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Transition from island to continuous InP layer growth on (001) GaAs by MOCVD

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Abstract

Low pressure metal-organic chemical vapour deposition grown InP/GaAs layers were analysed using scanning and transmission electron microscopy and Rutherford backscattering spectroscopy to characterize the evolution of the InP layer morphology from the initial stages of the growth up to the complete substrate coverage. Up to nominal thicknesses of about 100-150 nm, an appreciable fraction of the GaAs substrate is not covered by InP. For higher thicknesses, a sudden transition to an enhanced lateral growth leading to island coalescence was observed. Finally, a third growth stage leads to the complete filling of the valleys, leading to continuous layers. The results are discussed in terms of the phenomenological models proposed in the literature.

Keywords: Epitaxy of thin films; MOCVD; Indium phosphide; Nucleation

1. Introduction

Recent developments both in crystal growth technology and in the theoretical analyses of low-dimensional semiconductors structures, from quantum wells to quantum wires and quantum dots, give access to a wide range of new quantum-mechanical phenomena which are promising for device applications. In fact, in addition to the traditional band gap modulation produced by the heteroepitaxial growth, the band structure of a given material can be modelled by means of quantum confinement (0D, 1D or 2D), by means of strain [1] and, in the case of semiconductor alloys, by manipulating the internal degree of ordering of the crystal sublattices [2]. In principle, the desired electro-optical properties could be given by different combinations of these three parameters. Of course, from the structural point of view, it is important to select the most simple and easy-to-fabricate structures. In this respect, the most promising approach seems to be the direct growth of the nanostructures without using any ex situ processing techniques. Most of the self-organization processes which occur during the epitaxial growth are driven by the mismatch between the substrate and the deposited material. In this paper we consider one of these self-organization effects which is not a new problem in epitaxial growth but which has been considered as a major drawback to be avoided so far.

Although 3D growth is undesirable to obtain a good-quality epitaxial layer, this may not be the case if we are interested in islands of nanometric dimensions. It has already been shown that in high-mismatch systems such as InP/GaAs [3] and InGaAs/GaAs [4], nanometric-scale islands behaving like quantum dots can be obtained. It has been shown that in systems with small interface energy and large lattice mismatch,

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Stransky–Krastanov growth is favoured, with respect to the layer by layer growth, by the overall reduction of the elastic energy per unit volume due to the relaxation of each island at the cost of a local strain field in the substrate [5]. It is the balance between this elastic energy reduction and the surface and interface energy associated to the islands which determines the morphology of the deposited material [6]. Since the strain is lower in 3D islands with respect to a uniform layer, it is reasonable to expect that the islands can grow coherently, well above the critical thickness for the generation of misfit dislocations in epitaxial films [6]. In other words, coherent and partially strained islands should be obtainable by optimizing the growth conditions and the substrate orientation, as suggested by the results of Leonard et al. [4].

2. Experimental details

To understand the evolution of the islands from the first stage of the deposition to the coalescence stage, and finally to the complete coverage of the substrate, we analysed a set of InP/GaAs samples grown by low pressure metal–organic chemical vapour deposition (MOCVD) at a substrate temperature of 600 °C. The working pressure was 100 mbar and the carrier gas was argon with a total flow rate of 7 l min^{-1}. The InP layers were deposited using trimethyllindium (TMIn) and pure phosphine (PH_3) as precursors of group III and V, respectively. Another set of InP/GaAs samples were grown by atomic layer epitaxy (ALE) for comparison. ALE growth was performed in the same system by alternately introducing PH_3 and TMIn spaced by an argon purge step and by using a growth temperature of 340 °C at a working pressure of 76 Torr. The total flow rate was 7 slpm, giving a gas velocity of about 100 cm s^{-1}. The as-deposited layer thicknesses were monitored at the end of the growth stage by means of a stylus profilometer and etching. We shall refer in the following to the thickness measured in this way as to the "nominal thickness". Scanning (SEM) and transmission electron microscopic (TEM) and Rutherford backscattering spectroscopy (RBS) analyses were performed to obtain information on island shape, dimensions and distribution. SEM observations were performed using a model 360 Cambridge Stereoscan electron microscope. TEM in cross-section (XTEM) was performed with an analytical 2000FX JEOL microscope. The specimens were prepared by standard mechanochemical procedures followed by Ar^+ and I^+ ion milling in a model 600 DUOMILL Gatan system. RBS measurements in random geometry were performed by using a 2.0 MeV $^4He^+$ beam at the Laboratori Nazionali di Legnaro.

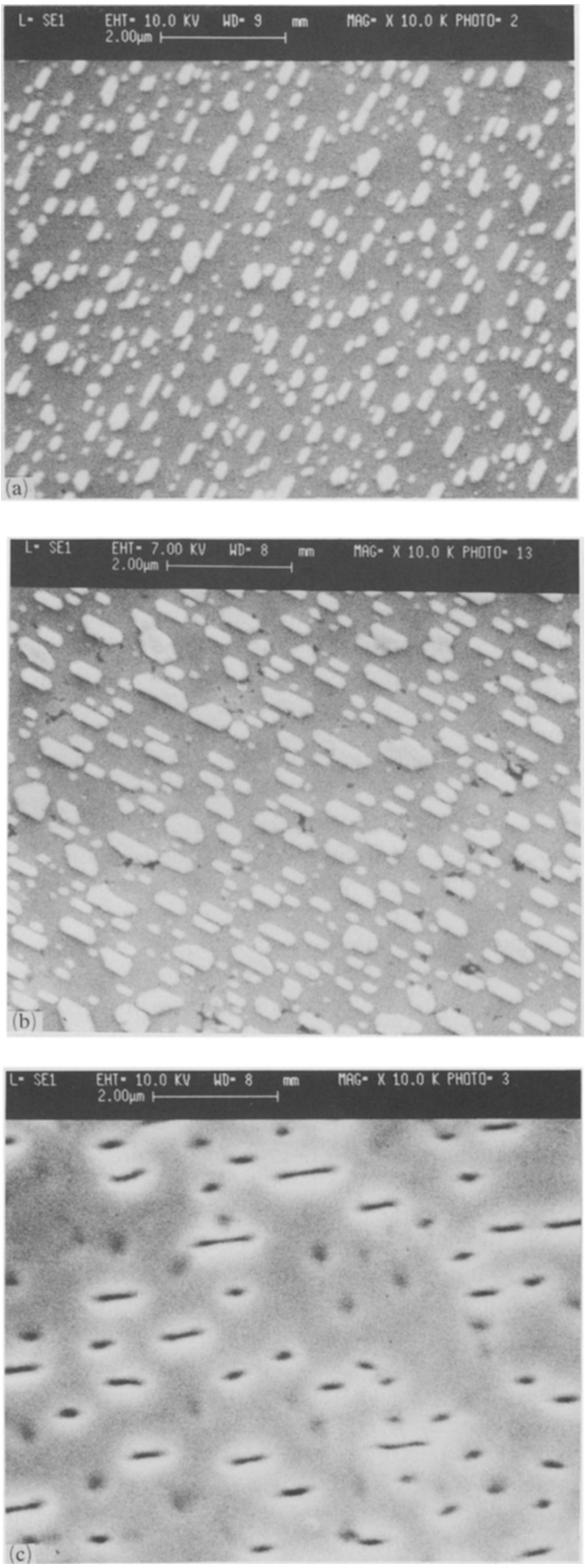

Fig. 1. SEM image of the surface of some MOCVD-grown structures of different nominal thicknesses: (a) 75; (b) 150; (c) 260 nm. The magnification is shown by the marker.

3. Results and discussion

Fig. 1 shows scanning electron micrographs corresponding to three different stages of the growth process. The image in Fig. 1(a) shows the surface of an InP/GaAs sample after a growth of nominally 75 nm. InP islands with the borders aligned along crystallographic directions cover only a small fraction of the substrate and appear to be slightly elongated in shape with lateral dimensions ranging from a few tens to a few hundred nanometres. By increasing the nominal thickness to 150 nm (Fig. 1(b)) the lateral dimensions of the islands increase up to several hundred nanometres, but nevertheless the substrate is still largely uncovered. Above a nominal thickness of 260 nm (Fig. 1(c)), the micrograph shows that nearly complete coalescence has taken place, the substrate being covered by an almost continuous film in which the partially unfilled valleys between the islands appear as dark segments.

Fig. 2 shows two XTEM observations of the sample shown in Fig. 1(a). Fig. 2(a) shows that, although the lateral size can vary from island to island, their height is fairly constant and is estimated to be about 50 nm. At higher magnification the presence of defects at the island–substrate interface and inside the islands themselves is observed (Fig. 2(b)). Further, high-resolution electron microscopy revealed that both 60° type and pure edge misfit dislocations were present at the heterointerface, in addition to planar defects (Fig. 2(c)). The resolution of the TEM (Scherzer resolution ≈ 3 Å) did not allow the determination of the nature of partial dislocations bounding planar defects.

The analysis of the RBS spectra of the structures allows the main features of the growth process to be quantified. Fig. 3 shows the superposition of two RBS spectra corresponding to an ALE-grown film (38 nm thick) in which the layer by layer growth mode led to the formation of a continuous InP/GaAs heterostructure and to an MOCVD-grown structure (150 nm nominal thickness). The height of the In signal in the ALE-grown sample corresponds to the backscattering yield from a continuous InP layer. This is not the case with the MOCVD-grown sample, where the In signal is considerably lower and the Ga and As signals exhibit a significant yield at the energies corresponding to the surface scattering. These two effects are direct evidence that the substrate is not fully covered by the growing islands.

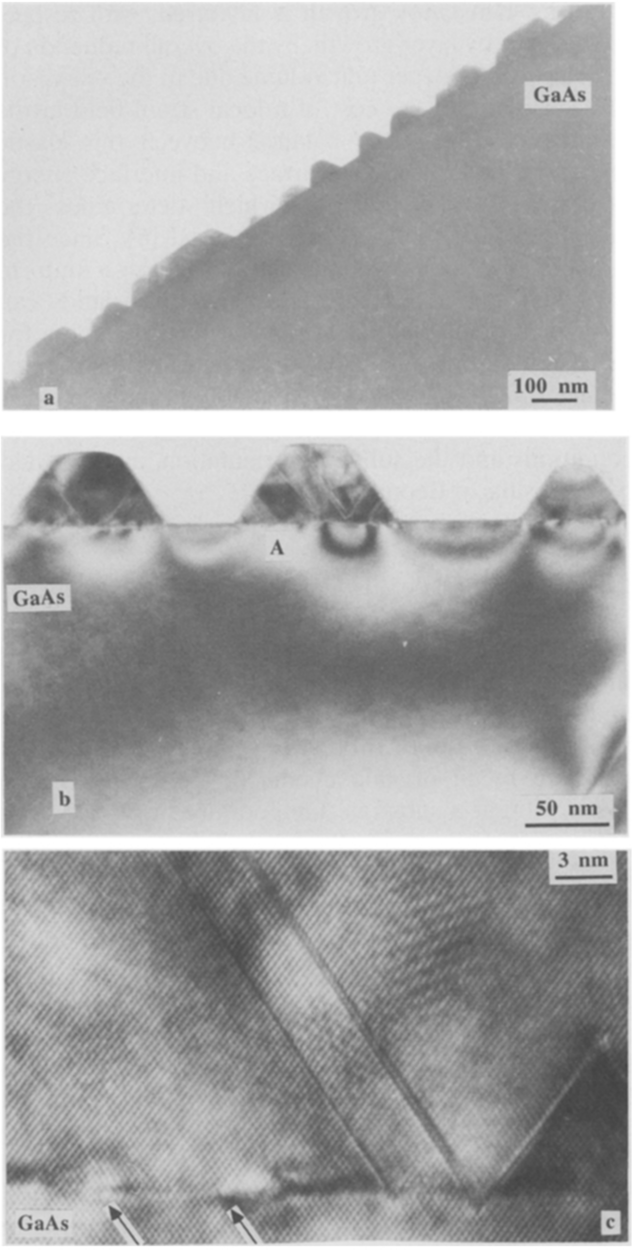

Fig. 2. XTEM image of 75 nm structure: (a) panoramic view showing the shape of the islands; (b) magnifications of a few islands showing the defect distribution; (c) high-resolution TEM image showing perfect dislocations (arrowed) at the interface and planar defects.

The RBS spectra of the MOCVD grown structures were analysed by means of a computer simulation code. In this procedure the GaAs surface is assumed to be partly covered by islands of square pyramidal shape with a truncated upper surface and {111}-oriented lateral faces, in agreement with the XTEM observations. The variables are the mean distance between the islands, their height and the dimension of their upper surface. Two of these were chosen as independent variables to fit the experimental spectrum. This procedure allows one to quantify the maximum thickness of the islands and the substrate surface coverage. It must be noted, however, that RBS is not able to discriminate whether or not a continuous InP film of a few monolayers is present at the substrate surface.

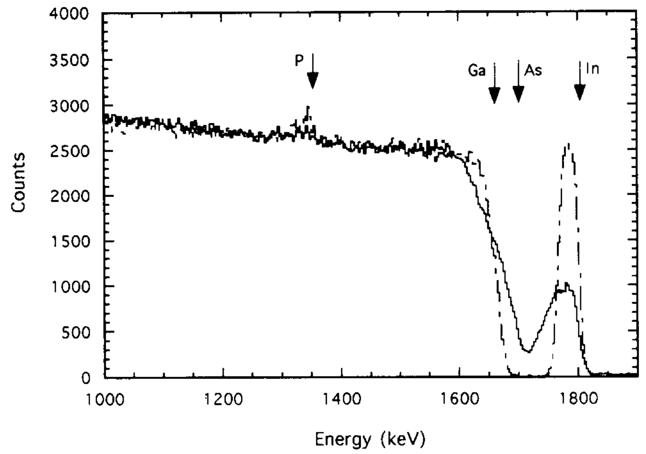

Fig. 3. Superposition of the RBS spectra of an ALE-grown (38 nm) layer (broken line) and of a MOCVD-grown (150 nm) structure (solid line). $E_0 = 2.0$ MeV; $\theta = 170°$.

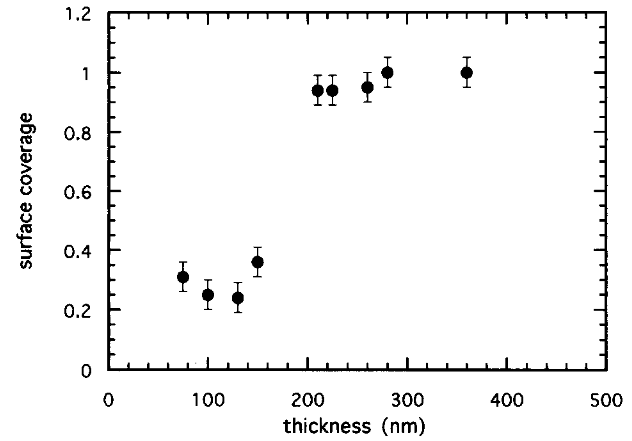

Fig. 4. Surface coverage as determined from the RBS spectra.

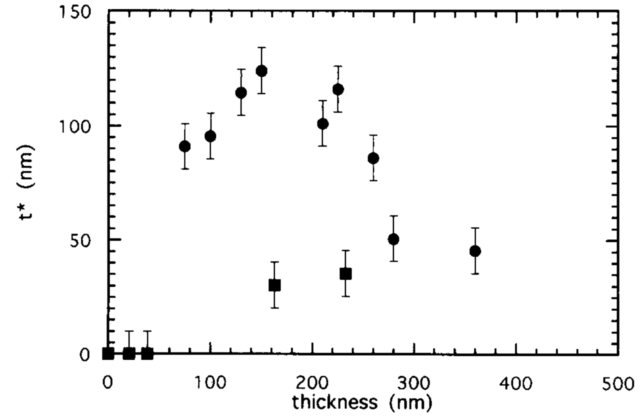

Fig. 5. t^* as determined from the RBS spectra: ●, MOCVD-grown structures; ■, ALE-grown samples.

The resulting surface coverage is reported in Fig. 4 as a function of the nominal thickness of the InP growth. Up to thicknesses of the order of 150 nm the coverage is low (25%-35%), confirming the SEM observations in Fig. 1(a) and (b). At increasing thicknesses the surface coverage abruptly rises to nearly 100%. The low-energy tail of the In signal gives the measure of a film "roughness" corresponding to the maximum thickness t^* from the top of the islands to the bottom of the valleys. This means that t^* is a measure of the maximum island thickness or of the surface roughness when partial or full surface coverage is observed, respectively. Fig. 5 shows t^* as a function of the nominal film thickness for several MOCVD-grown structures. The island thickness appears to increase up to a maximum value of about 130 nm, the substrate coverage being only 40%, after which a filling mechanism takes place. Above nominal thicknesses of 200 nm, the substrate is almost completely covered (see Fig. 4) and the surface roughness progressively decreases in value, reaching that of ALE-grown samples of comparable thickness (see Fig. 5). This suggests that once a "critical height" of the islands is reached, lateral growth proceeds much faster than vertical growth, leading to planar surfaces with the same quality as that produced by layer by layer growth.

Our experimental results indicate that the MOCVD growth of InP/GaAs is characterized by two main regimes. In the first stage the growth proceeds by island formation and the surface coverage is nearly constant with increasing growth time. It follows that vertical growth of the islands is favoured over lateral growth. After a "critical height" of about 130 nm is reached, a sudden transition leading to layer planarization takes place.

On the basis of these experimental results and also literature results, a qualitative description of the 3D island evolution to the coalescence stage can be inferred. At the very beginning the islands grow almost coherently [6], possibly with some minor plastic deformation which does not cause relevant strain relaxation. In fact, the strain field in the island is lower than it would be in a uniform layer of the same thickness, the relaxation being obtained by locally stressing the substrate in a region just underneath the island [5]. One of the effects of the substrate stress is a local bending of the interface area, giving rise to a strain gradient between the bottom and the top of the island [5] (the strain reduction rate being proportional to the interface curvature). The strain gradient causes the migration of the deposited atoms to the top of the island [6] until a "critical height" is reached where the strain field vanishes and lateral growth prevails. In fact, the growth velocity on the (111) planes is higher than on the (001) plane. A consequence, the space between the islands decreases rapidly, the substrate curvature decreases and the strain field in the coalescing islands tends to reach the level of a continuous film. Further work is necessary to formulate a complete model of the transition. In particular, at this stage, it is not clear whether substantial plastic relaxation occurs already in the island stage of the growth or during the coalescence stage. Lastly, detailed calculations of the strain fields in the island–substrate system, within an equilibrium model for the determination of the dimensions and the shape of the islands, are in progress and will be reported elsewhere.

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