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Si/Si_{1-x}Ge_x/Si heterostructure growth by ultraclean low-temperature LPCVD for the fabrication of novel heterodevice

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Abstract.—Low-temperature epitaxial growth of Si/Si_{1-x}Ge_x/Si heterostructures at high Ge fractions on Si(100) was investigated under the cleanest possible reaction environment of SiH₄, GeH₄ and H₂ or Ar using an ultraclean hot-wall low-pressure chemical vapour deposition (LPCVD) system. It was found that relatively lower deposition temperatures were suitable for higher Ge fractions in order to prevent island growth of the layers during deposition. Atomically flat surfaces and interfaces for the heterostructure containing Si_{0.8}Ge_{0.2}, Si_{0.5}Ge_{0.5} and Si_{0.3}Ge_{0.7} layers were obtained by deposition at 550, 500 and 450°C, respectively. Cross-sectional transmission electron microscope (TEM) images and Raman spectra show that such samples have excellent epitaxial qualities which are not degraded by wet oxidation for 2 hours at 700°C. The Si_{0.5}Ge_{0.5}-channel metal-oxide-semiconductor field-effect transistor (MOSFET) having a flat surface has the highest peak field-effect mobility, resulting in the large mobility enhancements of about 70% at 300K and over 150% at 77K compared with those of the MOSFET without the Si_{1-x}Ge_x-channel.

1.—Introduction.

The low-temperature epitaxial growth of Si/Si_{1-x}Ge_x/Si heterostructure has attracted interest for utilizing the improved hole mobility in p-channel MOSFET's [1-3] as well as in heterojunction bipolar transistors [4]. As a growth method, CVD offers many advantages, such as high throughput, in-situ doping and selective deposition. Recently, improvements in the quality of gases and CVD equipment have enabled low-temperature epitaxial growth processing [5-8]. For excellent Si_{1-x}Ge_x-channel pMOSFET's, high Ge fractions in the strained Si_{1-x}Ge_x layer are necessary. However, devices with an expected good performance have been fabricated only for Si_{1-x}Ge_x layers with x around 0.25 or less, deposited by use of CVD [1-2]. At a higher Ge fraction, heterojunction appears to be degraded by island growth as well as by generation of misfit dislocations due to the larger mismatch between the Si and Si_{1-x}Ge_x layers [9]. Therefore, it is important that the epitaxial growth process of the Si/Si_{1-x}Ge_x/Si heterostructure is optimized in order to obtain atomically flat surfaces and interfaces at high Ge fractions. In the present work, a low-temperature epitaxial growth process of the Si/Si_{1-x}Ge_x/Si heterostructure has been investigated under the cleanest possible reaction environment of SiH₄, GeH₄ and H₂ or Ar using an ultraclean hot-wall low-pressure CVD system [7], enabling to achieve Si/Si_{1-x}Ge_x/Si heterostructures with atomically flat surfaces and interfaces for high Ge fractions. In addition, high-performance Si_{1-x}Ge_x-channel pMOSFET's has also been achieved.

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Fig.1.-Schematic diagram of an ultraclean hot-wall LPCVD system.

Fig.2.-Typical process sequence for Si/Si_{1-x}Ge_x/Si heterostructure growth by ultraclean hot-wall LPCVD system.

2.-Contamination-minimized LPCVD processing.

The ultraclean hot-wall LPCVD system used in our experiments is schematically shown in Figure 1 [7]. The LPCVD system was made ultrahigh vacuum compatible with gate valves and a turbo molecular pump system. The turbo molecular pump system was improved to vacuum-evacuate from atmospheric pressure. To minimize air-contamination in the reactor during the wafer load and unload, a N₂ purged transfer chamber was combined with the reactor inlet. The typical process sequence for Si/Si_{1-x}Ge_x/Si heterostructure growth is shown in Figure 2. The substrates used were n-type Si wafers of 1-3 ohm-cm with mirror polished (100) surfaces. The wafers were cleaned in several cycles in a 4:1 solution of H₂SO₄ and H₂O₂, high-purity DI water, and 1% HF with a final rinse in DI water, and the wafers, placed on a quartz boat, were transported into the reactor under ultraclean N₂ atmosphere through the transfer chamber. After closing the gate valve, the N₂ flow stopped and the reactor tube was purged with high-purity H₂. In order to prevent any contamination from the exhaust line, the wafers were transported into the reactor at a reactor temperature of about 100°C, and then heated-up to the deposition temperature while purging with H₂ gas under a pressure of about 200 Pa [8]. All three layers of the Si/Si_{1-x}Ge_x/Si sandwich were grown by thermal decomposition of SiH₄ and GeH₄. To reduce oxygen and carbon pile-up at the interface between the deposited layer and the Si substrate, a Si buffer layer was deposited at 750°C on the Si substrate because impurities adsorbed on substrate were reduced by both thermal desorption and reduction by SiH₄ at 750°C as shown in Figure 3. The strained Si_{1-x}Ge_x layer with a typical thickness of 7 nm was deposited at rather low temperatures between

450 and 550°C. Finally, on the top of this heterostructure, a 10 nm-thick Si capping layer was deposited at temperatures between 500 and 550°C. For the deposition of the $\text{Si}_{1-x}\text{Ge}_x$ and the Si capping layers, the total gas pressure was about 25 Pa, and the partial pressures of SiH_4 and GeH_4 were in the range 1-1.4 and 0.03-0.75 Pa, respectively, with H_2 or Ar as carrier gas. Here, the moisture levels of N_2 , H_2 and SiH_4 gases used were 10 ppb or lower and that of GeH_4 was 23 ppb or lower at the reactor inlet.

Fig.3.-Depth-profiles of oxygen and carbon in the Si epitaxial growth sample, evaluated by secondary ion mass spectrometry. (a) and (b) are the results for the deposition at 600 and 750°C after heating-up from about 100°C. (c) is the result for the deposition at 600°C after pre-heating at 750°C.

3.-Si/Si_{1-x}Ge_x/Si heterostructure growth at high Ge fractions.

The influence of the deposition temperatures for the $\text{Si}_{1-x}\text{Ge}_x$ and Si capping layers, and of the Ge fraction of the $\text{Si}_{1-x}\text{Ge}_x$ layer on the surface morphology, observed by scanning tunneling microscopy (STM) is shown in Figures 4 and 5. It is found that a lower temperature during $\text{Si}_{1-x}\text{Ge}_x$ and Si capping layer depositions results in a smoother surface. At a Ge fraction around 0.2, atomically flat surfaces and interfaces can be obtained by depositing $\text{Si}_{1-x}\text{Ge}_x$ and Si capping layers at 550°C. For higher Ge fractions, however, much lower deposition temperatures are suitable, namely 500°C for a $\text{Si}_{0.5}\text{Ge}_{0.5}$ layer and 450°C for a $\text{Si}_{0.3}\text{Ge}_{0.7}$ layer, respectively, although no change of heterostructure surfaces with a Ge fraction around 0.7 was detected after the capping layer deposition at temperatures of 550°C or less [10]. The values of surface microroughness, obtained for the heterostructures containing the $\text{Si}_{1-x}\text{Ge}_x$ layers with $x=0.2$, 0.5 and 0.7 deposited at 550, 500 and 450°C, respectively, are comparable to that of the substrate (average surface microroughness < 0.4nm). Our results mentioned above clearly show that lowering the deposition temperature of the $\text{Si}_{1-x}\text{Ge}_x$ layers is necessary with increasing the Ge fraction to prevent island growth of the heterostructure. By electron diffraction measurements, Kikuchi lines were observed for such heterostructure samples as also shown in Figure 5.

Fig.4.-STM surface morphology of Si/Si_{1-x}Ge_x/Si heterostructures, where the Si_{1-x}Ge_x layer and the Si capping layer were deposited at 500 and 550°C. The deposition rate of Si_{0.8}Ge_{0.2}, Si_{0.5}Ge_{0.5} and Si_{0.3}Ge_{0.7} layers at 500°C were 0.46, 4.6 and 22nm/min, and those at 550°C were 9.7, 17 and 28nm/min, respectively. The deposition rates of the capping layer at 500°C and 550°C were 0.11 and 0.43nm/min respectively.

Fig.5.-STM surface morphology and electron diffraction pattern of Si/Si_{0.3}Ge_{0.7}/Si heterostructure, where the Si_{0.3}Ge_{0.7} and Si capping layers were deposited at 450 and 500°C, respectively. The deposition rate of Si_{0.3}Ge_{0.7} layer was 3.7nm/min.

Cross-sectional TEM images of Si/Si_{1-x}Ge_x/Si heterostructures are shown in Figure 6. In the case of Si/Si_{0.8}Ge_{0.2}/Si and Si/Si_{0.5}Ge_{0.5}/Si heterostructures deposited at 500°C with a flat surface shown in Figure 4, atomically flat interfaces are observed and the lattice image has no misfit dislocations as shown in Figures 6(a) and 6(b). In the case of Si/Si_{0.3}Ge_{0.7}/Si heterostructure deposited at 500°C with rough surfaces shown in Figure 4, island growth of the Si_{0.3}Ge_{0.7} layer is observed and dislocations are observed in the island growth region as shown in Figure 6(c). We believe that the critical thickness was exceeded in the island growth region. In the case of Si/Si_{0.3}Ge_{0.7}/Si heterostructure containing Si_{0.3}Ge_{0.7} layer deposited at 450°C with a flat surface shown in Figure 5, atomic order flat interfaces are observed, however, the interface position is indistinguishable as shown in Figure 6(d). By wet oxidation for 2 hours at 700°C to perform gate oxide formation, the interface position tends to become more vague than that without oxidation, comparing Figure 6(e) with Figure 6(b), but defect generation is not observed as seen in Figures 6(e) and 6(f). These results mean the possibility of interdiffusions between Si and Ge during Si/Si_{0.3}Ge_{0.7}/Si heterostructure growth and oxidation [11]. About the interdiffusions, further investigations are necessary.

Fig.6.- Cross-sectional TEM images of Si/Si_{1-x}Ge_x/Si heterostructures, where Si_{1-x}Ge_x layers of (a), (b) and (c) with the Ge fractions x of 0.2, 0.5 and 0.7, respectively, were deposited at 500°C under the conditions shown in Figure 4, and the deposition condition of (d) is the same as that in Figure 5. The samples of (e) and (f) were after wet oxidation for 2 hours at 700°C of the samples (b) and (d). Arrows indicate the interfaces in the heterostructure.

Fig.7.-Raman spectra of Si/Si_{0.5}Ge_{0.5}/Si heterostructure of Figure 6(b). The configurations of top and bottom spectra are $\bar{Z}(X,Y)Z$ and $\bar{Z}(X,X)Z$, respectively, where X, Y and Z denote [00 $\bar{1}$], [010] and [100]. The resolution of the spectrometer was set at 5cm⁻¹.

Fig.8.-Relationship between Raman intensity ratio of Ge-Ge peak to Si-Ge peak and Ge fraction determined by x-ray diffractometry for thicker relaxed Si_{1-x}Ge_x layers.

For the above samples, the Ge fraction x in very thin Si_{1-x}Ge_x layers was estimated from the lattice constant of a thicker relaxed Si_{1-x}Ge_x layer, deposited under the same conditions. For a cross check, the Ge fraction x in the very thin Si_{1-x}Ge_x layer of the heterostructure was directly estimated by Raman spectroscopy. The Raman spectra for the sample of Figure 6(b) are shown in Figure 7. The polarization selection rules of the Ge-Ge and the Si-Ge vibrations of the Si_{0.5}Ge_{0.5} layer are the same as that of the optical phonon of the Si(100) substrate. Figure 8 shows the relationship between Raman intensity ratio of Ge-Ge peak to Si-Ge peak and Ge fraction determined by x-ray diffractometry for thicker relaxed Si_{1-x}Ge_x layers. From Figures 7 and 8, the real Ge fraction is estimated to be about 0.5, which is nearly equal to that in the thicker relaxed layer. By wet oxidation for 2 hours at 700°C, the Raman spectra shown in Figure 7 scarcely changed although the decrease of Raman intensity ratio of Ge-Ge peak to Si-Ge peak was observed. Therefore, it is expected that the crystal qualities are not degraded by the above oxidation processing. It should be noted that the degradation of Ge profile was not observed by the above processing within the detection limit of x-ray photoelectron spectroscopy [10].

3.-Fabrication of a $\text{Si}_{1-x}\text{Ge}_x$ -channel MOSFET.

The MOSFET's with a 100 μm gate length and 300 μm width were fabricated on the $\text{Si}/\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ heterostructures deposited under the same conditions as the sample shown in Figure 6 using self-aligned Si gate process [12]. A 700nm field oxide was formed at 400 $^{\circ}\text{C}$ by CVD. A 10nm gate oxide was thermally grown by wet oxidation at 700 $^{\circ}\text{C}$. Then, in-situ phosphorous doped n^+ -polysilicon was deposited. The source /drain was formed by B^+ implantation ($1.2 \times 10^{15} \text{cm}^{-2}$ at 25keV). All anneal processes were performed at temperatures below 700 $^{\circ}\text{C}$.

Figure 9 shows threshold voltage and peak field-effect mobility of $\text{Si}_{1-x}\text{Ge}_x$ -

Fig.9-Threshold voltage and peak field-effect mobility of $\text{Si}_{1-x}\text{Ge}_x$ -channel MOSFET

channel MOSFET's having flat surfaces [12]. The $\text{Si}_{0.5}\text{Ge}_{0.5}$ -channel MOSFET having a flat surface has the highest peak field effect mobility (240 cm^2/Vs at 300k and 1500 cm^2/Vs at 77K), resulting in the large mobility enhancement of about 70% at 300K and over 150% at 77K compared with those of the MOSFET without a $\text{Si}_{1-x}\text{Ge}_x$ -channel [12]. This mobility enhancement is excellent compared with those reported by other investigators(1,2). The subthreshold slopes (about 80 mV/decade at 300K and about 30 mV/decade at 77K) of the $\text{Si}_{0.5}\text{Ge}_{0.5}$ -channel MOSFET were comparable to those of the MOSFET without a $\text{Si}_{1-x}\text{Ge}_x$ -channel. This indicates that defect density in the $\text{Si}_{0.5}\text{Ge}_{0.5}$ layer is low. On the other hand, the $\text{Si}_{0.3}\text{Ge}_{0.7}$ -channel MOSFET has larger threshold voltage and lower peak field-effect mobility, compared with those of the $\text{Si}_{0.5}\text{Ge}_{0.5}$ -channel MOSFET. Since the band gap of an unstrained $\text{Si}_{1-x}\text{Ge}_x$ layer decreases with decreasing Ge fraction and is larger than that of a strained layer [13], as is well known, it is considered that the Ge fraction decreases, and/or the heterostructure becomes unstrained by generating defects although such defects were not observed in Figure 6(f), during device fabrication. It is also found that the $\text{Si}_{0.3}\text{Ge}_{0.7}$ -channel with a rough surface, where the $\text{Si}_{0.3}\text{Ge}_{0.7}$ and capping layers were deposited at 500 $^{\circ}\text{C}$ (shown in Figure 6(c)), had markedly poor characteristics, that is, very low peak field effect mobility (51 cm^2/Vs at 300K and 55 cm^2/Vs at 77K) and very large leakage current. This result indicates that the nanometer order surface roughness of the heterostructure degrades the device performance. It was reported that the mobility of MOSFET with a $\text{Si}_{0.6}\text{Ge}_{0.4}$ -channel

was lower than that with a $\text{Si}_{0.7}\text{Ge}_{0.3}$ -channel, where both heterostructures were grown at around 600°C [1]. This reported finding should be caused by island growth of the $\text{Si}_{0.6}\text{Ge}_{0.4}$ layer. Our results mentioned above clearly show that lowering of the deposition temperatures of the $\text{Si}_{1-x}\text{Ge}_x$ layers is more essential for high Ge fraction to prevent island growth of the heterostructure. For improving MOSFET's with x around 0.7, further investigations will be necessary.

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