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Epitaxy of $\text{Si}_{1-x}\text{Ge}_x$ by Ultrahigh-Vacuum Chemical Vapor Deposition Using Si_2H_6 and GeH_4

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Disilane and germane were used to grow $\text{Si}_{1-x}\text{Ge}_x$ epilayers at 550°C by ultrahigh-vacuum chemical vapor deposition (UHVCVD). The solid composition x and growth rate of $\text{Si}_{1-x}\text{Ge}_x$ were evaluated from double-crystal X-ray rocking curves and show very strong dependence on the total source gas flow rate ($[\text{GeH}_4] + [\text{Si}_2\text{H}_6]$) and the gas ratio ($[\text{GeH}_4]/([\text{GeH}_4] + [\text{Si}_2\text{H}_6])$). The solid composition increases with increase of the gas ratio and also with increasing the total source flux by keeping gas ratio constant. The growth rate increases with the solid composition at lower values and then becomes saturated in the higher composition range ($x > 0.22$). The results can be explained by the relationships of the source fluxes, relative incorporation efficiency at activated surface sites and hydrogen desorption under different growth conditions.

KEYWORDS: $\text{Si}_{1-x}\text{Ge}_x$, low-temperature epitaxy, hydrogen desorption, disilane, germane

1. Introduction

The development of new high-performance devices has placed strong requirements on new materials such as $\text{Si}_{1-x}\text{Ge}_x$ strained epilayers. Si/ $\text{Si}_{1-x}\text{Ge}_x$ heterojunction bipolar transistors (HBTs) are candidates for extending the high-frequency limits of Si bipolar transistors.^{1,2} To improve the performance of p-channel metal-oxide-semiconductor field-effect transistor (PMOSFET), SiGe epilayers are also used as the MOSFET channel and are receiving increasing attention.^{3,4} Consequently, several new epitaxial technologies, such as molecular beam epitaxy (MBE) and ultrahigh-vacuum chemical vapor deposition (UHVCVD) have been developed to obtain better control of the quality of $\text{Si}_{1-x}\text{Ge}_x$ strained epilayers. Device-quality SiGe epilayers have been demonstrated at temperatures as low as 550°C using UHVCVD.⁵⁻⁷ Therefore, UHVCVD shows the most promising method for low-temperature SiGe epitaxy.

The usual SiH_4 -based process was used in the conventional UHVCVD invented by Meyerson and proved to be good enough for device applications. However, the growth rate of Si epitaxy is very low and it also shows some limits in selective epitaxial growth (SEG) application.⁸ Recently, a novel UHVCVD process with a cold-wall reactor using Si_2H_6 and GeH_4 gases has been developed to obtain high-quality $\text{Si}_{1-x}\text{Ge}_x$ epilayers and successful SEG capability.⁹⁻¹¹ In this study, we used a similar UHVCVD process to grow $\text{Si}_{1-x}\text{Ge}_x$ epilayers. We also demonstrated the controllability of the solid composition x and the growth rate of the $\text{Si}_{1-x}\text{Ge}_x$ epilayers. The dependence of the solid composition and growth rate on the gas ratio of Si_2H_6 and GeH_4 ($[\text{GeH}_4]/([\text{Si}_2\text{H}_6] + [\text{GeH}_4])$) and total reactant flux are evaluated from double-crystal X-ray rocking curves. A simple model proposed by Tweet *et al.*¹² is used to explain the result obtained for the first time in this study.

2. Experiment

The UHVCVD system used in this study includes a

water-cooled stainless steel growth chamber, a loading chamber, separate nozzles for process gases, and a computer-controlled gas switching box. The growth chamber is pumped with a 1000 l/s turbomolecular pump. A base pressure of 2×10^{-10} Torr is achieved and maintained throughout. The chamber pressure is maintained below 10^{-3} Torr during the epitaxial process by the turbomolecular pump. Six-inch (100) Si substrates were subjected to a precleaning process composed of the following steps: (1) $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=3:1$ of 10 min at 120°C, (2) D.I. water rinse of 10 min, (3) 49% $\text{HF}:\text{H}_2\text{O}=1:50$ dip of 1 min, (4) $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:6:20$ of 5 min at 75°C and (5) D.I. water rinse of 10 min. The above steps reduce the accumulation of impurities by removing the surface native oxide and reform a protective thin oxide which is easier to remove during the thermal cleaning process before the epitaxial process is initiated. After the precleaning step, the wafers were loaded into the loading chamber and pumped down to $<10^{-6}$ Torr as soon as possible. Then the substrates were transferred into the growth chamber for the epitaxial process. Pure Si_2H_6 and GeH_4 are used for the growth of $\text{Si}_{1-x}\text{Ge}_x$. The flow rates of the reactants were controlled precisely by STEC mass flow controllers. The solid composition, growth rate, and crystal quality are evaluated from double-crystal X-ray rocking curves.

3. Results and Discussions

Si_2H_6 and GeH_4 were used to grow $\text{Si}_{1-x}\text{Ge}_x$ epilayers at growth temperatures between 525°C and 575°C. The growth pressure is about 1 mTorr. Figure 1 shows the dependence of the Ge solid composition x on the source gas ratio ($[\text{GeH}_4]/([\text{GeH}_4] + [\text{Si}_2\text{H}_6])$) and the total source gas flow rate ($[\text{GeH}_4] + [\text{Si}_2\text{H}_6]$). The total source gas flow rates were kept at 5, 10 and 20 sccm and the gas phase ratios were between 0.4 and 0.85. In order to obtain more precise results from double-crystal X-ray rocking curves, the thicknesses of $\text{Si}_{1-x}\text{Ge}_x$ epilayers were controlled around the critical thickness. The Ge solid composition x increased monotonically

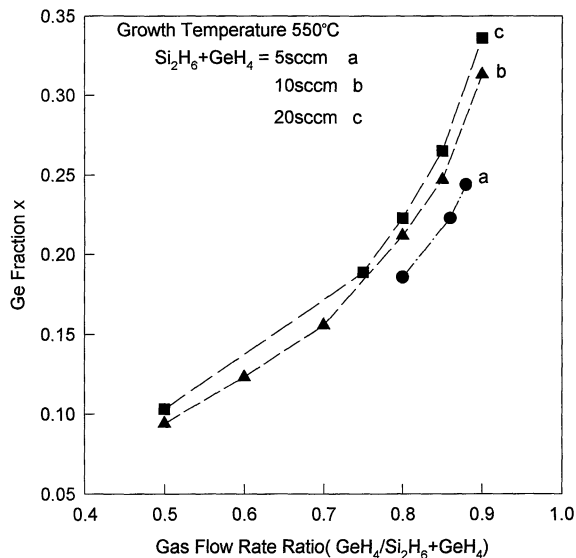


Fig. 1. The dependence of Ge solid composition x on the source gas ratio at different total source gas flow rates.

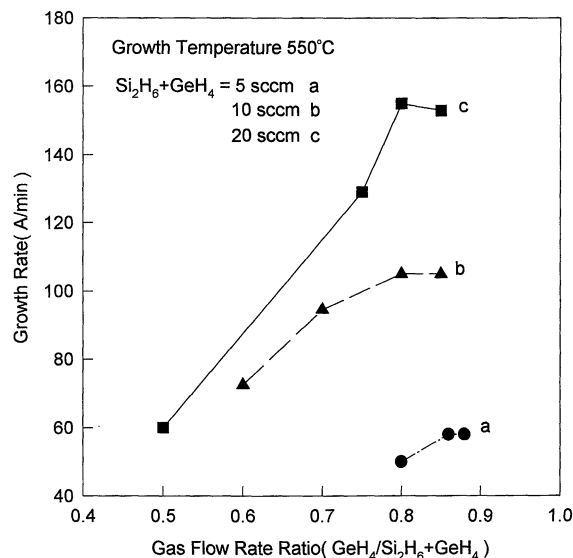


Fig. 2. The dependence of the growth rate of $\text{Si}_{1-x}\text{Ge}_x$ on source gas ratio at different total source gas flow rates.

with increase of the source gas ratio when the total source gas flow rate and the growth temperature (550°C) were kept constant. Another important result is that the Ge solid composition x also increases with increasing total source gas flow rate by keeping the source gas ratio and the growth temperature constant.

We also evaluate the dependence of growth rate on source gas ratio at different total source gas flow rates from double-crystal X-ray rocking curves and results are shown in Fig. 2. The growth rates increase rapidly at smaller values of the ratio and gradually at a slightly higher ratio, and finally become saturated at an even higher ratio. The growth rate also increases with increasing total source gas flow rate at the same source gas ratio. In order to explain the above results, Figs. 1 and 2 are combined and used to determine the dependence of growth rate on the Ge solid composition x at different total source gas flow rates. The relationship is shown in Fig. 3. The growth rates increase with increase of the Ge solid composition x and become saturated when the solid composition is greater than 0.22. The value of the solid composition at which the growth rate becomes saturated is independent on the total source gas flow rate. To obtain a further insight into the above results, we divided the $\text{Si}_{1-x}\text{Ge}_x$ growth rate R_{SiGe} into Si growth rate R_{Si} and Ge growth rate R_{Ge} , that is, R_{SiGe} is equal to $(R_{\text{Si}} + R_{\text{Ge}})$. Table I shows the values of R_{SiGe} , R_{Si} and R_{Ge} under the different growth conditions described above.

As observed from Fig. 1, the Ge solid composition x increases with the increase of source gas ratio at constant total source gas flow rate. From Table I, we also find that the Ge growth rate R_{Ge} increases monotonically and the Si growth rate R_{Si} increases and then decreases with the source gas ratio. Following Tweet *et al.*,¹²⁾ Ge and Si growth rates can be expressed as

$$R_{\text{Si}} = k_{\text{Si}} P_{\text{Si}} (1 - \Theta)^2 \quad (1)$$

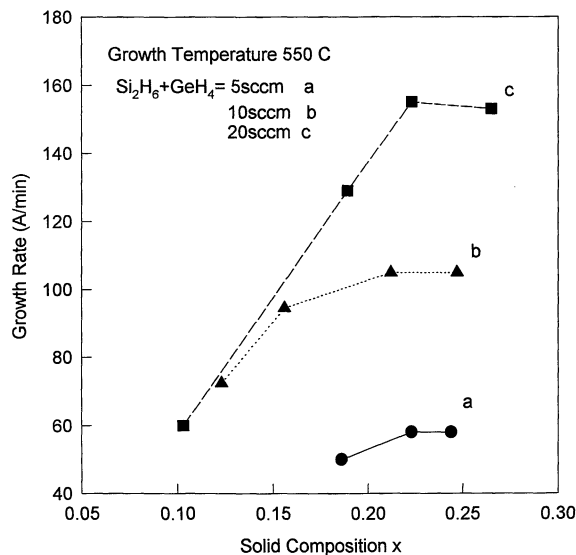


Fig. 3. The dependence of the growth rate of $\text{Si}_{1-x}\text{Ge}_x$ on Ge solid composition x at different total gas flow rates.

$$R_{\text{Ge}} = k_{\text{Ge}} P_{\text{Ge}} (1 - \Theta)^2 \quad (2)$$

where P_{Si} and P_{Ge} are the disilane and germane partial pressures, Θ is the fraction of the occupied sites and k_{Si} and k_{Ge} are the adsorption reaction rate constants. As shown, R_{Si} and R_{Ge} depend on the reactant flow rates, adsorption reaction rate constants and the hydrogen desorption rate. Si epilayers were also grown at 550°C under different Si_2H_6 flow rates and the results show that R_{Si} decreases slightly with decrease of the Si_2H_6 flow rate. Therefore, we assume that R_{Si} is strongly dependent on both the hydrogen desorption rate and the relative incorporation efficiency at activated sites on the wafer surface during the epitaxy process. However, R_{Ge} is strongly dependent on the GeH_4 flow rate, hydrogen desorption rate and the relative incorpo-

Table 1. Si Growth rate R_{Si} and Ge growth rate R_{Ge} extracted from Figs. 1 and 2.

Si ₂ H ₆ /GeH ₄ flow rate (sccm)	Ge Solid composition x	R_{Si} (A/min)	R_{Ge} (A/min)	R_{SiGe} (A/min)
1/4	0.186	40.7	9.3	50
0.7/4.3	0.223	45.1	12.9	58
0.6/4.4	0.244	43.9	14.1	58
4/6	0.123	63.6	8.9	72.5
3/7	0.156	79.8	14.8	94.6
2/8	0.212	82.7	22.2	105
1.5/8.5	0.247	79.2	25.9	105
10/10	0.103	54	6	60
5/15	0.189	104.6	24.4	129
4/16	0.223	120.4	34.6	155
3/17	0.265	112.9	40.1	153

ration efficiency at activated surface sites. Hence, R_{Ge} increases with the source gas ratio which mainly results from the increase of GeH₄ flux. The increase of R_{Si} at lower gas ratio is due to the enhancement of hydrogen desorption with GeH₄ incorporation.¹²⁾ However, the decrease of R_{Si} at higher gas ratio is due to the decrease of Si₂H₆ flow rate and the reduction in the number of useful activated sites for Si₂H₆ adsorption for the increase of GeH₄ adsorption. The different variation tendencies of R_{Si} and R_{Ge} at higher gas ratio result in monotonic and sharp increase in the Ge solid composition x with the source gas ratio. The effects of the increase of R_{Ge} and the decrease of R_{Si} with gas ratio on SiGe growth rate are balanced and result in the saturation of the SiGe growth rate R_{SiGe} when the solid composition is greater than 0.22 in this study. When we increase the total source gas flow rate and keep the gas ratio constant, the Si growth rate R_{Si} will be increased with increase of GeH₄ flow rate due to the enhancement of hydrogen desorption and suppressed by the reduction in the number of activated sites due to the increase of GeH₄ adsorption. Besides the above effects on R_{Si} , R_{Ge} is also strongly enhanced by increase of the GeH₄ flow rate due to the flux-controlled characteristics. Therefore, the relative incorporation efficiency of Ge is greater than that of Si and results in the increase of the solid composition x with the total gas flow rate at a constant gas ratio.

4. Conclusions

Si₂H₆ and GeH₄ are used to grow Si_{1-x}Ge_x at 550°C by cold-wall UHVCVD process. The Ge solid composi-

tion x and growth rate of Si_{1-x}Ge_x epilayers are evaluated from double-crystal X-ray rocking curves and found to depend on the source gas ratio and total source gas flow rates. The Si_{1-x}Ge_x growth rates R_{SiGe} for various solid compositions were separated into Si growth rate R_{Si} and Ge growth rate R_{Ge} . From the results obtained, R_{Si} is greatly enhanced by introduction of a small amount of GeH₄ and shows only a slight dependence on the Si₂H₆ flow rate. Furthermore, R_{Si} decreases when the Ge solid composition is greater than 0.22 due to the reduction of the relative incorporation efficiency at activated surface sites resulted from significant GeH₄ adsorption. Besides the above effects in R_{Si} , R_{Ge} shows a strong dependence on the GeH₄ flow rate. Therefore, the relative variations of the hydrogen desorption rate, relative incorporation efficiency at activated surface sites and source gas fluxes under different growth conditions are used to explain the above results consistently in this study. This work was supported by the National Science Council of the Republic of China under contract No. NSC 84-2622-E009-007-6.

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