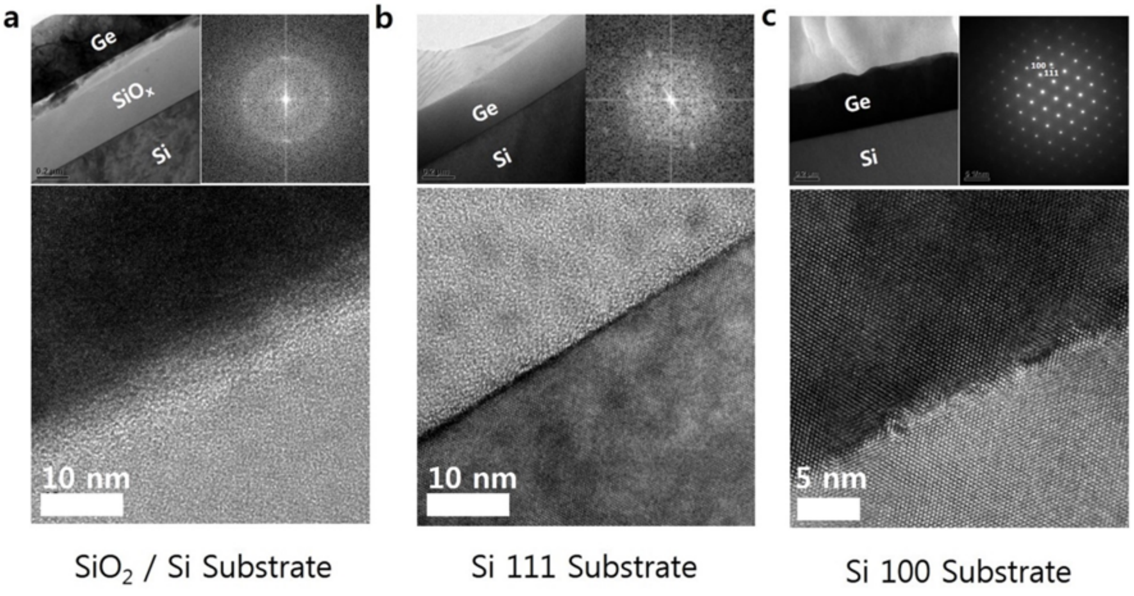

Fig. 2. TEM images of GeTFs grown on SiO_2, Si (111) and Si (100). Cross-TEM, HR-TEM and SAED patterns of (a) poly-crystalline GeTF formed on SiO_2, (b) poly-crystalline GeTF formed on Si (111), and (c) single-crystalline GeTF formed on Si (100).

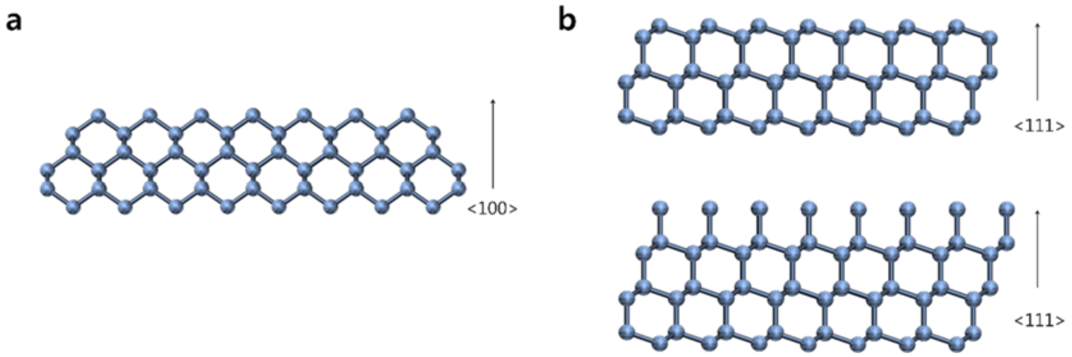

Fig. 3. Schematic images of the side projection view of atomistic Ge interlayer surface for (a) (100) Ge surface and (b) (111) Ge surface.

present.[19,20] Thus, the (111) Ge surface exhibits an asymmetric geometry as shown in Fig. 3(b), thereby causing the formation of small irregularly shaped three-dimensional islands. The presence of islands with different size and shape distributions could lead to the high growth rate of Ge films with the Stranski-Krastanow growth mode. The presence of islands with different shapes induces the formation of defects during Ge coarsening, which could lead to the high growth rate of the films. Thus, the rough (111) surface of Ge enhances the adsorption of Ge atoms owing to the large surface areas and larger number of adsorption sites, resulting in high growth rates.

In the case of Ge (100) film surfaces, every Ge atom exhibits a two-fold coordination[19] and the surface exhibits a symmetric geometry as indicated in Fig. 3(a). The symmetric geometry and the presence of one termination site tend to prevent the impinging Ge from forming islands on the surface, resulting in a flatter substrate and a homogenous coverage of Si substrates owing to the slow growth rate. The high growth rate generally results in poor crystallinity due to the lack of time for the growth of perfect epitaxial-, single crystalline films. Thus, single crystalline Ge films could be obtained with Si (100). Although the slow growth rate mainly contributes to the formation of single crystalline films, the annealing step enhances the growth of single crystalline Ge films on Si (100) by annihilating the defects and dislocations associated with strain relaxation, thereby allowing the growth of Ge on fully relaxed Ge interlayer.[21,22]

The growth rate of Ge on SiO_2 is higher than that on Si (100) and slower than that on Si (111). The quality of the GeTF formed on SiO_2 is higher than that formed on Si (111) within the framework of growth rate. However, in this study, the Ge films would grow without interaction between the Ge and SiO_2 films. In case of SiO_2, the Ge deposition induces the formation of Ge films without forming Ge wetting layers. The interaction of Ge with SiO_2 does not generally occur during the growth step under 430 °C.[13,23,24] Therefore, an amorphous Ge film is deposited relatively slowly on SiO_2, resulting in poor surface uniformity and morphology.

The crystallinity of GeTFs can be determined by estimating the threading dislocation density. Selective etching process based on chemicals is a simple and fast way to evaluate the structure perfection of the crystal,[25-28] and the threading dislocation density can be obtained by calculating the etch pit density (EPD) using wet chemical etching. The etchant used in this study was composed of CH_3COOH, HNO_3, HF and I_2 with a ratio of 5:3:3:1/10.[26] Figure 4 shows the EPD test results for GeTFs on SiO_2, Si (111), and Si (100). The GeTF formed on Si (100) exhibits a small dislocation density of 6.53×10^6 cm^{-2}. The dislocation densities of GeTFs formed on Si (111) and SiO_2 are 7.16×10^8 cm^{-2} and 1.57×10^9 cm^{-2}, respectively. Defects such as misfit dislocations and stacking faults are easily formed in the films prepared with high growth rates. Thus, high-quality single crystalline GeTFs are formed on Si (100) whereas low-quality crystalline GeTFs are formed on Si (111) and SiO_2. The growth rate that depends on the type of substrates plays a critical in the growth of high quality Ge films.

4. CONCLUSIONS

We grew GeTFs on SiO_2, Si (111), and Si (100). A high-quality crystalline Ge film is grown on Si (100), and low-quality crystalline Ge films are formed on Si (111) and SiO_2. The growth rate, which is closely related to the surface structure of the films, plays a critical role in the formation of flatter interlayer surfaces with lower defects, which could be controlled by selecting the substrate that determines the growth orientation of the Ge films. In conclusion, high quality- single crystalline Ge film with a low defect density can be grown by selecting suitable Si substrates.

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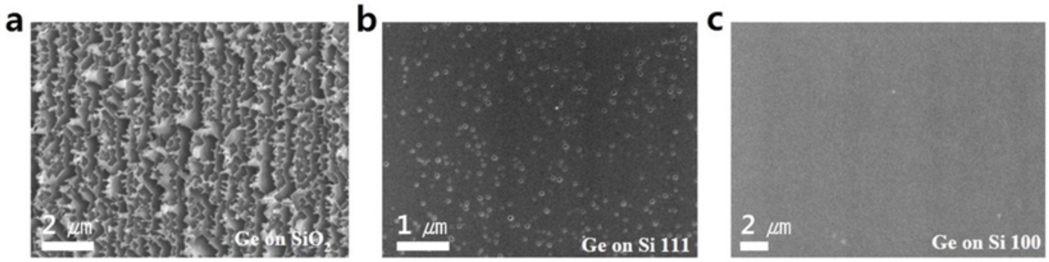

$1..57 \times 10^9$ cm^{-2} 7.16×10^8 cm^{-2} 6.53×10^6 cm^{-2}

Fig. 4. Defect density of GeTFs on (a) SiO_2, (b) Si (111), and (c) Si (100) examined using etch pit density methods.

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