# Kinetics of $Si_{1-x}Ge_x/Si(0\leqslant x\leqslant 1)$ growth by molecular beam epitaxy using disilane and germanium

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(Received 17 February 1995; accepted for publication 17 April 1995)

Molecular beam epitaxy of $Si_{1-x}Ge_x$ alloys, using gaseous $Si_2H_6$ and solid Ge as sources, has been studied over the entire composition range ($0\leqslant x\leqslant 1$). From the measured growth rates as a function of $x$, it is clear that the presence of Ge tends to decrease the Si incorporation rate. This establishes growth via adatom migration to kink sites in a dissociative chemisorption process. © *1995 American Institute of Physics.*

Coherently strained and relaxed $Si_{1-x}Ge_x/Si$ heterostructures have emerged as important materials for Si-based high-speed electronic and optoelectronic devices. Most of the epitaxy and application of $Si_{1-x}Ge_x$ have been done with alloy composition $x<0.35$. Very limited reports have been made on the growth and application of alloys with high Ge fractions.[1–4] Theoretical studies[5] clearly demonstrate that the Ge-rich alloys provide improved carrier transport through the removal of band edge degeneracies in both conduction and valence bands. Thus, the same advantages, as seen in *p*-type modulation-doped field effect transistors (MODFETs) realized with III-V-based materials (where the degeneracy in the valence band is removed), can be seen for electron- and hole-based devices with the SiGe system. Furthermore, it is expected that a Ge-rich based region of an *n-p-n* heterojunction bipolar transistor would improve the device performance.

High-quality SiGe alloys have been grown by a variety of epitaxial techniques. These include low-pressure chemical vapor deposition (LPCVD), molecular beam epitaxy (MBE), and gas-source MBE (GSMBE). The later growth technique, using $Si_2H_6$ (disilane) and $GeH_4$ (germane) provides several advantages and has been demonstrated by us[6] and Hirayama *et al.*[7] We have recently demonstrated excellent film quality using $Si_2H_6$ and solid Ge as sources.[8] An important aspect of the application of alloys with high Ge content is the understanding of the growth process of these alloys and the characterization of layer morphology, structural quality, and growth kinetics. In this letter we report on these issues related to growth of $Si_{1-x}Ge_x$ over the entire composition range ($0\leqslant x\leqslant 1$) using $Si_2H_6$ and Ge as sources.

Growth of the $Si_{1-x}Ge_x$ layers on (100)-oriented Si substrates was carried out in a three-chamber RIBER 32 molecular beam epitaxy (MBE) system with vacuum load locks. The growth chamber crysoshroud temperature was held constant at 77 K with liquid nitrogen and this chamber was pumped by a turbopump during growth. A series of 1 $\mu$m thick undoped $Si_{1-x}Ge_x$ ($0\leqslant x\leqslant 1$) layers were grown using $Si_2H_6$ from a low temperature (200 °C) injector and elemental Ge from a PBN crucible in a resistively heated effusion cell. The growth process was monitored using *in situ* reflection high energy electron diffraction (RHEED) and a (2×1) surface reconstruction pattern was obtained and maintained after removed of the substrate surface oxide at 840 °C for 10 min. All the layers were grown at a substrate temperature of 630 °C.

Two series of $Si_{1-x}Ge_x$ layers were grown. In the first, the Ge content was varied by keeping the Ge cell temperature constant at 1120 °C and varying the $Si_2H_6$ flow rate, with a mass-flow controller, in the range of 0 to 55 sccm. In the second set of samples, the Ge content was varied by holding the $Si_2H_6$ flow rate constant at 14 sccm and varying the Ge cell temperature in the range of 1000–1200 °C. The thickness of the layers was measured by scanning electron microscopy (SEM) and independently confirmed by Rutherford backscattering spectrometry (RBS). There was good agreement between the values obtained from both measurements. It may be noted that all the layers were strain relaxed, their thickness being larger than the critical thickness. The alloy composition was determined by double-crystal x-ray measurements, using Cu $K\alpha_1$ line, and was confirmed by RBS measurements. Typical x-ray rocking curve data are shown in Fig. 1 for a $Si_{0.17}Ge_{0.83}$ layer. The surface morphology of the layers did not have any special features.

The variation of alloy composition with change in $Si_2H_6$ flow rate and Ge flux for the two growth techniques described earlier are shown in Figs. 2(a) and 2(b), respectively. In the first the Ge cell temperature is held constant and

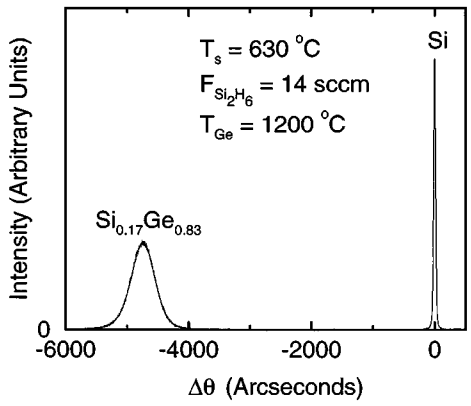


FIG. 1. The double-crystal x-ray rocking curve for relaxed $Si_{0.17}Ge_{0.83}$ alloy grown on a Si substrate at a substrate temperature of 630 °C, $Si_2H_6$ flow rate 14 sccm, and Ge cell temperature 1200 °C.

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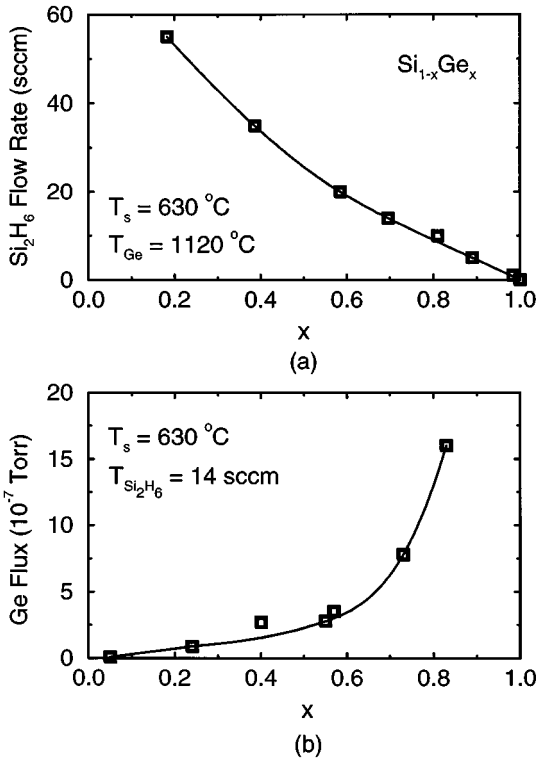


FIG. 2. Dependence of germanium content in $Si_{1-x}Ge_x$ alloys for the two methods of growth: (a) the Ge cell temperature is held constant at 1120 °C and the $Si_2H_6$ flow rate is varied; (b) the $Si_2H_6$ flow rate is held constant at 14 sccm and the Ge cell temperature is varied. The squares are experimental data and the solid lines are a guide for the eye.

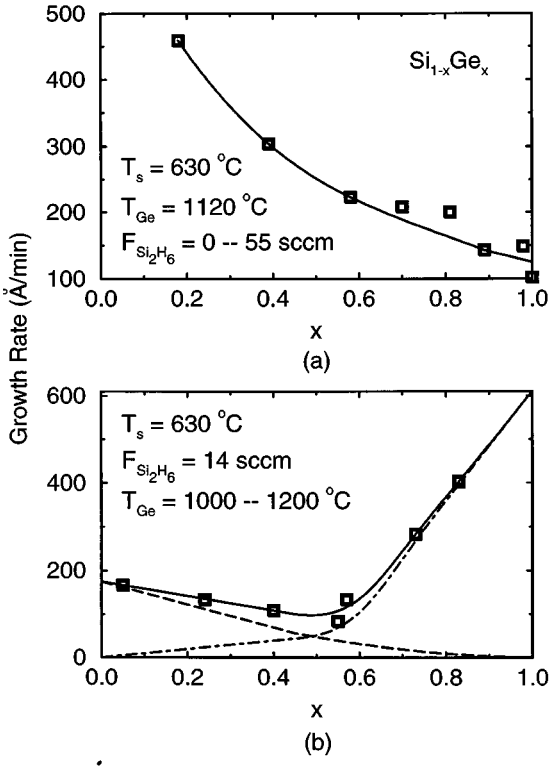


FIG. 3. $Si_{1-x}Ge_x$ layer growth rates as a function of germanium fraction for the two methods of growth: (a) the Ge cell temperature is held constant at 1120 °C and the $Si_2H_6$ flow rate is varied; (b) the $Si_2H_6$ flow rate is held constant at 14 sccm and the Ge cell temperature is varied. The squares are experimental data and the solid lines are a guide for the eye. In (b), the dashed line indicates the decreasing curve, the dot-dashed line, the increasing curve.

in the second the $Si_2H_6$ flow rate is held constant. As expected, the Ge content in the alloy increases with decrease of $Si_2H_6$ flow rate and with increase of Ge flux. Figures 3(a) and 3(b) show the variation of growth rate with Ge content in the alloy for the two methods of growth. In the first case, when the Ge cell temperature, or flux, is held constant, the growth rate monotonically decreases with Ge content in the alloy. However, when the composition is varied by varying the Ge flux, as shown in Fig. 3(b), the growth rate first decreases and then increases sharply. It is important to note that growth rate data for alloys with high Ge content ($x \geqslant 0.4$) have not been hitherto reported.

The growth behavior indicated by Fig. 3(a) is easily understood. As the $Si_2H_6$ flow rate is decreased, the Ge content in the alloy increases, but the growth rate decreases. A similar trend has been observed as reported by Mokler *et al.*[9] during growth of $Si_{1-x}Ge_x/Si$ from gaseous $Si_2H_6$ and $GeH_4$. The growth phenomenon represented by the data of Fig. 3(b) is more interesting. Here the $Si_2H_6$ flow rate is maintained constant, and the different alloy compositions are obtained by varying the Ge flux. One would expect that the growth rate would monotonically increase with Ge composition. However, it is noticed that the growth rate initially decreases up to $x=0.5$ and then increases. A curve-fitting indicates that the measured data can be the sum of two curves, one decreasing slowly with $x$ [shown in Fig. 3(b) by the dashed line] and the other increasing with $x$ [shown in Fig. 3(b) by the dot-dashed line]. The latter represents the increase of growth rate with increasing Ge flux. The first curve, however, would suggest that there is actually a surface phenomenon that tends to *decrease* the growth rate with increasing Ge flux.

The decrease in Si incorporation rates as a result of Ge flux sheds light on important details of the incorporation process of Si from $Si_2H_6$. The growing surface of the epitaxial layer has surface sites that are characterized by kink sites and nonkink sites. Kink sites correspond to sites that are at step edges and whose bonding energy would be high. Nonkink sites are sites whose bonding energy is rather low, as shown in Fig. 4. In principle, dissociative chemisorption can occur at both kink and nonkink sites. However, for a molecule like $Si_2H_6$, dissociative chemisorption is more likely at kink sites. If the kink sites are near Si atoms, this dissociation will be strongest. In the case of Ge, we expect that due to the weaker nature of the bonding, incorporation can occur at all surface sites. Also, due to the high migration rate of Ge atoms, they will rapidly move towards the step edges and occupy the kink sites. This would leave few available sites where Si can dissociate and thus results in a lower incorporation rate of Si. We expect the same phenomenon to occur in the growth of $Si_{1-x}Ge_x$ using $Si_2H_6$ and $GeH_4$, since the Ge–H bond is weaker than the Si–H bond, but should not occur for MBE using all solid sources. Indeed, up to $x=0.3$, a decreasing trend of the growth rate with increasing $GeH_4$ flow rate has been observed by us,[6] Hirayama *et al.*,[7] and Robbins *et al.*[10] If growth does not occur by a dissociative adsorption pro-

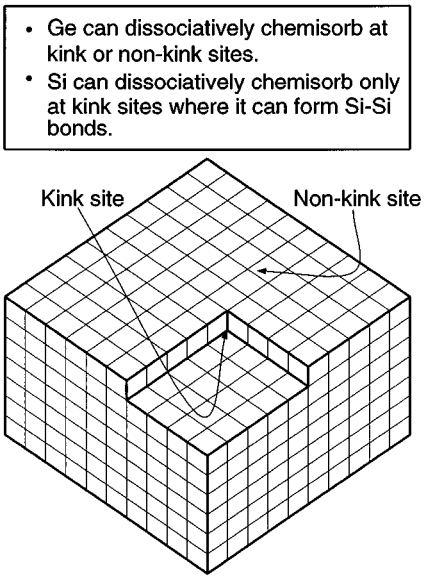


FIG. 4. Illustration of epitaxial growth via adatom migration to kink sites in a dissocative chemisorption process.

cess, but by thermal decomposition of source gases as in ultrahigh vacuum chemical vapor deposition (UHV/CVD), the growth rate will increase with increase of $GeH_4$ flow rate.[11,12] It is important to point out that at our relatively high growth temperature of 630 °C, the effects of hydrogen coverage on the surface,[13] and associated Ge segregation[11] do not play any significant role in the observed growth phenomena.

In conclusion, we have demonstrated MBE growth of high quality $Si_{1-x}Ge_x/Si$ alloys having composition in the range $0 \leqslant x \leqslant 1$ by using $Si_2H_6$ and elemental Ge as sources. The data conclusively establish growth via adatom migration to kink sites in a dissociative chemisorption process.

The authors thank J. Lee and Dr. S. H. Li for their help. The work is supported by the U.S. Air Force Office of Scientific Research under Grant Nos. F49620-95-1-0013 and F49620-94-1-0404.

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