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GaP-interlayer formation on epitaxial GaAs(100) surfaces in MOVPE ambient

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ABSTRACT

The challenge to embed a single monolayer of phosphorus during epitaxial gallium arsenide (GaAs) growth triggers numerous questions regarding practical preparation, effective analysis, and fundamental consideration of the resulting interlayers. Beyond better understanding of III-V heterointerface formation processes, precise interlayer incorporation may enable enhanced interface design, effective diffusion barriers, and advanced band structure engineering. We employ metalorganic vapor phase epitaxy (MOVPE) in various growth modes (continuous, with interruptions, pulsed, surface exchange) targeting the most abrupt incorporation of thinnest GaP films in the GaAs(100) matrix. The intensities of higher order interference fringes in high resolution X-ray diffraction (HR-XRD) serve as a measure of the effective GaP_xAs_{1-x} film thickness and P concentration, which is compared to compositional analysis based on scanning transmission electron microscopy (STEM). *In situ* reflection anisotropy spectroscopy (RAS) provided us with insights to the GaAs(100) surface configurations relevant during the P interlayer preparation.

1. Introduction

Flexible design and precise preparation of semiconductor heterostructures are among the major advantages of the III-V materials system. A wide range of technological applications bases (a) on superior material properties (e.g. charge carrier mobility for microelectronics) [1], (b) on ternary and higher order III-V compounds available via heteroepitaxial growth (e.g. (GaIn)P for solar cells) [2], (c) on the integration of multiple functional materials (e.g. for multijunction absorbers) [3], and/or (d) on the heterojunction itself (e.g. for tunneling contacts) [4]. Often, the perception of III-V heterointerfaces is indirectly qualified by their detrimental effects on subsequently grown functional materials. Examples include antiphase disorder in III-V/Si integration [5], step-graded buffers in metamorphic growth [3], or surface recombination rates in active optoelectronic layers [6]. The significance of structure and atomic configuration at the very interface increases for minimal functional layer thickness as required for quantum confinement [7] or where the interface itself has decisive influence on the physical properties such as in tunneling contacts [4] or in two-dimensional electron gases [8].

III-V device production and research largely rely on metal-organic vapor phase epitaxy (MOVPE) for precision and scalability. Process conditions typically involve a significant precursor overpressure for the more volatile group V elements [9] compared to the group III flow that determines the growth rate. Hence, very different factors may influence the ability to prepare abrupt III-V heterointerfaces. Group III transitions mainly depend on the surface diffusion and incorporation of the involved species as well as on the control of surface segregation and carry-over effects where applicable [10]. In contrast, several factors may complicate group V transitions: Beyond relevant general issues involving (a) the gas phase exchange, (b) the roughness of the growth surface, and (c) subsequent thermally induced interdiffusion, also (d) group V species desorbing from deposits in the vicinity of the sample and (e) the reconstruction of the growth surface, in particular its chemical composition and vertical extent, need to be considered.

The GaP/GaAs interface represents an archetype for a group V exchange [11]. Many applications rely on phosphide heteroepitaxy (particularly lattice matched GaInP) on GaAs(100) substrates [2,3]. Several studies explicitly consider the GaP/GaAs(100) interface formation and the growth of thinnest GaP films for GaAs surface passivation [12–14]. Thermal annealing in P-containing ambient induces an exchange of As with P within the surface reconstruction, particularly driven by the incongruent desorption of group V elements [9] and their replacement from the gas phase. The exchange may include subjacent As monolayers (ML), basically inducing the growth of a thin GaP film [12]. Subsequent GaAs growth confines the interlayer

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and allows multiple repetitions enabling superlattice structures for high-resolution X-ray diffraction (HR-XRD) analysis [12,15].

The present study focuses on embedding thinnest GaP-type interlayers in GaAs by MOVPE. We target the abrupt incorporation of a single ML of phosphorus (P) and discuss challenges in both preparation and characterization of the resulting structures. In practice, the group V concentration profiles smear out in the growth direction for several reasons. We compare results of various gas switching sequences including continuous growth, growth interruptions, group V surface exchange, and pulsed deposition regarding the effective GaP_xAs_{1-x} film thickness and P concentration derived from high resolution X-ray diffraction analysis of respective superlattice structures. *In situ* reflection anisotropy spectroscopy (RAS) provides insights into the GaAs(100) surface configurations relevant for P interlayer preparation, while scanning transmission electron microscopy (STEM) serves as an independent benchmark for compositional analysis.

2. Experiment

The GaP interlayer preparation took place in a commercial (Aixtron AIX 200) MOVPE system with horizontal reactor design, infrared heating, gas foil rotation, and palladium purified hydrogen (H_2) as carrier gas. We used semi-insulating GaAs(100) substrates without intentional misorientation, a process gas pressure of 50 mbar, a growth temperature of 600 °C, as well as tertiarybutylarsine (TBAs), tertiarybutylphosphine (TBP), and triethylgallium (TEGa) as precursors. A TEGa partial pressure of $3.85{\cdot}10^{-3}$ mbar resulted in a growth rate of about 0.25 nm/s equivalent to the deposition of a single ML per second, while TBAs and TBP flows were adjusted to V/III ratios of 10 ($3.85{\cdot}10^{-2}$ mbar) and 20 ($7.7{\cdot}10^{-3}$ mbar), respectively. After thermal oxide removal under TBAs flow at 750 °C, we first grew a homoepitaxial buffer layer of about 250 nm before depositing a superlattice of 20 repetitions, each consisting of the intended GaP ML covered by about 20 nm of GaAs serving as spacer and cap.

Among the conceivable gas switching sequences for the incorporation of a ML of P, we distinguish between 4 different concepts as depicted in Fig. 1:

- Continuous growth: Under constant TEGa flow, the group V precursor is abruptly switched from TBAs to TBP for a short period of t_{GaP}.
- Growth interruptions: The TEGa flow can be interrupted before (t^0) and/or after (t^1) t_{GaP} for short periods in TBAs (t^i_{As}), TBP (t^i_P), pure H_2 (t^i_f), or a combination of the above.
- Surface exchange: Instead of nominal GaP growth, the GaAs(100) surface is just exposed to a TBP ambient for an extended period (t_P) in which the surface reconstruction will change due to incongruent As desorption and simultaneous uptake of P.
- Pulsed growth: GaP growth is separated into short, alternating precursor doses (t^i_P; t^i_{Ga}) potentially separated by short periods without precursor flow (t^i_f).

The evaluation of our GaP_xAs_{1-x}/GaAs superlattice samples based on HR-XRD data measured by a commercial (Panalytical X'Pert Pro) setup with a monochromatized $Cu_{K\alpha}$ source (0.15405 nm X-rays). The (004) diffraction patterns were simulated by both proprietary commercial software (X'Pert Epitaxy) and custom code full dynamical simulation as detailed in Ref. [16] to validate position and intensity of higher order interference fringes. A commercial reflection anisotropy spectroscopy system (RAS; LayTec EpiRAS) served as an *in situ* probe of the GaAs(100) growth surface [17] prior to the GaP interlayer deposition. RA spectra were recorded under gas foil sample rotation (at typical frequency of 2–3 Hz) [18] directly measuring the absolute value of the signal intensity, its sign being restored subsequently based on reference data. For selected samples high angle annular dark field (HAADF) measurements were carried out in a double C_S corrected JEOL JEM 2200FS scanning transmission electron microscope (STEM) operating at 200 kV. Series of atomic resolution images of the GaP_xAs_{1-x} layers were acquired and aligned non-rigidly using the Smart-Align software [19] to improve the signal-to-noise ratio. The images were normalized to the intensity of the impinging beam following the procedure described in [20]. Complementary simulations were carried out using the frozen phonon approximation in the

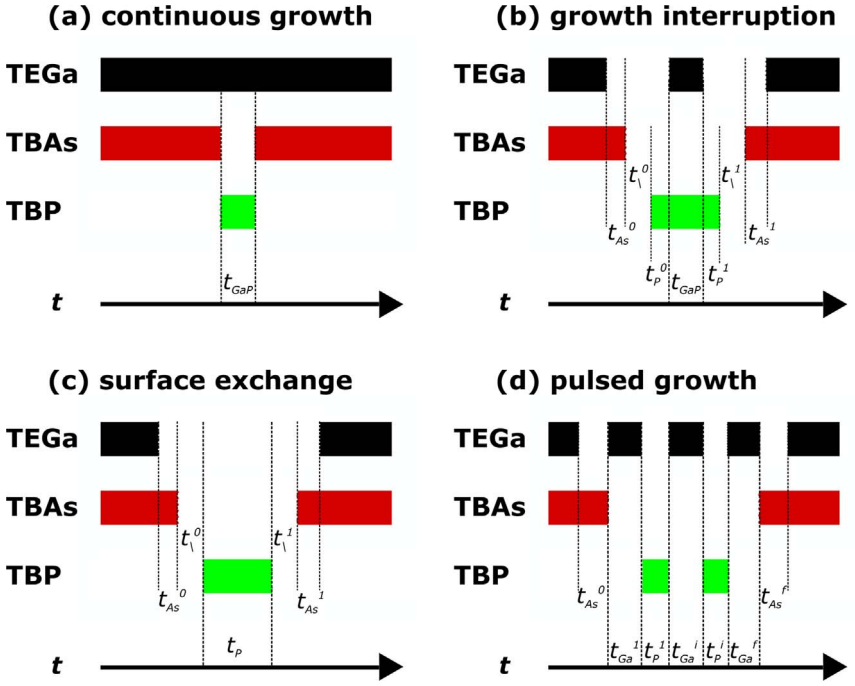

Fig. 1. Potential gas switching sequences for embedding thinnest GaP interlayers into a GaAs matrix during MOVPE growth: (a) continuous growth – just replacing TBAs by TBP for a short period; (b) growth interruption – pausing growth before and/or after GaP deposition with optional supply of group V precursors; (c) surface exchange – thermal annealing of the GaAs(100) surface in TBP ambient with optional growth interruption before and after; (d) pulsed growth – alternating supply of TEGa and TBP in short pulses, with optional pauses in between.