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JOURNAL DE PHYSIQUE

Colloque C5, supplément au n°12, Tome 43, décembre 1982 *page* C5-11

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Centre National d'Etudes des Télécommunications, 196 rue de Paris, 92220 Bagneux, France

Résumé - Nous montrons en utilisant un MEBT en modes image et microanalyse X qu'un champ de déplacement quasipériodique et une modulation de composition associée existent dans des couches de InGaAsP épitaxiées sur substrat InP orienté (001). Nous vérifions que cette modulation n'est pas un artefact dû à des effets de canalisation. Le domaine de température et de composition pour lequel la structure quasipériodique est observée est en bon accord avec la prédiction théorique d'une zone d'instabilité spinodale dans la phase solide.

Summary - We show by STEM imaging and X-ray microanalysis that a quasiperiodic strain field and an associated composition modulation exist in InGaAsP layers LPE-grown on (001) InP. This modulation is checked not to be an artefact due to channelling effects. The composition and temperature range for which the quasiperiodic structure is observed is in good agreement with the theoretical prediction of a spinodal instability zone in the solid phase.

I - Introduction - The use of $In_xGa_{1-x}As_yP_{1-y}$ III-V quaternary alloys for the fabrication of opto-electronic devices for fibre-optic systems has grown rapidly over the last few years. The attraction of these alloys is that by choosing the composition x and y, the crystal lattice parameter and energy band gap may be selected independantly. This flexibility is important because (1) it permits epitaxial growth of InGaAsP layers lattice matched to single crystal substrates to provide the defect-free interfaces necessary for high quality heterostructure devices and (2) it allows a range of devices to be made operating in the wavelength range 1.1 to 1.7 µm, where loss and dispersion in SiO_2 based optical fibres are a minimum.

However, there is evidence that a solid phase instability occurs over a large part of the quaternary composition range at the usual growth temperature (1,2,3). This is in apparent contradiction to the fact that good-quality devices can be readily fabricated over the full composition range. It has been argued (1) that the composition of lattice-matched quaternary layers grown within the immiscibility zone are stabilized by strain induced by the substrate. Quillec et al. (3) have shown that for layers grown from the liquid phase on intentionally lattice mismatched (001) GaP substrates, phase separation does indeed occur for compositions grown within the immiscibility region. For perfect lattice matching ($\frac{\Delta a}{\Delta} \sim$ a few 10^{-4}), the epilayers are homogeneous at the micron scale. Henoc et at. (4) have shown by scanning transmission electron microscopy (STEM) that quaternary layers grown by LPE, lattice matched to (001) InP within the immiscibility zone display a quasiperiodic strain field with an associated composition modulation. A series of different quaternary compositions LPE grown at 650°C were examined in reference (4). It was shown that all compositions lying within the predicted spinodal isothermcurve (see fig.1) displayed "tweed"-like contrast (filled squares in fig.1) and those lying outside the curve (open squares) did not exhibit "tweed". All specimens were lattice matched to InP and lay on the iso-lattice parameter line a_0 = 0.587 nm.

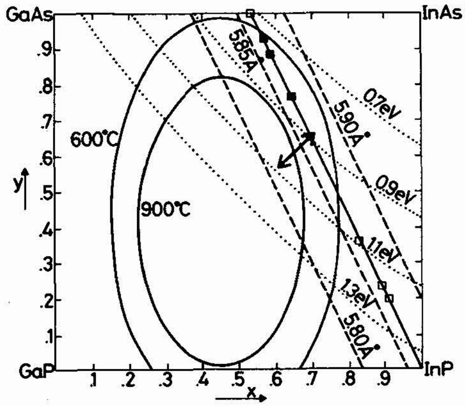


Fig. 1 : Composition representation of the $In_xGa_{1-x}As_yP_{1-y}$ alloy system showing the spinodal isothermal curves calculated by De Crémoux (1) and the isoparameter (---) and isobandgap (...) lines.

In this paper we extend the preceeding STEM results on composition modulations : (i) complements are given on the STEM analysis ; (ii) for given compositions (emitting wavelength 1.3 µm an 1.65 µm) we show that the composition modulations are observed only when the growth temperature lies in the immiscibility domain.

II - Experimental results - A series of lattice-matched InGaAsP/InP specimens were grown by LPE using either equilibrium cooling or step cooling. For examination by STEM, the specimens were thinned from the substrate side to a thickness of about 30 µm, first by mechanical and then by chemical polishing, using Br_2/CH_3OH solution. Final thinning was completed by etching a hole in the specimen using either Br_2/CH_3OH or ion-beam thinning. Specimens were glued onto nickel slot grids. Thin areas near the edge of the hole were examined in a Vacuum Generators Ltd. HB501 STEM equipped with an energy dispersive X-ray analyzer.

II.1 - STEM images and microanalysis - Fig.2 shows a STEM (220) dark field image of an InGaAsP layer (1.3 µm lasing wavelength) grown at 650°C within the expected immiscibility zone. The image shows the characteristic "tweed-like" contrast propagating in the [100] and [010] directions with a periodicity of about 200 nm. This contrast is quite different from the much narrower contrast due to a misfit dislocation network such as is observed in the [110] directions in similar compounds (but very rarely in our own samples).

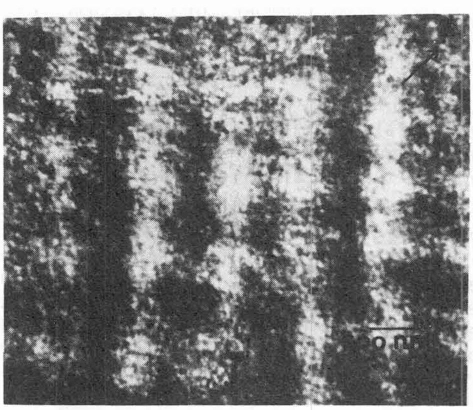


Fig. 2 : (220) STEM dark field image showing the quasi-periodic contrast

In fig.3 we show in more detail the image contrasts of fig.1 sample taken under (220) $(\bar{2}\bar{2}0)$ and (040) two-beam dark field conditions. Comparison of figs 3.a and 3.b ($\underline{g}$ = (220) and $(\bar{2}\bar{2}0)$ respectively shows that the "tweed" reverses contrast on changing the sign of $\underline{g}$. In the $\underline{g}$ = (040) image (fig.3.c), the tweed periodicity running along the [010] direction only is visible. These observations are consistent with a quasiperiodic displacement field $\underline{R}$ of the atom positions, with components in the [100] and [010] directions. The dark field image contrast arises mainly from the local bending of the diffracting planes relative to the beam direction causing a quasiperiodic excitation essor $\underline{g}.\frac{dR}{dz}$ of the Bragg reflection. Dilatation contrast caused by local changes in $\underline{g}$ itself is too weak to adequately explain the observed contrast.

A fine (∿ 15 nm) granular structure is also visible in fig.3. This granular structure is not easily correlated between different dark field images, and assumes a streaky nature in the $\underline{g}$ = (040) image. Granular contrast is visible in all specimens whether or not they are within the immiscibility zone, and is visible equally in specimens which have been chemically or ion-beam thinned. The origin of this contrast is not clear, but it may be related to short range ordering.

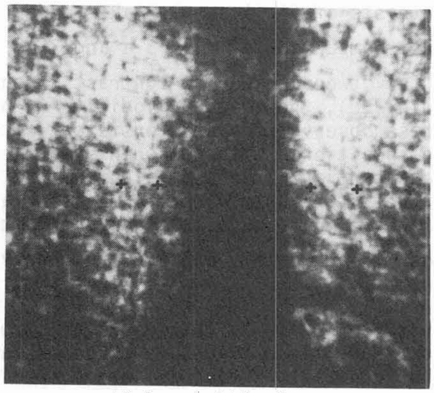
The area shown in fig.3 was microanalyzed in the three diffraction conditions using the energy dispersive X-ray spectrometer. The nominal probe used during microanalysis was about 1 nm, but because of probe spreading within the sample, about 100 nm thick, this increases to about 20 nm (5) at the sample exit face. The results for the P, Ga and In Kα emission energies (2.01, 9.22 and 24.00 keV respectively) are plotted in fig.4 relative to the As peak at 10.51keV.The Ga/As ratio changes by ± 4 % over the zone analyzed whereas the In/As ratio remains constant within statistical error. The P/As ratio follows the Ga/As ratio but the statistics is not as good. The weakly energetic PK X-rays are strongly absorbed in these specimens and if PK is compared with AsL peak (1.39 keV) which is still more absorbed, we also find that the P/As ratio is similar in amplitude to Ga/As. These results do not change significantly on changing the specimen diffraction conditions, so we can discount the hypothesis that these concentration fluctuations arise through anomalous channelling effects caused by the quasiperiodic Bragg reflection excitation error $\underline{g}.\frac{dR}{dz}$.

II.2 - Phase diagram exploration - Many samples grown at 650°C, and corresponding to 1.3 μm emission wavelength, were examined. In all cases, the composition modulations are observed and correspond to a constant value of x/y, in agreement with the observed tie-line direction of demixion (3). The composition range we find falls short of that observed by Quillec, and is sample dependant. The highest measured value is shown by the arrow in fig.1.

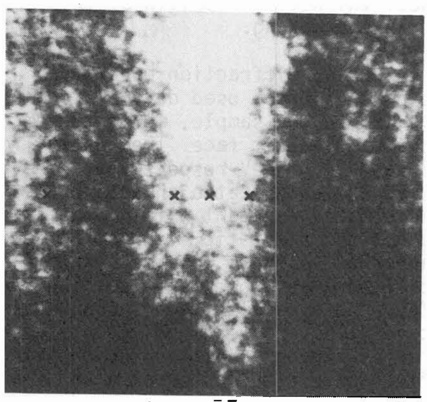
We find that strong image contrast is related to strong composition changes. Occasionally, contrasts suggestive of lamellar precipitates are observed (see fig.5.a). Such areas show the strongest composition modulations (fig. 5-b, c, d).

Further connection of these composition modulation with instability of the solid phase in these alloys is obtained by changing the growth condtitions.1.3 μm layers LPE-grown at the elevated temperature 750°C, taking the growth conditions outside the immiscibility zone, do not exhibit the quasiperiodic "tweed" contrast, although the granular contrast persists. Composition profiles along [100] directions show no significant deviation from constant value (6).

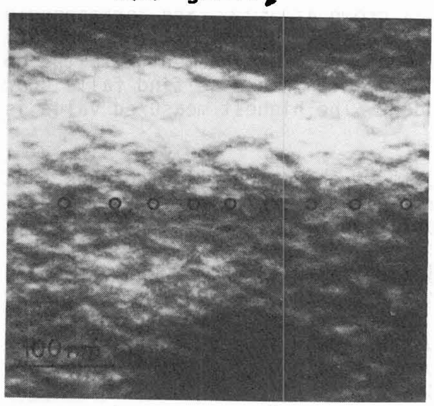
Similar effects are observed in the lattice-matched ternary layer $In_{0.53}Ga_{0.47}As/InP$. When grown at 650°C, it does not show the tweed, but when grown at the reduced temperatures of 550°C and 490°C, the "tweed" contrast appears with equal and opposite In and Ga concentration fluctuations of ± 5 %. Demixion has been observed at 550°C for mismatched ternary compounds (P.Henoc et M.C.Joncour, private communication).



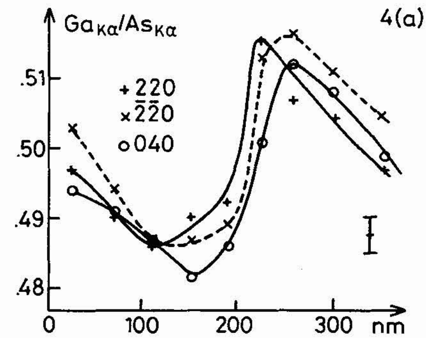
3(a) g=220 ↗

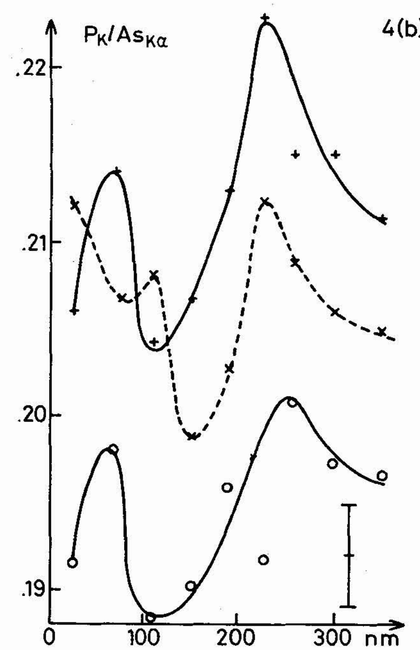


3(b) g=$\bar{2}\bar{2}0$ ↙



3(c) g=040 ↑





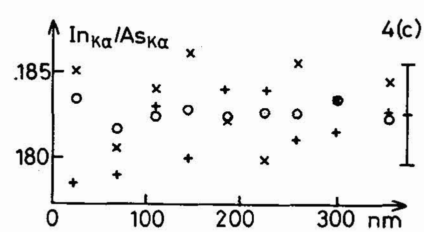


Fig. 3 and 4 : STEM dark fields images of the same area taken under three different diffraction conditions, and the results of X-ray microanalyses at the points indicated on the micrographs.

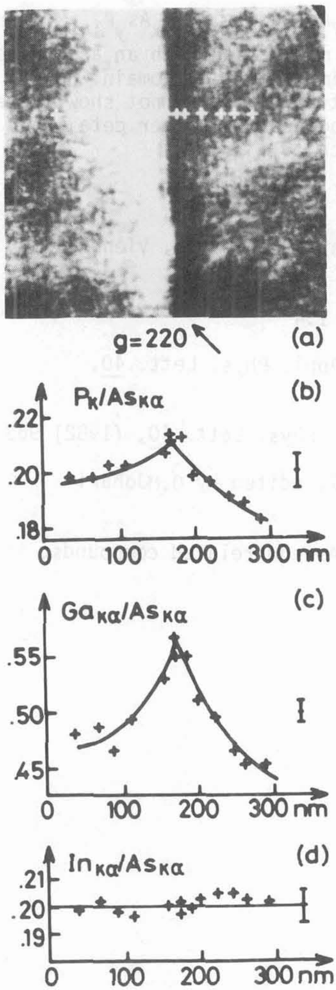


Fig. 5 : (220) STEM dark field image and X-ray results from an area thought to be a lamellar precipitate

Also examined was a series of 1.3 µm quaternary epilayers grown at 650°C by step cooling with various degrees of supersaturation. All exhibit "tweed" contrast, although rather weak. Samples thinned so as to observe the quaternary layer near the InGaAsP/InP interface were severely bent and difficult to examine under fixed diffraction conditions.

The development of these composition modulations in lattice matched layers is as yet not clearly understood. Diffusion coefficients in III-V alloys are too small to account for composition modulations on a 200 nm scale. Annealing of a 1.3 µm specimen at the epitaxy temperature for 15 hours produced no noticeable modification to the structure. This strongly suggests that the modulation happens at the solid-liquid interface.

Within a factor of two, the periodicity of the tweed does not depend on composition, growth conditions and parallel mismatch of the layers (within elastic limit). It is likely that the solid solution free energy is minimized by coherent unmixing.

In summary, we have shown that lattice-matched $In_{.53}Ga_{.47}As$ and $In_xGa_{1-x}As_yP_{1-y}$ layers grown on (001) InP exhibit a quasiperiodic composition modulation with an associated strain field, when the growth temperature lies in the immiscibility domain. For growth temperature above this domain, the same composition layers do not show these composition modulations, and the solid solution is homogeneous. Further details on the growth dynamics of the layers are given in reference (6).

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