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Studies of Interdiffusion in Ge_mSi_n Strained Layer Superlattices

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We present the results on the characterization and interdiffusion behavior of Ge_mSi_n strained layer superlattices (SLS's) composed of alternating monolayers of pure Ge and pure Si. Such Ge_mSi_n SLS's were grown on top of thick relaxed Ge_ySi_{1-y} buffer layers so as to symmetrize the strain distribution and to maintain the pseudomorphic growth of the superlattices. Samples with different superlattice periodicities (*i.e.* $d = d_{Ge} + d_{Si}$ and different layer thickness ratios (*i.e.* $d_{Ge}:d_{Si}$ were prepared for comparison. Raman scattering spectroscopy and x-ray diffraction were used to characterize these samples. Initial results on thermal stability of these Ge_mSi_n SLS's are also reported

Key words: Superlattice, x-ray, Raman, interdiffusion

INTRODUCTION

Heteroepitaxy of Ge_xSi_{1-x} layers on Si substrates grown by molecular beam epitaxy (MBE) has attracted considerable interests in recent years.[1-4] In spite of the 4.2% lattice mismatch between Ge and Si, device quality Ge_xSi_{1-x}/Si strained layer superlattices (SLS's) have been successfully grown. Several optical and electronic devices such as modulation doped field-effect-transistors (MODFET),[5,6] heterojunction bipolar transistors (HBT),[7,8] and photodetectors[9] based upon such Ge_xSi_{1-x}/Si heterostructures have been demonstrated. Recently, the resonant tunneling of holes through double barrier diodes[10,11] as well as the hole transport through minibands of a Ge_xSi_{1-x}/Si superlattice[12] have also been reported. It is known that, among the important properties of Ge_xSi_{1-x}/Si heterostructures, the most interesting and possibly potentially useful one is the predicted quasi-direct optical transition[13] in superlattices consisting of alternating monolayers of pure Ge and pure Si. Nevertheless, interface abruptness may drastically affect the optical properties of such SLS's. Therefore, a careful control over the growth conditions and subsequent thermal treatment is very important as they affect the interface abruptness. Interface diffusion makes the superlattice more alloy-like and the phonon zone-folding effect is reduced.[14,15] In this study, we use x-ray diffraction and Raman scattering spectroscopy to study the interface abruptness and the thermal stability of these Ge_mSi_n SLS's.

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SAMPLE PREPARATION

The samples used in this study were grown in a Perkin-Elmer MBE system with base and growth pressures of $\sim 9.0 \times 1^{-11}$ and $\sim 3.0 \times 10^{-9}$ Torr, respectively. Ge_mSi_n SLS's having different superlattice periodicities (*i.e.* $d = d_{Ge} + d_{Si}$) and thickness ratios (*i.e.* $d_{Ge}:d_{Si}$) of Ge and Si layers were prepared. Prior to the growth of the superlattices, relaxed Ge_ySi_{1-y} alloy buffer layers, with the Ge fraction in the buffer layers matching that in the superlattices,[16] were grown on Si (100) substrates to symmetrize the strain distribution and thus maintain the pseudomorphic growth of the superlattices. Details of the growth procedure have been described elsewhere.[14] Table I is a summary of the samples used in this study, where d_X is the superlattice period obtained from x-ray diffraction and d_{RS} is the superlattice period obtained from Raman scattering.

In order to study the thermal stability of the Ge_mSi_n SLS's, the samples were annealed using furnace (FA) or rapid thermal (RTA) annealings at different temperatures and times. The FA was carried out in an evacuated furnace backfilled with flowing nitrogen gas. Samples were placed on top of a quartz boat inside the furnace. The annealing temperatures were controlled by a calibrated thermocouple. A Peak System's rapid thermal processor[17] was used

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Table I. Summary of the samples used in this study

Sample	$d_{Ge}:d_{Si}$	d_X	d_{RS}	buffer
VA19	1:4	54Å	56Å	$Ge_{0.2}Si_{0.8}$
VA21	4:1	61Å	60Å	$Ge_{0.8}Si_{0.2}$
VA25	1:1	50Å	55Å	$Ge_{0.5}Si_{0.5}$
VA27	1:1	35Å	38Å	$Ge_{0.5}Si_{0.5}$
VA28	1:1	23Å	24Å	$Ge_{0.5}Si_{0.5}$
VA30	1:1	14Å	15Å	$Ge_{0.5}Si_{0.5}$
H 56	2:3	33Å	36Å	$Ge_{0.4}Si_{0.6}$

for RTA. The cold wall system uses a long arc, ac, gas discharge lamp with output spectrum tuned for absorption by Si.

EXPERIMENTAL DETAILS

Both Raman scattering spectroscopy and x-ray diffraction were used to characterize these Ge_mSi_n SLS's samples before and after annealing. The x-ray diffraction measurements were made using the Cu K_α radiation in the $\theta - 2\theta$ scanning mode on a powder diffractometer equipped with a graphite crystal diffracted-beam monochromator. The Raman scattering experiments were performed at room temperature with near-backscattering geometry. Samples were kept in vacuum in order to reduce stray light scattering from the air. Various lines (457.9, 488.0, 514.5nm) of an argon ion laser were used for excitation, and the laser light was manipulated with a cylindrical lens to minimize sample heating. Scattered light was analyzed with a Spex 1404 double spectrometer and an EG&G Ortec 941 photon counter. For superlattice samples, the layered structure with a repetition length, d, acts as artificial Bragg planes for x-ray reflection.[18] It is thus possible to determine the interface quality from the full-width at half-maximum (FWHM) and the number of orders of the low-angle $(000)_+$ x-ray reflection. By using Raman scattering,[14] we can also determine the interface abruptness from the relative intensity of the Ge—Si phonon vibration as well as the energy positions of the Ge—Ge and Si—Si phonons.

RESULTS AND DISCUSSIONS

The low-angle x-ray diffraction reflections for the as-grown samples VA19, VA21, and VA25 are shown in Fig. 1(a), (b), and (c), respectively. These superlattices had been grown with nominally identical periodicities of 40 monolayers, but they have 4:1, 1:4, and 1:1 ratios, respectively, for the individual Si and Ge layer thicknesses. The superlattice satellite x-ray peaks for samples VA19(4:1) and VA21(1:4) have narrow FWHM's and we can clearly observe multiples of the low-angle peaks up through the 7th order. Since these satellites about main diffraction lines correspond to individual Fourier components in the scattering function, that arise from modulation of the interplanar spacings for periodic structures,[18] more abrupt interfaces between the layers will give a greater number of satellite peaks. Consequently, the low-angle x-ray patterns in Fig. 1 imply that both Si and Ge enriched Ge_mSi_n SLS samples have more ideal square-wave like composition profiles than those SLS structures grown with a close or equal Ge and Si composition (or thickness) ratio such as sample VA25(1:1). This assertion is supported by the observed folded longitudinal-acoustic (FLA) phonon spectra. Figure 2(a), (b), and (c) are the Raman spectra of samples VA19, VA21 and VA25 in the acoustic phonon regions. It can be seen that samples VA19 and VA21 both showed clear 1st and 2nd order FLA phonon doublets[19,20] and a weak 3rd order FLA phonon peak. On the other hand, for sample VA25, the 1st order FLA phonon doublet is unclear and the 2nd order doublet is unresolvable and much weaker than those observed from samples VA19 and VA21. Thus, the FLA data also indicate that the interface quality is better for Ge and Si rich samples. The reason for this phenomenon is unclear at this moment; however, it might be related to the properties of the relaxed buffer layers beneath the superlattices. The Ge and/or Si rich SLS's were grown on Ge and/or Si rich buffers as designed for strain symmetrization. These buffer layers are more "bulk" like with

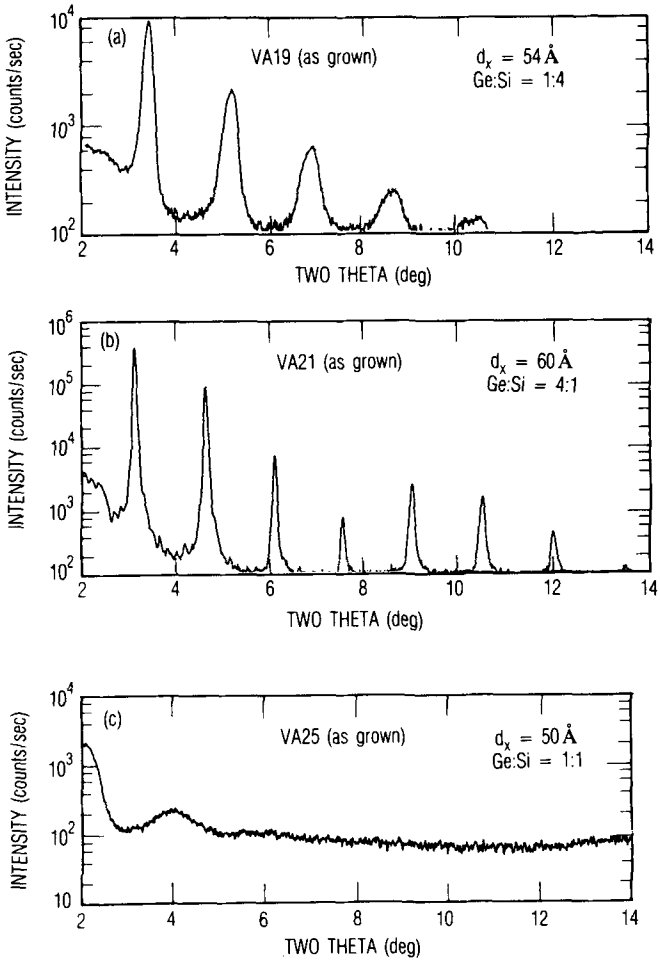

Fig. 1 — Low-angle x-ray diffraction spectra of (a) sample VA19, (b) sample VA21, and (c) sample VA25 before annealing.

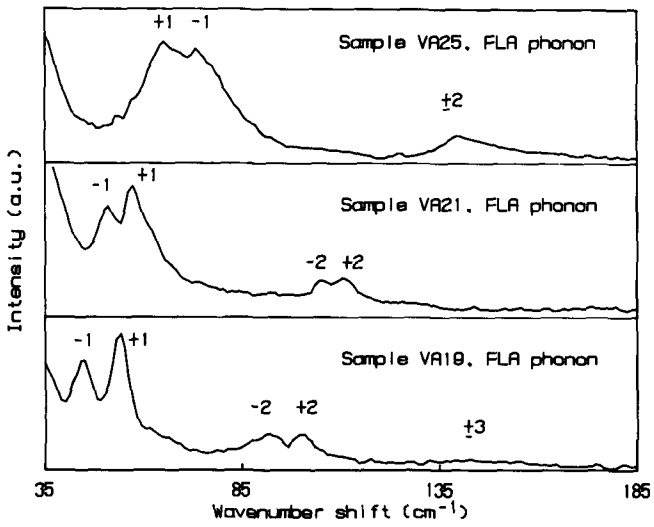

Fig. 2 — FLA phonon spectra of (a) sample VA19, (b) sample VA21, and (c) sample VA25 before annealing. The laser was operated at 514.5 nm.

less disorder, and can provide smoother superlattice/buffer interfaces than those buffer layers with equal Ge and Si concentrations. Transmission electron microscopy studies have been started on these samples to assess the nature of disorder and defects in these samples. The results will be reported elsewhere.

The effects of annealing induced Ge and Si interdiffusion can also be easily observed with both x-ray diffraction[21] and Raman scattering spectroscopy.[14] The optical phonon regions of the Raman scattering spectra for the as-grown and annealed sample VA25 are presented in Fig. 3. It can be seen that the relative intensity of the Ge—Si phonon vibration increases and both Ge—Ge and Si—Si phonon energies shift to the lower energy side for annealed samples. These results suggest that substantial interface mixing occurred in the annealed samples.[14] For a Si-rich sample (*i.e.* VA19), we also observed that the relative intensity of Ge—Ge phonon vibration decreased drastically as the sample was annealed (as indicated in Fig. 4). For the as-grown Si-rich sample VA19, even though only 20% of the atoms in the superlattice are Ge, the total number of Ge—Ge atomic bonds is still large. However, as the annealing process proceeds, the number of Ge—Ge bonds decreases significantly due to the increase of the number of neighboring Si atoms resulting from interdiffusion. Similarly, a decrease in the intensity of Si—Si phonon vibration is observed in the annealed Ge-rich sample (*i.e.* VA21). The FLA phonon spectra are also very sensitive to thermal treatment. As shown in Fig. 5, the Ge and Si atomic interdiffusion induces interface smearing which results in the merging of the FLA phonon doublets and a decrease in the overall FLA phonon signal intensity.

X-ray diffraction can also be used to monitor the interdiffusion process.[21–23] The gradual loss of the interlayer order can be examined from the decrease in the intensities of the superlattice satellites to the x-ray diffraction peaks. From the temperature dependence of the intensity decay time, we can also quantitatively determine the activation energy of the interdiffusion process and thus assess the dominant interdiffusion mechanism. The decay in the intensity of the 1st order satellite x-ray peak, I, is directly related to the interdiffusion coefficient, D_λ, by:[22]

$$\frac{d}{dt}\ln\left(\frac{I}{I_0}\right) = \frac{-8_\pi^2}{\lambda^2} D_\lambda \qquad (1)$$

where λ is the superlattice periodicity and I_0 is the initial satellite x-ray peak intensity before annealing.

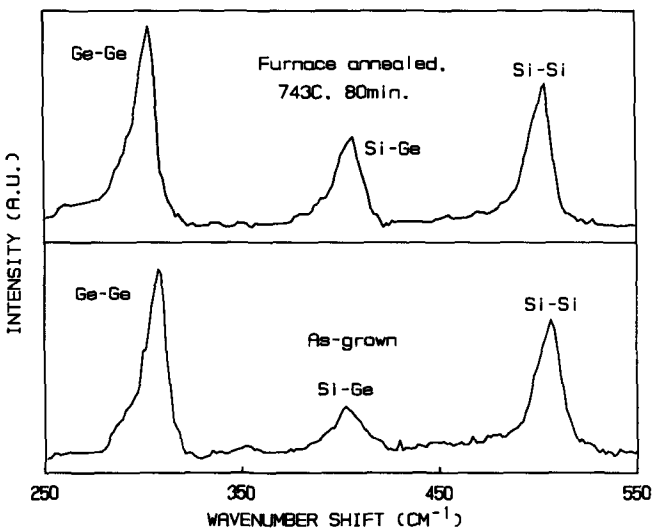

Fig. 3 — Optical phonon regions of the Raman spectra for as-grown (lower panel) and annealed (upper panel) sample VA25. The laser was operated at 457.9 nm and the annealing was done using FA at 743° C for 80 min.

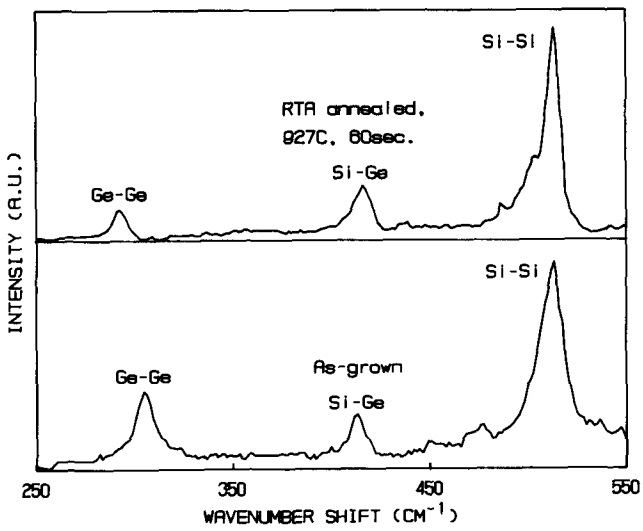

Fig. 4 — Optical phonon regions of the Raman spectra for as-grown (lower panel) and annealed (upper panel) sample VA19. The laser was operated at 457.9 nm and the annealing was done using RTA at 927° C for 60 sec.

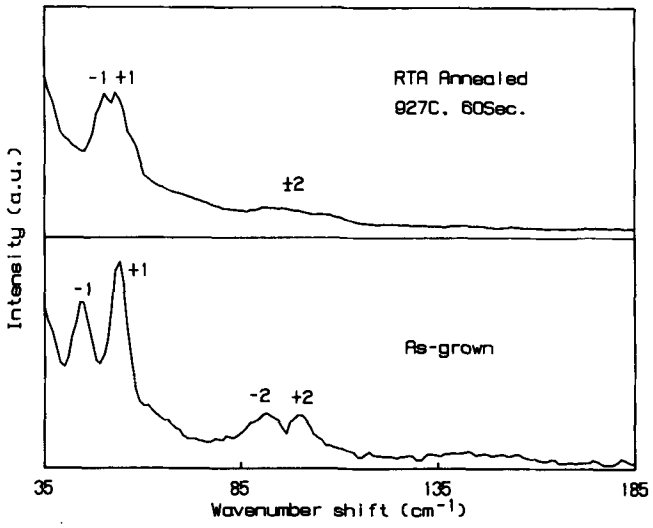

Fig. 5 — The FLA phonon spectra of sample VA19 before (lower panel) and after (upper panel) annealing. The laser was operated at 514.5 nm and the annealing was done using RTA at 927° C for 60 sec.

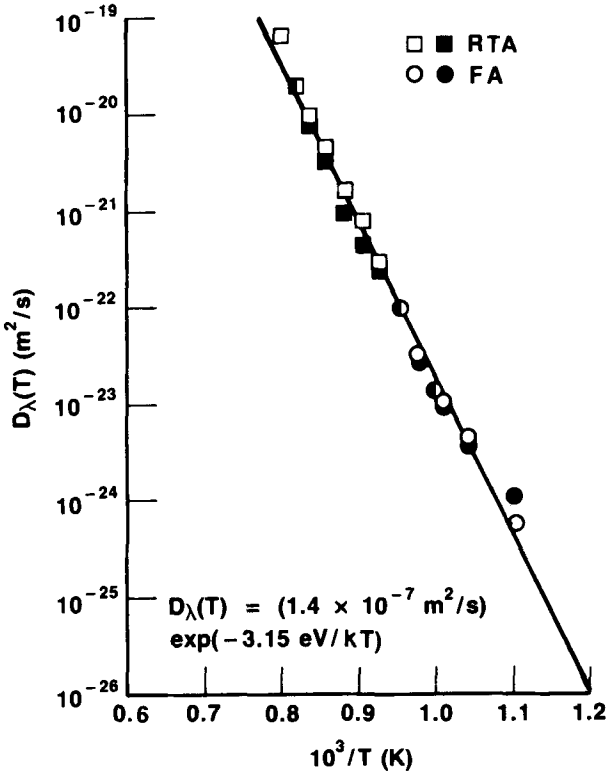

Fig. 6 — Temperature dependence of the interdiffusion coefficient $D_\lambda(T)$ for sample H 56. The solid symbols were obtained from the low-angle superlattice peak and the open symbols were obtained from the (−1)-satellite of the (400)-reflection after furnace and rapid thermal annealings.

We have previously reported[21] that under furnace annealing (FA) for temperature between 640 and 780° C, an activation energy (E_a) was obtained for interdiffusion coefficients for a sample (H56) which has a layer thickness ratio $d_{Si}:d_{Ge} = 3:2$ and a superlattice periodicity d = 33Å. Through the use of the RTA procedures, additional measurements of the interdiffusion coefficients for this sample have been made at higher temperatures. As shown in Fig. 6, the Arrhenius expression is valid for the entire set of $D_\lambda(T)$ values over the temperature range of 640° C – 985° C, to give an activation energy of 3.1 ± 0.2 eV. The data represented in Fig. 6 were obtained from the low-angle superlattice peak (solid symbols) as well as from the (−1)-satellite of the (400)-reflection (open symbols) after both furnace (FA) and rapid thermal (RTA) anneals. Similar combined FA and RTA treatments have also been performed on two of the 1:1 ratio samples (*i.e.*, VA27 and VA28). Analyses of their low-angle x-ray satellites for temperatures between 680 and 851° C lead to E_a values of 3.2 ± 0.2 and 2.8 ± 0.2 eV for VA27 and VA28, respectively. These results suggest that the common activation energy of 3.1 ± 0.2 eV represents the initial stage of interlayer diffusion for both 2:3 and 1:1 Ge_mSi_n SLS structures. Unfortunately, the thicknesses of the nominal 40 monolayer samples (*i.e.*, VA19, VA21, and VA25) precluded observation of their first order low-angle satellites with the Cu K_α x-rays. Since eqn. (1) is valid only for these first order satellites,[17,21] it was not possible to obtain the interdiffusion parameters for these samples.

It should be noticed that the activation energies of Ge self-diffusion and Si impurity diffusion in Ge are ~3 eV,[24,25] while the activation energies of Si self-diffusion and Ge impurity diffusion in Si are ~5 eV.[26,27] The measured 3.1 ± 0.2 eV activation in sample H 56 seems to suggest the interdiffusion process in this case is dominated by the diffusion of Si atoms into Ge layers via mono-vacancy mechanism.[21]

SUMMARY

In this study, Ge_mSi_n strained layer superlattices with different layer thickness ratios and superlattice periodicities were grown and characterized by x-ray diffraction and Raman scattering spectroscopy. An activation interdiffusion energy of 3.1 ± 0.2 eV was obtained and this value when compared with other studies seems to imply Si diffusion into Ge layers as a dominant process. Additionally, it is found that Ge and Si rich samples have smoother interface than the samples having an equal Ge and Si contents. The reason for this is being investigated.

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