Real-time Monitoring of Heteroepitaxial $Ga_xIn_{1-x}P$ Growth on Si(001) by P-Polarized Reflectance

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Abstract

We report the application of the real-time optical monitoring techniques p-polarized reflectance (PR) and laser light scattering during low temperature growth of epitaxial $GaP/Ga_xIn_{1-x}P$ heterostructures on Si(001) and GaAs(001) substrates by pulsed chemical beam epitaxy (PCBE). The high surface sensitivity of PR allows to follow growth processes with sub-monolayer resolution during the sequential precursor exposure of the surface that causes periodic alterations in composition and thickness of a surface reaction layer (SRL), the effect of which is monitored by PR as a periodic fine structure. This fine structure is superimposed on interference fringes, resulting from back reflection at the substrate-layer interface with increasing layer thickness. The amplitude modulation and the turning points in the fine structure are accessed and compared to experimental results, showing that an average complex dielectric function of an ultra-thin SRL can be quantified, independent of the average thickness of the surface reaction layer. The PR response during the growth of $Ga_xIn_{1-x}P$ correlates as a function of the interference fringe position with the Ga:In composition.

Introduction

The increasingly complexity of electronic and optoelectronic structures and the trend toward smaller device dimensions requires more stringent tolerances in the control of thickness and composition of tailored artificial materials and structures. The understanding of surface reactions chemistry during the deposition process involving organometallic chemical precursor molecules becomes essential for optimizing the growth process. Surface-sensitive optical real-time sensor techniques are very well suited for this task since their application is not limited to a high vacuum environment. Optical real-time process techniques have been successfully applied during the last decade, focusing on the monitoring of either bulk-film properties [1-4] or surface processes by reflection high energy electron diffraction (RHEED), or reflectance difference spectroscopy (RDS[5-7]). For the characterization of both, bulk and surface, we added recently p-polarized reflectance spectroscopy (PRS) and demonstrated its capability during pulsed chemical beam epitaxy (PCBE) of III-V heteroepitaxial growth. Single wavelength PR and laser light scattering (LLS) data are obtained simultaneously during heteroepitaxial film growth under pulsed chemical beam epitaxy conditions, as described previously [8-13].

Experimental

PR and LLS data are simultaneously obtained to monitor heteroepitaxial film growth under pulsed chemical beam epitaxy conditions. The surface of the substrate is exposed to pulsed ballistic beams of tertiary-butyl phosphine [TBP, $(C_4H_9)PH_2$], triethylgallium [TEG, $Ga(C_2H_5)_3$] and trimethylindium [TMI, $In(CH_3)_3$] at typically 350°C-400°C to accomplish nucleation and overgrowth on Si or GaAs substrates by an epitaxial GaInP film. The fluxes of the pre-

cursor and hydrogen are established by mass flow controllers and are directed via computer-controlled valves to either the reactor chamber or a separately pumped bypass chamber. The switching of the sources is synchronized with the data acquisition of the PR (λ=632.8nm at 75 deg) and LLS signals in order to correlate the changes in the reflected intensity to the changes in the optical properties of the heteroepitaxial stack that encompass chemistry-induced changes in the surface composition and changes due to the thickness and optical properties of the epitaxial film. Typical growth rates under the chosen pulsed chemical beam epitaxy (PCBE) growth conditions are in the order of 1Å/s, with TBP:TEG flux ratios in the range 30:1 to 40:1 and a constant hydrogen flux of 5 sccm in the background. The GaAs substrates are ex-situ chemically etched in Br:Methanol (0.02%) solution, follow by a DI-H_2O rinse, a NH_4OH:H_2O (1:1) dip and a final DI-H_2O rinse prior loading in the growth chamber. Further details on the experimental conditions are given in previous publications[8-11,14-17].

Results and Discussion

Figure 1 shows a typical evolution of the PR signals during GaP growth on a Si(001) substrate. The pulsed supply of the precursor causes of fine structure oscillation in the PR signal (see insert in fig. 1) which can be analyzed in more detail using the first derivatives of the PR signals. In the experiments here, the precursor cycle sequence is 3 sec, composed of a TBP pulse (0.0-0.8 s), a pause, a TEG pulse from 1.5-1.8 s, followed by a second pause. A continuous flow of H_2 (5 sccm) is supplied during the complete cycle sequence.

The fine structure observed in the PR signal can be understood as the optical response to the alternative supply of precursors, where one oscillation in the fine structure corresponds to a complete precursor cycle. The start of an oscillation (marked with dashed lines in the insert in fig. 1) coincides with the leading edge of the first precursor pulse in the cycle sequence. As shown in fig.

1, the amplitude in the fine structure undergoes periodic changes during deposition time. The amplitude increases on the raising flank of the interference oscillation with a maximum at the top, and then decreases on the falling flank. The relative locations of these decreases and increases in the fine structure amplitude and the film interference oscillation strongly depend on the chosen growth conditions, such as precursor pulse width and height, pulse sequence time, or supply of additional activated hydrogen. Characteristic features can be identified using the first derivative of the PR signals, shown in fig. 1.
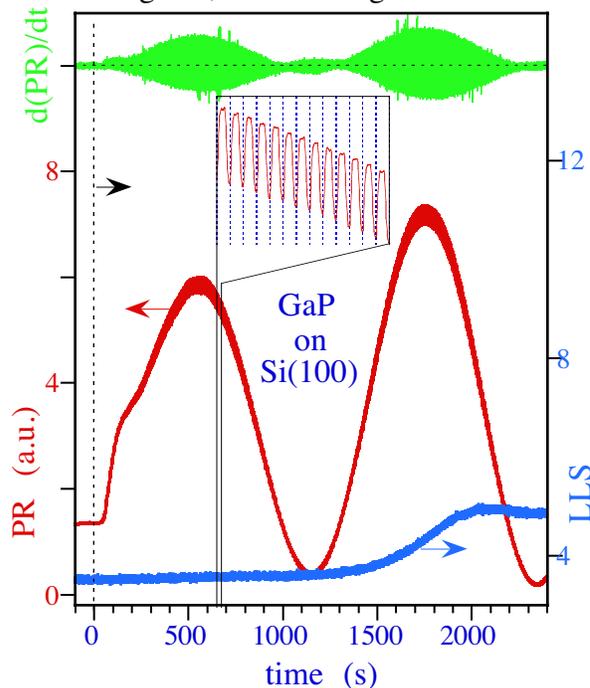

Figure 1: PR, LLS and d(PR)/dt evolution for heteroepitaxial GaP growth on Si under PCBE conditions at 350°C. PR is monitored under an angle of 75 deg. The insert shows an enlargement of the fine structure as a response to the sequential precursor exposure of the surface

The envelope function of d(PR)/dt reveals two important features: (1) the zero crossing points in d(PR)/dt mark the positions where the response to the first precursor pulse changes sign (turning points) and (2) during steady-state growth conditions, the d(PR)/dt envelope evolution undergoes period

oscillations, where one oscillation consists of a long period with a large amplitude and a short period with a small amplitude. The ratio of these periods and their amplitude depends on the chosen precursor dose and exposure times.

The mathematical modeling of the fine structure under the simplified assumption of a periodically in phase modulated SRL with an average dielectric function ε_1' [11,18] describes the overall observed evolution of the PR signal, using Fresnel's equations and a four-layer (ambient / surface layer / film / substrate) stack model. A more detailed model that accounts for changes in both thickness and dielectric function of the SRL during one precursor cycle, requires a correlation of structure in the PR intensity to changing of defragmentation products and their concentrations in the surface reaction layer, which is discussed in more detail elsewhere [19].

Figure 2 shows the simulated four layer stack reflectivity, $R_4(t)$, built up by the substrate Si with $\varepsilon_3(\lambda=632.8nm) = (15.25, 0.17)$, the growing GaP film with $\varepsilon_2(\lambda=632.8nm) = (11.1, 0.01)$ and an average growth rate of 0.85Å/sec, a periodically modulated SRL with $\varepsilon_1(\lambda=632.8nm) = (9.5, 2.5)$ and a maximal thickness of $d_{1max}=5$Å, and an ambient with $\varepsilon_0= 1$. Also drawn in are the calculated difference between the four-layer and the three layer stack reflectance, $[R_4(t) - R_3(t)]$, and the derivative $dR_4(t)/dt$. The values for the average dielectric function of the SRL are chosen such that it matches typical experimental results for GaP on Si(001) monitored at an angle of incidence of 75 deg (see fig. 2). Under these specific growth conditions $Re(\varepsilon_1)$ is smaller than $Re(\varepsilon_2)$ with a significant absorption of $Im(\varepsilon_1) = 2.5$.

Figure 3 shows the temporal evolution of the PRS and LLS signals during the growth of $Ga_xIn_{1-x}P$ on Si(001). The flow ratio TMI:TEG was set nominally 1:4 with a TEG:TBP ratio 1:40. The cycle sequence time is 6 sec, where the surface is sequentially exposure to two TBP pulses from
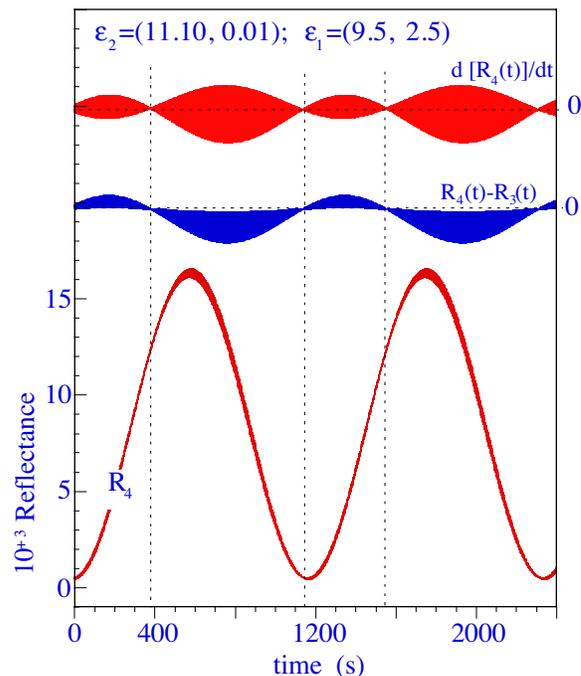

Figure 2: Simulation of the temporal evolution of the PR signal in a four layer stack model. Also shown are the first derivative of the PR signal and SRL contributions to the reflectance (see text).
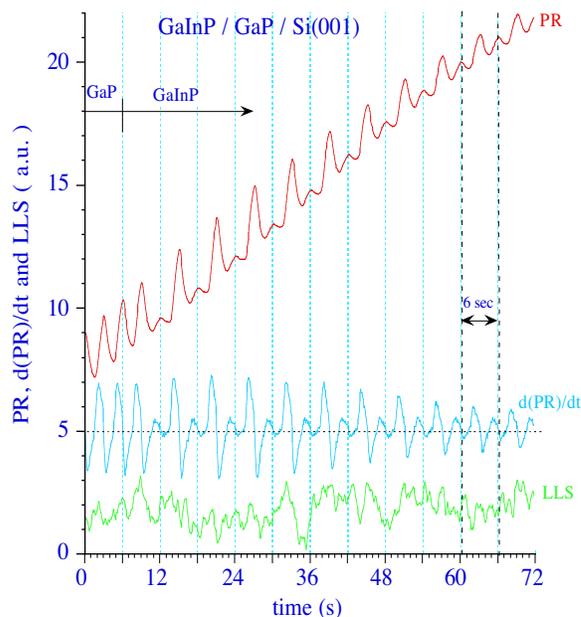

Figure 3: PR, LLS and d(PR)/dt evolution during $Ga_xIn_{1-x}P$ growth on Si substrate at 400°C.

0.0-0.8s and 3.0-3.8s, one TEG pulse from 1.5 - 1.8 s and one TMI pulse from 4.5 - 4.8 s. Also shown (lower curve) is the evolution of the LLS intensity during the deposition

process and the derivative, $dR_4(t)/dt$, of the PR signal. The begin of each cycle sequence is marked by a dashed line.

Fig. 4 shows the evolution of the PR signal during the growth of lattice-matched $Ga_{0.5}In_{0.5}P$ on GaAs(001) (flow ratio TMI:TEG=1:1), the first derivative of the PR signal and the precursor cycle sequence. The begin of each cycle is marked by a solid line and the begin of a precursor pulse as a dashed line. The fine structure amplitude differs for the TEG and TMI exposure due to their different induced SRL thickness and SRL composition. The PR response to the TMI is increased compared to the PR response shown in Fig. 3, where the flow ratio TMI:TEG was =1:4. Comparison with ex-situ composition analysis[17] shows that the ratio of PR responses to TMI and TEG exposure correlates with the Ga:In composition. However, since the PR response-ratio for a given Ga:In composition depends on the position of the PR interference fringe, a simulation of the PR signal over an extended interference fringe is required to extract the composition of the film.
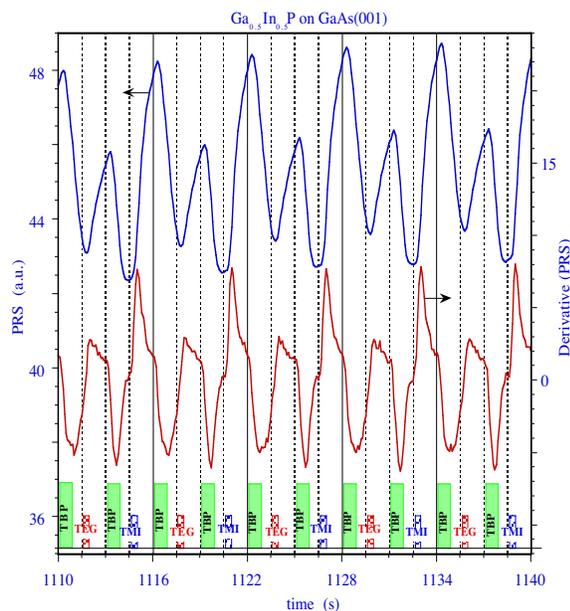

Figure 4: PR, LLS and d(PR)/dt evolution during GaInP growth on GaAs substrate at 400°C.

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