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Spontaneous formation of nanostructures by surface spinodal decomposition in GaAs$_{1-x}$Bi$_x$ epilayers

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We report on the spontaneous formation of lateral composition modulations (LCMs) in Ga(As,Bi) epilayers grown by low-temperature (<300 °C) molecular beam epitaxy (MBE) on GaAs(001). Both cross-section and plan-view transmission electron microscopy techniques are used to investigate the nature of the LCMs, consisting of Bi-rich cylinder-like nanostructures lying along the [001] growth direction. The observed LCMs are the consequence of a two-dimensional phase separation process occurring at the surface of the growing epilayers, and their columnar nature is consistent with a surface-directed spinodal decomposition process. Although LCMs are thermodynamically driven, we show how they can be kinetically controlled, in particular, through the As/Ga flux ratio and the substrate temperature. This is a result of LCMs developing from surface atomic diffusion processes, since the atomic dimer configurations on the surface alter adatom diffusivity. The significant role of the surface reconstructions is also discussed. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

The development of III-V-Bi compounds has recently emerged as a strong research field in semiconductor science and technology. In particular, GaAs$_{1-x}$Bi$_x$ alloys exhibit, among other advantageous properties, a large band gap reduction upon the incorporation of a few percent Bi (~90 meV/% of Bi) and a strong enhancement of the spin-orbit splitting. Hence, the use of bismide compounds could bring important benefits for the development of mid-infrared lasers, detectors, high-efficiency solar cells, and other photonic and/or spintronic devices. Furthermore, interest in this novel material goes beyond optoelectronics and basic material-related properties such as alloy stability, segregation, or solubility limits are still unknown. GaAs$_{1-x}$Bi$_x$ belongs to the so-called highly mismatched alloys (HMAs), which are formed by the isoelectronic substitution of elements with very different size and/or electronegativity (in the present case, As would be replaced by Bi, a much larger atom with lower electronegativity). As a consequence, HMA are often affected by a miscibility gap, which makes their growth challenging due to the tendency of the alloy to phase separate in addition, phase separation has direct implications on the optical response and on the electronic properties. Extensive work on the HMA (In,Ga)(As,N) material system has evidenced that the occurrence of composition fluctuations and morphological instabilities have a detrimental effect on the optical response and hence limits optoelectronics applications. In this respect, little is known about morphological instabilities in III-V-Bi compounds.

In general, the microstructure of GaAs$_{1-x}$Bi$_x$ layers and its correlation with the molecular beam epitaxy (MBE) growth conditions have been largely unexplored. This is in contrast with the large amount of published works on the electronic and optical properties of GaAs$_{1-x}$Bi$_x$, where, interestingly, the occurrence of peculiar or not well understood properties is often mentioned. Recently, using transmission electron microscopy (TEM) techniques, Norman et al. and Reyes et al. reported the occurrence of both CuPt-type atomic ordering and phase separation in MBE grown GaAs$_{1-x}$Bi$_x$ layers. In particular, Norman et al. found that the phase-separated microstructure took the form of irregular, anisotropic platelets.

In this work, we show that GaAs$_{1-x}$Bi$_x$ layers exhibit an intricate microstructure which is strongly dependent on the MBE growth conditions. In the detailed microstructural analysis performed using TEM, we show that while the layers grown at “higher” substrates temperatures (T_s) show a homogeneous Bi incorporation and are free of clusters and/or morphological instabilities, the growth at lower T_s results in pronounced and well-defined quasi-periodic lateral composition modulations (LCMs), where the phase separation takes the form of spontaneously developed vertical stripes. In particular, LCMs consist of a regular array of columnar-like nanostructures with their axis oriented along the optic [001] growth direction. In addition, TEM experiments reveal that the columnar structure is consistent with the occurrence of surface spinodal decomposition during growth.

II. EXPERIMENTAL DETAILS

The investigated samples consist of 270 nm thick GaAs$_{1-x}$Bi$_x$ epilayers grown by solid-source MBE on GaAs(001) substrates. Conventional effusion cells were used for Ga and Bi and a two-zone cracker source was used for As$_2$. Prior to the GaAs$_{1-x}$Bi$_x$ layer growth, a ~140 nm thick GaAs buffer layer was grown at T_s = 580 °C, after which T_s...
was significantly reduced for the growth of GaAs$_{1-x}$Bi$_x$. In the investigated samples, $T_s$ varied between 220°C and 315°C and the estimated atomic As/Ga flux ratio ranged between 1.2 and 1.9. The growth rate was 0.4–0.5 μm/h for all samples. The Bi content varied between 1.3% and 4.7%, and it was determined from the lattice mismatch between Ga(As,Bi) and GaAs measured by X-ray diffraction (XRD) after assuming Vegard’s law and a GaBi lattice parameter of 6.33 Å. Detailed growth conditions are reported elsewhere. Cross-sectional TEM foils were prepared in the [110] and [110] projections using mechanical thinning followed by Ar-ion milling. TEM investigations were carried out using a Jeol JEM 3010 microscope operating at 300 kV equipped with a GATAN slow-scan CCD camera. The investigated samples are summarized in Table I.

### III. RESULTS AND DISCUSSION

#### A. Lateral composition modulations

Figure 1(a) displays a cross-section two-beam dark-field (DF) TEM micrograph obtained using the chemically sensitive diffraction vector $g=002$ of the pseudomorphic layer with 1.3% Bi grown at the higher $T_s=315°C$ (sample A in Table I). The homogeneous intensity contrast in the $g_{002}$ DFTEM image indicates a homogeneous layer, where no extended defects, clustering, or contrast modulations are detected. Furthermore, quantitative chemical determination from the analysis of the $g_{002}$ diffracted intensity, following the procedure proposed by Bithell and Stobbs, yields [Bi] ~ 1.4%, which is in good agreement with the Bi content extracted from XRD (1.3%). In the analysis, we assume that Bi incorporates substitutionally at As positions, as well as the validity of Vegard’s law. Similar results (images not shown here) are obtained for sample B (4.7% Bi and $T_s=315°C$).

On the contrary, the layers grown at $T_s=220°C$ reveal an unexpected quasi-periodic lateral variation of the image contrast taken under $g_{002}$ two-beam conditions, as observed in Figures 1(b), 1(c), and 2. The DFTEM micrographs in Figures 1(b) and 1(c) correspond to sample C (1.5% Bi) and are taken along the two perpendicular [110] zone axes. This sample was grown under identical conditions as sample A except for its lower $T_s=220°C$. Since $g=002$ DFTEM micrographs are chemically sensitive, the contrast modulation directly reflects the presence of lateral composition modulations perpendicular to the (001) growth plane. Assuming that the substitutional incorporation of Bi also holds when growing at $T_s=220°C$, the bright vertical stripes in Figures 1(b) and 1(c) correspond to Bi-rich areas, whereas the dark vertical stripes correspond to As-rich ones. In analogy to the 315°C samples, no extended defects and/or clusters are detected in the pseudomorphic layers. In some cases, V-shaped or “semi” V-shaped domain structures are observed close to the sample surface [Figure 1(c)]. These intriguing features correspond to areas with triple-period atomic ordering (TPO). A detailed investigation on TPO in these samples is reported elsewhere.

As observed in Figures 1(b) and 1(c), LCMs are detected along both the [110] and [110] directions, with a modulation period of $λ=15–20$ nm along [110] directions [cf. Figure 1(d)]. Interestingly, all investigated epilayers grown at 220°C show clear LCMs regardless of their Bi content. Apparently, the layer composition (namely, an increased Bi content in the layer) has a negligible impact on the modulation period $λ$, since samples with 4.7% Bi and 1.5% Bi exhibit the same period: $λ=20$ nm for samples C and E. Similarly, $λ=14–15$ nm for samples D and F. We find, however, slight differences in $λ$ for series of epilayers with identical growth parameters except for the As/Ga ratio: $λ=20$ nm for sample E with an As/Ga ratio of 1.2 and $λ=14$ nm for sample F with an As/Ga ratio of 1.4. Similarly, $λ=20$ nm for sample C with an As/Ga ratio of 1.6, whereas $λ=15$ nm for sample D with an As/Ga ratio of 1.9. We attribute the small variation in the period of the LCMs to variations in the growth kinetics, which in this case arise from the different As/Ga flux ratios. Interestingly, investigations on LCMs in other III–V semiconductor alloys have established a correlation between the modulation wavelength $λ$ and the atom surface diffusion length $λ^*$. In a rough approximation, $λ^* ≈ λ$. In the case of III–V–Bi compounds, there is a lack of data regarding atomic surface diffusion lengths, with

### Table I. Summary of the investigated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_s$ (°C)</th>
<th>As/Ga ratio</th>
<th>[Bi]%</th>
<th>$λ_{002}$ (nm)</th>
<th>$λ_{Bi-rich}$ (nm)</th>
<th>$λ_{As-rich}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>315</td>
<td>1.6</td>
<td>1.3%</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>B</td>
<td>315</td>
<td>1.5</td>
<td>4.7%</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>C</td>
<td>220</td>
<td>1.6</td>
<td>1.5%</td>
<td>20 ± 1</td>
<td>12 ± 2</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>D</td>
<td>220</td>
<td>1.9</td>
<td>1.4%</td>
<td>15 ± 2</td>
<td>9 ± 2</td>
<td>6 ± 2</td>
</tr>
<tr>
<td>E</td>
<td>220</td>
<td>1.2</td>
<td>4.7%</td>
<td>20 ± 2</td>
<td>5 ± 1</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>F</td>
<td>220</td>
<td>1.4</td>
<td>2.9%</td>
<td>14 ± 2</td>
<td>8 ± 2</td>
<td>6 ± 2</td>
</tr>
</tbody>
</table>
only few works commenting on the topic.\textsuperscript{19,20} The same is true for LCMs in bismide alloys.\textsuperscript{11} Furthermore, it is unclear whether $\Lambda$ is determined by $\lambda_{Ga}$, $\lambda_{As}$, or $\lambda_{Bi}$. For a qualitative discussion of $\Lambda$ in Ga(As,Bi), we have then to rely on available data on surface diffusion rates from other III-As alloys. Among them, the GaAs system and $\lambda_{Ga}$ are the most investigated.\textsuperscript{21–23} Since most of the experiments on surface diffusion on GaAs were done at $T_s > 550^\circC$ and on the $(2 \times 4)$ surface reconstruction,\textsuperscript{21,22} we rely on the recent experiments by Bietti et al., which were carried out at $T_s = 300–375^\circC$.\textsuperscript{23} Using their values for the diffusion activation energy and diffusion prefactor, we estimate $\lambda_{Ga}$ at $T_s = 220^\circC$ to be about 2–3 nm. On the other hand, the reported persistence of reflection high-energy electron diffraction (RHEED) oscillations in Ga(As,Bi)(001) at $T_s < 350^\circC$ compared to GaAs, where RHEED oscillations are difficult to observe at these low $T_s$,\textsuperscript{24,25} indicates a significantly enhanced surface diffusion length on Ga(As,Bi), even at this low temperature. It is then reasonable to assume that $\lambda_{Ga}$ on Ga(As,Bi)(001) would be on the order of 10–20 nm, similar to our measured $\Lambda$. The change in $\Lambda$ with the As flux can explain our experimentally observed reduction in $\Lambda$ from about 20 nm to about 14–15 nm with the increase in As/Ga ratio, since the increase in As (at constant $T_s$ and growth rate) reduces $\lambda$.\textsuperscript{22,23} The modulation amplitude, i.e., the relative variation in Bi content from the Bi-rich to the As-rich regions, amounts to about $\Delta[Bi]/[Bi] = 30\%$ in sample E. $\Delta[Bi]/[Bi]$ has been experimentally determined from the difference in [Bi] between Bi-rich and Bi-poor areas, where [Bi] is extracted from the analysis of the chemically sensitive $g_{002}$ DFTEM images, following the method proposed by Bithell and Stobbs.\textsuperscript{15} We could not find a clear correlation between the modulation amplitude and the period $\Lambda$.

B. Surface spinodal decomposition

LCMs have already been reported in other III–V semiconductor alloys and have been attributed to the presence of a miscibility gap. Due to the large miscibility gap between GaAs and Bi, there is a strong thermodynamic driving force for phase separation in this material system. In addition, it is well established that in layers grown from the vapor phase (like the present MBE-grown samples), LCMs and phase separation processes often proceed via surface spinodal decomposition, i.e., at the growing surface, where the higher surface diffusivity facilitates the decomposition compared to the slow bulk diffusion processes in (bulk) spinodal decomposition.\textsuperscript{17,26} Thus, LCMs spontaneously develop in the very early stages of film growth and the frozen two-dimensional decomposed areas serve as a template for the subsequently deposited material.\textsuperscript{27} Moreover, theoretical and experimental works reveal that layers undergoing surface-directed spinodal decomposition frequently exhibit a distinctive decomposition morphology characterized by nanometer-sized columnar-like structures along the growth direction where the columns are enriched in one of the (decomposed) phases.\textsuperscript{17,26–28} From our cross-section TEM observations, we have strong evidence that the spontaneous LCMs in the GaAs$_{1−x}$Bi$_x$ epi-layers are due to surface spinodal decomposition, where the LCMs have the form of cylinder-like or columnar nanostructures along the growth direction. The supporting evidence is as follows: (i) LCMs are observed along the two perpendicular $(110)$ projections with the same periodicity $\Lambda$ in both directions [cf. Figure 1], i.e., $\Lambda_{[110]} \approx \Lambda_{[\bar{1}10]}$; (ii) the transition from Bi-rich to As-rich regions seems to be smooth with a diffuse interface, as is characteristic of spinodal decomposition. Concerning (i), although the LCMs are better defined in the $(110)$ zone axis [cf. Figure 1], in all samples we find that $\Lambda_{[110]} \approx \Lambda_{[\bar{1}10]}$, where $\Lambda_{[110]}$ are average values obtained from the statistical analysis of more than 20 $g_{002}$ DFTEM micrographs in each zone axis. The values of $\Lambda$ with their standard deviations shown in Table I correspond to $\Lambda_{[110]}$. Regarding (ii), a first analysis of the modulation [cf. Figure 2(c) displaying a representative intensity line-scan] reveals a transition width between the Bi-rich and As-rich areas (10%–90%)\textsuperscript{29} of about 25 ML (7 nm). The quantitative determination of the transition width was achieved by fitting to a sigmoidal function\textsuperscript{29} as shown in Figure 2(d). In the analysis, we consider LCMs at different positions of the sample. We focused on modulation fringes which were very well-defined, highly uniform and with a size ($\Lambda_{Bi-rich}$) close to the average value (cf. Table I). Due to the contribution from the LCM morphology (i.e., cylinder-like nanostructures), we are not able to deconvolute the chemical width of the transition. The data exposed here constitute a first attempt to estimate the width of the decomposed area. For a most elaborated analysis, however, the specific geometry of the decomposed areas has to be carefully considered.

In order to further investigate the nature of the composition modulations, we have performed plan-view TEM on sample E. We select this sample since, for these growth conditions, no TPO domains close to the surface are

![Image](https://via.placeholder.com/150)

**FIG. 2.** TEM micrographs of GaAs$_{0.98}$Bi$_{0.02}$/GaAs grown at $T_s = 220^\circC$ and As/Ga ratio of 1.2 (sample E). (a) Cross-section chemically sensitive $g_{002}$ DFTEM micrograph, (b) plan-view $g_{002}$ bright-field TEM micrograph, displaying the columnar morphology of the two-dimensional decomposition. (c) Intensity line-scan displaying the LCMs. (d) The analysis of the modulation [the data are extracted from (c)] reveals a transition width (10%–90%) of about 25 ML (7 nm). The solid line represents the fit to a sigmoidal function and the red marks, the transition width.
detected, which would hinder the plan-view TEM observations. The results are presented in Figure 2(b). The plan-view TEM reveals a regular array of columnar-like structures. Furthermore, the size of the Bi-rich areas [cf. the dark circular spots in the g = 002 bright-field plan-view TEM micrograph in Figure 2(b)] matches the size of the bright stripes observed in cross-section TEM observations along (110) directions: \( \Lambda = 20 \text{ nm} \) with about 15 nm (As-rich) + 5 nm (Bi-rich) (cf. Table I). The observed decomposition morphology fully agrees with experimental and theoretical works on surface spinodal decomposition in other III–V semiconductor systems.18,26,30,31

As observed in Figure 1(c), LCMs seem to develop after a certain thickness \( t_{\text{LCM}} \), i.e., LCMs are not detected close to the GaAs buffer but initiate some distance away from the GaAs buffer/Ga(As,Bi) interface. The origin might be related to the buildup of a Bi wetting layer due to Bi surface segregation.19 The analysis of Bi composition profiles at the Ga(As,Bi)-on-GaAs interface reflects traces of Bi segregation and delayed Bi incorporation, although it is not possible to make a direct correlation with \( t_{\text{LCM}} \) neither with \( \Lambda \), since traces of Bi segregation are also detected in the homogeneous layers \( (T_s = 315^\circ \text{C}) \). Following the work of Spencer et al., \( t_{\text{LCM}} \) is considered as a “kinetic critical thickness” for the onset of LCMs and is very sensitive to relative differences in adatom mobilities.32 The importance of surface mobility was also pointed out by Venezuela and Tersoff,33 who demonstrated that differences in atomic mobility on the surface could lead to substantial decomposition even when atomic sizes were identical. On the other hand, it is well-known that surface reconstructions have a significant impact on the adatom surface diffusion.17,21,22 Based on Monte Carlo simulations of phase separation in semiconductor alloys, Kaspi and Barnett predicted that semiconductor surfaces with stable dimers reconstructions would exhibit reduced decomposition compared with surfaces with less stable reconstructions.17 Therefore, segregated Bi will likely not only affect adatom surface diffusion but also trigger a change towards a surface reconstruction which could favor decomposition.

Both experimental and theoretical works reveal the complexity of the surface reconstruction phase diagram in Ga(As,Bi)(001).24,34–36 From the reported data, it is clear that the boundaries of Bi-related reconstructions at \( T_s < 370^\circ \text{C} \) are relatively insensitive to changes in \( T_s \) but extremely sensitive to small changes in the As/Ga ratio.24 In Ga(As,Bi)(001), there are two main surface reconstructions: the \((2 \times 1)\) reconstruction occurring at low As/Ga ratios close to stoichiometry (this reconstruction enables high quality layers with the highest Bi incorporation19,24,34); and a set of \((n \times 3)\) reconstructions with multiple stable configurations and dimer disorder among the individual \((4 \times 3)\) surface units.34–36 The surface reconstruction and stoichiometry not only regulates the total Bi incorporation but also likely determines the compositional uniformity across the surface.10,34 Furthermore, some groups predict that the configurational disorder of the \((n \times 3)\) reconstructions can induce clustering, atomic ordering, and/or composition fluctuations.34–36 Due to technical limitations in our MBE chamber, we could not identify the surface reconstruction of the investigated samples. However, comparison with the only reported phase diagram by Masnadi-Shirazi et al.24 reveals that for the growth parameters of the layers at \( T_s = 315^\circ \text{C} \), the \((2 \times 1)\) is the stable surface reconstruction, as schematically represented in Figure 3. This may explain the observed composition homogeneity in this case. Figure 3 shows the location of our experimental data points within the GaAs,Bi) phase diagram drawn using the data from Masnadi-Shirazi et al.24 While there is a lack of data for \( T_s < 250^\circ \text{C} \) in this case, the surface reconstruction may be a mixture of \((2 \times 1)\) and \((2 \times 3)\) phases [the \((2 \times 3)\) phase is addressed as a mixture of \((2 \times 1)\) and \((1 \times 3)\)24] at the growth conditions of samples C–F, with contribution of \((1 \times 3)\) at higher As/Ga ratios, as proposed in Figure 3. Although we can only discuss LCMs at the speculative level, it is clear that the specific dependence of surface reconstructions in Ga(As,Bi)(001) on the As/Ga flux ratio can explain our intriguing experimental findings of: (i) the presence of LCMs at \( T_s = 220^\circ \text{C} \) but not at \( T_s = 315^\circ \text{C} \) and (ii) the different \( \Lambda \) in samples grown at the same \( T_s \) but with different As/Ga flux ratios, since small variations in the As/Ga flux ratio would promote changes in the surface stoichiometry and surface reconstruction, and, thus, in the adatom surface diffusion.19,24,34

Finally, we would like to note that the microstructure (LCMs and TPO) of \( T_s = 220^\circ \text{C} \) Ga(As,Bi) as-grown epilayers significantly modifies with post-growth thermal annealing treatments. In particular, rapid thermal annealing at \( T_{\text{anneal}} > 600^\circ \text{C} \) results in the disappearance of both LCMs and TPO, as well as in the formation of Bi-rich quantum dot-like nanoclusters.37

IV. SUMMARY

We demonstrate the spontaneous formation of columnar-like nanostructures by means of surface spinodal decomposition in Ga(As,Bi) epilayers. The modulated structures are very regular in size and distribution and can be controlled by a careful selection of the growth conditions, in particular, of the As/Ga flux ratio and the surface reconstruction. Although not yet explored, the presence of LCMs in this material system may not necessarily be detrimental, since the highly uniform Bi-rich nanostructures may constitute new functional

FIG. 3. Schematic representation of the location of the investigated samples on the phase diagram of surface reconstructions in Ga(As,Bi)(001) as determined by Masnadi-Shirazi et al.24 The dashed lines are to guide the eye.
units for future optoelectronic and/or spintronic devices, expanding the potential application of dilute bismides alloys.

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