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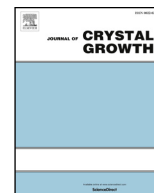
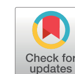


Homoepitaxy of Ge on ozone-treated Ge (1 0 0) substrate by ultra-high vacuum chemical vapor deposition



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ABSTRACT

Germanium (Ge) homoepitaxy is still a big challenge due to the immature surface cleaning of Ge, which often results in imperfect Ge epitaxial growth in terms of surface roughness, pits and islands. In this work, high crystal quality Ge and GeSi with very smooth surface were epitaxially grown on Ge (0 0 1) substrates, which were thermally cleaned at 650 °C in an ultrahigh vacuum chemical vapor deposition system after ozone oxidation. The ozone oxidation of Ge substrates at optimal duration could strongly diminish Ge suboxides which should be responsible for the formation of square concave or islands in Ge epilayers. The complete removal of fully stoichiometric GeO_2 on Ge substrates by thermal annealing provided a clean surface for almost perfect Ge homoepitaxy or GeSi heteroepitaxy with a low temperature Ge epilayer. This technology would solve the dilemma of epitaxy on Ge for micro- and opto-electronic device applications.

1. Introduction

Germanium (Ge) attracted extensive studies in recent years for its high carrier mobilities, high absorptance at wavelength around 1550 nm (telecommunication wavelength), quasi-direct band structure and compatibility with standard silicon (Si) processing technology. The superiority impulses Ge to be a promising material for Si-based microelectronic and optoelectronic devices, such as metal-oxidesemiconductor field-effect-transistor, modulator, and photodetector et al [1–3]. The heteroepitaxy of Ge on Si substrate has been considerably studied from the aspects of film-growth technology to surface science. However, there is little attention on the growth of Ge or $Si_{1-x}Ge_x$ on Ge (1 0 0) surface due to two impediments mainly. For one thing, to obtain a clean substrate for further epitaxy is difficult due to various Ge suboxides which are easily formed in air and cannot be totally removed through chemical cleaning and thermal annealing [4,5]. In the existing methods of cleaning Ge substrates, ultraviolet light and oxygen plasma exposure have been demonstrated more effective than the other chemical cleaning methods. Both techniques remove carbon contamination from the Ge surface and simultaneously form an oxide passivation layer impeding the formulation of Ge suboxides [6]. For another thing, it is too hard to grow Ge homoepitaxially with a flat surface through vapor phase deposition due to a tendency of formation of islands as well as pits on Ge substrates. Actually, for ultra-high vacuum chemical vapor deposition (UHV/CVD) using germane (GH_4) as source, incoming Ge atoms from the gas phase have a much higher possibility of migrating due to GeH_x partially dangling bond terminated surface resulting in the formation of three-dimensional epilayer [7–9]. In contrast, for MBE with a solid-source, a flat surface of Ge epitaxial layer is more easily obtained than UHV/CVD with germane (GeH_4), whatever Ge substrates are cleaned and to form stable GeO_2 by chemical methods or ozone treatment [10–12]. In that case, insufficient hydrogen atoms originating from the residual gas allow the free migration of Ge adatoms and further result in formation of the two-dimensionally flat surface [13]. Zhang et al. [14] has reported that a highly perfect Ge single crystal at 400 °C employing MBE was obtained in collaboration with the ultraviolet ozone treatment to form stable GeO_2 which can be thermally decomposed due to interface reaction (GeO_2+Ge → GeO↑) on substrates to protect surface without other Ge suboxides and carbon contaminations. Bosi has reported that a flat Ge homoepitaxial layer with a good Ge/Ge interface and a low defect density was obtained by metal-organic vapor phase epitaxy (MOVPE), but multiple pits were formed on the epilayer [15]. Few years later, a perfectly adapted lattice and a barely detectable interface between the Ge epilayer and the substrate

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was obtained through MOVPE by Bosi using AsH_3 dopant [16]. However, to our knowledge, perfect Ge or SiGe epitaxial layers on Ge substrates grown by UHV/CVD have not been reported yet.

In this work, we investigate the effect of ozone treatments on Ge substrate on Ge homoepitaxy in an UHV/CVD equipment. The ozone exposure time and growth temperature are optimized, in which almost perfect crystal quality Ge and SiGe alloys with very smooth surface are epitaxially grown on Ge (0 0 1) substrates. The mechanisms on the formation of pits and islands in Ge epilayers are discussed in terms of the impact of Ge suboxides.

2. Experiments

Intrinsic Ge (1 0 0) wafers with resistivity in the range of 55–65 Ω·cm were ultrasonically immersed in acetone, alcohol and deionized (DI) water orderly to remove organic contaminants, then were dipped in diluted HCl solution to remove metals contaminants. Then Ge substrates were treated by two methods: (a) etched by HF and drying in N_2. (b) exposed to ozone in one atmosphere pressure at room temperature for various durations ranging from 15 min to 60 min after drying in N_2. Subsequently, all of the substrates were immediately loaded into chambers of UHV/CVD with a base pressure of 5×10^{-8} Pa, and then were thermally annealed from 450 °C to 700 °C for 30 min. After that, Ge thin layers were epitaxially grown on Ge substrates using GeH_4 precursor at a fixed flow rate of 5 sccm (sccm denotes cubic centimeter per minute) at various temperatures from 260 °C to 600 °C to optimize the growth temperature and ozone treatment duration. Finally, 50 nm thick Ge and 85 nm thick $Si_{0.21}Ge_{0.79}$ were grown on Ge substrates at 500 °C for 30 min, respectively, with a 70 nm thick Ge buffer layer grown at 260 °C (denotes as LT-Ge buffer). Prior to Ge epitaxy, Ge substrates were oxidized by ozone for 45 min and thermal annealed at 650 °C for 30 min in the chamber of UHV/CVD for fresh surface. For the growth of SiGe, the ratio of flow rates of Si_2H_6 to GeH_4 was about 0.5:8. The chart flow of preparation of Ge substrate and growth of Ge and SiGe epialyers are shown in Fig. 1. The surface morphologies of the samples were analyzed by atom force microscopy (AFM). The Ge oxide components were analyzed by X-ray photoelectron spectroscopy (XPS). The strain and crystal quality of Ge and GeSi were evaluated by high resolution double crystal X-ray diffraction (DCXRD) and transmission electron microscopy (TEM) Fig. 1.

3. Results and discussion

3.1. Optimization of Ge growth and thermal cleaning temperature

In order to study transition temperature between roughening and smoothing of Ge epilayer surface, Ge epilayers were grown at 260 °C, 310 °C and 600 °C, respectively, on Ge substrates etched by diluted HF and thermally annealed at 600 °C for 30 min in UHV chamber. The AFM images of surface morphology of those samples are shown in Fig. 2. It is observed that the pits are formed in the Ge epilayer grown at low temperature of 260 °C, whereas the islands are formed at comparatively high temperature of 310 °C and 600 °C. At low temperature of 260 °C, decomposition rate of GeH_4 and migration rate of Ge atoms are slow, so that the atoms have adequate time to form cluster, and then cluster is tightly fixed as a new nucleus. On the other hand, H atoms on the surface are sufficient for impeding migration of Ge atoms. Consequently, the relatively flat surface of the Ge epilayer is formed in layer-by-layer mode as judged by sharp (2 × 1) RHEED pattern (not shown), even though its RMS roughness presents a big value due to the existence of deep pits. At higher temperature of 310 °C and 600 °C, the delivery of GeH_x species to the partially dangling bond terminated at surfaces and the accelerated migration of Ge atoms result in nonuniform nucleation that creates the islands [8,13]. It is suggested that Ge epilayers should be grown at low temperature (such as 260 °C) for two dimensional flat surface. The low temperature causes low migration of Ge and low decomposition of GeH_x to make adequate H atoms on surface.

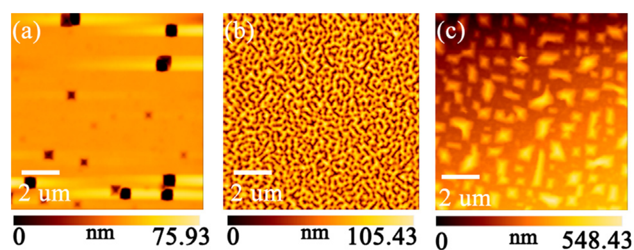

Fig. 2. AFM images (10 μm × 10 μm) of the surface morphology of Ge epilayers at (a) 260 °C, (b) 310 °C, and (c) 600 °C, respectively, with the Ge substrates thermally annealed at 600 °C for 30 min. The RMS surface roughness of Ge epilayers is 23 nm, 18 nm, 94 nm, respectively.

Inspecting the AFM image of Ge epilayer grown at low temperature of 260 °C (Fig. 2(a)) reveals that the epilayer would be quite smooth, if all of the pits are eliminated. The depth of pits is about 70 nm, indicating that the Ge substrate seems to be covered by some obstacles that cannot be removed through HF treatment and thermal annealing, resulting in nucleation of Ge atoms on surface being impeded.

In order to investigate the possible reason for the formation of deep pits, we checked the effect of thermal cleaning temperature on the surface morphology of Ge epilayer. Fig. 3(a–c) shows AFM images of the surface morphology of Ge epilayers grown at 260 °C with Ge substrates thermally annealed in UHV chamber for 30 min at 450 °C, 650 °C, and 700 °C, respectively. The number of pits was significantly reduced with increase of thermal annealing temperature from 450 °C to

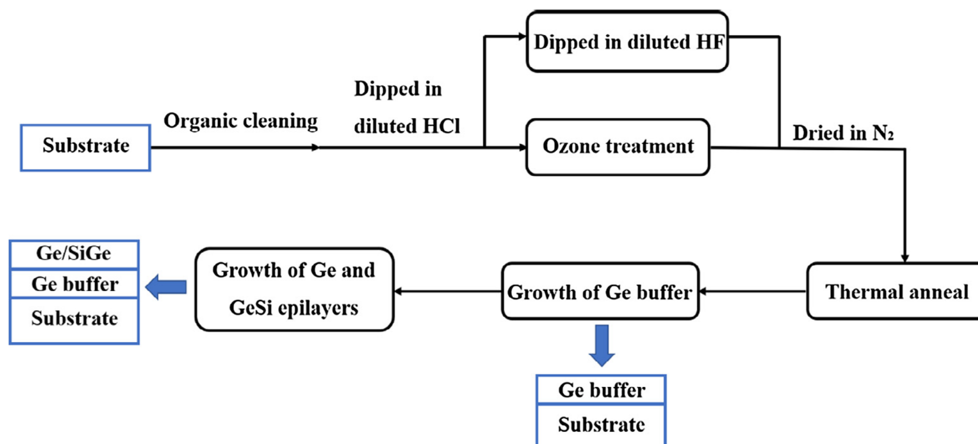

Fig. 1. Chart flow of preparation of Ge substrate and growth of Ge and SiGe epilayers.

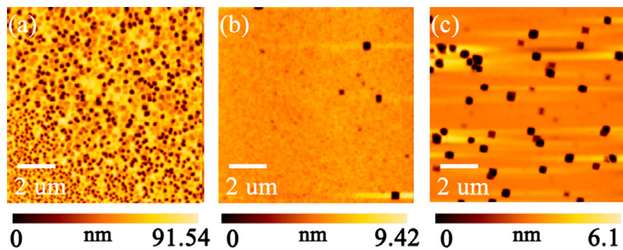

Fig. 3. AFM images (10 μm × 10 μm) of the surface morphology of Ge epilayers at 260 °C with the Ge substrate thermally annealed for 30 min at (a) 450 °C, (b) 650 °C, (c) 700 °C, respectively. The RMS surface roughness of Ge epilayers is 16 nm, 0.7 nm, 12 nm.

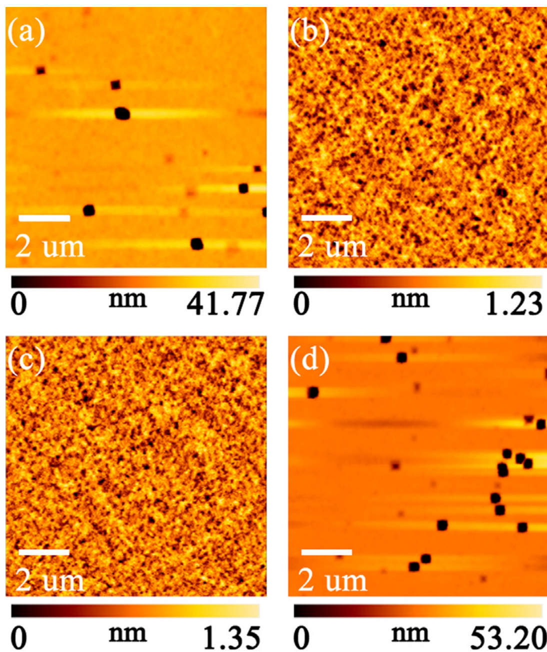

Fig. 4. AFM images (10 μm × 10 μm) of surface morphology of the Ge epilayers on Ge substrates treated with ozone oxidation for various durations. (a) 15 min, (b) 30 min, (c) 45 min, (d) 60 min. The RMS surface roughness is 4.6 nm, 0.19 nm, 0.21 nm, and 6.1 nm, respectively.

650 °C. Furthermore, when annealing temperature was raised up to 700 °C, Ge epilayer became rougher and the number of pits increased again. Those results indicate that 650 °C was optimal thermal annealing temperature that could desorb some of barriers on surface of substrate. If the annealing temperature is lower than 650 °C, hydrogen-termination and other barriers might not be desorbed from surface, leading to high density of pits in Ge epilayer. Furthermore, once the temperature is higher than 700 °C, more pits appear again, which might be due to the move and aggravation of defects. Hence, optimal thermal annealing temperature is essential of "epi-ready".

Though the Ge epilayer is relatively smooth and the density of visible pits is less than 6×10^6 cm^{-2}, the pit density is still unacceptable for device application. The nucleation obstacles cannot be completely removed from surface by thermal annealing at 650 °C or above. The amount of pits is strong evidence that obstacles on surface of substrate play an important role in forming pits, so cleaning method on Ge substrates should be improved to obtain quite clean surface for further epitaxy growth.

3.2. Thermal clean of Ge with ozone oxidation

As is well known, Si substrates can be cleaned by Radio Corporation of American (RCA) method and dried by N_2 before loading into the

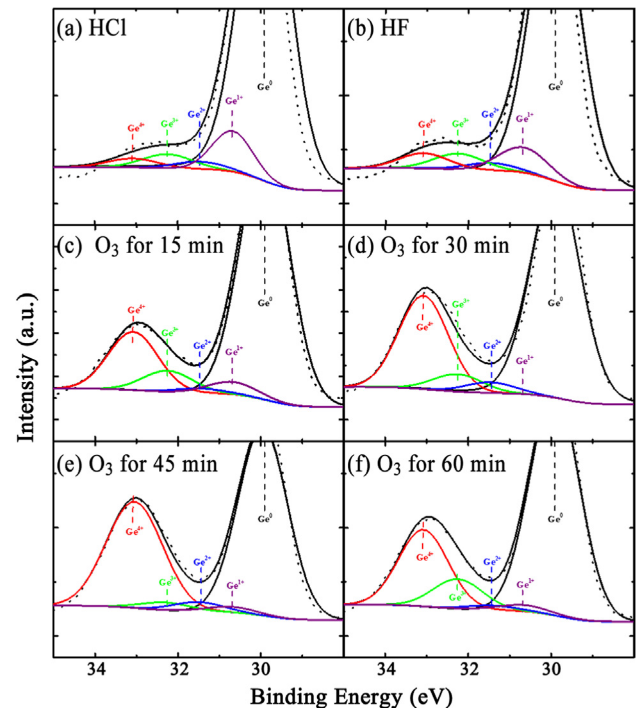

Fig. 5. Detailed Ge 3d XPS spectra with fitting curves of all samples after chemical cleaning and ozone treatment: the samples were ultrasonically immersed in acetone, alcohol and DI water orderly, then (a) dipped in dilute HCl solution, (b) clean by HF after HCl, and exposed to ozone for (c) 15 min, (d) 30 min, (e) 45 min, and (f) 60 min, respectively.

growth chamber. The last step is carried out by using aqueously chemical solution (HCl: H_2O_2: H_2O) to form newly oxide layer of stable SiO_2. The Si substrate is then transferred to UHV-CVD system to remove protective oxide layer at thermal annealing temperature ranging from 800 °C to 1100 °C for obtaining a very fresh surface for further epitaxial growth. However, for Ge substrate, it is too difficult to form an oxide layer of stable GeO_2 in aqueously chemical solution since GeO_2 is soluble in water with a solubility of 5.2 g/l [4]. On the other hand, although HF cleaning after HCl can remove GeO_2 and form H-terminated surfaces, suboxide still remains and a perfect hydrogen-terminated surface cannot be achieved, even by solutions with very high HF concentration [17].

Therefore, as mentioned above, cleaning method should be developed to grow a stable oxide layer of GeO_2 and then eliminate all of obstacles on surface in UHV chamber. From this point of view, Ge substrates were exposed to ozone to grow a protective oxide layer might be the possible way to achieve clean surface. In order to determine the effect of ozone oxidation, Ge substrates were exposed to ozone in one atmosphere pressure at room temperature for various durations ranging from 15 min to 60 min. After that, the Ge substrates were thermally annealed at 650 °C for 30 min in the UHV chamber and then 70 nm Ge layer was grown at 260 °C. The AFM images of the samples are shown in Fig. 4. It is clearly seen that the RMS roughness of Ge epilayers for the samples treated in ozone for 30 min and 45 min is quite smooth without any pits, whereas there are some pits in Ge epilayers for the samples treated in ozone for 15 or 60 min. The density of pits is more than 1.5×10^7 cm^{-2} and the depth of those pits is near 50 nm. Those results indicate that nucleation obstacles still exit after the Ge substrate exposure to ozone for 15 min and present again after 60 min. Carbon contamination and Ge substoichiometric oxides might be responsible for the pits formation.

To verify our speculation, Ge oxide components on surfaces of Ge substrates after the chemical cleaning and ozone treatment were analyzed using XPS. In XPS measurements, the take-off angle of the

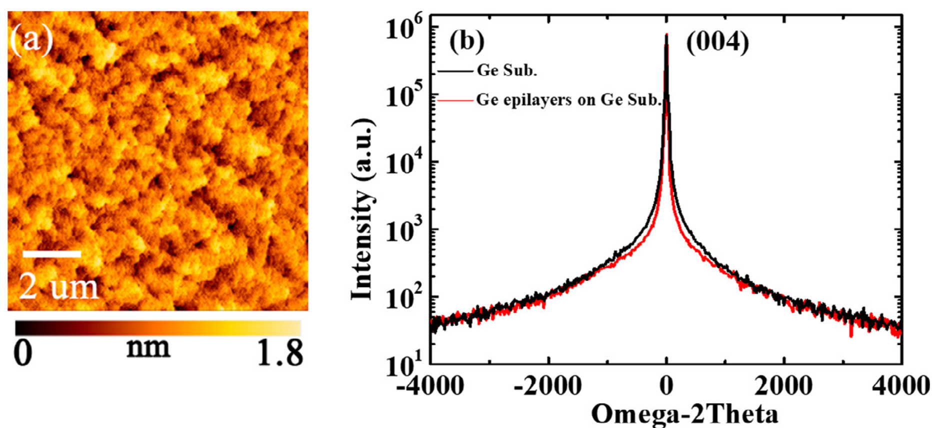

Fig. 6. (a) AFM image of surface morphology of Ge epilayer. The RMS roughness is about 0.26 nm and (b) DCXRD rocking curves of (0 0 4) facet of Ge substrate and Ge epilayer on Ge substrate.

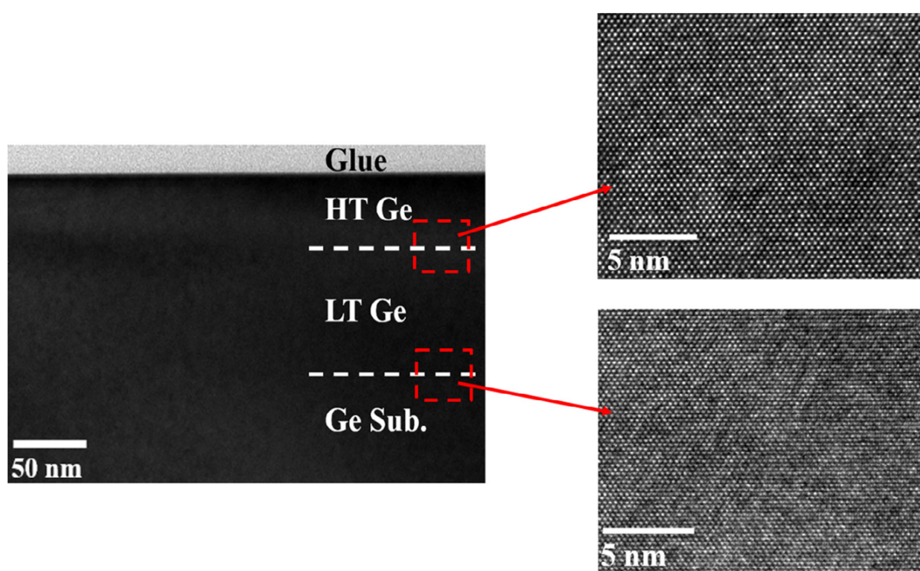

Fig. 7. Cross-sectional TEM images of Ge epilayers on Ge substrate.

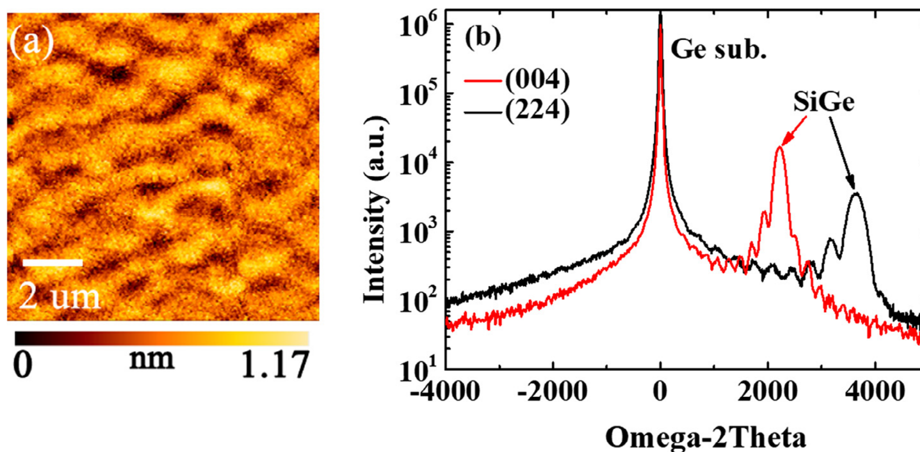

Fig. 8. (a) AFM image of the surface morphology of $Si_{0.21}Ge_{0.79}$ layer. The RMS surface roughness is 0.18 nm and (b) HRXRD rocking curves of (0 0 4) and (2 2 4) facets of fully stained SiGe epilayer on Ge substrate.

photoelectrons from these samples was set up to 45° in order to enhance signals from surfaces. The XPS spectra were fitted with that Ge^{0}, Ge^{1+}, Ge^{2+}, Ge^{3+} and Ge^{4+} peak positions are set as 29.9 eV, 30.68 eV, 31.47 eV, 32.25 eV, and 33.08 eV, respectively, and the full width at half maximum (FWHM) of Ge^{4+} peak is set as the same value of 1.4 eV [18,19]. The detailed Ge 3d XPS spectra with fitting curves of all of the samples after chemical cleaning and ozone treatment for 15–60 min are shown in Fig. 5.

Fig. 5(a) and (b) show XPS spectra of Ge wafers after etched with HCl and HF, in which various chemical states of Ge can be distinguished by fitting the XPS peaks. Chemical states including Ge^{1+}, Ge^{2+}, Ge^{3+} and Ge^{4+} can be clearly observed after Ge wafers are treated by HCl. For the Ge wafers after HF cleaning, the chemical states can still be distinguished clearly although the relative peak intensities presenting various chemical states are changed.

When Ge wafers are exposed to ozone after HCl cleaning, suboxide can be easily oxidized to higher oxidation states. As shown in Fig. 5(c), the XPS peaks of Ge^{4+} and Ge^{3+} can be fitted clearly distinguishing Ge^{2+} and Ge^{1+} components. When the samples are exposed to ozone for 30–45 min, it can be seen that Ge suboxides decrease due to increasing oxidation time, as shown in Fig. 5(d–e), suggesting that lots of the Ge suboxides have been transformed into Ge^{4+} component. In other words, stable GeO_2 with a few of Ge suboxides is successfully grown under ozone treatment for 30–45 min. When oxidation time increases to 60 min, Ge suboxides appear again especially Ge^{3+} component, as shown in Fig. 5(f). It can be attributed to the retardation of oxygen diffusion into the interface between Ge and oxide with the increase of thickness of Ge oxides along with oxidation time. The insufficient of oxidant at the Ge interface causes the formation of substoichiometric oxides again. Those results suggest that the pits in the Ge epilayers might be originated from suboxide components on Ge surface, which cannot be removed completely by subsequently thermal annealing in UHV chambers. The better way to avoid the formation of pits is to form Ge^{4+} component only.

3.3. Growth of Ge and GeSi epilayers on ozone-treated Ge substrates

In order to confirm the cleaning method of Ge substrate, two samples of 50 nm thick Ge and 85 nm thick $Si_{0.21}Ge_{0.79}$ layer were grown at 500 °C on LT Ge buffer layer on ozone-treated Ge wafers, respectively. Fig. 6 shows the AFM images and DCXRD rocking curves of the sample with 50 nm Ge. The surface is very smooth and the RMS surface roughness is only about 0.26 nm for 10 µm × 10 µm scaling. Full width at half maximum (FWHM) of Ge (0 0 4) XRD peak is similar with that of Ge substrate within the experimental error, demonstrating the achievement of high crystal quality of the Ge epilayers. The cross-sectional TEM images of the samples and corresponding atomic high resolution images are shown in Fig. 7. No obvious interface between Ge and LT-Ge buffer, as well as LT-Ge buffer and Ge substrate, can be detected and only a few of defects can be observed at the LT-Ge buffer regions. Growth of high crystal quality Ge on Ge substrate treated by ozone oxidation with LT-Ge buffer layer has been demonstrated successfully.

Fig. 8 shows AFM image and DCXRD rocking curves of a 85 nm thick $Si_{1-x}Ge_x$ layer grown at 500 °C on ozone-treated Ge substrate. Prior to the growth of $Si_{1-x}Ge_x$ layer, 70 nm thick Ge epilayer was grown at 260 °C. The RMS surface roughness is only about 0.18 nm. The Ge content x and tensile strain in the $Si_{1-x}Ge_x$ layer is evaluated about 0.79 and 0.89%, respectively. Those results demonstrate that high crystal quality, almost fully strained SiGe epilayer with high Ge content can be successfully grown on Ge substrates treated with ozone oxidation. This technique would be helpful for realization of high performance Ge-based optoelectronic devices.

4. Conclusion

High crystal quality Ge and SiGe with high Ge content has been grown on ozone-treated Ge substrates with a LT Ge buffer layer in an UHV/CVD system. Ge substrates exposed to ozone in one atmosphere pressure at room temperature for optimal duration could strongly diminish Ge substoichiometric oxides, rendering clean surface of Ge after thermal annealing in UHV chamber and smooth surface of epitaxial Ge layer without pits. The experimental evidence suggests that Ge suboxide components cannot be well removed by thermal annealing in the UHV chamber, which acts as nucleation obstacles to be responsible for the formation of pits in the Ge epilayers.

Acknowledgements

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