Delayed Relaxation by Surfactant Action in Highly Strained III-V Semiconductor Epitaxial Layers

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It is demonstrated that the concept of surfactant applies to the epitaxial growth of highly strained III-V semiconductors. The pseudomorphic growth regime of InAs on GaAs(001) is extended from 1.5 to 6 monolayers by the use of Te as surfactant. This delayed plastic relaxation of the strain is correlated with the modification of the growth mode via surface energy minimization.

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One of the main goals in contemporary material science research is to associate materials with different properties in thin epitaxial layers. This is especially true in the field of semiconductor physics and technology. There are, however, two fundamental limitations in the choice of materials from which highly perfect epitaxial structures can be made: the surface free energy of the deposit must not be greater than that of the substrate and the strain energy due to the lattice mismatch stress must be low enough to be elastically accommodated. If these particular conditions are fulfilled, the epitaxial growth follows the ideal layer-by-layer 2D growth mode [Franck-van der Merwe (FM) mode]. When the surface free energy of the deposit is higher than that of the substrate, 3D growth occurs as predicted by the theory of wetting phenomena [Volmer-Weber (VW) mode]. Finally, for lattice mismatched materials with suitable surface free energies, the growth mode generally undergoes a 2D-3D transition which allows the reduction of the strain energy of the system [Stranski-Krastanov (SK) mode]. This is the case for the growth of Ge on Si (lattice mismatch $\approx 4.2\%$), which has been a subject of intense study in recent years [1-5]. In this system, the 2D growth is limited to 3-4 monolayers (ML) [6]. The SK growth mode is also well known to occur in III-V semiconductors, the prototypical system being InAs/GaAs (lattice mismatch $\approx 7.2\%$). Islands begin to form after only 1-2 ML of InAs deposited on GaAs(001) [7,8], limiting the development of devices based on InAs/GaAs heterostructures in spite of their considerable potential interest for both microwave and optoelectronic applications. One of the most promising ways to increase the thickness for which pseudomorphic 2D growth can be maintained is the use of surfactants. This has been recently demonstrated by Copel and co-workers [1,4,9] for the Ge/Si system using As and Sb as surfactant species.

Analogously to the effect of column-V elements on Si surface, column-VI elements are known to strongly modify the surface electronic properties of III-V semiconductors [10] giving passivating effects [11] and are expected to lower the surface energy. In this Letter we show that Te acts as a surfactant for the growth of InAs on GaAs. While beyond the first InAs monolayer the formation of islands is observed when the growth is performed directly on GaAs, the 2D coherent growth is sustained up to ~6 ML when using a Te surfactant layer. Moreover, the onset of lattice relaxtion is delayed from 1.5 to 6 ML.

The growth of InAs on GaAs(001) by molecular-beam epitaxy was performed at 400 °C with a constant growth rate of 0.14 ML/s, precisely measured by using reflection high-energy electron diffraction (RHEED) specular beam intensity oscillations during the growth of both InAs and $In_xGa_{1-x}As$ layers on GaAs. For the surfactant modified growth experiments, the GaAs buffer layer surface was exposed to a Te flux in order to obtain a 6×1 reconstructed GaAs(001) Te surface (which corresponds to the ordered surface phase with the maximum Te surface coverage, roughly 1 ML) [12]. This surface was prepared just prior to the growth of InAs and Te was not added during growth. The variation of the in-plane lattice parameter $a_\parallel$ as well as intensity variations of characteristic diffraction features were followed during the growth by RHEED using a high sensitivity charge-coupled-device camera based video recording system.

The variation of $a_\parallel$ during the growth of InAs on GaAs is shown in Fig. 1(a). In agreement with previous results [8] it is found that the lattice relaxation occurs above 1.5 ML. An important question is whether or not the onset of lattice relaxation is concomitant with island formation. We have thus precisely measured the variation of the diffracted intensity at a Bragg position on the RHEED pattern from the beginning of the growth. Figure 1(b) shows the variation of the 115 Bragg intensity as a function of InAs thickness. From these data it is clear that there are different stages in the islanding process. Plateaus in the Bragg intensity variation indicate that growth of islands is not a linear process, as also noted in the case of the growth of Ge on Si [6]. The most relevant result in the context of the present Letter is that islands begin to form just before the onset of the $a_\parallel$ relaxation, as indicated by the fact that the first significant increase in the Bragg intensity occurs after only 1 ML of InAs growth. As in the case of the Ge/Si system [2,6], it seems therefore that the formation of islands is not a consequence of strain relaxation but rather one mechanism of this relaxation.

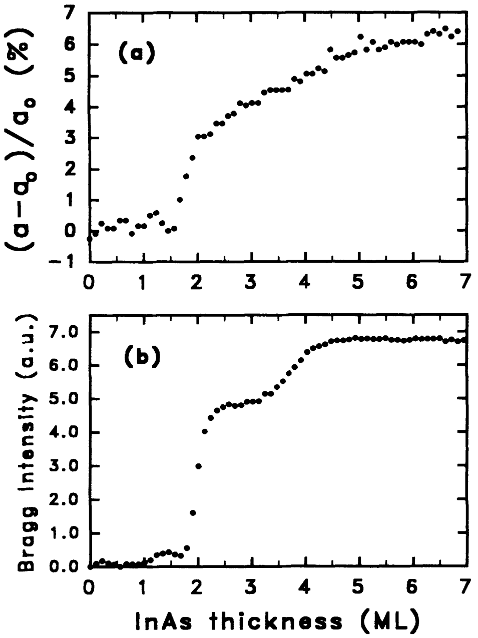

FIG. 1. Variation of the (a) in-plane lattice parameter and (b) 115 Bragg reflection intensity during the growth of InAs on GaAs. In order to eliminate the 2D (streak) contribution to the intensity measured at the location of the Bragg reflection, this contribution is measured in the vicinity of the Bragg position and subtracted from the raw Bragg intensity data (similar data have been obtained at different Bragg positions).

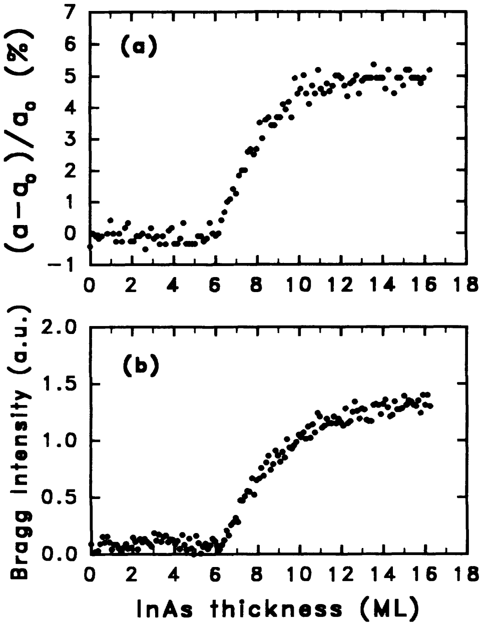

FIG. 2. Variation of the (a) in-plane lattice parameter and (b) 115 Bragg reflection intensity during the Te modified growth of InAs on GaAs.

Let us now consider the Te mediated growth of InAs on GaAs. Figure 2(a) shows the $a_\parallel$ variation as a function of InAs thickness. The key result is that the pseudomorphic growth is maintained up to ~6 ML, instead of 1.5 ML without the Te surfactant action. On the other hand, Fig. 2(b) indicates that now the increase of Bragg intensity exactly coincides with the onset of the $a_\parallel$ variation. Moreover, this increase in intensity is considerably lower than that for growth without the preadsorbed Te layer [the data of Figs. 1(b) and 2(b) have been normalized so that the intensity levels can be compared]. Such a limited increase in the 3D contribution to the diffracted intensity is more a consequence of the roughening of the growth front than of a true 2D-3D transition such as that observed in standard InAs/GaAs growth.

The growth behavior of InAs on GaAs with and without the Te surfactant layer has also been studied by x-ray photoelectron spectroscopy (XPS). As a preliminary remark, it should be noted that since the XPS analysis can only be performed upon growth interruptions, such experiments are not strictly comparable to those corresponding to the RHEED study (continuous growth), at least from the point of view of relaxation kinetics. However, valuable additional information on the growth mode can be obtained from XPS. As long as the growth mode of InAs on GaAs(001) is 2D and the interface is flat, we can evaluate the overlayer thickness from the ratio of In and As XPS peak intensities which is given by

$$I_{\mathrm{In}}/I_{\mathrm{As}}=[I_{\mathrm{In}}/I_{\mathrm{As}}]_{\mathrm{InAs}}\{1-\exp[-h/(\lambda\sin\Theta)]\}\,, \qquad (1)$$

where h is the InAs thickness, λ the escape length of the In photoelectrons (25 Å for In $3d$), Θ the emission angle ($\Theta=45°$), and $[I_{\mathrm{In}}/I_{\mathrm{As}}]_{\mathrm{InAs}}$ the intensity ratio for semi-infinite InAs. As shown above, the growth mode of InAs on GaAs(001) without Te is of the 2D type for only 1 ML. Therefore for more than 1 ML of InAs, Eq. (1) fails. In order to account for the XPS data corresponding to the SK growth regime we have used a simple island model. In this model, a given volume V of InAs deposited on a GaAs surface S considered in terms of a $N\times N$ lattice is written as $V=\sum_{i=1}^{N}\sum_{j=1}^{N}h_{i,j}\sigma$, where $h_{i,j}$ is the height of the element of volume and σ the unit surface. The ratio of In and As intensities is then

$$I_{\mathrm{In}}/I_{\mathrm{As}}=[I_{\mathrm{In}}/I_{\mathrm{As}}]_{\mathrm{InAs}}\sum_{i=1}^{N}\sum_{j=1}^{N}\{1-\exp[-h_{i,j}/(\lambda\sin\Theta)]\}\,.$$

The terms $h_{i,j}$ depend on the overlayer morphology which is assumed to be formed by one pseudomorphic InAs monolayer and egg-shaped islands (due to the well-known anisotropy of [$\bar{1}$10] and [110] surface diffusion) whose size is proportional to the thickness of the deposited InAs. Since we have neglected the coalescence of islands, this model is in fact only strictly relevant for relatively thin InAs layers. The density of islands is taken to be 5×10^{14} m^{-2} as deduced from previously reported transmission electron microscopy observations [13]. Figure 3 shows

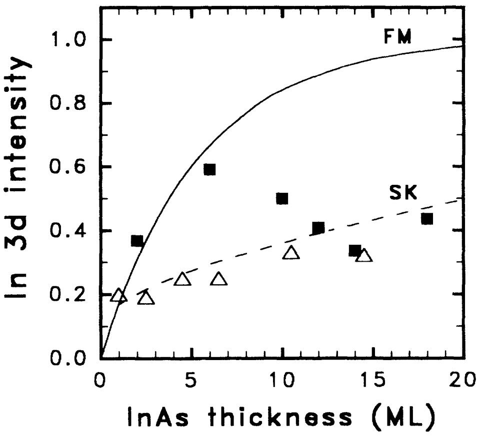

FIG. 3. Normalized In 3*d* XPS intensity variation as a function of InAs thickness in monolayers (ML). Squares and triangles are for InAs growth with and without Te preadsorbed layer, respectively (the triangle corresponding to 1 ML is taken from Ref. [7]). Solid and dashed lines are for the Frank-van der Merwe and Stranski-Krastanov growth mode models, respectively.

the XPS data of In 3*d* intensity for InAs/GaAs (triangles) and InAs/Te/GaAs (squares). The solid and dashed lines correspond respectively to the FM and SK growth mode models. For InAs directly grown on GaAs, the data diverge from the ideal FM intensity variation after the deposition of only 1 ML, in agreement with the RHEED data. Actually, the In 3*d* photoelectron intensity follows reasonably well the SK curve in spite of the simplicity of the model used. If now we consider the growth of InAs on GaAs using the Te surfactant layer, the XPS data follow the FM curve up to 6 ML in excellent agreement with the result deduced from the RHEED study, despite the growth interruptions performed for the XPS measurements. However, for thickness greater than 6 ML the data deviate considerably from the FM curve and finally join the SK curve above an equivalent InAs thickness of ~10 ML. This behavior does not agree with that observed by RHEED during continuous growth which indicates that the formation of islands is strongly reduced by the surfactant action. As confirmed by RHEED analysis of growth with interruptions, this behavior is the consequence of a relaxation process taking place during growth interruption, kinetically inhibited for continuous growth. This point will be the subject of a subsequent report. Finally, the XPS analysis also indicates that Te is segregated at the InAs layer surface when the growth proceeds (however, it is estimated from the data that the Te surface coverage has decreased by ~20% after the growth of ~20 ML of InAs). This is a prerequisite for the surfactant action [1].

As mentioned above, the critical thickness (h_c) has been delayed from 1.5 to 6 ML when Te is used. A very simple theoretical approach can explain this result. Generally, the critical thickness theories consider that the growth mode is of the FM type. In this case, for a thin overlayer on a thick substrate, Matthews and Blakeslee have given an expression for h_c based on mechanical equilibrium theory [14]. In this model, h_c is determined by the function φ when

$$\varphi(h)=h-b(1-\sigma/4)[\ln(h/b)+1]/2\pi f(1+\sigma)=0\,, \qquad (2)$$

where h is the overlayer thickness, b the Burgers vector ($b=a/\sqrt{2}$), σ the Poisson ratio, and f the misfit strain. For InAs/GaAs, Eq. (2) gives $h_c=5.4$ ML. This value agrees quite well with the experimental value (6 ML) for the 2D growth regime obtained with Te. In the case of InAs directly grown on GaAs, we have to take into account that above the first deposited monolayer the growth is no longer 2D. For this purpose, we have applied Eq. (2) to the case of the SK growth mode with the same model which was described for XPS data analysis. The critical thickness is then reached when

$$\sum_{i=1}^{N}\sum_{j=1}^{N}\varphi(h_{i,j})=0\,.$$

This gives $h_c=1.8$ ML, i.e., plastic relaxation should start for an equivalent thickness of 1.8 ML (experimental value of 1.5 ML). We can therefore conclude from both experimental and theoretical grounds that when using Te as a surfactant the lattice relaxation is delayed because of a suppression of islands. This is basically due to a decrease in the surface energy by the continuously segregated Te layer: In and As atoms are rapidly incorporated into the subsurface layer in order to allow Te atoms to occupy the surface sites. With indium surface diffusion strongly reduced, island formation is inhibited. This probably occurs following a mechanism similar to the one recently proposed for the Ge on Si surfactant modified epitaxial growth [5]. However, as shown above, when partial lattice relaxation occurs by dislocation formation, a 2D-3D like growth mode transition is observed in RHEED, although it is far from being as pronounced as in standard growth. Such behavior does not seem to be observed for the surfactant modified Ge/Si growth [1,5,9]. There are at least two possible reasons for this: (i) since the strain is largely higher for the InAs/GaAs system and relaxation is inhomogeneous [15], 3D islands can be favored in relaxed areas despite the surfactant action; (ii) in our case the surfactant is not continuously added during growth in contrast to experiments performed on Ge/Si [1,5,9]. With regard to this second point, it should be noted that even if the Te incorporation into the growing layer is very limited, a slight decrease of the Te surface coverage occurs as growth proceeds and this may well be sufficient to change the arrangement of Te atoms at the surface, thus altering the microscopic mechanism of the surfactant action [16].

In summary, we have demonstrated that surfactants can be used to modify the growth mode of highly strained III-V epitaxial layers and then significantly increase the so-called critical thickness for which strain relaxation by dislocation formation occurs. Using Te as the surfactant for the growth of InAs on GaAs, plastic relaxation begins at 6 ML of InAs instead of 1.5 ML without the surfactant action. This is because the formation of 3D islands, which allows a rapid relief of the strian, is delayed by the presence of Te at the growing surface.

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[16] If this is indeed the case, purely 2D growth, as is observed on Ge/Si, could be maintained by a continuous Te flux during InAs growth (however, this is not possible in our present experimental configuration).