# **Real-time Optical Control of Ga<sub>1-x</sub>In<sub>x</sub>P Film Growth**

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### Abstract

This paper describes results on open- and closed-loop controlled growth of epitaxial GaP /  $Ga_{1-x}In_xP$  heterostructures on Si(001) substrates. The layers are grown in a low pressure pulsed chemical beam epitaxy (PCBE) reactor utilizing real time optical p-polarized reflectance (PRS) probing. The results of the implemented closed loop controlled growth favorably compare to the films grown using pre-designed source injection profiles based on an experimental data base.

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#### INTRODUCTION

The development of surface-sensitive optical characterization techniques of thin film growth opened up the possibilities to obtain detailed information in real time that is highly relevant to the growth kinetics. The significance of these techniques for growth monitoring is that they move the observation point close to the surface of the film where the growth occurs. These developments make it feasible to improve thin film deposition applying closed loop control techniques. Areas of interest include fabrication of advanced nanostructure devices, improved densities of integrated electronic devices.

In this work we describe our monitoring and control method for thickness/composition control of Si(001)/GaP/Ga<sub>1-x</sub>In<sub>x</sub>P growth in low pressure PCBE system. The films grown with our control algorithm have been analyzed by ex-situ methods such as x-ray diffraction (XRD) and Secondary Ion Mass Spectroscopy (SIMS). The test results show the superiority of the closed loop controlled growth over open loop control designed using our data base, which was built up from accumulated growth data. In our experiment we use p-Polarized Reflectance Spectroscopy (PRS) as the primary probing method of our thin film growth process. PRS is based on the changes in reflectivity *R* of the p-polarized laser light shone on a dynamically changing stack of dielectric media and its sensitivity for the growth kinetics is based on choosing the incident angle to be the pseudo-Brewster angle (to *Si* and *GaP* substrates in our case ).

In earlier papers<sup>1-3</sup> we have reported on our approach of modeling the surface kinetics of epitaxial GaP and  $Ga_{1-x}In_xP$  growth on *Si*. For both the GaP and  $Ga_{1-x}In_xP$  growth stages we introduced reduced order surface kinetics (ROSK) models to represent the essential chemical processes in the surface reaction layer (SRL). In this paper we utilize our model to monitor and control the growth rate and composition of the growing film as follows. First, for the modeling of the PRS reflectance measurement we use Fresnel's equation and a virtual interface method, introduced by D.E Aspnes<sup>4,5</sup>, for the multi-layer stack of GaInP where the change of composition and thickness of the growing layer is determined by our model dynamics and the flow rates are entered as input variables. We formulate the control of thin film growth as an optimal control problem. Second, we use a nonlinear filtering algorithm<sup>6</sup> to estimate growth rate and composition of growing  $Ga_{1-x}In_xP$  film and based on these estimates then determine optimal flow rates of our source vapors to achieve the desired composition and growth per cycle in real time.

Due to the limited space for a detailed description of the experimental setup we refer to previous publications<sup>7-9</sup>.

Figure 1: Schematic representation of a precursor pulsing sequence used in the growth of the ternary compound semiconductor  $Ga_{1-}$ <sub>x</sub>In<sub>x</sub>P grown via the organometallic precursors TBP, TEG and TMI.



#### DATA BASE ANALYSIS/OPEN LOOP CONTROL DESIGN

In the PCBE growth of GaInP film layers, the quality of the grown film strongly depends on ambient pressure, temperature, the flow rate and the pulse timing of the three source gases. We adjusted appropriately those by selecting optimal background pressure, temperature and the injection rate of TBP, as well as pulsing profile over the various growth conditions. Thus the control authority we used are the flow rates of TEG and TMI source gases. A series of test runs was conducted to obtain data base on the effect of the changes in the TMI/TEG injection ratio on the growth of  $Ga_xIn_{1-x}P$  film. To identify the effects on the growth rate and composition we have grown GaInP films using set flows for TEG and TMI, i.e.,  $u_{TMI} / u_{TEG}$ was set to a constant value that varied from 0 to 1.2 (with fixed nominal flow  $u_{TEG} = 0.545$ sccm) on top of an initial GaP film. We analyze the corresponding the PRS data and XRD measurements to establish the functional relationships  $x = \Phi(y)$ ,  $gr = \psi(y)$ , where y denotes TMI/TEG flow ratio, x composition and gr the  $Ga_{1-x}In_xP$  film's growth rate as depicted in Figure 3.

We utilize this data base to perform the open-loop control synthesis. That is, given a discretization  $z_k$  with the thickness step size  $\Delta z$  and a corresponding average desired composition sequence  $x_k$  we select the flow ratio to be  $y_k = \Phi^{-1}(x_k)$  and the corresponding duration  $t_k = \Delta z / \Psi^{-1}(y_k)$ . Thus we can design predetermined flow rates of TMI and TEG to achieve the desired composition/growth profile.





#### **REAL-TIME MONITORING/CONTROL**

In this section we describe our approach to utilize the real time optical observations and apply feedback control methodology for controlling GaInP film growth. Consider the four layer stack composed of ambient / surface-reaction layer / film / substrate. We assume an effective media with the homogeneous dielectric function  $\varepsilon_1$  in the surface reaction layer. Let us denote the four media by the indices labeled from the ambient to substrate. The reflection coefficient  $r_{n-1,n}$  from the (n-1) –st layer to n-th media is given by

$$r_{n-1,n} = \frac{\varepsilon_n \sqrt{\varepsilon_{n-1} - \varepsilon_0 \sin^2 \varphi} - \varepsilon_{n-1} \sqrt{\varepsilon_n - \varepsilon_0 \sin^2 \varphi}}{\varepsilon_n \sqrt{\varepsilon_{n-1} - \varepsilon_0 \sin^2 \varphi} + \varepsilon_{n-1} \sqrt{\varepsilon_n - \varepsilon_0 \sin^2 \varphi}}$$
(1)

where  $\varepsilon_n$  is the dielectric constant of the n-th media. The phase factor  $\Phi_n$  for the n-th media is given by

$$\Phi_{n} = \frac{2 \pi d_{n}}{\lambda} \sqrt{\varepsilon_{n} - \varepsilon_{0} \sin^{2} \varphi} , \qquad (2)$$

where  $d_n$  is the thickness of the n-th media.

For the case of multi-later stack of films by applying the theory of the virtual interface method by Aspnes<sup>10,11</sup>, the reflectance amplitude r of the p-polarized light is then given by

$$\mathbf{r} = \frac{r_{01} - \hat{r} \, e^{-2\,\mathrm{i}\,\Phi_1}}{1 + r_{01}\,\hat{r} \, e^{-2\,\mathrm{i}\,\Phi_1}} \quad \text{with} \quad \hat{\mathbf{r}} = \frac{r_{12} - r_k \, e^{-2\,\mathrm{i}\,\Phi_2}}{1 + r_{12} \, r_k \, e^{-2\,\mathrm{i}\,\Phi_2}} \,. \tag{3}$$

The virtual reflection index  $r_k$  is updated by

$$r_{k} = \frac{\eta_{k,k-1} - \eta_{k-1} e^{-2i\Phi_{2}}}{1 + \eta_{k,k-1} \eta_{k-1} e^{-2i\Phi_{2}}} \quad \text{with} \quad r_{k} = A_{k} e^{-i\theta_{k}} ,$$
(4)

at the end of cycle, where  $\theta_k$  defines the phase factor. Based on the phase factor we estimate the thickness of the grown layers. For each homogeneous layer we have the estimate of the thickness d<sub>2</sub> by

$$d_2 = \frac{\lambda}{4 \pi \sqrt{\varepsilon_2 - \varepsilon_0 \sin^2 \varphi_0}} \left( \theta_{end} - \theta_{begin} \right),$$
(5)

where the  $\theta_{end}$ ,  $\theta_{begin}$  is the phase factor at the end and beginning of the layer. Similarly the growth  $gr_k$  per each cycle k is given by

$$gr_k = \frac{\lambda}{4\pi\sqrt{\varepsilon_2 - \varepsilon_0 \sin^2 \varphi_0}} \left( \theta_k - \theta_{k-1} \right).$$
(6)

We use the nonlinear filtering algorithm<sup>6</sup> for estimating the state consisting of the virtual reflection index  $r_k = e^{x_1 + i x_2}$ , the film dielectric constant  $\varepsilon_2 = x_3 + i x_4$ , and growth per cycle  $x_5$  in real time. In turn the thickness of the specific compound is estimated by (5). The growth ratio of GaP and InP for each cycle determined by (6) provides a composition estimate. Let  $y_k$  denote the PRS signal at the end of the k-th cycle. Then the filtering problem is to estimate the signal process  $x^k$  defined by

$$\begin{pmatrix} x_{I}^{k} \\ x_{2}^{k} \\ x_{3}^{k} \\ x_{4}^{k} \\ x_{5}^{k} \end{pmatrix} = \begin{pmatrix} f_{1}(x^{k}) \\ f_{2}(x^{k}) \\ x_{3}^{k-1} \\ x_{3}^{k-1} \\ x_{4}^{k-1} \\ x_{5}^{k-1} \end{pmatrix} + \omega_{k}$$

$$(7)$$

based on the observation process  $y_k = h(x^k) + v_k$ . Here we assumed that  $|r_{k,k-1}|$  is sufficiently small and used  $r_k = r_{k-1} e^{-2 + \Psi_2}$  for updating the virtual index  $r_k$ . If we let  $f_{r_k}$  be the growth ratio of GaP or InP to each nominal flow rate, then the functions  $f_1$ ,  $f_2$  and h are defined by

$$f_1 + i f_2 = x_1 + i x_2 + 2 i \phi_2; \quad h = \frac{r_{02} + r_v}{1 + r_{02} r_v}$$
(8)

where  $d_2 = f_{r_k} x_5$ . We assume that noise processes  $w_k$ ,  $v_k$  are independent (identically distributed) Gaussian random variables with mean zero and covariance Q and R, respectively.

The growth of GaP and InP is determined in terms of  $n_{GaP}$  and  $n_{InP}$  which are given by

$$\frac{d n_{GaP}}{dt} = k_4 n_p n_{Ga}, \quad \frac{d n_{InP}}{dt} = k_5 n_p n_{In}$$
(9)

where  $n_P$ ,  $n_{Ga}$ , and  $n_{In}$  denote the concentration of surface active phosphorous, gallium and indium, respectively. We consider the model for the concentration change of active Ga in the SRL by

$$n_{Ga} = u_{TEG} S_{GaP} - n_{GaP} , \qquad (10)$$

where  $S_{GaP}$  is a pre-determined constant. Integrating the first equation in (9) we obtain

$$n_{GaP}(t_{k+1}) = e^{-C} \left( n_{GaP}(t_k) - S_{GaP} u_{TEG} \right) + S_{GaP} u_{TEG}$$

$$(11)$$

where  $t_k$  is the starting time of the k-th cycle and  $C = k_4 \int_{t_k}^{t_{k+1}} n_p(t)$ . The rate constant  $k_4$  varies and we estimate it in real time. We use our filtering algorithm to estimate the concentration  $n_k$  of  $n_{GaP}$  and the accumulated rate constant  $C_k$  for the k-th GaP cycle based on

$$\binom{n_k}{C_k} = \binom{n_{k-1} + C_{k-1} (u_{TEG} - n_{k-1})}{C_{k-1}} + \tilde{w}_k$$
(12)

with measurement  $gr_k = V_{GaP} n_k + \tilde{v}_j$ . Here  $gr_k$  is the growth rate of *k*-th GaP cycle, determined by Equation 6. The growth of the InP is modeled analogously. We determine the input flow rates  $u_{TEG}^k$  and  $u_{TMI}^k$  by performing

$$\min_{u_{TEG}^{k}} \left| \left( 1 + z_{k} \right) n_{GaP}^{+} - gr_{d} \right|^{2} + \beta \left| u_{TEG}^{k} - u_{TEG}^{k-1} \right|^{2}$$

$$\min_{u_{TMI}^{k}} \left| \frac{n_{InP}^{+}}{n_{GaP}^{+}} - \frac{z_{k}}{1 - z_{k}} \right|^{2} + \beta \left| u_{TMI}^{k} - u_{TMI}^{k-1} \right|^{2},$$

$$(13)$$



subject to

programming.

$$n_{GaP}^{+} = e^{-C_{TEG}^{k}} \left( n_{GaP}^{c} - S_{GaP} u_{TEG}^{k} \right) + S_{GaP} u_{TEG}^{k}$$

$$n_{InP}^{+} = e^{-C_{TMI}^{k}} \left( n_{InP}^{c} - S_{InP} u_{TMI}^{k} \right) + S_{InP} u_{TMI}^{k} , \qquad (14)$$

respectively.  $C_{TEG}^{k}$  and  $C_{TMI}^{k}$  are the current estimates of *C* for GaP and InP cycle, and  $z_{k}$  is the desired composition at the *k* cycle. That is, we control the growth rate by  $u_{TEG}$  and then by  $u_{TMI}$  the composition for each cycle.

#### FINDINGS: OPEN LOOP AND CLOSED LOOP RESULTS

We conducted a number of tests to compare open loop and closed loop control performance in the GaInP growth. We present the test results for specified thickness-composition profiles, depicted in Figures 5 and 6, for single - and for multiple parabolic graded  $Ga_{1,x}In_xP$  heterostructures.

The specifications include constant, linearly and parabolically graded composition segments in terms of the film thickness. We varied the thickness of the parabolically graded quantum wells between the 200 - 1000 Å range. Direct analysis of film thickness and composition of the films was conducted using SIMS measurements. The calibration of the SIMS data has been made using constant composition samples with compositions measured by XRD, as well as using a linear estimate for the sputtering rate throughout the composition range. In tracking the prescribed composition profile the feedback control clearly proved to be superior.



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Figure 6:

SIMS analysis of closed loop (top) vs. open loop (bottom) controlled growth results. Specifications include a repetition of 200 Å, wide parabolic composition graded structures.



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Figure 7:

GaInP

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