Real-time Optical Monitoring of $Ga_xIn_{1-x}P$/GaP Heterostructures on Silicon

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ABSTRACT

In this paper we report the combined application of p-polarized reflectance spectroscopy (PRS), reflectance difference spectroscopy (RDS), and laser light scattering (LLS) to investigate the heteroepitaxy of $Ga_xIn_{1-x}P$/GaP on Si by pulsed chemical beam epitaxy (PCBE) with tertiarybutylphosphine (TBP), triethylgallium (TEG), and trimethylindium (TMI) precursors. Both, PRS and RDS follow the growth process with submonolayer resolution utilizing a periodic fine structure signal, which is caused by a periodic alteration of thickness and composition of an ultra-thin surface reaction layer during the periodic TEG and TBP exposure of the surface. After the transition from GaP growth to $Ga_xIn_{1-x}P$ growth, the RDS oscillations are reoriented after about five precursor cycles in a new oscillation periodicity, where the response to the TBP pulse has the opposite direction. The ratio of the changes in the amplitudes of RDS signals as a response to TEG and TMI surface exposure is used to estimate the composition fo $Ga_xIn_{1-x}P$. The PRS fine structure is maintained after switching to $Ga_xIn_{1-x}P$ growth with a separate feature for each TEG and TMI surface exposure. The amplitude ratio of these features changes during growth.

INTRODUCTION

The application of optical techniques to the real-time monitoring of epitaxial deposition processes is attractive because of their non-invasive character. A variety of methods, such as normal incidence reflectance spectroscopy (NRIS)[1] and pyrometric interferometry (PI)[2] have been successfully applied to monitor the growth rate and the composition of the growing film. In order to gain a higher sensitivity to surface- and interface- related growth properties, alternative in-situ optical methods such as reflectance difference spectroscopy (RDS)[3,4] surface photo-absorption (SPA)[3,4] and spectroscopic ellipsometry (SE)[5,6] have been developed. We added to these methods a real-time optical monitoring technique, p-polarized reflectance spectroscopy (PRS), which achieves both (i) a high sensitivity to surface chemistry under quasi steady-state growth conditions and (ii) the capability of monitoring film thickness and optical properties with submonolayer resolution [7-12]. PRS is also sensitive to any changes of the dielectric function of the initially conditioned silicon surface, which may be due to temperature-induced changes in the dielectric function of the substrate, surface roughening, surface chemical modifications, or coverage by a thin film having a dielectric function that differs from that of the Si substrate.

EXPERIMENT

The heteroepitaxial growth of $Ga_xIn_{1-x}P$ on GaP-coated Si substrates is examined through simultaneous measurements by single-wavelength PRS and LLS (HeNe laser source, λ=6328Å) and by RDS (1.8eV to 5.5eV) under pulsed chemical beam epitaxy conditions. Specifically, surfaces are exposed to pulsed ballistic beams of tertiarybutyl phosphine [TBP, $(C_4H_9)PH_2$], triethylgallium [TEG, $Ga(C_2H_5)_3$] and trimethylindium [TMI, $In(CH_3)_3$] at substrate temperature from 350 to 400°C. The flows of precursors and hydrogen are established by mass flow controllers and are directed by computer-controlled 3-way valves to either the reactor chamber or a separately pumped bypass chamber. This allows the substrate to be exposed sequentially to the individual pulses of the precursor molecules with no overall pressure

variations. The switching of the sources is synchronized with the data acquisition of the PRS and LLS signals to correlate changes in the reflected intensity to chemically induced changes in the surface condition and/or the optical properties of the growing film. Typical growth rates under the present conditions are about 1Å/sec. Further experimental details are given in a previous publication [8]. The LLS intensity is detected with a photomultiplier tube (PMT) located 45° away from the plane of incidence. RDS measures the spectral-resolved optical anisotropy between the $[\bar{1}10]$ and [110] principal axes of the (001) surface. The configuration and approach have been described in detail elsewhere[13].

RESULTS

Figure 1 shows the temporal evolution of the PRS and LLS signals during the growth of GaP and $Ga_xIn_{1-x}P$ on a Si(001) substrate at 350°C. During the preconditioning period the reflected intensity changes due to the changed dielectric function of the substrate and surface conditioning. At t = 700 s GaP growth is initiated with precursor cycle sequence times of 3s. The surface exposure sequence consists of a TBP pulse of length 0.8 s, a delay of 0.7s, a TEG pulse of 0.3 s and a second delay of 1.2 s. During the entire sequence an activated hydrogen beam impinges onto the substrate surface. The reflected intensity oscillates due to interference as the film grows. Superimposed on these oscillations is a fine structure (not resolved in fig. 1) that is strongly correlated to the time sequence of the supply of precursors. This fine structure

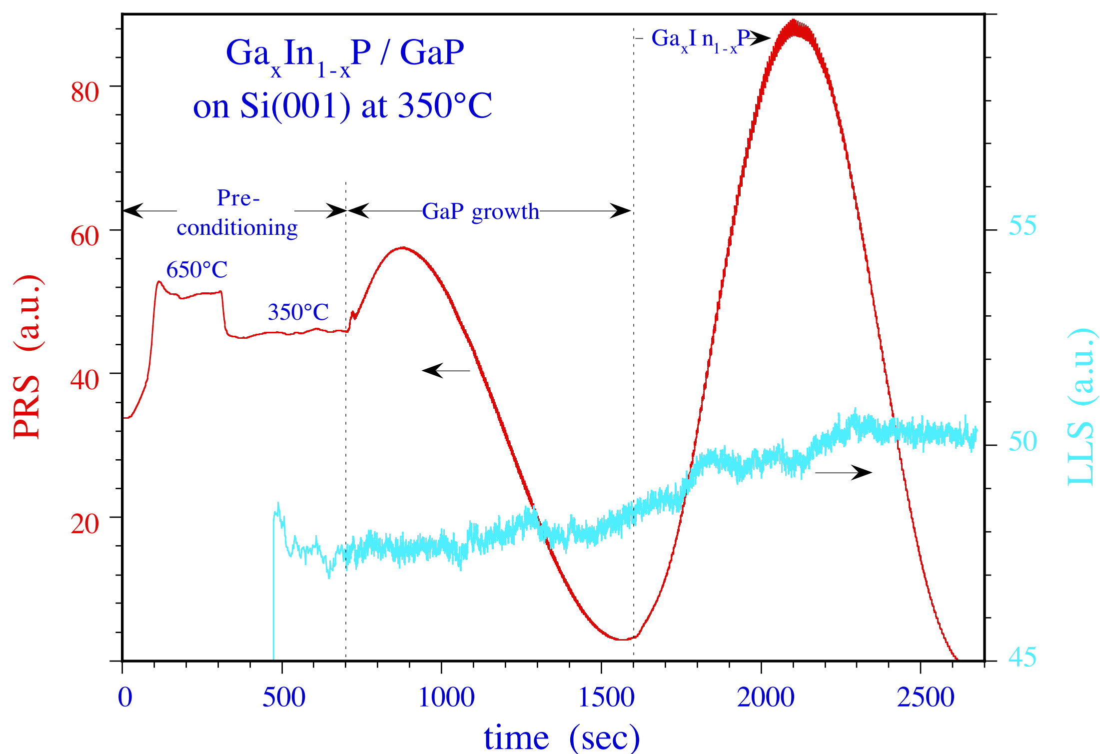


Figure 1 Evolution of PRS and LLS transients during $Ga_xIn_{1-x}P$ epitaxial growth on a GaP-coated Si(001) substrate.

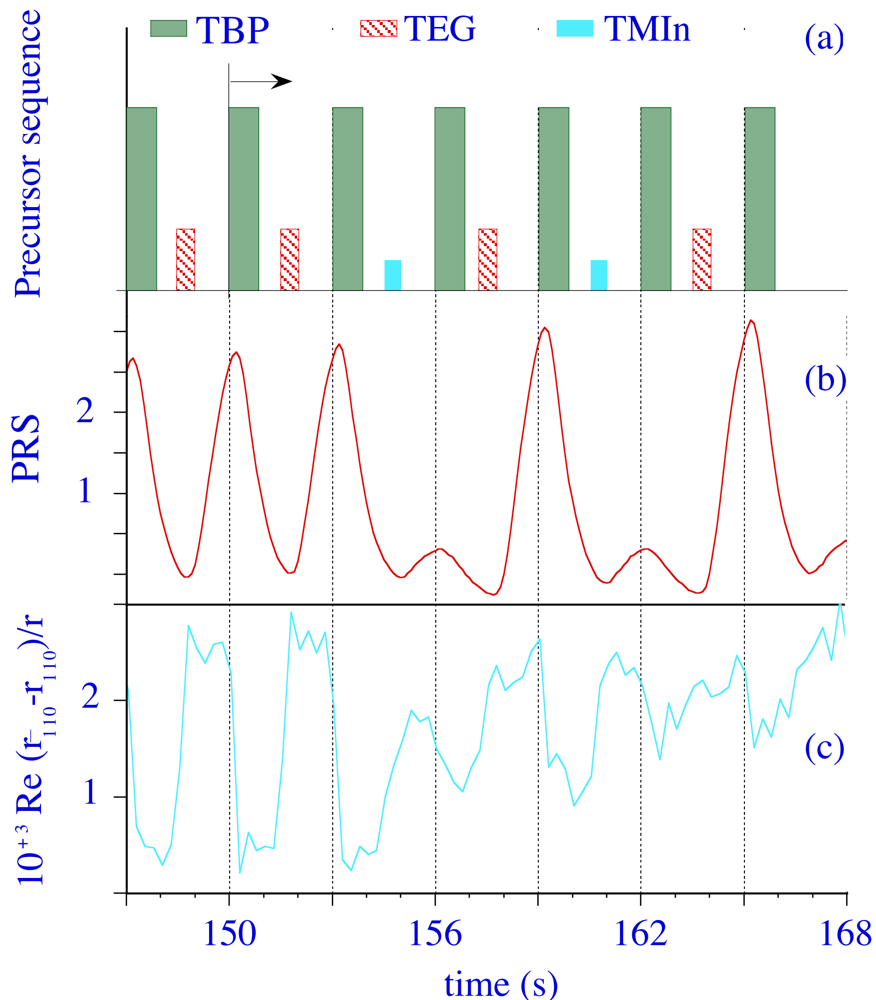
relates to a periodic modification of the dielectric function and/or thickness of a surface reaction layer due to sequential exposure to the TEG and TBP pulses. At t=1600 sec, the deposition process is switched to $Ga_xIn_{1-x}P$ growth with a precursor cycle sequence of 6 sec, where the

surface is exposured to two TBP pulses from 0.0-0.8s and 3.0-3.8s, one TEG pulse from1.5 - 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.

Figure 2 shows the PR and RD responses during a transition from GaP growth to $Ga_xIn_{1-x}P$ growth with fluxes of 0.06 sccm and 0.035 sccm for TEG and TMI, respectively. The evolution of the RD transient is monitored at 2.6 eV. The PR signal immediately follows a 6 s periodicity, which consists of unchanged oscillations associated with the TBP and TEG exposure sequences and a smaller oscillation associated with the TBP and TMI sequential exposure.

Figure 2

Transition from steady-state GaP growth to $Ga_xIn_{1-x}P$ growth on a GaP-coated Si(001) substrate.



However, the RDS response shows a transition period of about 5 cycles before the surface stabilizes in a new configuration. This behavior is shown in more detail in Figure 3 where the RDS transition is shown for a longer time period. After approximately five $Ga_xIn_{1-x}P$ cycles the RDS oscillation is modified to a 6 s period and a reduced amplitude. In addition, the rising edge of the RDS signal that coincides with the onset of the TEG pulse during steady-state GaP growth and the falling edge that coincides with the onset of the TBP pulse are inverted. After

the transition to $Ga_xIn_{1-x}P$ the TEG pulse causes a dip to occur while after the TBP exposure the RDS signal proceeds to a higher level. TMI exposure causes a dip that is only about one-third as deep as that caused by TEG.
This behavior shows that the surface completely changes its character upon TMI exposure. We propose that the activities of phosphorus and metal-related precursors to growth undergo cyclic changes with a periodicity corresponding to that of the source vapor exposure. In this picture the larger dip associated with TEG exposure indicates a Ga/In ratio of approximately 3, which is in good agreement with ex-situ Rutherford backscattering (RBS) analysis that shows 25 at-% In in the grown $Ga_xIn_{1-x}P$ layer. After prolonged growth no response of the RD signal to either TEG or TMI is observable. Therefore, the surface must be highly saturated with phosphorus such that any arriving cations immediately reacts with the surface, which maintains the RD response at the upper position [14].

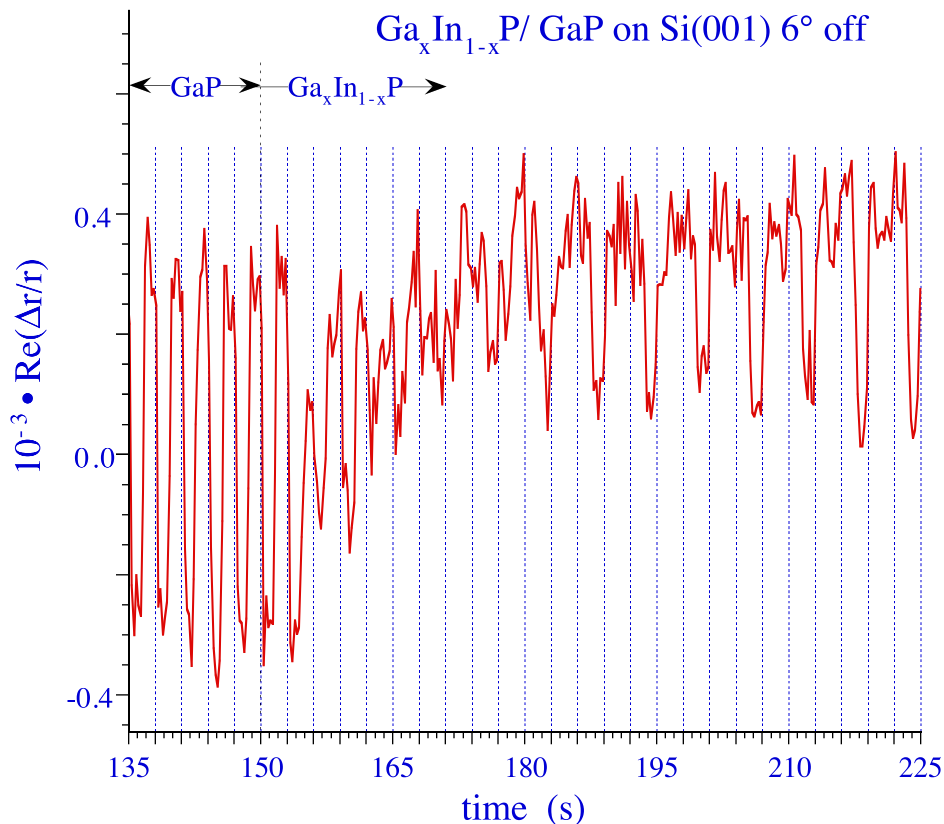


Figure 3 RDS data during the transition from GaP to GaInP growth.

Figure 4 shows RD spectra taken during interruptions of $Ga_xIn_{1-x}P$ / GaP heteroepitaxy on vicinal Si(001). For layer thicknesses above the penetration depth of light, spectra are obtained that bear some resemblance to the dielectric function of GaP and to RD spectra of GaP on Si(113) but with reduced amplitude. This indicates that for a Si(001) substrate offcut by 6° towards (111) anti phase boundaries (APD) are present that partially cancel the RD signal.

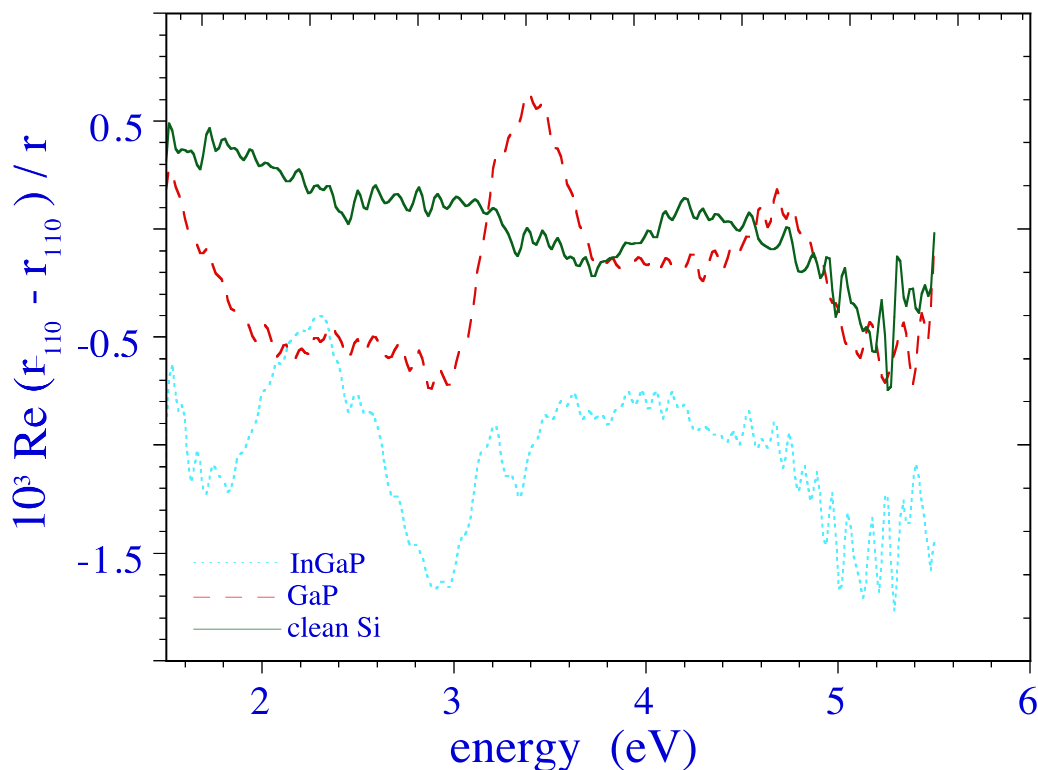


Figure 4 Comparison of RDS spectra of $Ga_xIn_{1-x}P$, GaP and Si(001) at 350°C obtained under phosphorus - stabilized conditions during growth interruptions.

CONCLUSION

In conclusion, we have applied PRS, RDS, and LLS to monitor low-temperature hetero-epitaxial growth of $Ga_xIn_{1-x}P$ and GaP on Si during pulsed chemical beam epitaxy. RDS and PRS show that alternately supplying V-III precursors results in a periodic change of the surface chemistry, which appears either as a periodic oscillation of the anisotropy as measured by RDS or as fine-structure oscillations as measured by PRS. The RDS oscillations are modified where GaP growth is changed to $Ga_xIn_{1-x}P$ growth, that is, after the change the response to the TBP pulse has an opposite direction as observed under the conditions of GaP epitaxy. The amplitude ratio of the changes in RDS signals during TEG and TMI exposure of the surface can be used to estimate the $Ga_xIn_{1-x}P$ composition. The PRS oscillation originating from TBP and TEG exposure of the surface is maintained after switching to $Ga_xIn_{1-x}P$, but an additional periodic feature is inserted into the signal in response to the TMI exposure. The amplitude ratio of these two TBP-TEG and TBP-TMI related PRS features is also related to the $Ga_xIn_{1-x}P$ composition. However, this ratio changes during growth as a complex function of composition ratio and properties of the surface reaction layer in a manner not completely understood at present.

ACKNOWLEDGMENT

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