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AFM and TEM study of the lateral composition modulation in etched and photo etched $In_xGa_{1-x}P$ epitaxial layers

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Abstract

An alternative way to characterise composition modulation in $In_xGa_{1-x}P$ ALMBE layers grown on GaAs (001) substrate at a temperature of 420 °C by selective etching and photo etching is presented for the first time. AFM and TEM examinations revealed characteristic quasi-periodic surface structures consisting of ridges oriented along $\langle 110 \rangle$. We propose that morphology features observed in the experiments are related to composition modulation effects. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Surface morphology; Etching; Transmission electron microscopy; Atomic force microscopy

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1. Introduction

After TEM observations the layers of the ternary system $In_xGa_{1-x}P$ grown by MBE in the miscibility gap show specific defects due to lateral composition modulation over a spatial range from a few to hundreds nanometers. Fine scale modulation in all ternary systems is associated now with spinodal decomposition. Long wavelength quasi-periodic fringes are also supposed to be decomposition related [1,2]. There are numerous papers devoted to examination of composition modulations by TEM [1,4–9]. Nevertheless, the origin and properties of lateral composition modulation as well as many peculiarities remain unclear. An understanding of the microscopic nature of this phenomenon is very important, due to its influence on both the semiconductor band structure and charge carriers scattering as well as on the performance of optoelectronic devices. On the other hand, understanding and control of composition modulation can provide a new approach for band structure engineering or, on the contrary, suppressing decomposition.

Composition modulation features have been usually studied by TEM. However, this technique presents some intrinsic problems, such as the small field of view, complex sample preparation procedure as well as the difficulty to localise a certain place of observation.

In this paper, an alternative way to reveal and characterise the long-wavelength composition modulation in $In_xGa_{1-x}P$ by selective etching and photo etching techniques has been presented for the first time. These techniques possess the very high sensitivity to local elastic stresses and chemical inhomogeneities as well as to local electronic properties of the semiconductors [10,11]. The latter two cases are of particular interest because an additional information about the presence and distribution of electrically active impurities can be obtained. These techniques are also very effective for defect characterisation. It was clearly demonstrated in GaAs bulk and epitaxial materials, containing structural and compositional inhomogeneities, using special diluted etching solutions [10]. In this work the experiments were performed to show the suitability of the

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techniques for revealing and characterisation of the lateral composition modulation. The AFM and TEM imaging techniques have been used for analysis of the etching topography and correlation between topography and structural features.

2. Experimental details

The samples under study were undoped, Si-doped (n-type) and Be-doped (p-type) In$_x$Ga$_{1-x}$P layers grown by atomic layer molecular beam epitaxy (ALMBE) on GaAs (001) substrate at temperature of 420 °C [12]. The doped layers ($n = 1.9 \times 10^{18}$ cm^{-3}, $p = 8.8 \times 10^{18}$ cm^{-3}) were lattice-matched ($x = 0.48$). The undoped layer had an In content $x = 0.56$. Selective etching was performed in (1–3 parts) HBr + (1 part, 50% aqueous solution) CrO$_3$ [13]. The diluted Sirtl-like etchants were used for photo etching similar as reported in [10]. One hundred and fifty W xenon lamp and 15 mW He–Ne lasers were used as light sources. The layers were examined by TEM in plan-view mode. The samples were thinned both by chemical etching and Ar$^+$-ion milling. TEM was performed with JEOL 1200EX and JEOL 200CX microscopes at accelerating voltage of 120 kV. AFM images were recorded with Nanoscope II (DI) and P47 'Solver' (MDT Russia).

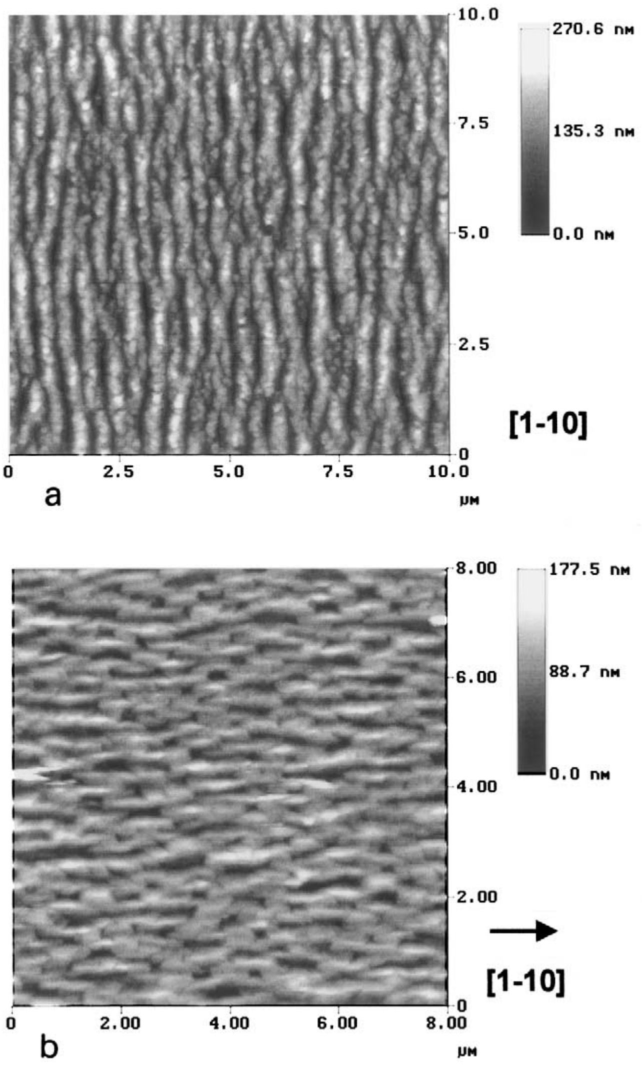

Fig. 1. AFM topographic images of selectively etched InGaP layers: (a) n-type, (b) p-type.

3. Results and discussion

3.1. *Fig. 1a and b show AFM images of n- and p-type InGaP layers, respectively, after selective etching*

It is seen that in n-type material the etching reveals quasi-periodic extended ridges with different length oriented mainly along [1–10] direction (Fig. 1a). Ridges in orthogonal ⟨110⟩ direction are practically not seen. We find a similar morphology in the surface of selectively etched undoped InGaP layers. However, in p-type layers (Fig. 1b) although quasi-periodic ridges are also observed along the same direction, the ridges and valleys form a distinct cellular structure. One can see that valleys between ridges are shorter than in n-type or undoped layers. Periodicity of the ridges in n-type material is ~400–500 nm and ~300–400 nm in p-type layers. The height of ridges changes from ~250–270 nm for n-and undoped layers to ~150–170 nm for p-type. AFM profiling has shown a triangle pyramid shape of the ridges with narrow valleys and heights.

3.2. *Plan-view TEM observations (Fig. 2a and b) revealed surface structures of quasi-periodic ridges in all investigated etched layers*

The micrographs show pronounced bands of contrast along [1–10] direction with the periodicity correlated with that obtained from AFM measurements (Fig. 1a and b). However, the contrast had not shown noticeable changes with the reflection of observation at such magnification.

Direction ⟨110⟩ is not trivial and differs from well-known contrast modulations aligned along ⟨100⟩ directions. However, there are reported TEM observations of contrast modulation bands along ⟨110⟩ in as-grown layers of InGaAs [7], InPSb [8], AlInAs [9], which are attributed to composition modulations due to spinodal decomposition. In coincidence with these results, our TEM results in as-grown InGaP layers, in particular, in undoped material as reference, also show contrast fringes oriented mainly along [1–10] (Fig. 3a). The contrast features are similar in all respects to the long wavelength quasi-periodic contrast previously observed [1,2,4–9] and discussed in detail in [5].

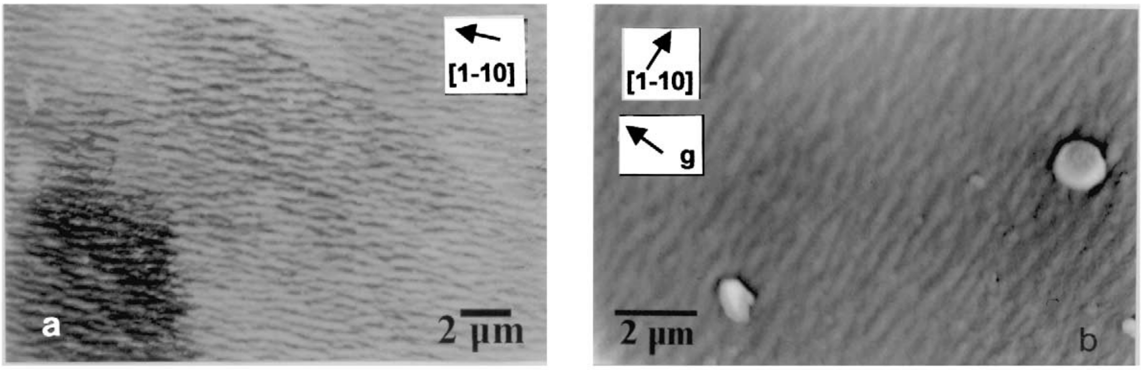

Fig. 2. Typical plan-view TEM images of the same selectively etched layers shown in Fig. 1: (a) n-type, (400) reflection, (b) p-type, (220) reflection.

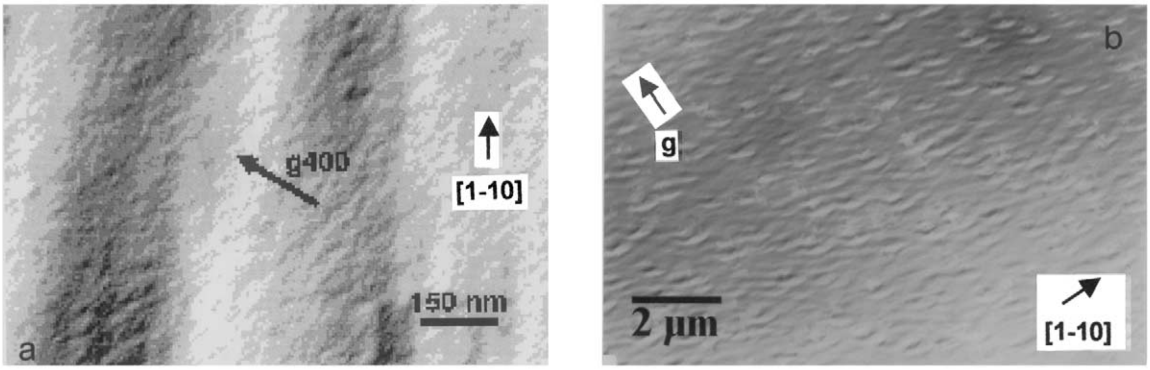

Fig. 3. (a) TEM plan-view of the coarse composition modulations in undoped as-grown InGaP layer, (400) reflection. Fine speckle contrast is seen. (b) TEM plan-view of photo etched n-type InGaP layer, (220) reflection.

So, it is seen that the contrast fringe direction and lateral scale in as-grown layers related to composition modulation coincide with whose in etched layers. Nevertheless, there are differences in TEM images of etched and as-grown layers determined by the conditions of TEM observations. Really, the conditions of image formation in the etched layers are completely different from as-grown layers, because the foil contrast is overlapped with strong topography contrast from the ridges and one may expect appearance of additional contrast features. Indeed, more detail analysis has shown that the contrast of the ridges changed significantly under different reflections, particularly along the boundaries of ridges. Some features of the contrast under different diffraction conditions are shown in Fig. 4 and described in Section 3.3. It should be noted that the fine scale speckle contrast was also observed in etched layers.

Thus, the presented observations lead us to assume that the quasi-periodic structures revealed by etching are related to composition modulation. TEM imaging of photo etched InGaP n-type layer is an additional strong argument for such conclusion. In this sample, the structure revealed by photo etching and observed by TEM (Fig. 3b) have shown contrast features oriented in the same direction as in the selectively etched sample (Fig. 2a) but obtained by an independent method. However, in this case as shown in Fig. 3b, the contrast features oriented along $[1-10]$ direction are seen as cellular structure of short and small ridges instead of long ridges (Fig. 2a). AFM imaging of photo-etched n-type InGaP layer reveals a surface roughness height of ~ 10–30 nm. The Fourier transformations of the AFM images has shown periodicity in orthogonal $\langle 110 \rangle$ direction of ~ 300 nm, which is close to the periodicity on the TEM image.

The most acceptable explanation of this result is that the cellular structure of ridges is related to regions of local recombination activity and their distribution is essentially similar to the fringe contrast shown in Fig. 2a. In this connection it would be very interesting to carry out experiments similar to those presented in [2] to analyse the electrical activity dependence on intrinsic point defects and, if possible, to compare the observations with EBIC or DLTS measurements of deep levels.

3.3. A quite unusual result has been obtained under TEM observation at high magnification

Different features of the TEM contrast and specific morphology of ridges were revealed. Detailed analysis of the morphology features under different reflections was carried out in selectively etched undoped layers (Fig. 4). The ridges were found to have, as a rule, rectilinear boundaries and part of them has characteristic direction ⟨240⟩ as shown in Fig. 4c and d. Specific very fine lines are seen along the edges of ridges (marked A in Fig. 4b and c). Their origin is not clear and may be the subject of special investigation. It is very likely that there exists some unknown kind of chemical separation. One may assume that the selective etchant has low sensitivity to elastic stresses, but has high selectivity to composition in specific coherent-chemical domains or platelets of some intermediate phase. Such domains-ridges contain probably a GaP-rich phase. The assumption is speculative, but it should be noted that the selective etchant used in the experiments has high selectivity to InP [13]. It means possibly that InP-rich alloy domains can be removed selectively by etching. So, maximum contrast changes are seen near the boundary of ridges-Gap-rich phase. It is interesting to note that different contrast peculiarities such as relatively sharp traces of narrow lamellar features [5], rectilinear boundaries [14] and nucleation of the platelets of GaP-rich phase in InGaAsP layers have been earlier discerned [15]. Of course, further detailed analysis of micro-diffraction pattern and influence of the diffraction conditions are necessary for more precise interpretation of the contrast origin.

4. Conclusions

The presented experimental data lead us to some important conclusions. In all InGaP layers the selective etching and photo etching reveal characteristic quasi-periodic structures of ridges, oriented mainly along ⟨110⟩, which supposingly are related to composition modulation. We have found that selective etching based on HBr and diluted Sirtle-like system are effective for revealing of the local changes of composition and potentially for the distribution of electrically active impurities in InGaP layers and possibly in other ternary alloys. In fact, this can give the possibility for separation of recombination active regions in as-grown layers. In this case near-field optical microscopy in photoluminescence mode or CL in a TEM could be a powerful instrument for characterisation of both structural and optical properties of epitaxial layers. Another interesting observation is finding the differences of the ridges morphology in etched p-type layers. It is very likely that the results can point out possible link between layer structure and the extremely low experimental values of the hole mobility in p-type material.

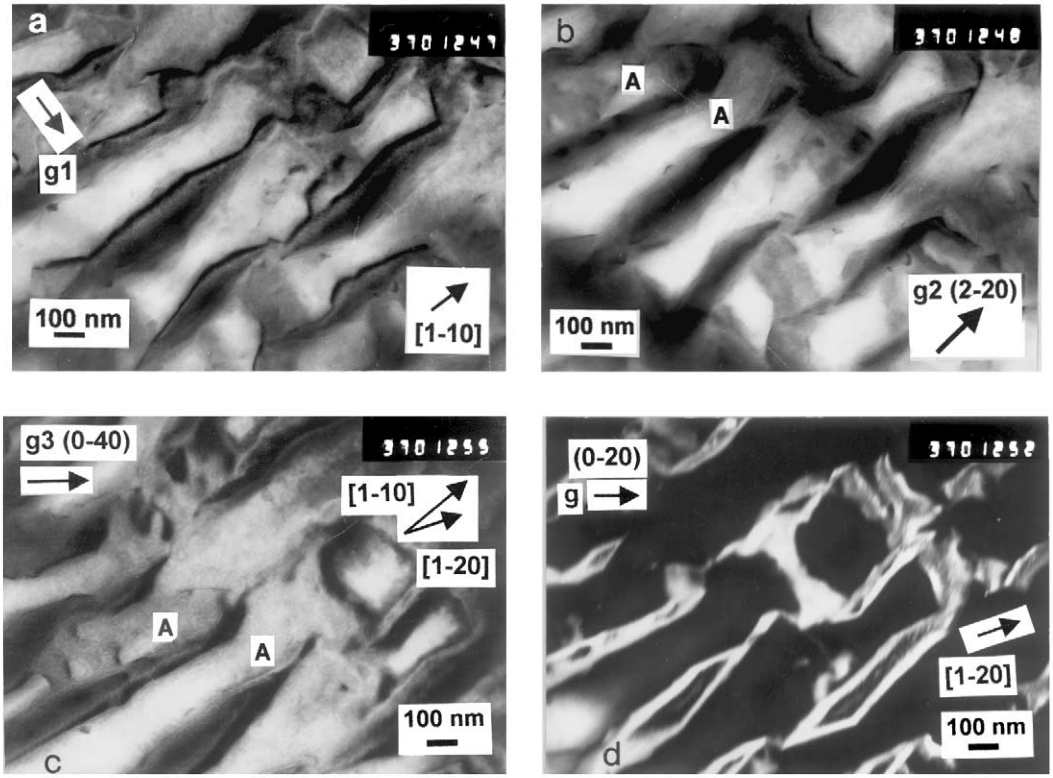

Fig. 4. TEM plan-view micrographs of selectively etched undoped InGaP layer: (a) $g_1(-2$ to $20)$ reflection, (b) $g_2(2-20)$ reflection, (c) $g_3(0-40)$ reflection, (d) dark-field image, (0–20) reflection. In Fig. 4b and c some fine contrast lines are marked with A.

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