TEM AND STEM OBSERVATIONS OF COMPOSITION VARIATIONS IN III-V SEMICONDUCTORS

Frank Glas
Centre National d’Etudes des Télécommunications
196, avenue Henri Ravéra
92220 Bagneux, France

INTRODUCTION

In first approximation, the quaternary A_{1-x-y}B_xC_yIII-V semiconducting alloys have the same sphalerite structure as their constituent binaries AC, AD, BC and BD; their lattice parameter and their band gap energy vary continuously with the compositions x and y. These materials are thus attractive for the fabrication of optoelectronic devices, because a suitable choice of these in principle independent compositions usually allows both the epitaxy of a thin alloy layer on a bulk binary substrate and the subsequent obtaining of a device emitting or detecting light at a given wavelength. Conversely, any inhomogeneity in the alloy is likely to induce local variations of its structural and electronic properties. Such composition variations are either introduced intentionally to obtain novel effects, for instance in superlattices, or unintentionally. In the latter case, they are often caused by changes in the growth conditions of the layer: this may happen in Liquid Phase Epitaxy (LPE) when the liquid bath changes composition as growth proceeds, or in Chemical Vapor Deposition, because of instabilities in the growth process; the composition then varies only in the growth direction.

However, inhomogeneities of a more fundamental origin (with isoconcentration surfaces not necessarily planes parallel to the growth front of the layer) may exist even in samples grown under temporally uniform conditions. This is expected to be the case if the homogeneous alloy is thermodynamically unstable against disproportionation. Surprisingly, most III-V alloys are now generally believed to be partially immiscible. Early investigations showed that the restricted available portions of their phase diagrams are described rather satisfactorily by a regular solution model. In this model, the enthalpy of mixing of a ternary alloy A_{1-x-y}C is \( \omega_x(1-x) \), where \( \omega \) is the 'interaction parameter'; the alloy is immiscible under some critical temperature \( T_c \) if the interaction parameter is positive. Similarly, the quaternary alloys are immiscible if the interaction parameters relative to the pairs of constituent binaries are positive. For the III-V alloys, the \( \omega \)'s are all found strictly positive provided the constituent binaries are not latticed-matched. This predictable immiscibility was in apparent contradiction with the existence under \( T_c \) of lattice-matched layers with well defined emission wavelengths, and was not commented upon until the first experiments of Hénoc et al. revealed that composition inhomogeneities indeed exist in some III-V alloys.
In this paper, we will first review the Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) microanalysis experiments demonstrating that, in a range of average composition and growth conditions, In\textsubscript{G}a\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} layers display very specific composition modulations with components parallel to the substrate surface and a characteristic coarse scale of about 100 nm. The complexity of this phenomenon, happening during growth and subsequently frozen, but clearly related to the predicted immiscibility, will then be discussed. However, these often confirmed data leave open the question of the homogeneity of the alloy on a smaller scale. Thus, the TEM study of the fine scale contrast (~10 nm) universally observed in alloys with lattice-mismatched constituent binaries will then be reviewed and its strain nature proven; its often admitted relation with smaller scale composition modulations will be critically discussed, in relation with the recent microscopical thermodynamic models of the III-V alloys, which, although they rightly insist on the existence of strains at the atomic level, will be shown not to describe suitably disordered materials.

In a ternary A\textsubscript{B},B\textsubscript{C} alloy, we call mixed the sublattice occupied by A and B; both the sublattices of a quaternary alloy are mixed. We qualify as disordered a model alloy where the occupation probabilities of the different sites of the mixed sublattices are uncorrelated. We call intrinsic the value \(a(x,y)\) of the lattice parameter of the alloy in its bulk homogeneous stress-free form; it varies linearly with \(x\) and \(y\) (Vegard’s law).

EXPERIMENTAL STUDY OF THE QUASIPERIODIC COMPOSITION MODULATIONS

In this section we recall that characteristic composition modulations exist in lattice-matched In\textsubscript{G}a\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} layers epitaxially grown by LPE on (001) oriented InP substrates. The experimental evidence is given for layers of average composition \(x=0.72, y=0.60\) grown at temperatures \(T\), between 620 and 650°C. The micrographs were taken in a Vacuum Generators HB5 STEM at an energy \(E_0=100\) keV, and are interpreted in the usual TEM terms; X-ray spectra were recorded in the same instrument with a Kevex Si:Li detector. For a Bragg reflection \(g\) of modulus \(g\), we denote by \(F_g\) and \(d_g\) respectively the structure factor and the extinction distance, and by \(w=g_d\) the deviation parameter, if \(M\) is the angle between the electron beam and the exact Bragg incidence.

The quasiperiodic contrast

The study of numerous ‘plan view’ specimens thinned from the substrate side either mechano-chemically with a solution of bromine in methanol, or by Ar\textsuperscript+ ion bombardment, confirms and expands the first experiments of Hénoc et al.:

(a) The Bright Field (BF) and Dark Field (DF) (Fig. 1 a,b,c) two-beam images, taken at or near the exact Bragg position for reflection \(g\), display contrast elements roughly parallel to the directions [100] and [010] normal to the growth direction, repeated respectively along the directions \(u=[010]\) and \([100]\) about every 100-200 nm; hence the term ‘quasiperiodic’ (QP).

(b) Both contrast directions appear for \(g\) of 220 type (Fig. 1 a); only the direction \(u\) colinear to \(g\) appears for \(g\) of 400 type (Fig. 1 b). The quasiperiod is the same in both types of images.

(c) DF images show one sharp black/white (bw) transition per quasiperiod (the ‘whiteness’ of a pixel grows with the number of electrons contributing to it); this transition is reversed to wb if \(g\) is changed in \(-g\) (Fig. 1 a,c). In a given image and for a given repeat direction \(u\), these sharp transitions are always in the same sense, such that \(g.u>0\) if \(u\) is chosen from black to white.

(d) BF images are less contrasted. Two black bands flanking a whiter one correspond to the most pronounced transitions of the DF images.

(e) In images formed with other reflections than 220 and 400, the