Optical spectroscopic studies of InAs layer transformation on GaAs surfaces

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The optical properties of InAs monolayer and submonolayer coverage formed in a GaAs matrix by molecular-beam epitaxy have been studied. Prolonged growth interruptions were introduced after the InAs layer was deposited. In samples with intentionally deposited submonolayer InAs coverage, the luminescence efficiency was maintained and no emission line broadening was observed up to very long interruption times, suggesting this arrangement is stable. On the other hand, one InAs ML was found to be unstable with a tendency towards transformation into two surface arrangements: InAs anisotropic multilayer islands and uniform submonolayer distribution of InAs molecules over the surface. For InAs coverage larger than 1 ML, it was found that long growth-interruption times favor the formation of thicker three-dimensional InAs islands and may result in a local strain relief. It was found that in the case of monolayer coverage, the luminescence line shape broadens and the intensity decreases as the growth interruption time increases. Our results explain how the marked improvement of the optical quality of structures grown by submonolayer epitaxy may arise.

The growth of highly strained InAs-GaAs heterostructures on GaAs substrates with different orientation has attracted much interest.[1-4] In addition to a strong fundamental interest in growth-related phenomena,[5-6] these structures have numerous practical applications in optoelectronics and microelectronics.[7] These systems were also seen as possible candidates for the creation of quantum wires and dots.[8,9] InAs quantum wires and dots were grown selectively on SiO_2-patterned GaAs substrates[8] or on terraced GaAs surfaces with submonolayer InAs coverage.[9] More recently, the transformation of inherently unstable strained layers into quantum dots and wires was explored in various strained heterostructures. Mo *et al.*[10] investigated the transition from two-dimensional (2D) to 3D growth of Ge on Si(001) by scanning-electron microscopy. They demonstrated the formation of pyramidlike 3D Ge clusters with a specific facet crystallography and alignment of their principal axes with respect to the substrate. The clusters have a lateral aspect ratio from 1:1 (dots) to 8:1 (wires). Similar island formation was observed in the earlier stages of growth of highly strained $In_xGa_{1-x}As$ on GaAs(001).[11] A 3D island morphology was evolved from an initial 2D wetting surface. Again, such island formation provides a mechanism for strain relaxation without dislocations.[12] Further theoretical and experimental studies by Tersoff and Tromp[13] revealed that these shape transitions are generally involved in the growth of highly strained heterostructures. Strained epitaxial layers tend to grow initially as dislocation-free islands. Above a critical size, the islands transform into a long thin shape with an aspect ratio as high as 50:1 in order to allow better elastic relaxation of the island's stress. Therefore, with proper control of growth parameters, spontaneous formation of quantum wires and dots can be achieved in strained-layer systems.

In this paper we report spectroscopic studies in InAs layer transformation in strained InAs/GaAs heterostructures on both (100)-oriented and high-index surfaces with different growth interruption times. The results demonstrate the coexistence of uniformly distributed InAs molecules and anisotropic InAs islands and explain the possible mechanism for such transformation in the highly strained InAs-GaAs system.

The structures were grown by elemental-source molecular-beam epitaxy (MBE) side by side on (100)- and (311)A-oriented GaAs semi-insulating substrates. Growth rates were 0.8 μm/h for GaAs and 0.3 μm/h for InAs. After oxide desorption, a 0.3-μm-thick GaAs buffer layer was grown at 600°C. This layer was followed by a 40-period 25-Å GaAs/25-Å $Al_{0.4}Ga_{0.6}As$ superlattice (SL) to trap impurities and to prevent nonequilibrium carriers from spreading into the semi-insulating substrate. The SL was followed by a 2000-Å GaAs layer, then the substrate temperature was lowered to 450°C and the arsenic beam equivalent pressure was increased to 10^{-5} torr. After this, a 100-Å-thick GaAs layer was deposited, which was followed by the InAs layer. At this stage, different growth interruption times ranging from 10, 100, and up to 1000 seconds (s) were introduced. After the growth interruption, 20 Å of GaAs was grown on the top. Then the substrate temperature was increased to 600°C and the arsenic pressure was reduced to 3×10^{-6} torr to grow a 2000-Å-thick GaAs layer. Finally, a 40-period 25-Å GaAs/25-Å $Al_{0.4}Ga_{0.6}As$ SL was grown to prevent surface recombination and to avoid

surface-related electric fields. The low substrate temperature and the high arsenic pressure minimized In segregation effects.[14] InAs layers with an average thickness varying between 1 Å and 4 monolayers (ML) were grown for this investigation. The samples with the InAs coverage of 1 Å and 1 ML were extensively studied in this work.

For photoluminescence (PL), PL excitation (PLE), and polarizability studies, Ar^+ and Ti-sapphire lasers were used. The PL signal was analyzed with a 1-m double monochromator and a cooled photomultiplier operating in the standard photon-counting mode. Samples were chemically polished on the back face and held by paper frames in a He-flow cryostat to avoid any possible source of external strain.

PL spectra of (100)-grown structures with 1-ML-thick InAs coverage for three different growth interruption times were investigated thoroughly and are shown in Fig. 1. The GaAs free-exciton emission can be seen on the high-energy side of the spectra and the InAs-related PL line at lower energies. Structures grown with 10-s growth interruption show essentially the same PL line position and width as structures grown without growth interruption.[15] Increasing the growth interruption time results in (i) a relative decrease of InAs-related luminescence intensity, (ii) broadening and splitting of the main InAs-related peak, (iii) the appearance of a polarized low-energy band (band centered at ~ 1.45 eV of the spectrum in the 1000-s sample in Fig. 1). Therefore, in samples grown with growth interruptions, the InAs monolayer-related peak splits into a broader feature that shifts to lower energies with respect to luminescence line of an initial InAs monolayer grown without growth interruption. At the same time, a sharper peak appears on the high-energy side.

In Fig. 2, PLE spectra of the two main luminescence features of (100)-grown samples with 1000-s growth interruption time are shown. Both the high-energy feature and the main PL peak show two similar peaks in the respective PLE spectra with similar energy positions. This is demonstrated in Fig. 2(a), where only the PLE

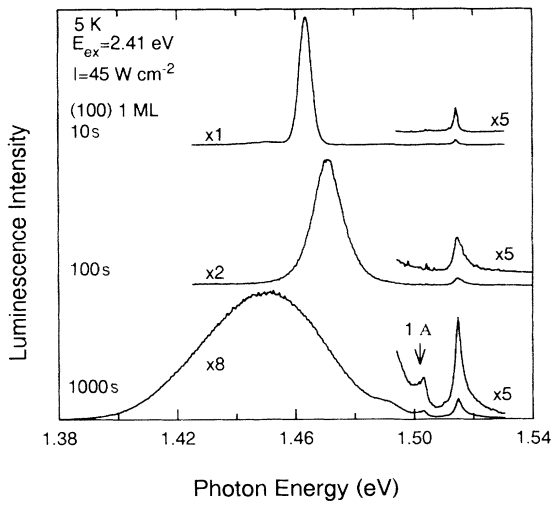

FIG. 1. Photoluminescence spectra of 1 ML InAs grown with three different growth interruption times.

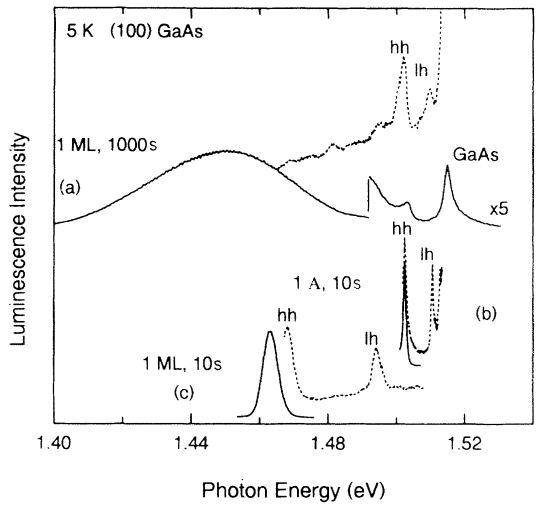

FIG. 2. PL (solid line) and PLE (dotted line) spectra of 1-ML InAs samples grown with a 1000-s growth interruption (a); of a 1-Å InAs sample grown with 10-s growth interruption (b); of a 1-ML InAs sample grown with a 10-s growth interruption (c). The decomposition of InAs monolayer coverage with long growth interruption into stable submonolayer InAs coverage is demonstrated.

spectrum of low-energy emission is shown. The two peaks have heavy-hole and light-hole characteristics, confirmed by circular-polarization measurements; however, their energy positions are different from those found for a 1-ML InAs sample grown with a much shorter interruption time, corresponding effectively to a "thinner" InAs coverage[15] (< 1 ML). Figure 2 (b) shows PL and PLE spectra of an InAs submonolayer sample where the average InAs layer thickness is equivalent to 1 Å. One can see that the PLE spectra of the 1-Å, 10-s InAs sample and of the low-energy feature of the growth-interrupted 1-ML, 1000-s sample are very similar. In contrast, the 1-ML InAs sample growth with 10-s growth interruption [see Fig. 2(c)] exhibits strong hh and lh excitonic oscillator strength associated with the main PL line. Comparing Figs. 2(a) and (c), no exciton resonances due to 1 ML InAs were found in the PLE spectrum of the main peak of the growth-interrupted sample. Thus, one may conclude that most of the surface after the growth interruption is covered with a uniform submonolayer distribution of InAs.

The low-energy PL band shown in Fig. 1 (bottom) and Fig. 2 (a) is attributed to InAs islands with thickness greater than one monolayer. A relatively strong PL intensity of InAs islands means that there is an effective trapping of nonequilibrium carriers and excitons. Moreover, the luminescence peak position of this low-energy band depends strongly on the excitation power, demonstrating the low densities in these clusters (Fig. 3). Moreover, this luminescence is polarized along the $\langle 110 \rangle$ direction, as shown in Fig. 4, especially under resonant excitations, indicating that the islands are elongated along the $[\bar{1}10]$ direction. It is clear that the islands or cluster have anisotropic shape. A similar situation was observed by reflection high-energy electron diffraction (RHEED) pat-

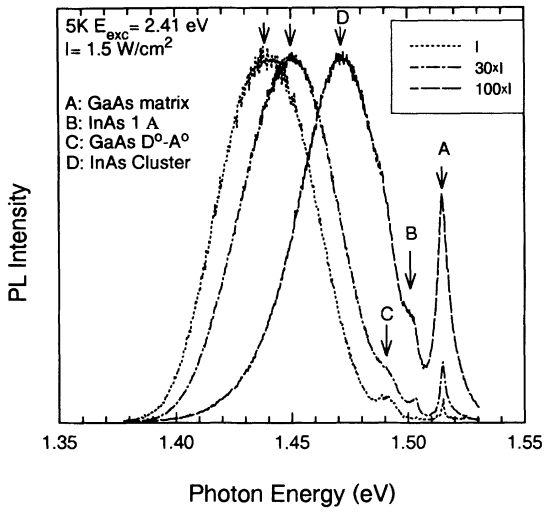

FIG. 3. Three spectra with nonresonant optical pumping under three different excitation intensities. The spectra are normalized to the low-energy broad-band transitions. With increasing excitation intensity the broad band shifts to higher energy, indicating high density of states in the uniform 1-Å InAs regime. This is also confirmed in the PLE spectra. 1-Å PL emission line can be observed clearly in the 1-ML sample with 1000-s growth interruption.

tern during the growth of ultrathin InAs/InP quantum wells by chemical-beam epitaxy.[16] The RHEED pattern showed a mixed streaky and spotty state along the [110] azimuth, and strongly spotty state along the [$\bar{1}$10] azimuth. This was attributed to islands elongated in the [$\bar{1}$10] direction, with (114) facets. Shape changes such as island formation therefore constitute a major mechanism

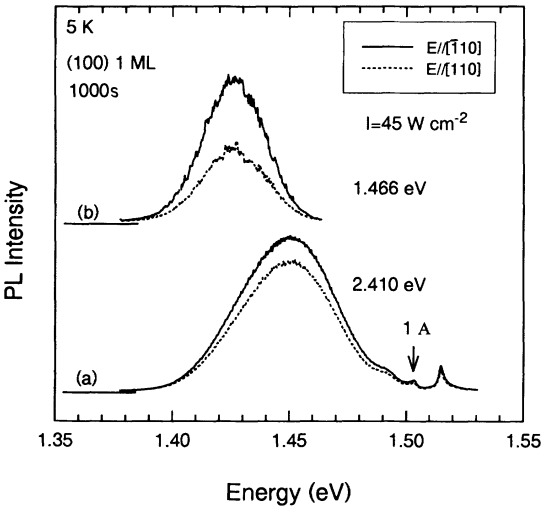

FIG. 4. PL spectra under different excitation energies. (a) Nonresonant excitation with an Ar^+ laser. (b) Resonant excitation at the 1-ML heavy-hole transition (see Ref. 15). It should also be noted that the broad-band luminescence is anisotropic, indicating that it originates from the elongated InAs clusters during the growth interruption. The intensity ratios $I_{\bar{1}10}/I_{110}$ are 1.2 and 2.05 for 2.410- and 1.446-eV excitation energy, respectively.

for strain relief.[12,17] On the other hand, such strained layers are metastable against formation of dislocations. This is more evident in our luminescence-intensity analysis. The persistently high integrated luminescence intensity of the 1-ML InAs samples with different interruption times indicates that the possibility of dislocation-induced nonradiative recombination channels is relatively small. Nevertheless, at increased observation temperatures (70 K), InAs submonolayers exhibit higher PL efficiency.

Figure 5 shows PL spectra at 100 K of samples with 1-ML InAs grown with long growth interruption (1000 s). At this temperature, the luminescence intensity of the peak associated with the InAs submonolayer is rather strong. This is true especially in the (311)-oriented 1-ML sample, which shows negligible cluster emission. PL spectra of 1-Å samples with short growth interruption were also shown for comparison. The same trend was found in this study for structures with 1.6-ML InAs coverage.

However, a completely different situation occurs when the growth interruption experiments were carried out in samples with ultrasmall InAs (1 Å) coverage on both (100) and (311) orientations. In this case, the InAs PL peak showed neither broadening nor splitting with growth-interruption time. Instead, it shifted continuously to higher energies with increasing growth interruption time and finally merged with the GaAs exciton emission. This effect may be explained by the uniform evaporation of InAs molecules from the surface. The above results demonstrate that the surface arrangement of InAs molecules in the case of submonolayer coverages provides a minimal available surface energy. It is stable against shape transformation, despite the absolute intensity of InAs-related emission decreases while the GaAs free-exciton emission increases with growth-interruption time. InAs monolayers grown with very short growth-interruption times (10 s) do not show significant transformations, although the integrated PL intensity is lower

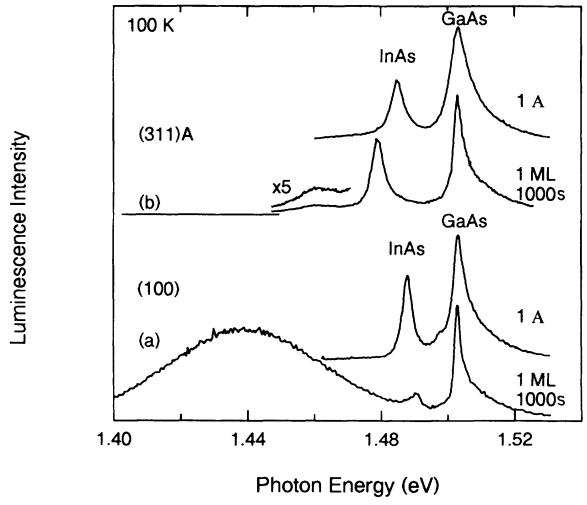

FIG. 5. PL spectra at 100 K of 1 ML InAs with 1000-s growth interruption for (100) (a) and (311) (b) orientation.

than those structures with submonolayer coverage. It is thought that the InAs monolayer decomposition, including the formation of relatively large and stable InAs clusters, results in a local strain relief before the strain can be further reduced by the formation of dislocations. However, the local formation of larger, relaxed InAs clusters is also possible.

The above explains the high emission intensity and narrow emission lines of (In,Ga)As-GaAs structures grown with InAs submonolayer superlattices compared to the emission from structures grown with InAs monolayer superlattices or by conventional MBE (In,Ga)As alloy growth.[15] In the latter case, the formation of InAs-rich surface is unavoidable because of the segregation effects.[18] In fact, by appropriately choosing of growth-interruption conditions, one may create structures with isolated InAs clusters on GaAs surfaces using the one-monolayer annealing technique, attractive for *in situ* fabrication of quantum dots.[19]

The transformation effect studied above can be explained by the strong enhancement of the solid-phase InAs monolayer Gibbs energy induced by the strain.[20] In this situation, it may be more energetically favorable for the system to transform into coherent InAs clusters[11–13] to accommodate the significant strain relief, in contrast to traditional critical-thickness theories. Furthermore, the islands are elongated along the $[\bar{1}10]$ direction, indicating that most of the strain is accommodated by the elastic deformation along the [110] direction. Both the lateral-strain and lateral-confinement effects intermix the hh and lh states in (001) samples, causing the optical anisotropy. On the other hand, InAs submonolayers exhibiting uniform distribution over the GaAs surface[15] are subjected to relatively small strain; thus, transformation is energetically prohibited. Other mechanisms for InAs monolayer transformation include the anisotropic adatom diffusion. The anisotropy of islands is controlled by the energetics at the step edges.[21] Therefore, the observed anisotropy of InAs islands indicates that during the growth interruption, the arsenic-terminated edge (along the [110] direction, or *B*-type edge) is more reactive and the diffusion barrier in the $[\bar{1}10]$ direction is lower than that in the [110] direction. This mechanism accounts for the anisotropic growth mode in lattice-matched systems.[22] Again, anisotropic islands elongated in the $[\bar{1}10]$ direction have been observed after homoepitaxy of GaAs on GaAs surfaces.[23–25]

To conclude, we have studied the transformations of InAs monolayer and submonolayer coverage during the MBE growth interruptions. We found that these two types of structures showed remarkably different behavior. While submonolayer coverage is stable, monolayers show a marked tendency toward transformation into different arrangements, even in the case where the InAs layer thickness is far below the critical value. This study provides spectroscopic evidence of the initial strain relaxation in thin films, confirming the analytical studies involving various scanning-probe microscopies.[10–13,19]

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