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EPILAYER THICKNESS INFLUENCE ON COMPOSITION MODULATION OF LOW TEMPERATURE GROWN InGaAs/GaAs(001) LAYERS

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We have developed a Transmission Electron Microscopy study of $In_{0.2}Ga_{0.8}As$ layers grown on GaAs (001) substrates by Atomic Layer Molecular Beam Epitaxy at 200 ºC. Our results show that the apparition of composition modulation in these samples depends on the layer thickness, the thinnest being homogeneous. Therefore, the phase separation in these low temperature grown systems should have occurred in bulk on arriving to a critical layer thickness between 80 nm and 300 nm and not at the surface during growth as it has been widely reported. Accumulated elastic energy due to an increasing epilayer thickness seems to be a crucial factor in this critical thickness. On the other hand, we have observed a high asymmetry in the contrast modulation wavelength for these low temperature grown samples for the $[110]$ and $[\bar{1}10]$ directions, contrary to the symmetrical ones found in structures grown by conventional MBE at 500 ºC.

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1. Introduction

In the last decade, extensive efforts have been carried out to predict the thermodynamic stability of III-V semiconductors, leading to the general result that most ternary and quaternary systems such as InGaAs or the recently created InGaAsN show a miscibility gap. However, even now there is no agreement on the precise temperatures and compositions for the beginning of the spinodal decomposition process responsible for the composition modulation, due to the diversity of theoretical and experimental results. The knowledge of these parameters is essential to optimize the performance of the optoelectronic devices obtained from semiconductor alloys. On the one hand, composition modulation in III-V semiconductors broadens photoluminescence curves [1,2] and reduces the carrier mobility [3,4], causing the degradation of high-speed devices as HEMTs. But, on the other hand, the confinement properties of the composition modulation has led to the fabrication of light emitting diodes (LEDs) and lasers with modulated active layers [5,6].

The mechanism by which the spinodal decomposition process occurs is also controversial. Although early studies considered spinodal decomposition as a bulk process[7,8,9], latter works have shown experimentally that, at least at conventional growth temperatures, it occurs at the surface of the structure during growth, being related to surface morphology [10,11]. This work is focused on the mechanism of formation of composition modulation in InGaAs/GaAs(001) heterostructures grown at low temperature considering the effect of the epilayer thickness on the composition modulation.

2. Experimental

InGaAs simple layers with a nominal In content of 20% were grown at 200 ºC on (001) on-axis GaAs substrates by Atomic Layer Molecular Beam Epitaxy (ALMBE). The epilayer thickness

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is 300 nm for samples A300 and A300Ct, and 80 nm for A80Ct. A300Ct and A80Ct suffered a post growth thermal annealing at 500 ºC for half an hour. $In_{0.2}Ga_{0.8}As$ layers grown at 500 ºC by Molecular Beam Epitaxy (MBE) were also considered for comparison. These structures are B50 and B190, with 50 and 190 nm of epilayer thickness, respectively.

Samples were prepared for Transmission Electron Microscopy by mechanical thinning followed by ion-milling for cross-sectional (CS) observation. The TEM study was performed using a JEOL 1200EX transmission electron microscope operating a 120 kV.

3. Results

3.1 Low thickness InGaAs structures (< 150 nm)

TEM results for low thickness InGaAs layers have shown a different behaviour for structures grown at high and low temperatures. Fig. 1 shows CSTEM micrographs of sample B50 (grown at 500 ºC). Periodic dark and light contrasts are observed with g220BF reflection (Fig. 1a), which disappear with g400BF reflection (Fig. 1b). This behaviour is typical in the TEM study of III-V semiconductors on (001) substrates [12]. Patriarche et al. [13] showed by x-ray microanalysis that these dark and light fringes are due to areas with different composition. Composition modulation in InGaAs/GaAs(001) is bidimensional along $\langle 110 \rangle$ planes, which are stressed. That is the reason why the contrasts associated to composition modulation are observed by TEM with g220 reflection and not with g400. Therefore, we will consider that the contrasts observed in sample B50 are due to composition modulation in the growth plane, formed by Ga- or In- rich fringes. With regard to plastic relaxation, misfit or threading dislocations have not been observed in this structure.

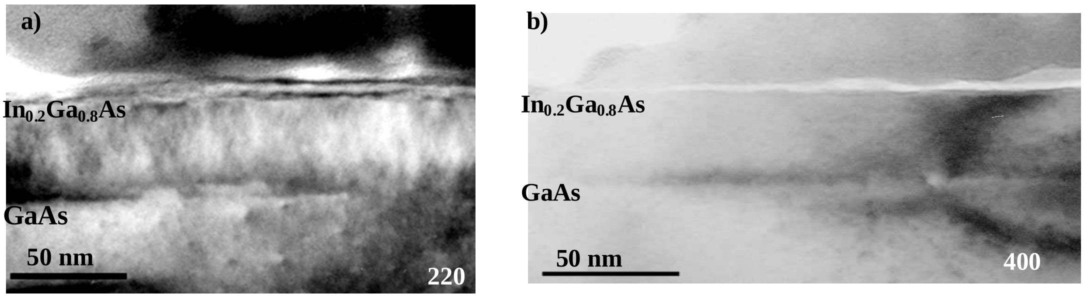

Fig. 1. XTEM images with g220BF (a) and g400BF (b) of sample B50. Dark and light contrasts are observed with g220BF, which disappear with g400BF, showing that composition modulation is parallel to $\langle 110 \rangle$ directions in the growth plane.

Sample A80Ct, similar in structure to the previous one but grown at 200 ºC and with a thermal annealing, has not shown the composition modulation-associated contrasts. Fig. 2 exhibits a TEM micrograph where an epilayer with uniform contrast is observed. Moreover, the structure is plastically relaxed, with a density of misfit dislocations of $18\times10^4 cm^{-1}$. Therefore, in contrast to the samples obtained at high temperature, low temperature growth allows to obtain homogeneous layers, without composition modulation.

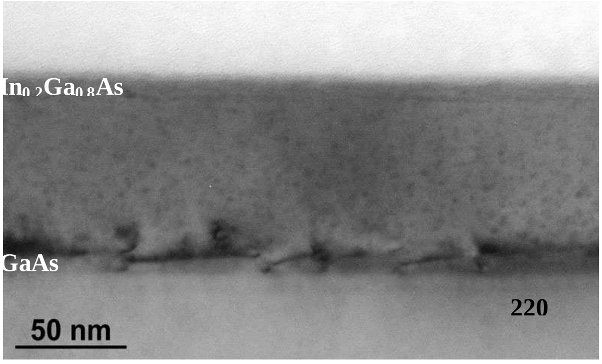

Fig. 2. XTEM micrograph with g220BF reflection for sample A80Ct. Periodic contrasts have not been found in this structure.

3.2 High thickness InGaAs structures (> 150 nm)

Fig. 3 shows g220BF CSTEM micrographs of sample A300 (grown at 200 ºC). As it can be easily observed, periodic contrasts have been found in this structure, showing the existence of composition modulation. This means that the increase in epilayer thickness from 80 to 300 nm causes the apparition of the phase separation in low temperature grown samples. To our knowledge, this is the first time that this fact has been observed.

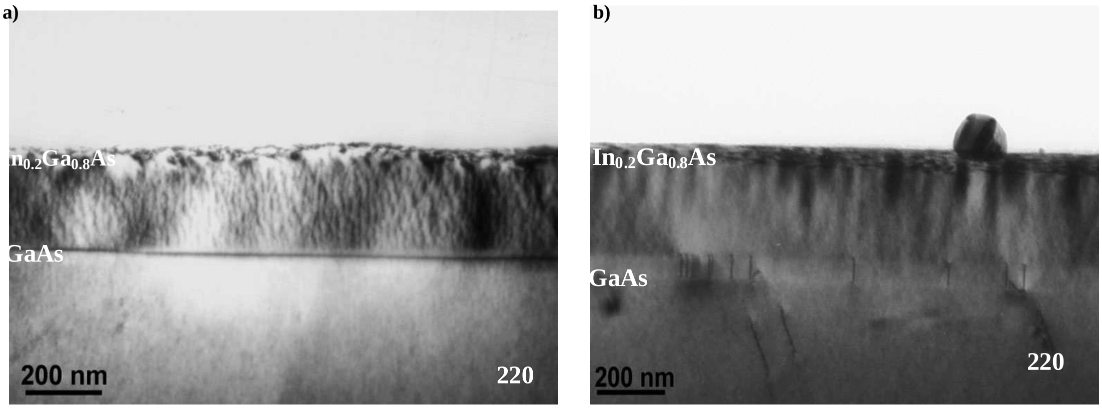

Fig. 3. XTEM images with g220BF reflection for sample A300: (a) $\langle 110\rangle$ direction, (b) $\langle 1\bar{1}0\rangle$ direction. It should be noted the asymmetry in composition modulation contrasts for both cross sections.

It is also worth mentioning the differences in contrasts found for both $\langle 110\rangle$ directions in the growth plane in samples A300 and A300Ct. In both structures, TEM micrographs obtained for $\langle 110\rangle$ direction show short-wavelength contrasts (approx. 25 nm), as it can be observed in Fig. 3a for A300. However, $\langle 1\bar{1}0\rangle$ direction exhibits longer wavelength contrasts, approx. 60-70nm. The similarity in contrasts found in both A300 and A300Ct shows that the application of a thermal treatment at 500 ºC does not affect the characteristics of the composition modulation in these structures. With regard to the high thickness sample grown at high temperature B190, composition modulation has also been found, but with symmetric characteristics for both $\langle 110\rangle$ directions. Fig. 4 shows the fine speckle contrasts observed in this structure, which are similar to that in $\langle 110\rangle$ direction of A300 and A300Ct.

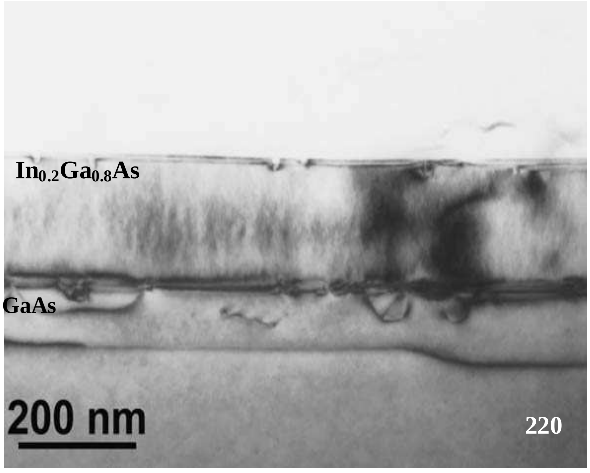

Fig. 4. XTEM micrograph with g220BF reflection for sample B190, where fine speckle contrasts are observed.

A difference in plastic relaxation degree for samples grown by the two methods considered in this work (MBE and ALMBE) has also been found. The planar density of misfit dislocations in samples A300 and A300Ct is 8×10^4cm^{-1} and 26×10^4cm^{-1}, respectively, lower than that in B190 (45×10^4cm^{-1}), which furthermore has lower thickness. Therefore, it seems that low temperature grown samples should have a considerable amount of accumulated elastic energy.

4. Discussion

4.1 Effect of the layer thickness on spinodal decomposition for low temperature grown samples

As it has been described above, our results have shown the existence of composition modulation in the high temperature grown sample B50, but not in A80Ct, obtained a 200 ºC. This means that phase separation in low temperature grown samples is inhibited for low thickness epilayers. Several authors have reported that spinodal decomposition is inhibited in low temperature growth of InGaAs/GaAs or SiGe/Si heterostructures [14,15], but we have not found any report on the influence of the epilayer thickness on this process.

Several thermodynamic models based in Cahn´s theory for metals [16] to calculate the critical temperature below which the spinodal decomposition process takes place in bulk have been reported [8,9]. Critical temperatures obtained with these models are really low, and can not explain the experimental results [17]. Thus, recent models regard the spinodal decomposition process as a surface phenomenon, introducing kinetic factors [10,11]. In this case, despite the fact that composition modulation is unstable in bulk material, it is considered to remain inside the material because of kinetic barriers for its homogenization.

However, our results have shown that phase separation can take place in bulk. Epitaxial growth at 200 ºC of an 80 nm thick InGaAs epilayer is homogeneous, whereas the 300 nm thick layer is modulated. Spinodal decomposition should have taken place in bulk in a specific moment, given that it could not be produced on the surface of the structure since the beginning of the growth. The apparition of composition modulation in bulk have been observed in the thermal annealing of low temperature grown SiGe heterostructures [15], but in our case this thermal treatment seems not to affect the phase separation.

We believe that the reasons for the apparition of phase separation in bulk in these InGaAs structures are related to its relaxation characteristics. Sample A300 has 300 nm of epilayer thickness, and a lattice mismatch with the substrate of f = 1.5%. However, the plastic relaxation degree obtained by TEM is very low (~5%) in comparison with the theoretical values for conventional growth temperatures (~76%) [18]. Therefore, this sample should have a considerable amount of accumulated elastic energy, because of its difficulties for the plastic relaxation.

Guyer and Voorhees [19][1] proposed a theoretical model for the apparition of composition modulation in epitaxial layers, where it is considered the influence of the elastic relaxation on the apparition of composition modulation in bulk. According to this model, in a structure where the elastic relaxation in the surface of the crystal is allowed, the thermodynamic condition for the spinodal decomposition $G_m{}^{f''} < 0$ becomes less restrictive, as $G_m{}^{f''} + V_0 E\eta^2 < 0$, where $G_m{}^{f}$ is the Gibbs free energy, V_0 is the molar volume, E is the Young's modulus and η is the solute expansion coefficient. In this way, the critical temperature for phase separation in structures where the surface elastic deformation is allowed is higher than that for rigid epitaxial layers. It is shown that the capacity of a structure to be elastically relaxed in the surface favours the apparition of a phase separation in bulk.

The experimental results obtained in this work are qualitatively in good agreement with this theoretical prediction. Given that the low temperature growth inhibits the formation of misfit dislocations, these structures tends to relax elastically. The sample with epilayer of 80 nm (A80Ct) have a relatively high plastic relaxation degree (30%, approx.) acquired during the thermal annealing. During its growth, and although the structure is stressed, its surface elastic relaxation is low because of a low epilayer thickness, therefore the layer remains homogeneous. However, in the sample A300, the accumulated elastic energy is really high because of a high epilayer thickness. This could favour the apparition of phase separation in bulk, as predicted theoretically by Gooyer et al. [19][1]. We have found that there should be a critical layer thickness in the range 80-300 nm for these InGaAs epilayers where the structure has such elastic strain that spinodal decomposition occurs. Before reaching such a thickness, the layer should be homogeneous.

4.2 Characteristics of composition modulation in low temperature grown samples

Our Transmission Electron Microscopy study of InGaAs samples has shown a change in the composition modulation characteristics with growth temperature. Samples A300 and A300Ct (grown at 200 ºC) are asymmetric with regard to the periodic contrasts (wavelength of 25 nm for $\langle 110 \rangle$ direction vs. 60-70 nm for $\langle 1\bar{1}0 \rangle$), whereas B190 (grown at 500 ºC) is symmetric. This is due to the fact that in each case, spinodal decomposition takes place through a different mechanism. When growing by MBE at high temperature, composition modulation is formed at the surface of the structure during growth [20,21,22], but in our low temperature grown samples, it should have taken place on bulk when arriving to a critical layer thickness.

The observed asymmetry in composition modulation features consist of a variation in the wavelength of the periodic contrasts for both <110> directions. Mirecki et al. [23] found the same asymmetry in AlAs/InAs structures, and they propose a difference in the surface diffusion length of the adatoms because of a (2×4) surface reconstruction as the cause for this asymmetry. However, the wavelength of coarse contrasts is too high to take place by surface diffusion in the available time between the depositions of two consecutives monolayers [20,22].

Lee et al. [24] propose a different explanation for the coarse contrasts composition modulation. They suggest that it could be induced by the undulation of the crystal surface produced by stresses in the structure. According to them, atoms with high volume would be placed in tension zones, and those with low atomic radius in compression areas, in such a way that each fringe would be enriched in a different type of atom and the composition would result modulated. In our case, these arguments are not valid because spinodal decomposition seems to have been produced in bulk and not in the surface of the structure. The observed asymmetry could be due to an asymmetry in the material, in such a way that when growing at so low temperature, the diffusion rate of Ga and In atoms would be different for both <110> directions. However, McDevitt et al. [25] state that coarse contrasts composition modulation can not be produce in bulk because diffusion of atoms in bulk is extremely slow.

McDevitt [25] try to corroborate Mahajan's hypothesis [20] that fine speckle contrasts and coarse contrasts are coupled. They applied a thermal cycle to structures with both types of modulation, and observed that coarse contrasts disappeared even sooner that fine speckle contrasts. If coarse contrasts were due to a real variation in composition, they should take more time to disappear because atoms had to diffuse a longer distance. Because of this, McDevitt says that coarse contrasts are a thickness-dependent artefact of TEM thin foils because of stresses in the structure due to the fine speckle modulation. Choi et al. [26] born out this assumption when they found, for the same specimen preparation for TEM of an InGaAs/InP sample, areas with coarse contrast and others without it, whereas fine speckle contrasts were observed all through the sample. Thus, the author associates the coarse contrasts to an artefact of TEM thin foils and not to a composition modulation.

This argument could be valid to explain the coarse contrasts observed in our study. However, it can not explain the reasons for the observed asymmetry. If we consider that coarse contrasts are just an artefact and not a real phase separation, then we would have composition modulation just in one of the <110> directions. To find an accurate explanation for this asymmetry more studies are needed.

5. Conclusions

In this work, the influence of epilayer thickness on the composition modulation of low temperature grown $In_{0.2}Ga_{0.8}As$/GaAs (001) heterostructures is studied. We have observed that in samples grown at 200 ºC, spinodal decomposition takes place in bulk, contrary to the general idea for high temperature grown structures that it is a surface process. Spinodal decomposition has been found to be a thickness-dependent process, occurring when the epilayer reaches a critical layer thickness in the range 80-300 nm. Elastic strain due to the reticular misfit in a structure with inhibited plastic relaxation seems to be a fundamental factor in this process. Furthermore, asymmetric composition modulation features have been observed in 300 nm thick InGaAs epilayers.

Fine speckle contrasts are observed in one $\langle 110 \rangle$ direction in the growth plane, while coarse contrasts appears in the other, the latter are likely to be an artefact of the sample preparation for TEM study. On the other hand, a post-growth thermal annealing does not change the characteristics of composition modulation in low temperature grown $In_{0.2}Ga_{0.8}As/GaAs(001)$ epilayers.

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