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Influence of boron surface enrichment on the growth mode of BGaAs epilayers grown on GaAs by metalorganic vapour phase epitaxy

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Abstract

BGaAs epitaxial layers were grown by metalorganic vapour phase epitaxy (MOVPE) on (100) GaAs vicinal substrates using diborane, triethylgallium and arsine as precursors. For growth temperatures of 580 and 610 °C, we studied the boron incorporation in the epilayers, their boron surface composition and their growth mode as a function of the diborane flow-rate, using respectively X-ray diffraction, X-ray photoelectron spectroscopy and Atomic Force Microscopy. We observed that increasing the diborane flow-rate strongly favours the development of step-bunching. This trend was related to a pronounced boron enrichment of the surface, as a consequence of a surface segregation of boron. These results suggest that boron behaves as a surfactant during the MOVPE growth of BGaAs and particularly increases the surface diffusion length of gallium adatoms. For excessive diborane flow-rates, a dramatic roughening of the epilayer surface is first observed and then, phase separation occurs.

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1. Introduction

Boron arsenide (BAs) and its related alloys remain some of the least explored semiconducting III–V materials. Due to the very small covalent radius of boron, BInGaAs can be grown lattice-matched to GaAs and has been demonstrated to be a promising material for solar cell applications as an alternative to InGaAsN [1]. This quaternary alloy is also a candidate for the active layer of devices used for fibre-optical telecommunications networks. Indeed, incorporating boron into InGaAs/GaAs quantum wells may allow extending their emission wavelength towards 1.3 µm by reducing the compressive strain. Since the pioneering work of Geisz et al. [2], there were few reports on the epitaxy of BGaAs and BInGaAs alloys on GaAs substrates. BGaAs alloy has been grown by molecular beam epitaxy [3,4] and metalorganic vapour phase epitaxy (MOVPE) [2,5–9] while the quaternary alloy, BInGaAs, has only been grown by MOVPE [2,5–7].

Various factors contribute to the complexity of B(In)GaAs epitaxy. First, a large miscibility gap exists between GaAs and BAs: theoretical calculations predicted a boron solubility limit in bulk GaAs, at thermodynamic equilibrium, ranging between 4 and 7% at 600 °C [10,11]. To date, $B_xGa_{1-x}As$ epilayers with a boron concentration x up to about 8% have been grown [4]. On the other hand, boron and arsenic can form a rhomboedral $B_{12}As_2$ phase as well as the zinc-blende BAs phase. During MOVPE growth, the V/III ratio appears as a key-parameter in order to stabilize zinc-blende B(In)GaAs alloys. Indeed, high V/III ratios seem to be required to inhibit the formation of B–B bonds in the solid [5]. Moreover, the mechanism of boron incorporation into B(In)GaAs by MOVPE appears complex and is still not well understood. Low growth temperatures promote boron incorporation [5–7]. But, whatever the growth temperature and the boron precursor nature (diborane, triethylboron...),

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boron incorporation efficiency remains low [12]. It has also been shown that good-quality BGaAs epilayers could only be obtained on a relatively narrow range of boron gas-phase concentrations. Indeed, increasing boron precursor flow-rate leads, beyond a critical point, to a pronounced surface roughening and to a structural breakdown [5–9]. For such epilayers, with a rough surface morphology, we evidenced a strong surface segregation of boron [13].

The aim of this paper is to clarify how the boron gas-phase concentration influences the boron surface composition, the surface morphology and the growth mode of BGaAs epilayers grown on GaAs by MOVPE. In our growth conditions, we show that boron surface segregation is a quasi-general phenomenon, not limited to epilayers with degraded surface morphologies. Moreover, we demonstrate that a close correlation exists between the boron accumulation on the epilayer surface and the development of a step-bunching growth mode. This study proposes an advance in the understanding of the growth mode mechanisms of BGaAs epilayers.

2. Experimental details

The growth of $B_xGa_{1-x}As$ layers ($x \leq 2.3\%$) has been performed by atmospheric-pressure MOVPE in a T-shaped horizontal reactor. The layers were deposited on (100) GaAs substrates misoriented 1° towards [001] direction. Diborane (B_2H_6), triethylgallium (TEG) and arsine (AsH_3) were used as precursors and hydrogen as carrier gas. Prior to BGaAs growth, a 70 nm thick GaAs buffer was deposited at 650 °C. BGaAs epilayers were then grown at 580 or 610 °C. AsH_3 and TEG flow-rates were kept constant, respectively at 2.7×10^{-3} and 4.2×10^{-6} mol min^{-1}. Diborane flow-rate was varied from 8.9×10^{-7} to 8.9×10^{-6} mol min^{-1}, leading to V/III ratios ranging between 125 and 460. We used high V/III ratios in order to favour BGaAs alloy stabilization. The boron gas-phase concentration was quantified by the initial molar flow-rate ratio: $X_v=2[B_2H_6]/(2[B_2H_6]+[TEG])$. In the range of diborane flow-rates used in this study, X_v varied between 30 and 81%.

Surface morphologies were observed by ex-situ Atomic Force Microscopy (AFM) using a Scientec Molecular Imaging microscope in constant-force mode. Surface roughness root-mean square (RMS) was measured on 5×5 µm^2 areas. Step heights were determined using profile cross-sections. The boron composition (x) of the epilayers was deduced from X-ray diffraction (XRD) patterns, using the (400) reflection, assuming Vegard's law and a coherent strain between the layer and the substrate. The Poisson ratio was estimated to 0.31 for our epilayers, using for BAs the elastic coefficient values calculated by Meradji et al. [14].

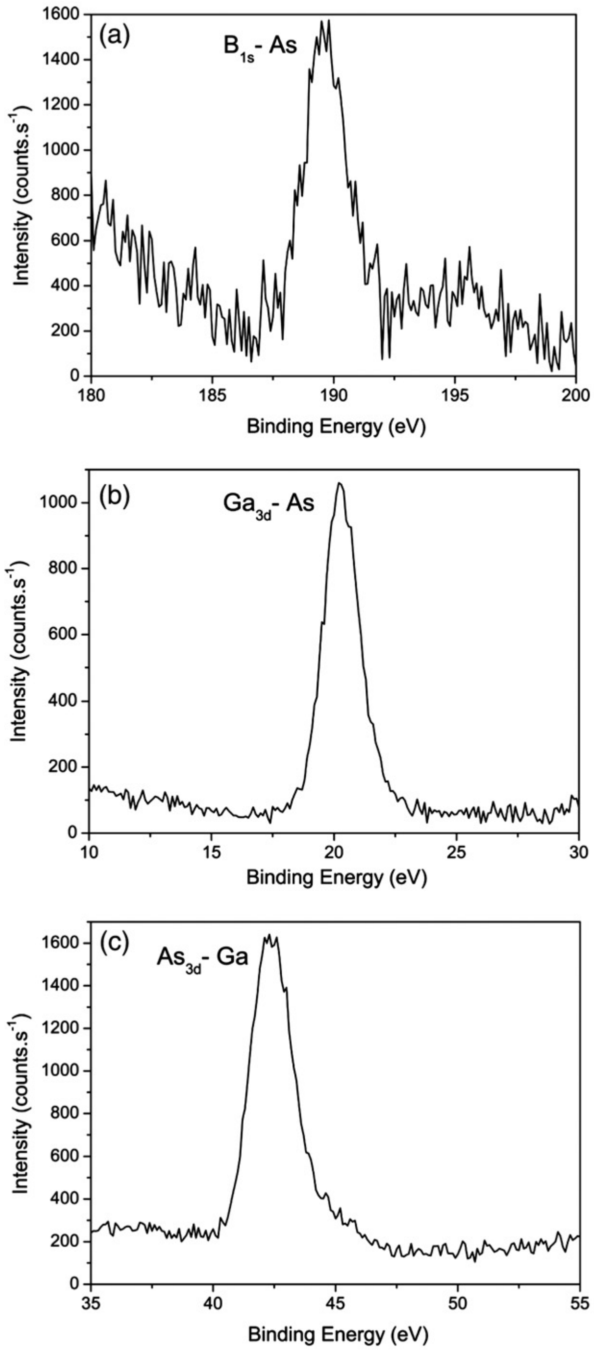

Fig. 1. Detailed XPS spectra of the (a) B_{1s}, (b) Ga_{3d}, and (c) As_{3d} photoelectron core levels for a BGaAs/GaAs epilayer grown at 580 °C with $X_v=62\%$.

X-ray photoelectron spectroscopy (XPS) experiments were performed with a 5950A Hewlett-Packard photoelectron spectrometer equipped with a monochromatic Al K_α X-ray source ($h\nu=1486.6$ eV) and a concentric hemispherical analyser with a resolution of 0.5 eV. No cleaning procedure was performed prior to analysing epilayers near-surface. As a consequence, the analysed samples had always a thin superficial naturally-grown oxide layer. In addition to wide binding-energy range survey scans (0–1000 eV), detailed XPS spectra (20 eV range) were recorded for the strongest photoelectron lines of each element, corresponding to the following core levels: B 1s, Ga 3d and As 3d. Fig. 1 shows detailed spectra obtained for a BGaAs epilayer grown at 580 °C with $X_v=62\%$. The boron surface composition (x_s) was estimated from B_{1s} and Ga_{3d} peak areas, using atomic sensitivity factors for our instrument which take into account both the X-ray cross-section and the transmission function of the spectrometer. The boron quantification threshold, estimated for our