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Fabrication of high quality strained SiGe on Si substrate by RPCVD

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In this study, the growth kinetics of SiGe in a reduced pressure chemical vapor deposition system using dichlorosilane (SiH_2Cl_2) and germane (GeH_4) as the Si and Ge precursors were investigated. The SiGe growth rate and Ge content were found to depend on the deposition temperature, GeH_4 flow and reactor chamber pressure. The SiGe growth rate escalates with increasing deposition temperature, while the Ge content is reduced. The SiGe growth rate accelerates with increasing GeH_4 flow, while the Ge content increases more slowly. According to the experimental data, a new relationship between Ge content (x) and $F(GeH_4)/F(SiH_2Cl_2)$ mass flow ratio is deduced: $x^{2.5}/(1-x) = nF(GeH_4)/F(SiH_2Cl_2)$. The SiGe growth rate and Ge content improve with increasing reactor chamber pressure. By selecting proper precursor flows and reactor pressure, SiGe films with the same Ge content can be fabricated at various temperatures. However, the quality of the SiGe crystals is clearly dependent on the deposition temperature. At lower deposition temperature, higher crystalline quality is achieved. Because the growth rate dramatically drops with lower temperatures, the optimum growth temperature must be a compromise between the crystalline quality and the growth rate. X-ray diffraction, Raman scattering spectroscopy and atomic force microscopy results indicate that 650°C is the optimum temperature for fabrication of $Si_{0.75}Ge_{0.25}$ film.

SiGe, epitaxial growth, growth rate, Ge content

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Over the years, there has been keen interest in fabricating high performance metal oxide semiconductor field effect transistors (MOSFETs) with strained Si/SiGe channels [1–3], as the carrier mobility in the strained layer is notably enhanced compared with that of Si MOSFETs. Defects in the strained layer, however, degrade carrier mobility and increase the leakage current. Thus, the crystal quality of the strained layer is an important factor in improving the performance of the MOSFETs. High quality strained SiGe/Si heterostructures can be fabricated by molecular beam epitaxy (MBE) [4,5] or by chemical vapor deposition (CVD) [6,7]. Compared with MBE, CVD technology is more satisfactory for industrial semiconductor production.

Several CVD technologies, such as atmospheric pressure CVD (APCVD) [8,9], ultra-high vacuum CVD [10], and reduced pressure CVD (RPCVD) [11,12], have been applied to fabricate SiGe/Si heterostructures. Among them, RPCVD is the most convenient method to grow high quality SiGe layers at reasonable growth rates in the semiconductor industry [13–15].

During SiGe deposition in an RPCVD chamber, all the growth parameters such as deposition temperature, Ge/Si precursor flow ratio and reactor chamber pressure can affect the SiGe growth rate and Ge content; thus SiGe layers with the same Ge content can probably be grown with different combinations of growth parameters. However, their crystal-

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line quality may differ distinctly. In fact, the growth parameters have a crucial role in reducing the defect density. Thus, research on how the SiGe growth rate and Ge content depend on growth parameters serves as the basis for selecting appropriate parameters to fabricate high quality strained SiGe.

1 Experimental

All the strained SiGe samples were grown on p-type Si(100) substrates (10–20 Ω cm) in an Epsilon 2000 ASM CVD system, which is a horizontal, single wafer, load-locked reactor. Before SiGe films were deposited, Si substrates were cleaned in the standard RCA-1 and RCA-2 solutions and rinsed in deionized water. After the Si substrate was loaded into the chamber, an *in-situ* bake in H_2 at 1060°C was performed to remove any remaining oxide. Keeping the reactor chamber pressure at 1.33–10.64 kPa, epitaxial growth was carried out at 550–900°C using dichlorosilane (SiH_2Cl_2) as the Si precursor and 10% germane (GeH_4) in H_2 as the Ge precursor. During deposition, the flow of H_2 carrier gas was set at a fixed value of 20 slms, and the flow of SiH_2Cl_2 at a fixed value of 75 sccms. The structural properties of the SiGe samples were investigated by high-resolution X-ray diffraction (XRD), Raman scattering spectroscopy and atomic force microscopy (AFM).

2 Results and discussion

2.1 The dependence of SiGe growth rate and Ge content on deposition temperature

After growing pseudomorphic SiGe/Si heterostructures using particular deposition parameters, the thickness and Ge content of the SiGe layers were determined by X-ray diffraction. Since the XRD peak of relaxed SiGe moves towards higher diffraction angles with increasing extent of relaxation, the exact Ge content can only be extracted from the XRD pattern once the relaxation degree of the SiGe sample has been determined. Figure 1 shows the high resolution XRD patterns of SiGe samples fabricated at varied deposition temperatures with fixed precursor flow and reactor chamber pressure. The presence of thickness interference peaks in these XRD spectra indicates that all these SiGe samples are fully strained, i.e., their relaxation degrees are all 0%. As the deposition temperature declines, the SiGe peak deviates away from the Si substrate peak, which means that the Ge concentration has increased. However, when the temperature drops to 550°C, the SiGe peak disappears from the XRD pattern (not shown in Figure 1), because it is difficult to decompose SiH_2Cl_2 at this temperature. For those SiGe samples fabricated at 600–900°C, the SiGe layer thickness and the Ge concentration were extracted based on the Takagi-Taupin dynamical scattering theory [16].

Table 1 lists the Ge content and growth rate (thickness/

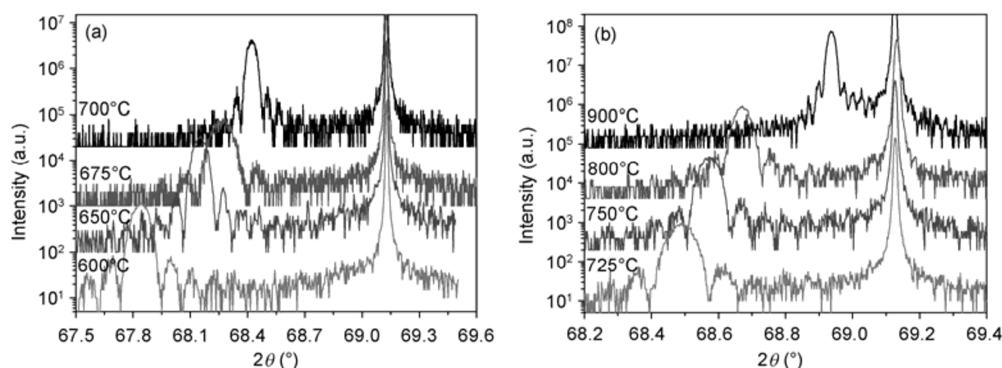

Figure 1 XRD patterns of SiGe samples deposited at different temperatures with fixed precursor flow and reactor chamber pressure.

Table 1 Dependence of SiGe growth rate (GR) and Ge content on deposition temperature at fixed reactor pressure and precursor flows

Temperature (°C)	SiGe GR (nm/min)	Ge (%)	Ge GR (nm/min)	Si GR (nm/min)	Ge:Si composition ratio
600	3.5	24.4	0.85	2.65	0.32
650	6.7	18.4	1.23	5.47	0.23
675	10	17.0	1.7	8.3	0.2
700	20	14.4	2.88	17.12	0.17
725	40	12.4	4.96	35.04	0.14
750	51.7	10.8	5.58	46.12	0.12
800	83	9	7.4	75.5	0.10
900	200	5.5	11	189	0.06

deposition time) determined from the XRD patterns of Figure 1. As shown in Table 1, the SiGe growth rate rises sharply from 3.5 to 200 nm/min when the temperature increases from 600 to 900°C, but the Ge content decreases from 24.4% to 5.5% over this temperature range. The SiGe samples fabricated at 800 and 900°C are particularly noteworthy. Although the deposition temperature is rather high, the SiGe layers remain fully strained (as confirmed from Raman spectra, which are not shown here) because of the low Ge content. Based on the Ge content and SiGe growth rate, the respective growth rates of Si and Ge in the SiGe layer were calculated and plotted in Figure 2 as a function of the inverse absolute temperature. It can easily be seen from this Arrhenius plot that the Si and Ge growth rates are thermally activated. The calculated activation energies for Si and Ge are 1.79 and 1.27 eV, respectively. According to Figure 2, the relationships between the Si growth rate (R_{Si}), Ge growth rate (R_{Ge}) and absolute temperature (T) can be described as

$$R_{\mathrm{Si}} \approx C_{\mathrm{Si}} \mathrm{e}^{-\frac{E_{\mathrm{A(Si)}}}{kT}}, \tag{1}$$

$$R_{\mathrm{Ge}} \approx C_{\mathrm{Ge}} \mathrm{e}^{-\frac{E_{\mathrm{A(Ge)}}}{kT}}, \tag{2}$$

where C_{Si} and C_{Ge} are constants, and $E_{\mathrm{A(Si)}}$ and $E_{\mathrm{A(Ge)}}$ are activation energies for Si and Ge growth, respectively. The relationship between the Ge content (x) of the SiGe layer and the deposition temperature can be deduced from eqs. (1) and (2):

$$\frac{x}{1-x} = \frac{R_{\mathrm{Ge}}}{R_{\mathrm{Si}}} \approx C_1 \mathrm{e}^{\frac{E_{\mathrm{A(Si)}} - E_{\mathrm{A(Ge)}}}{kT}} \quad (873\ \mathrm{K} \leqslant T \leqslant 1173\ \mathrm{K}), \tag{3}$$

where $E_{\mathrm{A(Si)}} - E_{\mathrm{A(Ge)}}$ is equal to 0.52 eV, and C_1 is a constant. Eq. (3) can be rewritten as

$$\ln\left(\frac{x}{1-x}\right) \approx \ln C_1 + C_2 \frac{1}{T} \quad (873\ \mathrm{K} \leqslant T \leqslant 1173\ \mathrm{K}), \tag{4}$$

where C_2 is a constant. The inset of Figure 2 shows the relationship between the actual Ge:Si content ratio and the inverse absolute temperature; the graph agrees with eq. (4).

2.2 Dependence of SiGe growth rate and Ge content on GeH_4 flow

As shown in Figure 3(a), the SiGe growth rate accelerates with increasing GeH_4 flow; the Ge content, however, climbs more slowly. Since the steady state concentration of free Ge sites is much higher than that of free Si sites during deposition of SiGe by RPCVD, equilibrium is achieved by transferring the H adatoms from Si to Ge. As the energy barrier for H_2 desorption from the Ge surface is lower than that for H_2 desorption from the Si surface, the growth rate enhancement with increasing GeH_4 flow can be explained by the lowering of energy barriers for hydrogen desorption

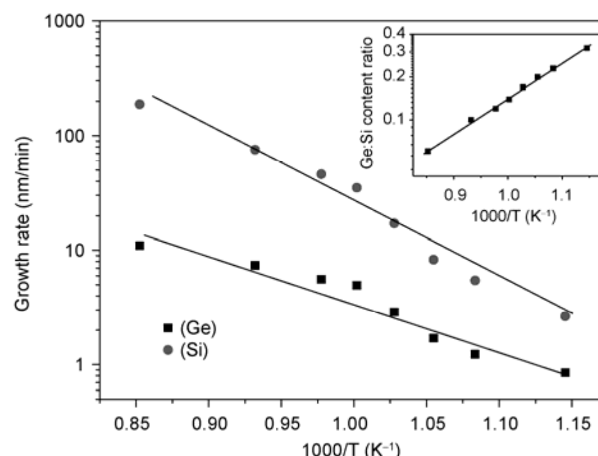

Figure 2 The growth rates of Si and Ge in the SiGe layer as a function of the inverse absolute temperature. The inset shows the dependence of Ge:Si content ratio on deposition temperature.

[17–20]. According to the literature [13,21], the ratio of $x^2/(1-x)$:F(GeH_4)/F(SiH_2Cl_2) should be a constant if the flows of H_2 carrier gas, HCl and SiH_2Cl_2 are all fixed. Our experimental data, however, indicate that a constant ratio is only obtained when the exponent of Ge content (x) is modified to give $x^{2.5}/(1-x)$:F(GeH_4) /F(SiH_2Cl_2), as shown in Figure 3(b). When F(HCl) = 0 and F(SiH_2Cl_2)/F(H_2) = 0.00375, the ratio $x^{2.5}/(1-x)$:F(GeH_4)/F(SiH_2Cl_2) is 0.7. Compared with the reported result [21], our revised relationship implies that a higher Ge content could be obtained if SiGe films were deposited with the same parameters. Considering the effect of temperature on SiGe epitaxy, a reasonable explanation for this difference is that our actual epitaxial temperature is lower than the nominal temperature, because the thermocouple is not in contact with the Si substrate when SiGe is deposited.

2.3 Dependence of SiGe growth rate and Ge content on reactor chamber pressure

The SiGe growth rate and Ge content as a function of reactor chamber pressure are plotted in Figure 4. The striking improvement in the SiGe growth rate is because more Si and Ge precursors are supplied with increasing reactor chamber pressure. A high reactor chamber pressure produces substantial quantities of Cl-based molecules, which, in turn, suppresses the decomposition of SiH_2Cl_2. As a result, the Ge content increases with the reactor chamber pressure.

2.4 The fabrication of high quality strained SiGe

The above analysis suggests that although SiGe layers with the same Ge content can be fabricated at different temperatures, the crystalline quality is, to a great extent, affected by the deposition temperature. Figure 5 shows the XRD patterns of two SiGe samples fabricated at 650°C (sample A)

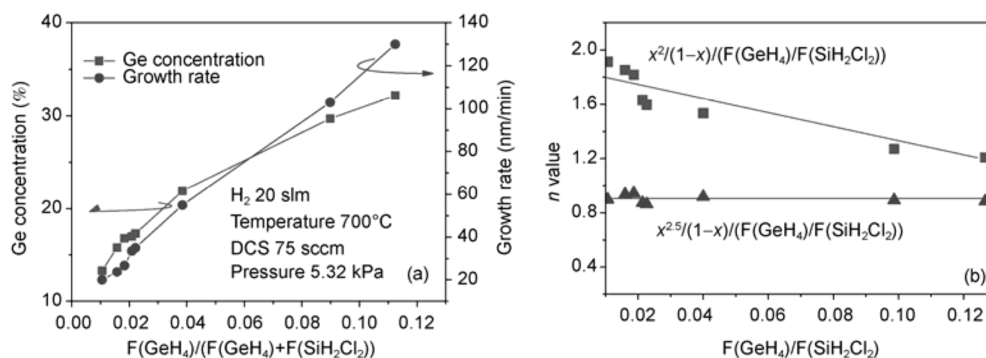

Figure 3 (a) The SiGe growth rate speeds up notably with increasing GeH_4 flow. However, the Ge concentration climbs more slowly; (b) the different relationships between Ge content (x) and $F(GeH_4)/F(SiH_2Cl_2)$ mass flow ratio.

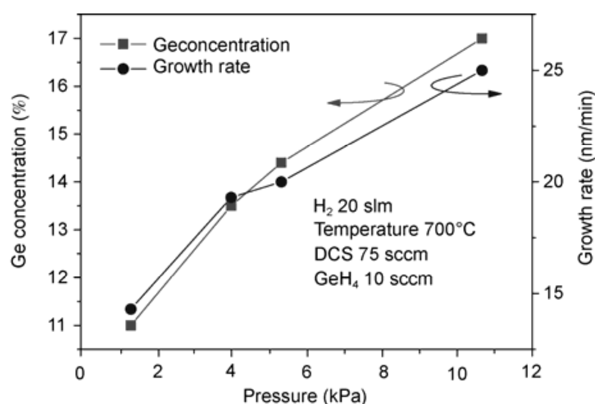

Figure 4 The SiGe growth rate and Ge concentration increase significantly with increasing reactor chamber pressure.

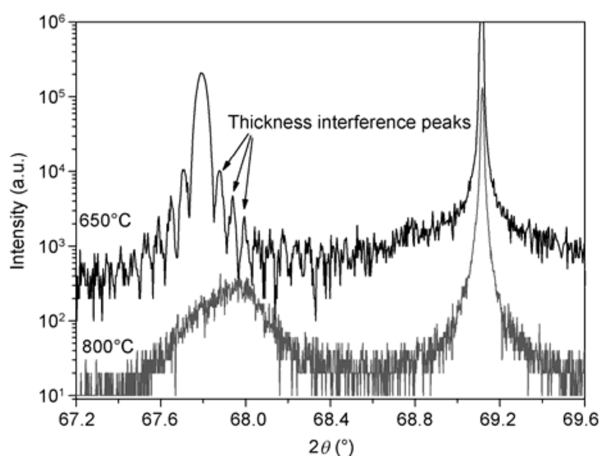

Figure 5 XRD patterns of SiGe fabricated at 650°C (sample A) and 800°C (sample B). The sharp SiGe peak and the presence of thickness interference peaks indicate the good crystalline quality of sample A. The broadened SiGe peak and the almost indiscernible thickness interference peaks demonstrate a decline in SiGe crystalline quality for sample B.

and 800°C (sample B). For sample A, the narrow full width at half maximum (FWHM) of the SiGe peak (only 0.1°) and the presence of thickness interference peaks indicate that the SiGe layer is pseudomorphic to the Si substrate, i.e. there is negligible dislocation density at the SiGe/Si interface. The SiGe layer thickness and the Ge content extracted from the XRD pattern are 151 nm and 25.0%, respectively. For sample B, the SiGe peak not only broadens significantly, but also becomes asymmetrical. In addition, the thickness interference peaks almost disappear from the XRD pattern. All of these features are associated with plastic relaxation of compressive strain and decline of the SiGe crystalline quality. As a result, the thickness and the Ge content of sample B become unidentifiable using XRD. To further evaluate the Ge content and relaxation degree, the Raman spectra of samples A and B were measured at room temperature using a JOBIN YVON HR800 spectrometer with a 514 nm excitation wavelength, and are shown in Figure 6. The in-plane strain and Ge content can be evaluated simultaneously from the Raman shifts of the Si-Si, and Si-Ge peaks [22]. Sample A is fully strained and its Ge content is 25%, which is consistent with the XRD result; sample B is partially relaxed with a relaxation of 14%, though its Ge content is only 21%.

As shown by the XRD and Raman results, sample B shows inferior crystalline quality although its thickness and Ge content are lower than those of sample A; this can be

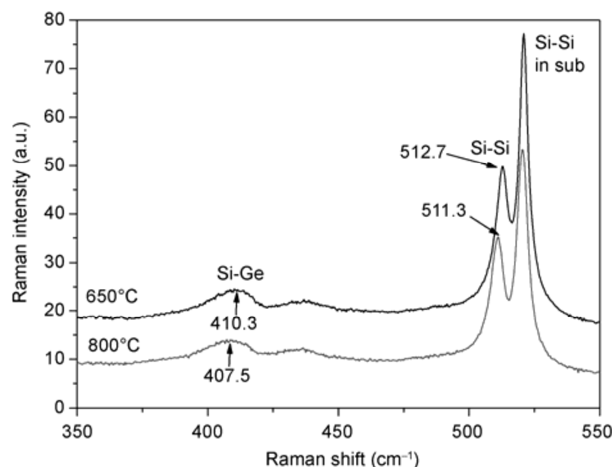

Figure 6 Raman spectra of sample A (650°C) and sample B (800°C).

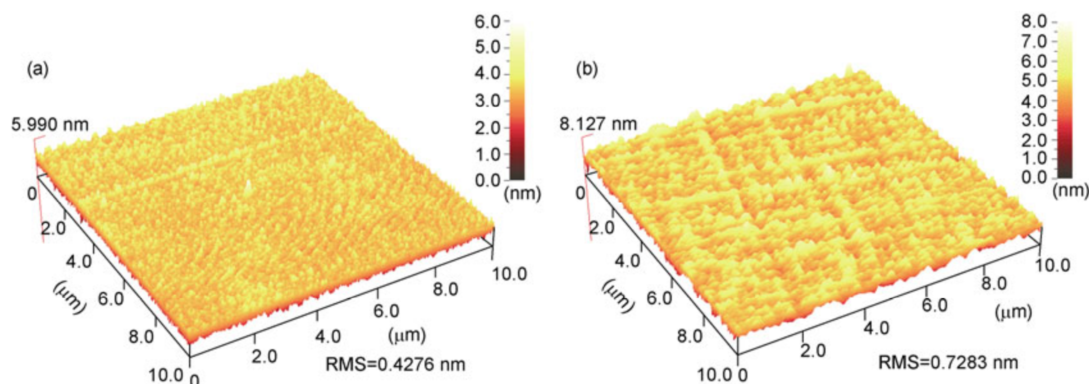

Figure 7 AFM images of samples A and B.

ascribed to its high deposition temperature. According to the suggested relaxation mechanism of a heteroepitaxial SiGe layer during growth on a Si substrate [23], the strain energy density plays a key role in the relaxation of the SiGe film. During growth of SiGe on a Si substrate, the strain energy density accumulates gradually as the SiGe film gets thicker. When the strain energy density reaches a critical value, it is relaxed by the formation of dislocations [24], resulting in the relaxation of the SiGe film and the decline of the crystalline quality. The higher the deposition temperature, the more strain energy is accumulated. Consequently, the SiGe layer fabricated at higher temperature begins to relax despite its thinner film thickness and lower Ge content.

Compared with sample B, sample A demonstrates not only superior crystalline quality, but also good surface morphology. Figure 7 shows the AFM images of samples A and B. The root-mean-square (RMS) roughness of sample A in a 10 μm square is only 0.43 nm; for sample B, the RMS roughness is 0.73 nm. Besides the bigger RMS value, a cross-hatch pattern was observed in the AFM image of sample B, where ridges and trenches extend in the <110> directions on the surface. It has been reported in the literature that the cross-hatch is caused by the relaxation of strain fields [25], which is consistent with the Raman result of sample B.

The XRD, Raman and AFM data for samples A and B suggest that a low deposition temperature is the essential factor to grow high quality SiGe. The higher the Ge content, the lower the required deposition temperature. However, the decrease in deposition temperature is necessarily accompanied by a drop in the growth rate. The optimal growth temperature must be a compromise between the crystalline quality and growth rate.

3 Conclusion

The dependence of the SiGe growth rate and Ge content on deposition temperature, GeH_4 flow and reactor chamber pressure was investigated. The SiGe growth rate escalates with increasing deposition temperature; meanwhile, the Ge content decreases, which can be explained by the Arrhenius equation. Because Ge incorporation lowers the energy barriers for hydrogen desorption, high GeH_4 flow also leads to rapid SiGe deposition rate. Although the decomposition rates of both SiH_2Cl_2 and germane increase notably at high pressure, high pressure is more favorable for the decomposition of germane, because the presence of substantial quantities of Cl-based molecules impedes the decomposition of SiH_2Cl_2. Consequently, the rise of SiGe growth rate at high reactor pressure is accompanied by an increase in Ge content.

Although SiGe layers can be fabricated at different temperatures, the rapid accumulation of strain energy at high temperature lowers the crystalline quality. To fulfill the semiconductor industry requirements for both crystalline quality and growth rate, SiGe deposition temperature must be carefully optimized.

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