Roughening transition and solid-state diffusion in short-period $InP/In_{0.53}Ga_{0.47}As$ superlattices

M. Gerling and A. Gustafsson
Department of Solid State Physics, Lund University, Box 118, 221 00 Lund, Sweden

D. H. Rich[a)]
Department of Materials Science and Engineering, University of Southern California, Los Angeles, California 90089-0241

D. Ritter and D. Gershoni
The Solid State Institute, Technion, Haifa 32000, Israel

(Received 24 July 2000; accepted for publication 8 January 2001)

We have examined the structural properties of $InP/In_{0.53}Ga_{0.47}As$ superlattices grown by metalorganic molecular beam epitaxy by varying the periodicity and the total thickness. We observed a roughening transition, which involves the formation of wavy interfaces, when the period and total thickness of the superlattice exceeded critical values. Interface roughening in the wake of the growth front reveals that solid state diffusion in subsurface layers can be induced by surface stresses associated with surface roughening. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1353839]

Phenomena related to strain have been observed previously in superlattices (SLs) of $InP/In_xGa_{1-x}As$.[1–7] The effects were attributed to either the *intrinsic* strain related to the unavoidable presence of an InAs or $In_{0.53}Ga_{0.47}P$ monolayer (ML) at the interfaces,[1,2] or to an *extrinsic* strain caused by intermixing of group V elements.[3] A third possibility for interface related strain is exchange of group III atoms across the interface.[4] However, it has been argued that this effect is negligible in comparison to the intermixing of the group V sublattice.[5,6] A strain-induced wavy growth mode, which involves Ga and In intermixing has been observed in the growth of lattice matched $InP/In_{0.53}Ga_{0.47}As$ SLs.[7]

In connection with the topics of wavy growth and surface strain, a question arises as to whether the composition undulation is purely a surface growth related phenomenon or whether a bulk phase separation occurs. Phase separation in strained III–V alloys is of particular interest, owing to its potential for an *in situ* one-step fabrication of optically active III–V nanostructures (i.e., quantum wires and dots).[8] A commonly held view is that the subsurface atomic arrangement is frozen into place in the wake of the growth front owing to the low atomic diffusion coefficients, thus precluding the possibility of a bulk spinodal decomposition under typical growth conditions.[9] In this letter, we examine the structural morphology of nominally lattice-matched $InP/In_{0.53}Ga_{0.47}As$ SLs grown by metalorganic molecular beam epitaxy (MOMBE). By performing cross-sectional transmission electron microscopy (TEM), atomic force microscopy (AFM), and high-resolution x-ray diffraction (XRD) of the SLs at various stages of the growth, we show that the composition undulation and formation of wavy interfaces can occur in the wake of the growth front (i.e., after the growth of several smooth atomic layers). These results provide strong evidence for solid-state diffusion in bulk subsurface layers in connection with the onset of a roughening transition. Using a simple model, we show that the surface and interface roughening is correlated with an increase in the total strain energy of the SL caused by the presence of an excess InAs ML at the $In_{0.53}Ga_{0.47}As$-on-InP interface.

Several different SL structures with periods varying between 660 and 50 Å were evaluated. The ratio between quantum well (QW) and barrier thickness was varied as well. The samples were grown by a compact MOMBE system[10] on exact (100)-InP:Fe substrates. Trimethylindium, triethylgallium, arsine, and phosphine served as group III and V sources, respectively. We employed the standard method for the MOMBE growth of thick layers containing a single anion in which arsine and phosphine were purged and switched during the growth interruptions before the group III materials were introduced. The growth temperature was 500 °C, and the growth rate was about 1 ML/s. Growth interruptions between consecutive layers were of the order of 30 s, to allow full stabilization of all gas flows. The quality of the layers degraded when the total SL period was less than ~100 Å and the number of SL periods exceeded ~10. Cross-sectional TEM images are shown in Fig. 1 for $InP/In_{0.53}Ga_{0.47}As$ samples with 10 periods [in Fig. 1(a)] and 20 periods [in Figs. 1(b) and 1(c)], each possessing a period of 60 Å and $In_{0.53}Ga_{0.47}As$ well thickness of 30 Å. The (002) dark field images in Fig. 1 were acquired with the electron beam along the [110] azimuth. Wavy interfacial regions between the QW and barrier layers are observed for the sample composed of 20 periods, whereas the sample with 10 periods is free of such large structural and composition undulations. Two different regions of the 20 period sample are shown in Figs. 1(b) and 1(c) to illustrate that some variations occurred between regions. The vertical arrows point to the undulations and the horizontal arrows point to the tenth layer or midpoint for the 20 period samples. A cross-sectional TEM analysis

[a)]Electronic mail: danrich@almaak.usc.edu

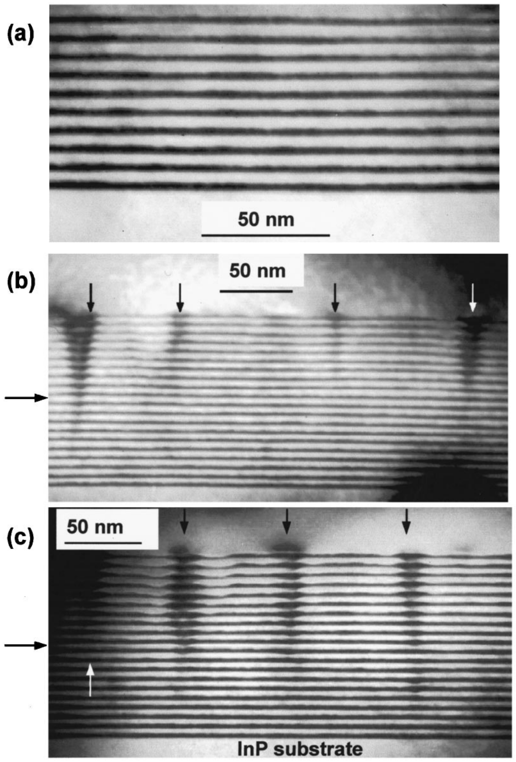

FIG. 1. (002) dark-field TEM images of two $InP/In_{0.53}Ga_{0.47}As$ samples possessing a period of 60 Å and well width of 30 Å. The total number of periods for the first sample is 10 in (a). The second sample contains 20 periods, as shown in (b) and (c) for two different regions of the same sample. The positions of the roughening for the second sample are indicated with vertical arrows in (b) and (c).

along the orthogonal azimuth, $[1\bar{1}0]$, showed an absence of such undulations in both samples.

The waviness in Figs. 1(b) and 1(c) is further characterized by vertically stacked three-dimensional (3D) hillocks of $In_{0.53}Ga_{0.47}As$ (dark regions) throughout most layers of the 20 period sample. We detect the onset of waviness in regions as close as the third or fourth layers from the substrate. The presence of the hillocks beneath the tenth layer of the SL (horizontal arrows) demonstrates that their formation occurs in the wake of the growth front and after more than 10 SL periods have been grown since no such 3D formations are observed in samples with 10 periods [Fig. 1(a)]. These data are strong evidence that solid-state diffusion occurs after 10 periods of the SL have been grown. AFM images of these samples are shown in Figs. 2(a) and 2(b) for the 10 and 20 period samples. Long wavy protrusions along the [110] direction are observed for the 20 period sample whereas a flat and featureless surface is observed for the 10 period sample. We therefore also find a strong correlation between surface roughening and wavy interfaces in these samples.

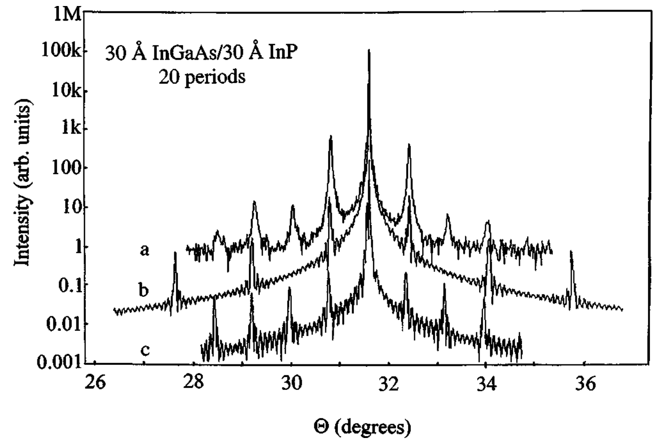

FIG. 3. Measured XRD profile (a) of a 20 period $InP/In_{0.53}Ga_{0.47}As$ SL with a period of 60 Å and well width of 30 Å. XRD simulations are shown assuming no InAs ML at the $In_{0.53}Ga_{0.47}As$-on-InP interface (b) and assuming the presence of an InAs ML (with a thickness of 3.0 Å) at the $In_{0.53}Ga_{0.47}As$-in-InP interface (c).

In order to evaluate the source of the strain in these samples, a set of XRD results for the 20 period $InP/In_{0.53}Ga_{0.47}As$ SL sample is shown in Fig. 3. The measured XRD profile is shown in Fig. 3(a). The well-resolved and intense satellite peaks indicate that the interfaces are smooth. Simulations of the rocking curves were performed in Figs. 3(b) and 3(c) using the Tagaki–Taupin approach.[11] Two simulations are shown for a structure without an InAs ML at the $In_{0.53}Ga_{0.47}As$-on-InP interface [Fig. 3(b)] and for a structure possessing an InAs ML at the $In_{0.53}Ga_{0.47}As$-on-InP interface [Fig. 3(c)]. Comparisons of the measured XRD spectra with the simulations yield a result most consistent with the assumption of the presence of an InAs ML at the interfaces, consistent with Refs. 1 and 2. We cannot, however, preclude the existence of some alloying to form a high-arsenic content InAsP ML,[5,6] owing to possible anion interdiffusion at the growth temperature. Our results thus exclude *extrinsic* interface strain, which is caused by a large intermixing of P and As, as the primary source for the degradation of short period SLs. We suggest that roughening in the SLs is caused by an *intrinsic* strain, owing to the

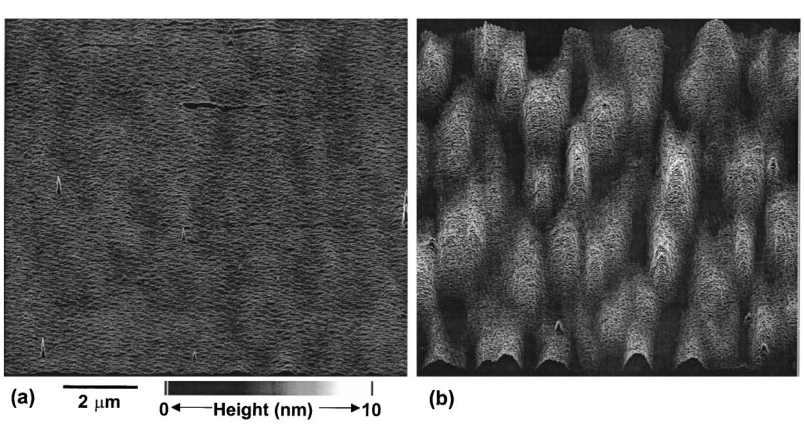

FIG. 2. AFM images of $InP/In_{0.53}Ga_{0.47}As$ samples with a total of 10 (a) and 20 (b) periods. Each sample possesses a period of 60 Å and well width of 30 Å.

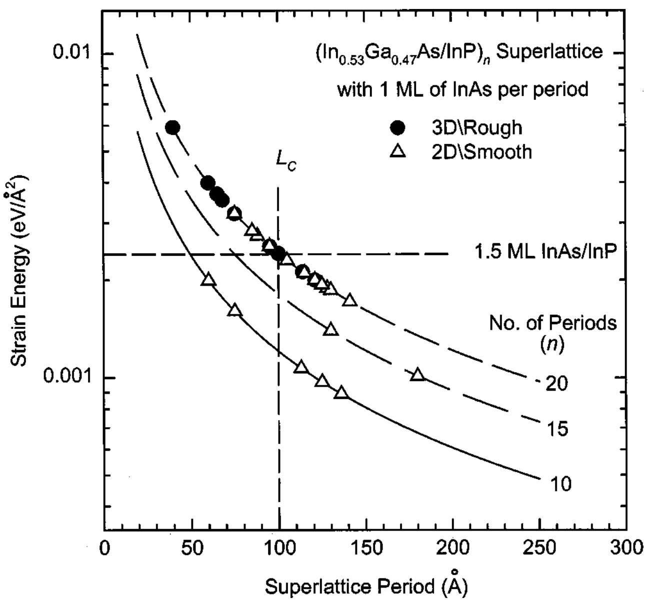

FIG. 4. Calculation of ε_S vs superlattice period (L) according to Eq. (1), for $n=20$, 15, and 10 periods. Solid and open symbols represent samples that have and have not exhibited a roughening transition, respectively.

presence of an excess InAs ML at the $In_{0.53}Ga_{0.47}As$-on-InP interfaces.

We hypothesize that the solid state diffusion that occurs in the wake of the growth front is a result of the increase in strain energy caused by the excess InAs at the $In_{0.53}Ga_{0.47}As$-on-InP interfaces. In order to demonstrate that the presence of excess InAs will raise the average total strain energy (ε_S) of the SL to a level where a morphological two-dimensional (2D)–3D transition can occur, we calculate ε_S as

$$\varepsilon_S = nG(x)\left[\frac{1+\nu(x)}{1-\nu(x)}\right]Lf(x)^2, \tag{1}$$

where $G(x)=1/2[c_{11}(x)-c_{12}(x)]$ is the shear modulus, $\nu(x)=c_{12}(x)/[c_{11}(x)+c_{12}(x)]$ is Poisson's ratio, L is the SL period (which is about twice the QW thickness), $f(x)$ is the misfit with respect to the InP substrate, n is the number of periods of the SL, and x is the average In composition.[12] The average In composition, x, is determined by averaging the In composition of the $In_{0.53}Ga_{0.47}As$ layer with the additional InAs ML of the SL.[13] The elastic constants $c_{11}(x)$ and $c_{12}(x)$ are given by $c_{11}(x)=(11.88-3.551x)10^{11}$ and $c_{12}(x)=(5.38-0.854x)10^{11}$ (in dyn/cm^2).[14] The calculation of $\varepsilon_S(T)$ for $n=20$, 15 and 10 periods is shown in Fig. 4 with the data interposed on the calculated curves. Solid and open symbols represent samples that have and have not exhibited a roughening transition, respectively. Further, we show the value of the strain energy (horizontal dashed line) for a 1.5-ML-thick film of InAs on InP(001), which is the coverage at which a 2D–3D growth mode transition is found to occur.[15] It is evident that the minimum strain energy associated with the roughening transition for $L_C \approx 100$ Å correlates well with the strain energy of the 1.5 ML InAs film. Therefore, we infer that SL samples, which exhibit waviness and surface roughness, undergo a similar 2D–3D morphological transformation.

Since the wavy interfaces are correlated with surface roughening, the solid-state diffusion may be induced initially by a surface roughening transition, which can effect the underlying strain fields in the SL. These strain fields will act to further laterally phase separate growth of successive layers through "lattice-latching," where the In and Ga species prefer larger and smaller, respectively, local in-plane lattice constants.[8,9] Further, the lateral strain field will also raise the critical temperature for the occurrence of spinodal-decomposition in the bulk of a ternary III–V compound,[9] thereby favoring the in-plane solid-state diffusion. These two effects may explain the appearance of vertically organized In-rich regions that are seen in TEM (Fig. 1). A similar phenomenon appears during the growth of multiple layers of InAs/GaAs quantum dots, in which vertically self-organized quantum dots form as a result of the vertically propagating strain fields.[16]

In conclusion, we demonstrate the importance of solid-state diffusion in the wake of the growth front, which occurs in conjunction with a 2D–3D surface roughening transition. The presence of an InAs ML at the $In_{0.53}Ga_{0.47}As$-on-InP interface provides the strain energy necessary to induce these transitions after a critical number of layers are grown. These results provide evidence for a spinodal decomposition behavior, and may help to explain the phase separation that leads to quantum nanostructures in similar highly strained SL systems.

M.G. gratefully acknowledges the Royal Physiographical Society of Lund, L. M. Ericsson, and the Swedish Natural Science Research Council. A.G. thanks the National Center for High Resolution Electron Microscopy at Lund University, D.H.R. acknowledges sabbatical support from the Lady Davis Fellowship Trust.

[1] J. M. Vandenberg, M. B. Panish, R. A. Hamm, and H. Temkin, Appl. Phys. Lett. **56**, 910 (1990).
[2] M. S. Hybertsen, Phys. Rev. Lett. **64**, 555 (1990); J. Vac. Sci. Technol. B **8**, 773 (1990).
[3] H. Y. Lee, M. J. Hafich, and G. Y. Robinson, J. Cryst. Growth **105**, 1210 (1990).
[4] M. Krishnamurty, A. Lorke, and P. M. Petroff, Surf. Sci. **304**, 493 (1994).
[5] R. Meyer, M. Hollfelder, H. Hardtdegen, B. Langeler, and H. Lüth, J. Cryst. Growth **124**, 583 (1992).
[6] A. R. Clawson, X. Jiang, P. K. L. Yu, C. M. Hanson, and T. T. Vu, J. Electron. Mater. **22**, 155 (1993).
[7] U. Bangert, A. J. Harvey, C. Dieker, and H. Hartdegen, Appl. Phys. Lett. **69**, 2101 (1996); J. Appl. Phys. **78**, 811 (1995).
[8] K. C. Hsieh and K. Y. Cheng, Mater. Res. Soc. Symp. Proc. **379**, 145 (1995).
[9] F. Glas, J. Appl. Phys. **62**, 3201 (1987).
[10] R. A. Hamm, D. Ritter, and H. Temkin, J. Vac. Sci. Technol. A **12**, 2790 (1994).
[11] P. F. Fewster, Semicond. Sci. Technol. **8**, 1915 (1993).
[12] R. People and J. C. Bean, Appl. Phys. Lett. **47**, 322 (1985).
[13] The XRD results and modelling of Ref. 1 demonstrates that the average strain in the QW of an InP/InGaAs SL is well approximated by averaging the strain of the single interfacial InAs monolayers over the whole InGaAs QW.
[14] S. Adachi, J. Appl. Phys. **53**, 8775 (1982).
[15] A. Ponchet, A. Le Corre, H. L'Haridon, B. Lambert, and S. Salaun, Appl. Phys. Lett. **67**, 1850 (1995).
[16] Q. Xie, A. Madhukar, P. Chen, and N. P. Kobayashi, Phys. Rev. Lett. **75**, 2542 (1995).