Accommodation of lattice mismatch in Ge_xSi_{1-x}/Si superlattices

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We present evidence that the critical thickness for the appearance of misfit defects in a given material and heteroepitaxial structure is not simply a function of lattice mismatch. We report substantial differences in the relaxation of mismatch stress in $Ge_{0.5}Si_{0.5}$/Si superlattices grown at different temperatures on (100) Si substrates. Samples have been analyzed by x-ray diffraction, channeled Rutherford backscattering, and transmission electron microscopy. While a superlattice grown at 365 °C demonstrates a high degree of elastic strain, with a dislocation density $< 10^5$ cm^{-2}, structures grown at higher temperatures show increasing numbers of structural defects, with densities reaching 2×10^{10} cm^{-2} at a growth temperature of 530 °C. Our results suggest that it is possible to freeze a lattice-mismatched structure in a highly strained metastable state. Thus it is not surprising that experimentally observed critical thicknesses are rarely in agreement with those predicted by equilibrium theories.

I. INTRODUCTION

Heterostructures composed of poorly lattice matched materials have received much attention.[1-3] Removing the constraint that structures be composed of lattice-matched materials increases the number of possible materials combinations and introduces strain as a new means of tailoring the properties of a device. However, stresses resulting from lattice mismatch can be the source of structural defects which may seriously degrade device performance.[4] The onset of misfit defect formation has traditionally been described in terms of a single "critical thickness" which, for a given lattice mismatch and materials system, has been assumed to represent the ultimate limit to defect-free growth. Critical thicknesses have been difficult to pin-down experimentally, with inconsistencies in the literature being ascribed to differing measurement techniques and changing structures.

We present evidence that the formation of defects in lattice-mismatched structures is strongly dependent on growth conditions. In particular, we see dramatic changes in dislocation densities in $Ge_{0.5}Si_{0.5}$/Si superlattices grown at different temperatures. Misfit dislocation densities drop from 2×10^{10} cm^{-2} at a growth temperature of 530 °C to levels undetectable ($< 10^5$ cm^{-2}) by transmission electron microscopy (TEM) in a sample grown at 365 °C. Our results are suggestive of a kinetic barrier against the formation of dislocations. The dislocation nucleation we observe cannot be explained in terms of different thermal expansion coefficients. While our results do not discredit the critical thickness theories of Matthews and Blakeslee[5] or Van der Merwe,[6,7] they demonstrate that equilibrium theories are not appropriate for describing metastable growths such as those obtained by the low-temperature technique of molecular-beam epitaxy (MBE).

II. EXPERIMENTAL

Compositionally identical $Ge_{0.5}Si_{0.5}$/Si superlattice samples were grown in a modified III–V MBE machine at temperatures between 330 and 530 °C. Growth temperatures were inferred from optical pyrometer and thermocouple readings, calibrated with the aid of eutectic reactions observed *in situ*. We estimate our growth temperatures to be accurate to within 20 °C. (100)-oriented Si substrates were cleaned following a modified Shiraki procedure[8,9] consisting of repeated *ex situ* oxide growths and etches. This was followed by a final oxide desorption at 800 °C in the growth chamber under ultrahigh vacuum (UHV) conditions. The cleaning procedure was followed by growth of an epitaxial Si buffer layer (≈ 1000 Å in thickness), during which the growth temperature was lowered continuously from 700 °C. Those superlattices fabricated at higher temperatures (530 °C) were grown without interruption on the Si buffer layers. Growth at temperatures lower than this required an interruption of < 30 min after deposition of the buffer layer to allow the substrate to cool further. The superlattice layers were grown by codeposition of Si and Ge at feedback-stabilized deposition rates of 1 Å/s, independent of the growth temperature.

In situ reflection high-energy electron diffraction (RHEED) patterns showed that the growth changes from amorphous to single-crystal at a temperature of 300 °C. TEM confirms the single-crystal nature of our superlattices. We did not observe any polycrystalline growth. Previous work had suggested "amorphous or disordered growth"[10] at 400 °C under certain circumstances and poor channeling yields under others. We saw no evidence of either of these in our films. The reason for this discrepancy is not clear at this point although it should be noted that the substrate cleaning procedure used here is substantially different from the sputter and anneal technique used in the previous study.[10] Discrepancies such as these highlight the difficulties associated with comparisons of data taken from different sources. It is clear that a mechanism affecting the crystallinity of a sample will play a significant role in determining defect densities in a structure. Thus, while data exist for Ge_xSi_{1-x} critical thicknesses at growth temperatures of 750 °C[11] and at 550 °C,[12] it is not clear that these data are directly comparable. Our work represents an attempt to isolate effects due to changing growth temperatures by keeping all other parameters and cleaning procedures constant.

Superlattice characteristics are listed in Table I. Four samples were grown with identical layer thicknesses, compositions, and numbers of superlattice periods. Growth temperature alone was varied between these samples. Two other superlattices (SL29 and SL37) were grown, at temperatures of 330 and 530 °C. Although the defect densities observed in these samples are consistent with results obtained from the other four samples, the different number of periods makes it impossible to conclusively isolate growth temperature as the cause of observed differences. X-ray diffraction measurements have confirmed the superlattice periods to be within ± 5 Å of the quoted values. Rutherford backscattering spectroscopy (RBS) shows a random variation in Ge content of < 5% from intended fractions.

Defect densities in the superlattices have been inferred from x-ray diffraction, channeled RBS, and TEM.[13] As illustrated in Fig. 1, x-ray diffraction reveals that superlattices grown at low temperatures accommodate lattice mismatch through elastic strain. The figure compares experimental $\theta/2\theta$ diffraction with the spectrum calculated for a single-period coherently strained superlattice. The experimental

TABLE I. $Ge_{0.5}Si_{0.5}/Si$ superlattice sample characteristics.

Sample	Layer thicknesses ($Ge_{0.5}Si_{0.5}/Si$) (Å)	Periods	Growth temperature (°C)
SL 78	65/65	36	365
SL 71	65/65	36	390
SL 77	65/65	36	450
SL 72	65/65	36	530
SL 29	70/70	34	330
SL 37	70/70	50	530

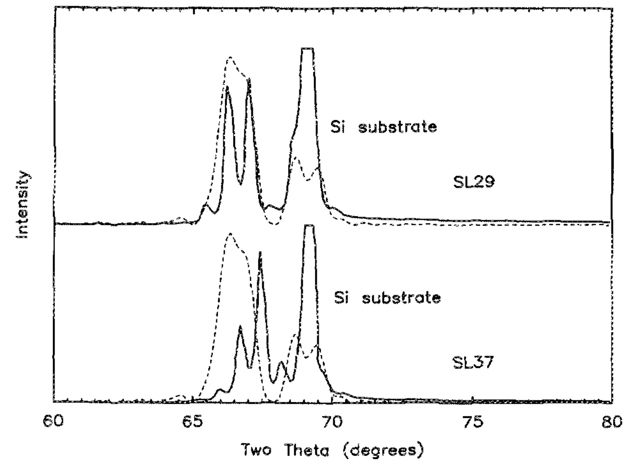

FIG. 1. $\theta/2\theta$ x-ray diffraction spectra for Ge_xSi_{1-x}/Si superlattices grown at 330 °C and 530 °C. Theoretical (---) spectra for diffraction from a single coherently strained superlattice period are included for comparison. Measured and calculated spectra are in good agreement for the sample grown at 330 °C. Experimental (—) x-ray diffraction is in poor agreement with theory at the higher growth temperature, indicating a high density of misfit dislocations in this sample.

diffraction consists of several narrow peaks modulated by broad envelopes. The positions of the narrow peaks yield the period of the superlattice, while the growth-direction lattice constants within the structure are inferred from the broad envelopes modulating these peaks.[14] The elastic strain within the superlattices can be determined by comparing the experimental peak heights with those expected from the broad envelopes calculated under the assumption of a coherently strained structure. While the agreement is excellent for sample SL29, grown at 330 °C, the $Ge_{0.5}Si_{0.5}$ (400)-like peaks are shifted towards those of Si in sample SL37, grown at 530 °C. While it is not possible to extract information as to the nature and density of the defects in SL37 from x-ray diffraction alone, it is clear that the sample is far from perfect. Growth at a higher temperature results in a substantial relaxation of stresses, whereas lattice mismatch appears to be accommodated largely elastically at lower temperatures.

Further structural information has been gathered from channeled RBS with an incident 2.275 MeV $^4He^{2+}$ beam aligned with the (100) growth direction. As illustrated in Fig. 2, the backscattered yield drops sharply as the growth temperature is lowered to 365 °C. The rapid rise in counts behind the Si surface peak (at ≈ 1.25 MeV) for the samples grown at 450 and 530 °C shows that these superlattices have many structural defects. Sample SL71, grown at 390 °C, shows no great increase in backscattering yield until the interface with the Si buffer layer (≈ 1.05 MeV). The counts rise dramatically at this point, however, indicating a great number of defects near this first superlattice interface. Superlattice SL78, grown at 365 °C, is unique in showing a low-backscattering yield throughout the film. The structure grown at 330 °C, although observed through x-ray diffraction to be highly strained, shows very poor channeling, indicative of a high number of defects incapable of relieving stresses due to lattice mismatch.

Several superlattices have been examined through cross-

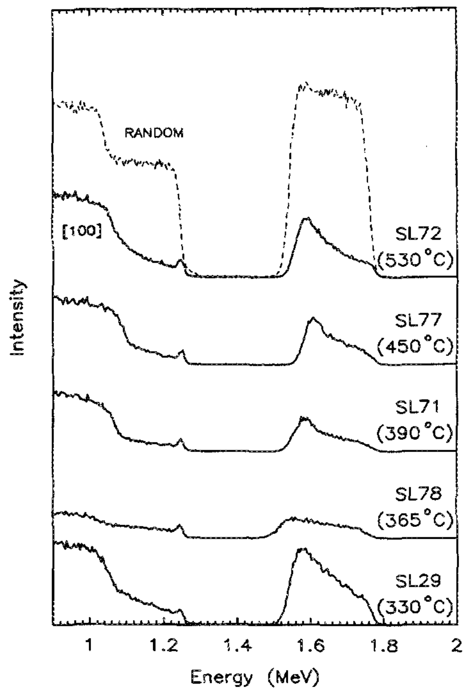

FIG. 2. Channeled Rutherford backscattering spectra (solid curves) for superlattice samples grown at temperatures between 330 and 530 °C. Spectra were accumulated at 168° with respect to the incident 2.275 MeV $^4He^{2+}$ beam, which was aligned with the [100] growth axis. Backscattered yield below the Si surface peak (around 1.25 MeV) rises substantially as the growth temperature is increased, indicating a growing density of structural defects. An unchanneled RBS spectrum for sample SL72 (dashed curve) is shown for comparison. The spectra are plotted on the same scale but are displaced vertically for clarity.

sectional and plan-view TEM to identify the types and densities of defects within the structures. Figure 3 shows a plan-view bright-field image taken from SL37, grown at 530 °C. A network of misfit-accommodating dislocations is clearly visible, at a density of $\sim 2\times 10^{10}$ cm^{-2}. Etching away the top-half of the superlattice had no significant effect on the dislocation density, which is consistent with the suggestion from channeling and from previous studies[14] that misfit defects are often confined to the first superlattice interfaces. Plan-view studies of SL78, grown at 365 °C, revealed no such network of misfit dislocations, nor any appreciable number of threading dislocations. Considering the area examined, the misfit dislocation density in this sample is $< 10^5$ cm^{-2}. Plan-view TEM of sample SL29, grown at 330 °C, also revealed no network of misfit dislocations but showed poor surface morphology. A cross-sectional micrograph taken from this superlattice is shown in Fig. 4. Although the sample appears to be single-crystal, a large number of dislocations thread through the superlattice. In addition, while the first superlattice layers appear to be quite planar, the morphology degrades higher in the superlattice, resulting in a poor top surface. This sample is unique in showing a high density of threading dislocations.

III. DISCUSSION

The experimental results can be summarized as follows. We observe single-crystal growth above 300 °C. Superlattice SL29, grown at 330 °C, accommodates lattice mismatch primarily through elastic strain. This sample displays a high number of threading dislocations, however. The structure grown at 365 °C (SL78) shows excellent surface morphology and a defect density too low to be detected by TEM ($< 10^5$ cm^{-2}). As the growth temperature is increased to 530 °C the superlattices display monotonically increasing densities of structural defects, with misfit dislocation densities reaching 2×10^{10} cm^{-2} for SL37, grown at 530 °C.

Our results clearly demonstrate that the appearance of misfit dislocations is strongly dependent on growth conditions. The nature of this temperature-driven process is not clear at present. Mismatched thermal expansion coefficients cannot explain the changes we observe. Differences in thermal expansion coefficients[15] stress samples at 530 °C by an additional 0.03% compared to those at 330 °C. As the lattice mismatch for Ge grown on Si is 4.2%, this temperature effect is equivalent to a change in Ge fraction of $<1\%$ (i.e., consideration of thermal expansion coefficients suggests that a superlattice at 530 °C will be under less stress than a superlattice with a 1% greater Ge fraction at 330 °C). Thus,

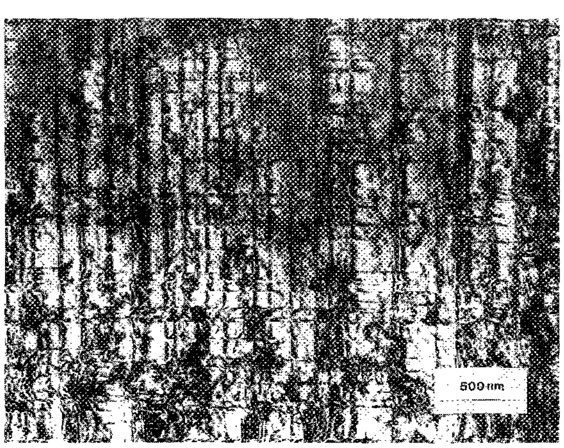

FIG. 3. Plan-view TEM image of sample SL37, grown at 530 °C, showing a network of misfit dislocations lying near the Si buffer-layer/superlattice interface. The dislocation density is $\sim 2\times 10^{10}$ cm^{-2}.

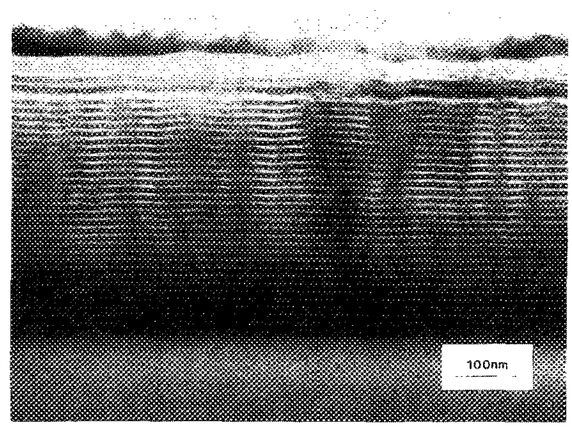

FIG. 4. Cross-sectional TEM micrograph of sample SL29, grown at 330 °C. Although superlattice layers near the Si buffer layer are quite planar, the morphology degrades considerably near the top surface. Note also the high density of threading dislocations.

the effect of thermal expansion coefficients is very small, and is more than compensated by the spread in composition of our samples, which exceeds 1%. Ge-rich structures grown at low-temperatures display lower defect densities than less-stressed samples grown at higher temperatures. Thus the temperature activation we observe is more likely associated with dislocation nucleation or glide. The precise nature of the process is presently under study.

Comparison with theoretical critical thicknesses suggests that our samples should be highly defective. Although individual layers within the superlattices are sufficiently thin to lie below the critical thicknesses predicted by all but the Van der Merwe model,[7] the superlattices as a whole lie beyond the energy-balancing limits,[6,7,12] and beyond the mechanical limit calculated by Matthews and Blakeslee.[5] Nevertheless, although samples grown at high temperatures lie beyond the critical thickness for the appearance of misfit dislocations, we find lattice mismatch to be elastically accommodated in a sample grown at 365 °C.

It is important to note that past critical thickness calculations have been based on *equilibrium* theories which neglect parameters such as temperature. Low-temperature growth techniques such as MBE clearly produce metastable structures[16] in which kinetics plays a dominant role. Thus it should not be surprising that the appearance of misfit dislocations is rarely seen to be in agreement with theory. Our results suggest that critical thicknesses are not uniquely specified for a given lattice mismatch and material system. Recent attempts to model the relaxation of misfit stresses in a metastable system have met with some success.[17] Whether models such as these can be used to predict the onset of dislocation formation in a variety of structures remains to be determined.

IV. CONCLUSIONS

We have demonstrated that the accommodation of lattice mismatch in Ge_xSi_{1-x}/Si superlattices is highly dependent on the conditions under which a sample is grown. We have seen dislocation densities of 2×10^{10} cm^{-2} and $<10^5$ cm^{-2} in compositionally identical superlattices grown at 530 and 365 °C, respectively. It is clear that by lowering growth temperatures it is possible to freeze a structure in a highly strained metastable state well beyond the critical thickness limits calculated by equilibrium theories. There appears to be a large kinetic barrier blocking dislocation nucleation or glide; the effect we observe cannot be explained by mismatched thermal expansion coefficients alone.

The film thickness at which dislocations appear is clearly dependent on growth conditions. While past theories provide equilibrium limits to defect-free growth, predicting the appearance of defects in samples grown at low temperatures will require consideration of the kinetics of defect formation. It should not be surprising that experimentally observed critical thicknesses vary substantially given the importance of fluctuations in fundamentally metastable structures. Recognizing that defect creation can be inhibited in severely mismatched systems should be important in growing heavily strained films of high quality. While the durability of these structures under prolonged use remains uncertain, by tailoring growth conditions it is possible to obtain defect-free structures well beyond the equilibrium critical thicknesses.

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