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Surface spinodal decomposition in low temperature $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ grown on $\text{InP}(001)$ by molecular beam epitaxy

G. Grenet ^{a,*}, M. Gendry ^a, M. Oustric ^a, Y. Robach ^a, L. Porte ^a, G. Hollinger ^a,
O. Marty ^b, M. Pitaval ^b, C. Priester ^c

^a Laboratoire d'Electronique, LEAME, UMR-CNRS 5512, Ecole Centrale de Lyon, F-69131 Ecully Cedex, France

^b Département de Physique des Matériaux, Université Claude Bernard, Lyon 1, F-69622 Villeurbanne Cedex, France

^c IEMN, Dpt ISEN, BP69, F-59652 Villeneuve d'Ascq, France

Abstract

The clustering development for lattice-matched $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ grown on (001) oriented InP substrates by molecular beam epitaxy (MBE) has been investigated by ex-situ transmission electron microscopy (TEM) and in-situ scanning tunnelling microscopy (STM). For a growth temperature of 450°C, a V/III beam equivalent pressure (BEP) ratio equal to 20 and a growth rate of $1\text{ }\mu\text{m h}^{-1}$, the clusters are strongly anisotropic: typically, 2 nm along the [110] direction, 30–50 nm along the $[\bar{1}\bar{1}0]$ direction and 20 nm along the [001] direction. We show theoretically that such a spinodal decomposition would be forbidden if the surface of the deposited film is perfectly flat. We also demonstrate that this decomposition appears to be possible if the surface roughness is sufficient to allow a partial elastic relaxation. © 1998 Elsevier Science B.V.

1. Introduction

The performance of devices for switching, microwave and optical applications depends on the atomic perfection of the interfaces but also on the intrinsic quality of the involved materials. However, most of the III–V semiconductor alloys develop clustering during their growth by molecular beam epitaxy (MBE). Such a phase separation induces a broadening of the photoluminescence (PL) linewidth and a lowering of the electron mobility. Among III–V alloys, the $\text{Al}_{1-x}\text{In}_x\text{As}$ alloy, used as a large band gap compound in heterostructure systems on InP, presents such a strong undesirable clustering behaviour [1]. Of fundamental importance in predicting such a deviation from randomness is the differ-

ence in lattice parameter and elastic properties between the two endpoint binary compounds [2–14]. However, the actual amount of clustering is also subjected to all the MBE growth parameters such as growth temperature, growth rate and V/III beam equivalent pressure (BEP) ratio because all these parameters influence the adatom mobility [15]. The present work reports both transmission electron microscope (TEM) and in-situ scanning tunneling microscope (STM) images with the aim of describing the clustering development for lattice-matched $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ grown on (001) oriented InP substrate by molecular beam epitaxy (MBE).

2. Experimental

The growth of the $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ layers was performed in a Riber 2300 reactor on $\text{InP}(001)$ epitaxially

* Corresponding author.

substrate from InPact. The surface reconstructions were monitored by reflection high energy electron diffraction (RHEED). Since AlInAs is very sensitive to oxygen, a careful deoxidation of the InP substrate was done previously to the growth via a progressive increase of the substrate temperature (50°C per min) up to 565°C under 10^{-5} Torr of As_4 . At this temperature, the surface reconstruction of the arsenic treated InP surface changes from As-stabilized (2×4) to cation-stabilized (4×2). The InP lattice matching of $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ on InP(001) was checked by double X-ray diffraction (DDX). The transmission electron images were recorded at 200 kV using a TOPCON EM-002B transmission electron microscope. To perform the plane view, the sample was mechanically thinned down to 50 μm and then chemically etched

using a bromine methanol solution. The electron transparency was obtained by ion milling using a Gatan model equipped with a nitrogen cold stage working under 3 kV and 0.5 mA per gun. The STM experiments were performed in a ultra-high vacuum chamber equipped with a Besocke Beetle scanning tunneling microscope and connected to the MBE chamber. The STM images were obtained with a tunnelling current of 0.5 nA and a tunnelling voltage of 2 V applied to the sample.

The phase separation appears to be strongly dependent on growth parameters [1]. It diminishes when the growth kinetic is limited by an increase of the V/III BEP ratio and/or of the growth rate. We have found that for a V/III BEP ratio equal to 20, and a growth rate equal to 1 $\mu\text{m h}^{-1}$, the phase separation

Fig. 1. Characteristic images of $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ grown on InP(001) using a V/III BEP ratio equal to 20, and a growth rate equal to 1 $\mu\text{m h}^{-1}$: (a) TEM plan view for the growth temperature $T = 450^\circ\text{C}$, (b) TEM plan view for the growth temperature $T = 525^\circ\text{C}$, (c) STM image for the growth temperature $T = 450^\circ\text{C}$, and (d) STM image for the growth temperature $T = 525^\circ\text{C}$.

increases versus the growth temperature to reach a maximum for the range 400–450°C. It disappears for temperatures greater than 475°C. Fig. 1 shows four characteristic images of $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ on $\text{InP}(001)$ acquired by TEM (Fig. 1a and b) and by STM (Fig. 1c and d) for two growth temperatures, i.e., at 450°C (the temperature corresponding to the phase separation maximum obtained by TEM) and at 525°C (a temperature corresponding to no phase separation by TEM). The TEM plan view for the sample grown at 450°C reveals a fine, quasi-periodic contrast elongated in the $[1\bar{1}0]$ direction, absent for the sample

grown at 525°C. Such a TEM contrast is interpreted in Fig. 2a as due to the elastic relaxation of strained clusters at the AlInAs surface. STM images for the sample grown at 450°C indicate a corrugation superposed on the overall morphology, showing the same kind of anisotropy with approximately the same period as the corresponding TEM image. This undulation is schematised in Fig. 2b. For the sample grown at 525°C, such a corrugation is not observed in the STM image (Fig. 1d), strengthening the result obtained by TEM.

Both the growth kinetic dependence and the ani-

Fig. 2. Schematic representation of: (a) the consequence of a lateral composition modulation on the TEM contrast via a surface elastic relaxation, and (b) a STM profile from Fig. 1c.

sotropy of the clustering effect clearly indicate a phenomenon appearing on the growth front. For a growth temperature equal to 450°C, a V/III BEP ratio equal to 20 and a growth rate equal to 1 $\mu\text{m h}^{-1}$ (Fig. 1a and c), typical cluster sizes are 2 nm in the [110] direction, 30–50 nm in the $[\bar{1}\bar{1}0]$ direction and 20 nm in the [001] direction. Finally, it should be noted that, the surface roughness is much greater for $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ (Fig. 1c and d) than for any binary III–V compound grown using similar growth conditions.

3. Discussion

Numerous III–V semi-conductor ternary alloys may be considered as pseudo-binary compounds $(\text{A}_{\text{III}}\text{C}_{\text{V}})_{1-x}(\text{B}_{\text{III}}\text{C}_{\text{V}})_x$ with x ranging from 0 to 1. In such alloys, the C_{V} atoms occupy all the crystallographic sites of one of the face-centred sublattices of the zinc blende structure while the atoms A_{III} and B_{III} are distributed on the second one with or without a deviation from the complete randomness. This deviation may take the form of a long range ordered phase and/or of a clustered phase [8,9]. Both of them have been observed in III–V alloys, separately or together [16–18]. When the lattice parameters for the two endpoint binary compound $\text{A}_{\text{III}}\text{C}_{\text{V}}$ and $\text{B}_{\text{III}}\text{C}_{\text{V}}$ are different, all bondlengths and interbond angles in the alloy are distorted (except for $x=0$ and $x=1$, the two endpoint compositions) from equilibrium even if no extra-strain is applied via a substrate. Fig. 3 (curve A) shows the so-developed strain energy per unit cell $U(x)$ evaluated for a true random alloy $(\text{AlAs})_{1-x}(\text{InAs})_x$ versus x , using the Keatings model [4–6]. This excess of energy $U(x)$, alias the excess enthalpy of mixing $(\Delta H)_m$ in a thermodynamic framework, may be approximated by $U(x) = x(1-x)\Omega$, where Ω is a constant called ‘interaction parameter’ estimated to 3600 cal mol^{-1} for $(\text{AlAs})_{1-x}(\text{InAs})_x$. Using the Gibbs alloy stability criterion $\partial^2 U / \partial x^2 < 0$ (or equivalently, $\Omega > 0$), a spinodal decomposition can occur in $(\text{AlAs})_{1-x}(\text{InAs})_x$ for temperatures below the critical value $T_c = \Omega / 2R = 905$ K, R being the gas constant, leading to two phases, viz., $(\text{AlAs})_{1-x-\varepsilon}(\text{InAs})_{x+\varepsilon}$ and $(\text{AlAs})_{1-x+\varepsilon}(\text{InAs})_{x-\varepsilon}$, with $\varepsilon > 0$.

Fig. 3. Energy $U(x)$ per deposited atom versus x for a free-substrate bulk $(\text{AlAs})_{1-x}(\text{InAs})_x$ (curve A) and for a 20 monolayers perfectly flat film of $(\text{AlAs})_{1-x}(\text{InAs})_x$ on InP substrate (curve B).

If we now consider such a composition fluctuation around the lattice-matching composition $x = 0.523$ given by the Vegard's law for an $(\text{AlAs})_{1-x}(\text{InAs})_x$ film on an InP substrate, the alloy film will either extend or contract in the growth direction depending on the strain sign as schematized in Fig. 2a. This ‘extrinsic’ strain energy (due to the mismatch with the substrate) contravenes the ‘intrinsic’ strain energy (due to the mismatch between the two end-point binaries within the alloy) at the origin of the spinodal decomposition. We have calculated and compared total energies for several different systems. In Fig. 3, we show the energy $U(x)$ per deposited atom versus x for a free-substrate bulk $(\text{AlAs})_{1-x}(\text{InAs})_x$ (curve A) and for a 20 monolayers perfectly flat film of $(\text{AlAs})_{1-x}(\text{InAs})_x$ on InP substrate (curve B). The negative curvature for free-substrate alloy turns to be positive for the alloy on InP prohibiting any spinodal decomposition. From this result, one can deduce that, as far as the surface is perfectly flat, $(\text{AlAs})_{1-x}(\text{InAs})_x$ grown on a InP substrate cannot demix. However, one has to remember that the alloy growth front is actually rough enough to allow part of the elastic strain to be relaxed via step edges. We have calculated, and we have shown that a 3 ML high roughness is sufficient to stabilize phase separation in the InAlAs film. We also show that, a given roughness can be sufficient to

enable demixion in InAlAs, but not in InGaAs (both of them lattice matched to the InP substrate). The observed surface lateral composition modulation appears thus as the result of an equilibrium between: (i) an intrinsic alloy strain energy which decreases if phase separation occurs, (ii) an extrinsic alloy strain energy induced by the mismatch between alloy phases and substrate, and (iii) a roughening which indeed increases the surface energy but allows both an intrinsic and extrinsic strain relaxation via step edges.

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