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Thermal stability of the $[(\mathrm{Si})_m/(\mathrm{Ge})_n]_p$ superlattice interface

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The structure of $[(\mathrm{Si})_m/(\mathrm{Ge})_n]_p$ superlattice interfaces and the onset of relaxation and interdiffusion initiated by annealing have been investigated with the use of extended x-ray-absorption fine structure and Raman scattering. For the as-grown material, the Ge-Ge bond length (0.2409 nm) was equal to that calculated for a fully strained Ge layer (0.2412 nm) while the Si-Ge bond length was significantly shorter. The results show conclusively that substantial intermixing along with partial relaxation of the Ge-Ge bonds occurs even for the shortest anneal at 700 °C.

Interest in $(\mathrm{Si})_m/(\mathrm{Ge})_n$ short-period superlattices consisting of m and n alternating layers of pure Si and Ge has increased because of the prediction of a direct-band-gap, silicon-based material.[1] The modification of the band structure will not be possible if perfection of the interfaces cannot be attained and maintained. There is general agreement that the growth of Ge on Si proceeds two dimensionally to a certain thickness [$n \sim 3$–6 monolayers (ML)], but after that thickness changes to a nonplanar mode.[2] Also of concern is the phenomenon of ordering which has been widely reported,[3–5] and will obviously limit the perfection of the interfaces. The use of surfactants[6] may be the solution to the problems of both nonplanar growth and ordering, but of equal concern is the ability to thermally cycle such superlattices and maintain the monolayer abruptness of interfaces which are so highly strained.

To date, the most commonly used approach in investigating interdiffusion has been x-ray diffraction[7,8] or Raman spectroscopy.[9,10] In x-ray measurements on annealed pseudomorphic structures,[8] an apparent enhancement of the diffusion was observed in the early stage of annealing. Strain or a concentration dependence of the diffusion coefficient could explain these observations, but measurements using a short-range probe would help to elucidate this question. Extended x-ray-absorption fine structure (EXAFS) can determine both the nearest-neighbor type and bond lengths,[11] neither of which are measured by the diffraction-based techniques. Thus EXAFS provides a means of testing the above premise and has been applied to problems in the Si-Ge system including amorphous layers,[12] strained alloys[13] and atomic-layer superlattices.[14]

EXAFS together with Raman scattering have been used to gain further insight into the results of an earlier x-ray-diffraction study[8] using samples taken from the same wafers. These were grown by molecular-beam epitaxy in a VG Semicon V80 system at ~ 400 °C and at a rate of ~ 0.02 nm s^{-1}, and subsequently capped with ~ 5 nm of Si. Sample No. 2 is a 100-period superlattice with $n = 2.2 \pm 0.1$ and $m = 8.0 \pm 0.1$ ML; sample No. 1 is similar, with 48 periods of $n = 2.0 \pm 0.1$ and $m = 6.6 \pm 0.1$ ML. Pieces of sample No. 2 were rapid thermal annealed (RTA) at 700 °C in a nitrogen atmosphere for 20, 200, and 2000 s. Pieces from both wafers were annealed at 750 °C in a vacuum furnace for 900 s.

X-ray diffraction is an extremely sensitive probe for investigating diffusion in very thin modulated structures.[15] An effective interdiffusion coefficient D_λ for a modulated structure of period λ can be obtained by monitoring the decay of the first-order superlattice satellite of the (000) Bragg peak as a function of time for a given annealing temperature. Figure 1 shows the evolution of the first (000) Bragg satellite of sample No. 2 as a function of time

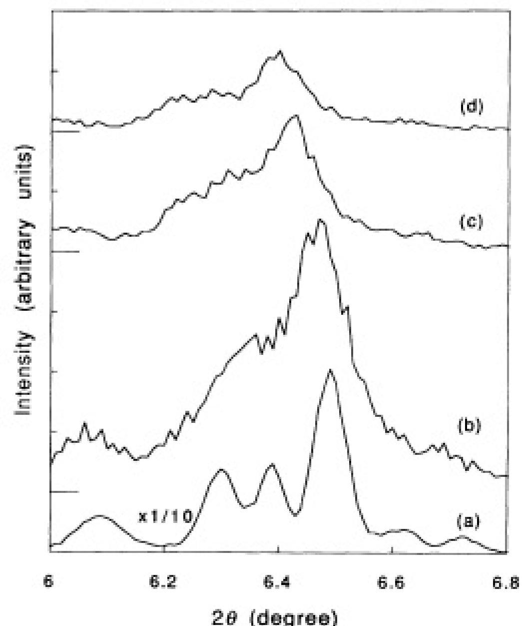

FIG. 1. First-order satellite of the (000) Bragg peak from sample No. 2: (*a*) as-grown, and after annealing at 700 °C for (*b*) 20 s, (*c*) 200 s, and (*d*) 2000 s.

at an annealing temperature of 700 °C. The as-grown sample [curve (*a*)] exhibits an intense peak at ~6.5° corresponding to the first-order superlattice reflection. Secondary intensity oscillations seen in the vicinity of that peak are due to interference effects arising from the finite thickness of the structure and the presence of three stacking mistakes within the superlattice. A tenfold decrease in intensity is observed after only a 20-s annealing treatment [curve (*b*)]. A much slower decay is observed for longer annealing times [curves (*c*) and (*d*)]. This nonlinear behavior in the satellite intensity decay in the early anneals is a common phenomenon and is generally attributed to some form of microstructural transformation.[15] Alternatively,[8] significant interdiffusion caused by the interfacial strain may have taken place together with relaxation [deduced from (400) diffraction measurements]. The smearing of the secondary features is consistent with this interpretation, since their intensity strongly depends on the interfacial abruptness.[16] Other samples, which were relaxed as grown, did not exhibit such a fast intensity decay.[8]

The Raman spectra of the superlattices[17] were recorded in a quasibackscattering geometry using 300 mW of argon laser light at 457.9 nm for excitation. The as-grown samples exhibited three strong peaks at frequencies above 250 cm^{-1} due to the longitudinal-optical (LO) phonons in the superlattice (see Table I). The peaks near 510 and 290 cm^{-1} are associated with vibrations confined largely to the Si and Ge layers, respectively. The peak near 410 cm^{-1} arises from LO modes propagating across the Si-Ge interface,[10] and thus their frequency and intensity are sensitive to the Si-Ge interface quality. Two other weaker LO peaks occur near 255 and 435 cm^{-1} and have been associated previously with ordering.[4] The relative weakness of these peaks in the Raman spectra of the as-grown samples indicates that little ordering has occurred at the Si-Ge interfaces. The strength and sharpness of the folded acoustic modes in these samples (see Fig. 2) imply reasonably sharp interfaces (i.e., the interface roughness is limited largely to the interfacial layers).

Annealing the superlattices affected their Raman peaks to varying extents. In the case of sample No. 1, the vacuum anneal (No. 1V) produced pronounced shifts in the three main LO-phonon peaks (see Table I) and changes in their peak intensities. The peaks near 290 and 510 cm^{-1} decreased and increased, respectively, in intensity after

TABLE I. Summary of LO-phonon frequencies for as-grown samples, after rapid thermal anneal (R) at 700 °C, and after vacuum anneal (V) at 750 °C for the duration stated.

Sample	Time (s)	Ge-Ge (cm^{-1})	Si-Ge (cm^{-1})	Si-Si (cm^{-1})
No. 1		294.3	414.4	511.7
No. 2		295.4	415.4	513.2
No. 2R1	20	291.1	411.2	508.4
No. 2R2	200	290.6	410.1	508.3
No. 2R3	2000	289.7	408.9	507.9
No. 1V	900	289.1	407.7	507.9
No. 2V	900	288.0	405.7	507.2

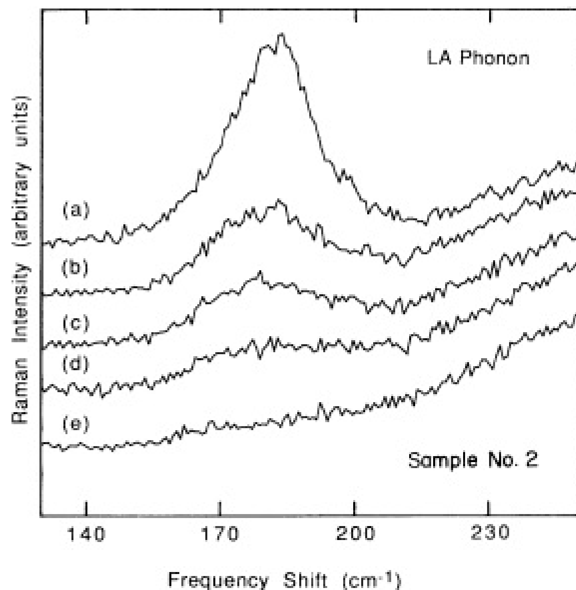

FIG. 2. Portion of the Raman spectrum (at 3-cm^{-1} resolution) showing the LA-phonon peak for sample No. 2: (*a*) as grown, after annealing at 700 °C for (*b*) 20 s, (*c*) 200 s, (*d*) 2000 s, and (*e*) vacuum annealed at 750 °C for 900 s.

the lengthy anneal, and both of the ordering peaks increased in intensity. In sample No. 2, vacuum or RTA annealing produced similar behavior. Beginning with the shortest anneal (No. 2R1), the frequencies of the three main LO-phonon peaks decreased (see Table I) and their relative intensities also changed slightly. The most dramatic intensity changes occurred after the longest anneal (No. 2R3). The intensities of the two weaker LO peaks were not affected except for the vacuum anneal, whereupon their intensities increased markedly. Calculations[10] have shown that for the Ge-Ge and Si-Si peaks, their frequency is most strongly affected by strain and confinement. Thus, the shift in frequency of these LO-phonon peaks indicates that strain relief has occurred, even after a 20-s anneal, consistent with the x-ray-diffraction results. What is more remarkable, however, is that the intensities of the LA modes also decrease immediately (see Fig. 2). This is qualitative evidence of diffusion across the Si-Ge interface, as the zone-folded LA-phonon intensities are very sensitive to interface sharpness.[10] The continued decrease in intensity with annealing is a clear indication of increased interface blurring. The 900-s vacuum anneal resulted in pronounced Si-Ge interdiffusion, as evidenced by the marked frequency shifts and large relative intensity changes in the LO modes and the disappearance of the folded acoustic modes. The sharp increase in intensity of the 255- and 435-cm^{-1} peaks in both superlattices after this anneal indicates a concomitant increase in the amount of ordering.

The EXAFS measurements were performed at the A3 and C2 beam lines at the High Energy Synchrotron Source (CHESS) at Cornell University. A gas-flow electron detector with sample rotation was used to eliminate diffraction artifacts while providing gas amplification of

the electron-yield signal.[18] Considering the small differences expected in bond lengths (0.235 and 0.245 nm for Si and Ge, respectively) one might conclude that EXAFS would be of marginal value. However, with the development of an analysis program,[19] which involves the simultaneous constrained-curve fits of four different but related EXAFS spectra, the *relative* errors in bond lengths and coordination numbers are *significantly* improved. This is *especially* applicable in the present case where one is interested in the changes that have occurred upon annealing of one sample.

Figure 3 shows the $k\chi(k)$ Ge K EXAFS spectra for the sample No. 2 series along with that of pure Ge crystal. The molecular compound, $Si[Ge(CH_3)_3]_4$, and pure Ge were used as model compounds. The increase in the EXAFS intensity near 4 $Å^{-1}$ is an immediate qualitative indicator of an increase in the Si content in the first shell (and thus intermixing) with annealing, since the Si (Ge) backscattering amplitude is at a maximum (minimum) at this wave number.[14] Quantitative results obtained from the constrained multiple file analysis are presented in Table II.

The ideal ratio of $N_{\text{Si-Ge}}/N_{\text{Ge-Ge}}$ bonds [given by $(n-1)^{-1}$] for an $n=2$ layer is 1.0, while for $n=2.2$ it is 0.83. The measured values of 1.43 and 1.35 of the two as-grown samples are consistent with an intermixing of the two Si-Ge interfaces of $\lesssim 20\%$ assuming that both interfaces mix equally. Alternatively, if the intermixing occurs predominantly at one interface, as has been postulated,[5] then this value would increase to $\sim 40\%$ in a first-order approximation. After the shortest anneal (No. 2R1) the ratio increased dramatically to 2.0. Without

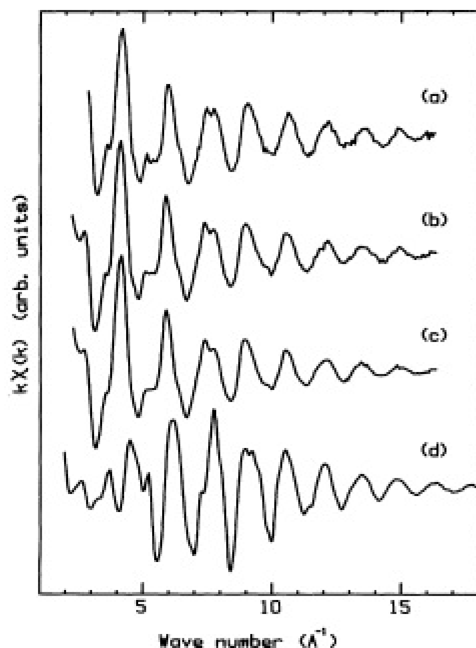

FIG. 3. $k\chi(k)$ Ge K-edge EXAFS spectra for sample No. 2: (a) as-grown, after annealing at 700 °C for (b) 20 s, (c) 2000 s, and (d) a bulk Ge crystal.

TABLE II. Summary of bond lengths (R) and coordination numbers (N) determined by EXAFS for as-grown samples, after rapid thermal anneal (R) at 700 °C, and after vacuum anneal (V) at 750 °C.

Sample	Time (s)	$R_{\text{Ge-Ge}}$ (nm) (± 0.0005)	$R_{\text{Si-Ge}}$ (nm) (± 0.0005)	$N_{\text{Si-Ge}}/N_{\text{Ge-Ge}}$ (± 0.15)
No. 1		0.2408	0.2396	1.35
No. 2		0.2409	0.2388	1.43
No. 2R1	20	0.2416	0.2391	2.0
No. 2R2	200	0.2419	0.2397	2.1
No. 2R3	2000	0.2425	0.2381	2.6
No. 1V	900	0.2415	0.2379	2.3

doubt, the initial loss in x-ray intensity is associated with a strain-enhanced intermixing, because this is the only process which can increase $N_{\text{Si-Ge}}$ at the expense of $N_{\text{Ge-Ge}}$. Using the diffusion constant of 10^{-24} m^2/s measured previously for long anneals,[8] negligible diffusion (<0.005 nm) would have been predicted. Upon further annealing (No. 2R2 and No. 2R3), the bond ratio continues to increase, but at a much slower rate, consistent with the previously observed lower diffusion constant.

The measured Ge-Ge bond length, $R_{\text{Ge-Ge}}$, for our as-grown, pseudomorphic strained atomic-layer superlattices ($n<4$), is always longer than the interface Si-Ge bond length.[19] $R_{\text{Ge-Ge}}$ agrees with the value calculated for a fully strained, tetragonally distorted layer of Ge (0.2412 nm), but *not* with the normal Ge bulk bond length, as has been reported for amorphous layers[12] and strained alloy layers.[13] Recent theoretical work has stated that the bond lengths should be a function of alloy composition[20] or, alternatively, should depend on the structure of the atomic-layer superlattices.[21] The bond length at the interface, between each Ge layer and the first Si layer (i.e., nominally a 50% alloy), has a bond length significantly shorter than $R_{\text{Ge-Ge}}$ and equal to the average value for a fully strained 60% alloy. Upon annealing, the $R_{\text{Ge-Ge}}$ bond length initially increases slightly (or remains constant, within the precision of the measurement) and then increases significantly for the longest anneal indicative of relaxation. $R_{\text{Si-Ge}}$ initially remains constant but at longer times becomes significantly smaller. Note that the error bars we quote in Table II are not at the accuracy level with which EXAFS is routinely thought to be capable of measuring *absolute* bond lengths (± 0.002 nm).[11] They represent the confidence level we have in the *relative* bond lengths[19] and thus the trends observed.

Together the techniques show that the structure of the layer during the anneal has evolved as follows. Initially, Ge and Si atoms interchange across the interface to reduce the total strain energy. This is clear from the significant increase in $N_{\text{Si-Ge}}$ and the concomitant reduction in $N_{\text{Ge-Ge}}$, and the decrease in the intensity of the LA-phonon line. The shift in the Raman Ge-Ge vibration (295 cm^{-1}), together with a small increase in $R_{\text{Ge-Ge}}$, shows that small areas of "pure Ge" have also begun to relax. As the anneal continues, $N_{\text{Ge-Ge}}$ continues to decrease while $R_{\text{Ge-Ge}}$ continues to increase. Unfortunate-

ly, neither the EXAFS nor the Raman measurements can distinguish between a partial relaxation of all Ge-Ge bonds or a mixture of fully strained and partially relaxed Ge-Ge bonds. The Si-Ge bond length is also a weighted combination of the bonds formed by the Si that has diffused into the Ge layer and the Ge that has diffused into regions of previously pure Si. This explains why $R_{\text{Si-Ge}}$ initially remains constant, as it is first dominated by Si diffusing into the Ge layer, creating a more Ge-rich alloy. $R_{\text{Si-Ge}}$ then decreases as Ge diffuses a significant distance into Si, creating a dilute alloy with a characteristically shorter bond length. This is supported by the continued decrease in $N_{\text{Ge-Ge}}$ (an indicator of the amount of original Ge bilayer) and the increase in $N_{\text{Si-Ge}}$. At this stage, EXAFS and Raman, both being short-range probes, can no longer follow the evolution of the layers and the analysis requires input from diffraction or microscopy techniques.

To summarize, EXAFS, in combination with Raman spectroscopy, has shown that the initial stages of strain relaxation in $(\text{Si})_m/(\text{Ge})_n$ superlattices begins with strain-enhanced intermixing across the interface together with partial relaxation. Further annealing leads to diffusion at a much slower rate and to the formation of an alloy layer. The Ge-Ge and Si-Ge bond lengths of the as-grown layers are different, and the Ge-Ge length (0.2409 nm) is that expected for a fully strained Ge layer (0.2412 nm), not that of a bulk-Ge crystal (0.245 nm).

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