Gas-source molecular-beam epitaxy using Si_2H_6 and GeH_4 and x-ray characterization of $Si_{1-x}Ge_x$ ($0 \leqslant x \leqslant 0.33$) alloys

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(Received 14 November 1991; accepted for publication 10 February 1992)

Gas-source molecular-beam epitaxy (MBE) has been used to grow SiGe alloys with Si_2H_6 and GeH_4 as sources on (100) Si substrates. Single-crystalline epilayers with Ge composition as high as 33% have been produced at 610 °C, the lowest temperature hitherto used for gas-source SiGe MBE. Growth parameters, growth modes, and the structural characteristics have been studied by a variety of *in situ* and *ex situ* techniques. Double-crystal x-ray diffraction data for the alloys have been obtained for the first time in thin mismatched layers.

I. INTRODUCTION

Mismatched and strained $Si_{1-x}Ge_x$ alloys, usually grown on Si substrates, have opened doors for the realization of Si-based heterostructure technology for use in electronic and optoelectronic devices.[1] In addition to obtaining a true semiconductor heterojunction, which was hitherto not possible with Si technology, the coherently strained alloys provide improved carrier transport through the removal of bandedge degeneracies in both the conduction and valence bands.[2] Thus, the same advantages, as seen in *p*-type modulation-doped field-effect transistors (MODFET) realized with the III-V–based systems (where the degeneracy in the valence band is removed), can be seen for electron- and hole-based devices with the SiGe system. The fundamental bandgap of the SiGe alloys falls within the 1.3–1.5-μm wavelength range, thereby making them attractive for fiber-optical communication applications.

High-quality SiGe alloys are essential for the realization of device structures, and these are being grown by a variety of epitaxial techniques. They include low-pressure chemical vapor deposition (LPCVD), molecular-beam epitaxy (MBE) using solid sources, and gas-source molecular-beam epitaxy (GSMBE) using hydrides. Growth by the MBE technique allows good controllability of film thickness and doping, and the realization of hyper-abrupt interfaces, both of which are important in the fabrication of state-of-the-art devices. Gas-source MBE, using silane (SiH_4) or disilane (Si_2H_6) and germane (GeH_4) as sources is very attractive since splitting defects, observed in layers grown by solid sources, are absent. Furthermore, gas sources assure a semi-infinite supply and ultrahigh vacuum (UHV) conditions in the growth chamber can be maintained for a long time. Disilane is a more attractive source material since silane tends to have a lower activity in chemical adsorption. This results in a higher growth temperature and lower growth rate.[3] There are two other advantages that have been observed in using disilane. First, it is trapped more effectively at the liquid-nitrogen-cooled cryoshrouds of the growth chamber, thereby helping to maintain a better vacuum in the growth ambience. Second, disilane provides a higher growth rate of the alloys since its incorporation involves both physisorption and chemisorption, as opposed to direct chemisorption with silane. In the case of disilane it is believed that the total sticking coefficient resulting from the physisorbed and chemisorbed states is higher than with silane.[4] However, these are issues which will require more study and understanding.

Several reports have been made on the growth of these alloys using gas sources, which include doping studies,[3] transport properties,[5] structural characteristics,[6] and dislocation generation.[7] To our knowledge, there is no explicit report on the x-ray characterization of the alloys grown by the above-mentioned techniques. It is difficult to observe x-ray data because of the high defect density resulting from the large lattice mismatch. For many device applications it will be necessary to grow mismatched layers,[8] and it is imperative to obtain x-ray peaks corresponding to the alloy composition. X-ray data cannot only give information regarding the crystalline quality of the alloys, but can also provide information regarding the growth modes of these highly strained layers. We report here our data obtained from growth studies and double-crystal x-ray measurements made on $Si_{1-x}Ge_x$/Si alloys ($0 \leqslant x \leqslant 0.33$) grown by GSMBE using Si_2H_6 and GeH_4.

II. EXPERIMENTAL TECHNIQUES

A. System description

Growth of SiGe was done in a two-chamber RIBER 32 MBE system with a vacuum load lock. The growth chamber is provided with an ion pump which maintains a background vacuum of $(5–10) \times 10^{-11}$ Torr, a liquid-nitrogen-cooled cryoshroud and equipment for *in situ* analysis and characterization of growth. During growth, a turbomolecular pump is used. The pumping rate is approximately 2200 ℓ/s. Pure Si_2H_6 and GeH_4 were selected as the source materials. The flow rates are controlled by precision mass flow controllers. The Si_2H_6 flow rate is fixed at 7 sccm. The GeH_4 flow rate is varied between 0.5 and 3 sccm. Due to the different GeH_4 flow rates, the system pressure during growth varies between $(5–20) \times 10^{-5}$ Torr. The tempera-

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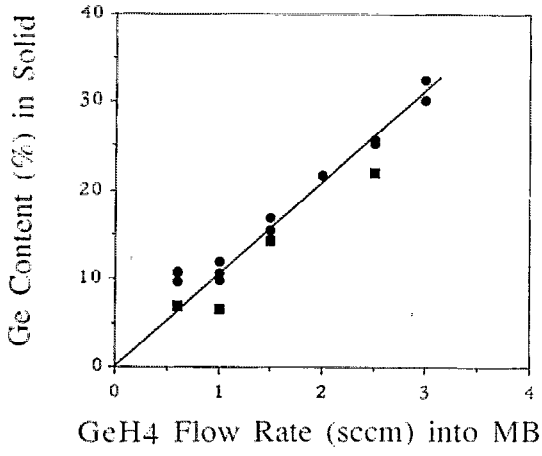

FIG. 1. Ge composition in the SiGe alloys as a function of the GeH_4 flow rate. The circles represent compositions determined by x-ray measurements. The squares represent compositions determined by electron microprobe. All samples were grown at 610 °C and the epitaxial layer thickness varied from 0.6 to 1.3 μm.

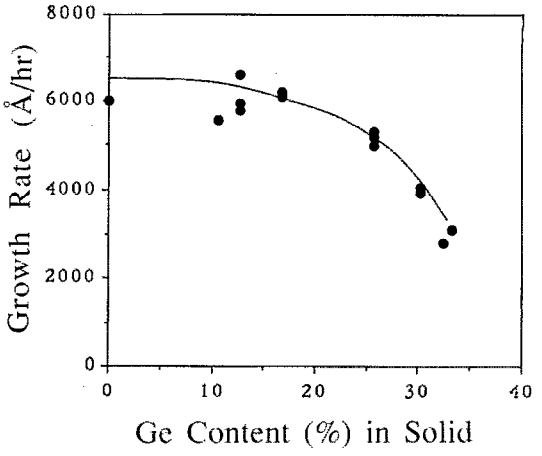

FIG. 2. Growth rate as a function of the Ge composition in the solids. The growth temperature was kept fixed at 610 °C. The data point for pure Si is taken from Ref. 16.

ture of the gas cell (or injector) was fixed at 200 °C. The liquid-nitrogen flow rate was adjusted to obtain the desired cryoshroud temperature. Growth at all alloy compositions was done at a fixed temperature of 610 °C.

B. Epitaxial growth

The substrates used were (100)-oriented, B-doped, p-type Si wafers with a resistivity between 10 and 20 Ω cm. To clean the surface and to form a protective thin SiO_2 film, the substrates were sequentially dipped in (1) $1NH_4OH:1H_2O_2:5H_2O$, (2) $1HF:50H_2O$, and (3) $1HCl:1H_2O_2:3H_2O$ solutions.[1] They are rinsed in H_2O after each solution. The substrate is loaded and degassed in the sample introduction chamber at 400 °C. The substrate is then transferred to the growth chamber and deoxidized by heating to 840 °C for 1 h prior to growth. *In situ* reflection high electron energy diffraction (RHEED) was used to monitor the surface crystallinity and smoothness. The epitaxial layer thickness, varying between 0.6 and 1.3 μm, was determined from selective epitaxy, using SiO_2 masks. It was observed that true selective epitaxy could be obtained.[6]

C. X-ray and microprobe measurements

Cu$K\alpha_1$ (004) rocking curve measurements[9] were performed on a double-crystal x-ray diffractometer. The separation between the substrate and epilayer peaks was used to determine the perpendicular lattice constant. Assuming that the grown layers are unstrained and Vegard's law is valid, the alloy compositions can be calculated. The validity of the assumptions is discussed in Sec. III A.

The composition of the alloys was also determined by direct electron microprobe measurements, where the electron beam is used to irradiate the grown materials, generating x rays with characteristic wavelengths from Si and Ge. From the x-ray intensities, the Si and Ge compositions are determined.

III. RESULTS AND DISCUSSION

A. Growth characteristics

The Ge composition in the SiGe alloys is plotted in Fig. 1 as a function of the GeH_4 flow rate. Each data point represents a single run. In general, the data points obtained from x-ray diffraction measurements deviate from the microprobe data. Although the actual cause for this is not clear, it could be due to the fact that the layers grown with low Ge mole fractions have a large critical thickness,[10] and therefore the layers have some residual strain. The apparent lattice constant in the (100) direction is then larger than the lattice constant of a totally relaxed layer with the same Ge composition. The possibility that Vegard's law does not hold is considered as less likely, because the deviation occurs in the low Ge range ($0 \leqslant x \leqslant 0.33$) where the bowing effect is normally insignificant. The spatial compositional nonuniformity is another reason for the observed discrepancy.

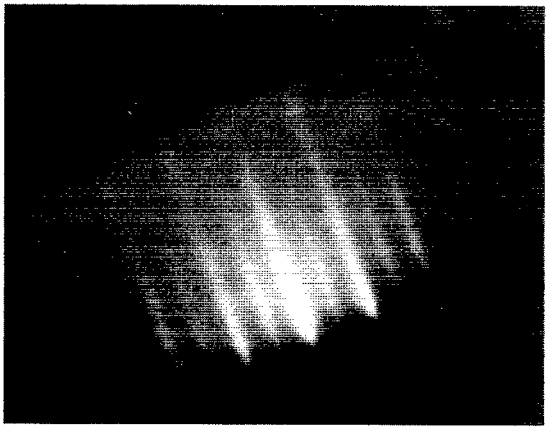

FIG. 3. 2×1 surface reconstruction pattern observed by RHEED from the $[1\bar{1}0]$ azimuthal direction during growth of a $Si_{0.83}Ge_{0.17}$ epitaxial layer.

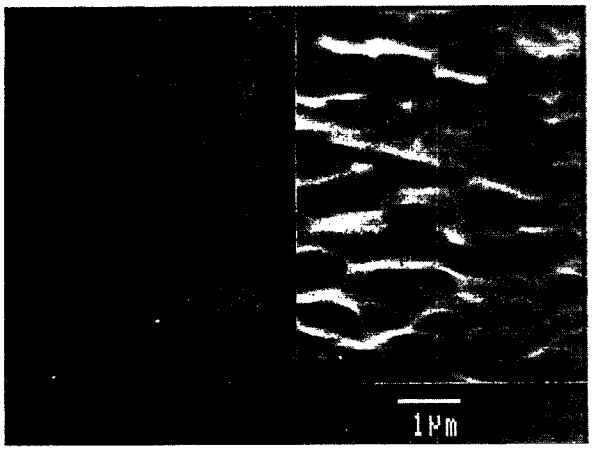

FIG. 4. Scanning electron micrographs of the surfaces of the (a) $Si_{0.89}Ge_{0.11}$ ($t = 1.3$ μm) and (b) $Si_{0.67}Ge_{0.33}$ ($t = 0.6$ μm) epitaxial layers.

It is worthwhile to note that in Fig. 1 the slope of the relationship between GeH_4 flow rate and the Ge solid composition can be changed if different liquid-nitrogen flow rates are used. This is because the liquid-nitrogen flow rate directly affects the cryoshroud temperature. At high liquid-nitrogen flow rates, or low cryoshroud temperatures, the Ge composition in the grown solid is very high and exceedingly sensitive to the input GeH_4 flow rate. However, on the other hand, at low liquid-nitrogen flow rates, the grown layers have little Ge content with high GeH_4 flow rates. It is believed that the pumping rate ratio between Si_2H_6 and GeH_4 is affected by the cryoshroud temperature. As a result, the gas-phase molar ratio between Si_2H_6 and GeH_4 is changed.

The measured variation of the growth rate with Ge composition in the alloy is shown in Fig. 2. A similar trend has been previously observed.[6] The trend is, however, contrary to that observed during growth of the alloys by ultrahigh vacuum (UHV)/CVD.[11,12] It is believed that at the lower pressure of GSMBE, growth occurs by dissociative adsorption, the efficiency of which decreases with higher GeH_4 flow to the surface. In UHV/CVD, where the background pressure is higher, thermal decomposition of the source gases results in a higher growth rate.[13]

B. Layer morphology

In situ RHEED measurements were made during oxide desorption from the substrate surface and subsequent growth. Measurements were made with an incident electron energy of 10 keV. A streaked (2×1) surface reconstruction pattern, as shown in Fig. 3, was observed for $Si_{1-x}Ge_x$ growth. However, for $x \geqslant 0.3$, the RHEED pattern turned spotty. This observation could be directly cor-

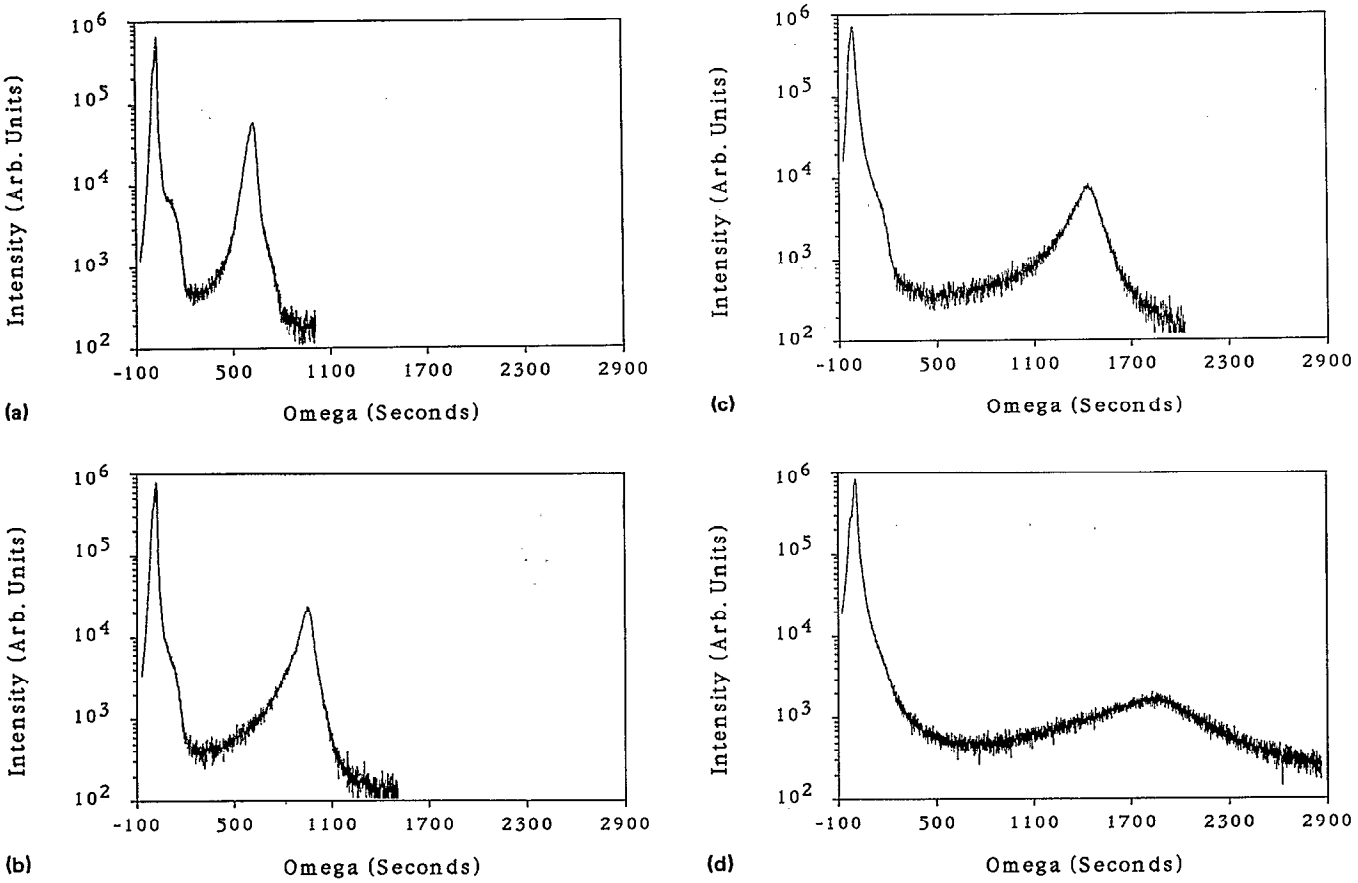

FIG. 5. Double-crystal x-ray diffraction results for (a) $Si_{0.89}Ge_{0.11}$, (b) $Si_{0.83}Ge_{0.17}$, (c) $Si_{0.74}Ge_{0.26}$, and (d) $Si_{0.68}Ge_{0.32}$.

related with the morphology of the layers, as observed by scanning electron microscopy (SEM). For $x < 0.3$, the surface was extremely smooth and featureless, whilst for $x \geq 0.3$ the surface has a hazy look. These are depicted in the SEM micrographs of Figs. 4(a) and 4(b). These observed trends can be related to an island mode of growth, instead of the layer-by-layer growth mode, that occurs for high values of misfit. Such island growth has been directly observed for InGaAs/GaAs epitaxy by scanning tunneling microscopy,[14] and explained by thermodynamic free-energy minimization considerations.[15]

C. X-ray diffraction results

Figures 5(a)–5(d) show the measured double-crystal x-ray data for alloys with increasing Ge content. In each case a sharp peak resulting from the reflection from the Si substrate and a broader peak from the SiGe epitaxial layer is observed. The alloy compositions for all the samples grown in this study were estimated from the angular position of this latter peak, assuming that the film is totally relaxed. The alloy compositions thus determined for the four samples in Fig. 5 are $x = 0.11$, 0.17, 0.26, and 0.32. It is evident that the peak corresponding to the alloy is broadened as x increases. This is mainly due to the increasing dislocation density and a resulting poorer crystalline quality. It is obvious that thicker layers or layers with effective dislocation filters such as superlattices need to be grown to preserve and improve the crystalline quality. However, to our knowledge, this is the first observation of x-ray peaks for SiGe grown by GSMBE and in such thin (≤ 1 μm) mismatched layers.

IV. SUMMARY

Gas-source MBE growth of $Si_{1-x}Ge_x$ alloys ($0 \leq x \leq 0.33$) using Si_2H_6 and GeH_4 has been done. Perfect crystallinity and surface smoothness have been obtained for alloys with $x < 0.3$. The growth rate was found to be approximately 0.3–0.6 μm/h depending on the growth parameters. The growth rate decreases as the Ge composition in the alloys increases. Peaks corresponding to the mismatched alloys could be obtained in double-crystal x-ray measurement data, even for layers approximately 1 μm thick.

ACKNOWLEDGMENTS

This work is being supported by the U. S. Air Force Office of Scientific Research and the Materials Research Laboratory, Wright-Patterson Air Force Base, under Grant No. AFOSR-91-0349 and by a grant from National Semiconductors, Santa Clara, CA. The authors would like to thank Professor J. Singh, Y. C. Chen, and D. Yang for help and useful discussions.

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