

Real-time optical Characterization and Control of Heteroepitaxial $Ga_xIn_{1-x}P$ Growth by P-Polarized Reflectance

N. Dietz^a, K. Ito^b, I. Lauko^b, and V. Woods^a

^aDepartments of Physics and Materials Science & Engineering, ^bCenter for Research in Scientific Computation; North Carolina State University, Raleigh, North Carolina 27696-7919

Abstract

The characterization and control of thin film growth processes requires improved methods of characterization and understanding of decomposition pathways and surface reaction kinetics under steady-state epitaxial growth involving organometallic precursors. In this contribution we present the application of p-polarized reflectance spectroscopy (PRS) for real-time monitoring and control of pulsed chemical beam epitaxy (PCBE) during low temperature growth of epitaxial $Ga_{1-x}In_xP$ heterostructures on Si(001) substrates by PCBE, where the growth surface is sequentially exposed to organometallic precursors. During the pulsed precursor supply the surface reaction kinetics can be followed by analyzing a periodically in composition and thickness modulated surface reaction layer (SRL), which is captured in the PR-signals as a fine structure that is superimposed to the interference fringes caused due to the underlying growing film. The optical response is linked to the growth process via a reduced order surface kinetics (ROSK) model and integrated as a control signal in the implementation of filter and control algorithms for closed-loop controlled growth of epitaxial $Ga_{1-x}In_xP$ heterostructures on Si(001) substrates. The control concept has been applied for thickness and compositional graded multi-heterostructure $Ga_xIn_{1-x}P$ epilayers and validated by ex-situ post-growth analysis, showing superior tracking of composition and thickness targets under closed loop controlled conditions compared to films grown using pre-designed source injection profiles (open-loop conditions).

I. Introduction

Real-time optical characterization of thin film inherits the challenge of relating macroscopic optical signatures to microscopic surface chemistry processes, that drive the growth process, to growth/film properties, such as composition, instantaneous growth rate or structural layer quality. The need is especially acute for chemical deposition methods, where organometallic precursor decomposition at the growth surface dominates the nucleation kinetics, surface atoms mobility, and steady-state growth reaction kinetics. The limited knowledge in these areas slowed the progress in understanding and controlling thin film growth. To improve the understanding of the driving mechanisms of growth processes, non-intrusive real-time techniques have been developed, focusing on the monitoring of surface processes by reflection high energy electron diffraction (RHEED)[1], reflectance difference spectroscopy (RDS)[2], surface photo absorption (SPA)[3] and p-polarized reflectance spectroscopy (PRS)[4].

Presently two techniques are available that combine the advantage of high surface sensitivity with bulk film properties characterization and are (a) an integrated spectral ellipsometry (SE) / RDS spectrometer[5] and (b) PRS[6]. Both techniques aim to integrate the optical response to surface processes with the optical response to bulk properties to monitor and control the deposition process with sub-monolayer resolution. The principle of (PRS) applied to thin film growth characterization has been described in recent publications[4,7] and the focus in this contribution will be on the integration of the optical PRS signals towards compositional and thickness control of heteroepitaxial $Ga_xIn_{1-x}P$ growth. The control of a growth process using the optical signature from the SRL that feeds the underlying growth requires detailed instantaneous simulation and prediction of the surface chemistry and its link to the optical properties of the outer most layer in a multilayer medium. For this, a reduced order surface kinetics (ROSK) model has been developed that describes the growth process with a mathematically reduced number of surface reactions equations using heteroepitaxial $Ga_xIn_{1-x}P$ growth as an example. The dynamic in the molar concentrations of surface constituents evolution gives information on SRL thickness, its optical

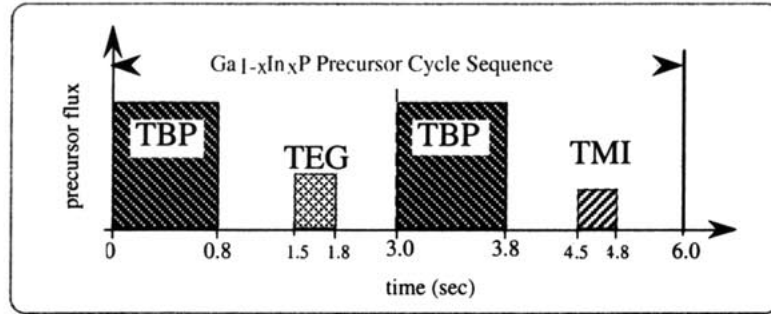
response in a four media layer approximation, the instantaneous growth rate, and the composition of the growing film. For real-time closed-loop deposition control a virtual substrate approach was adapted, based on an approach recently introduced by D.E. Aspnes for product-driven deposition control[8].

II. Reduced order surface kinetics model and real-time control for $Ga_{1-x}In_xP$

During heteroepitaxial $Ga_xIn_{1-x}P$ growth on Si under pulsed chemical beam epitaxy (PCBE) conditions, the surface of the substrate is exposed to pulsed ballistic beams of TBP $[(C_4H_9)PH_2]$, TEG $[Ga(C_2H_5)_3]$ and TMI $[In(CH_3)_3]$ at typically 350 - 470°C. The total pressure during growth in the reactor is kept in the range of 10^{-3} - 10^{-4} mbar and all precursors are supplied sequentially separated by pauses as shown schematically in Figure 1. Under these conditions, the decomposition processes occurs at the growth surface and no gas phase reactions have to be considered. In the reduced order surface kinetics (ROSK) model for the compound semiconductor $Ga_{1-x}In_xP$, we summarize all chemical reactions in one dominant bimolecular reaction for the TBP pyrolysis, two dominant molecular reactions for the TEG decomposition, and two dominant reactions for the TMI decomposition process. These simplifications lead to a set of coupled differential rate equations for the molar concentrations n_i of SRL constituents[7].

Figure 1:

Schematic representation of a precursor cycle sequence used for the growth of the ternary compound semiconductor $Ga_{1-x}In_xP$ grown via the organometallic precursors TBP, TEG and TMI.



To utilize the real time optical observations and apply feedback control methodology for controlling $Ga_{1-x}In_xP$ film growth, we consider a four layer media composed of ambient / surface-reaction layer / film / substrate as described previously[7]. For the case of multi-layer media of films we adapted a virtual substrate method[8,9], where the reflectance amplitude r of the p-polarized light is given by

$$r = \frac{r_{01} - \hat{r} e^{-2i\Phi_1}}{1 + r_{01} \hat{r} e^{-2i\Phi_1}} \quad \text{with} \quad \hat{r} = \frac{r_{12} - r_k e^{-2i\Phi_2}}{1 + r_{12} r_k e^{-2i\Phi_2}} \quad (1)$$

The virtual reflection index r_k is updated by

$$r_k = \frac{r_{k,k-1} - r_{k-1} e^{-2i\Phi_2}}{1 + r_{k,k-1} r_{k-1} e^{-2i\Phi_2}} \quad \text{with} \quad r_k = A_k e^{-i\theta_k} \quad (2)$$

at the end of cycle, where θ_k defines the phase factor. Based on the phase factor θ_2 the thickness d_2 of the grown layer is estimated by

$$d_2 = \frac{\lambda}{4\pi\sqrt{\epsilon_2 - \epsilon_0 \sin^2\phi_0}} (\theta_{end} - \theta_{begin}) \quad (3)$$

where the θ_{end} , θ_{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

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

We use the nonlinear filtering algorithm[10] 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 (3). The growth ratio of GaP and InP for each cycle determined by (4) provides a composition estimate. Let y_k denote the PR signal at the end of the k -th cycle. Then the filtering problem is to estimate the signal process x^k defined by

$$\begin{pmatrix} x_1^k \\ x_2^k \\ x_3^k \\ x_4^k \\ x_5^k \end{pmatrix} = \begin{pmatrix} f_1(x^k) \\ f_2(x^k) \\ x_3^{k-1} \\ x_4^{k-1} \\ x_5^{k-1} \end{pmatrix} + \omega_k \quad (5)$$

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 $r_k = r_{k-1} e^{-2i\varphi_2}$ 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

$$f_1 + i f_2 = x_1 + i x_2 + 2 i \varphi_2; \quad h = \frac{r_{02} + r_v}{1 + r_{02} r_v} \quad (6)$$

where $d_2 = f_{r_k} x_5$. We assume that noise processes w_k , v_k are independent (identically distributed) Gaussian random variables. The growth of GaP and InP is determined in terms of n_{GaP} and n_{InP} which are given by

$$\frac{d n_{GaP}}{dt} = k_4 n_p n_{Ga}, \quad \frac{d n_{InP}}{dt} = k_5 n_p n_{In} \quad (7)$$

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

$$n_{Ga} = u_{TEG} S_{GaP} - n_{GaP}, \quad (8)$$

where S_{GaP} is a pre-determined constant. Integrating the first equation in (7) we obtain

$$n_{GaP}(t_{k+1}) = e^{-C} (n_{GaP}(t_k) - S_{GaP} u_{TEG}) + S_{GaP} u_{TEG} \quad (9)$$

where t_k is the starting time of the k -th cycle and $C = k_4 \int_{t_k}^{t_{k+1}} n_p(t) dt$. 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

$$\begin{pmatrix} n_k \\ C_k \end{pmatrix} = \begin{pmatrix} n_{k-1} + C_{k-1} (u_{TEG} - n_{k-1}) \\ C_{k-1} \end{pmatrix} + \tilde{w}_k \quad (10)$$

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 4. The growth of the InP is modeled analogously. We determine the input flow rates u_{TEG}^k and u_{TMI}^k by performing

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

$$\min_{u_{TMI}^k} \left| \frac{n_{InP}^+}{n_{GaP}^+} - \frac{z_k}{1 - z_k} \right|^2 + \beta \left| u_{TMI}^k - u_{TMI}^{k-1} \right|^2, \quad (11)$$

subject to

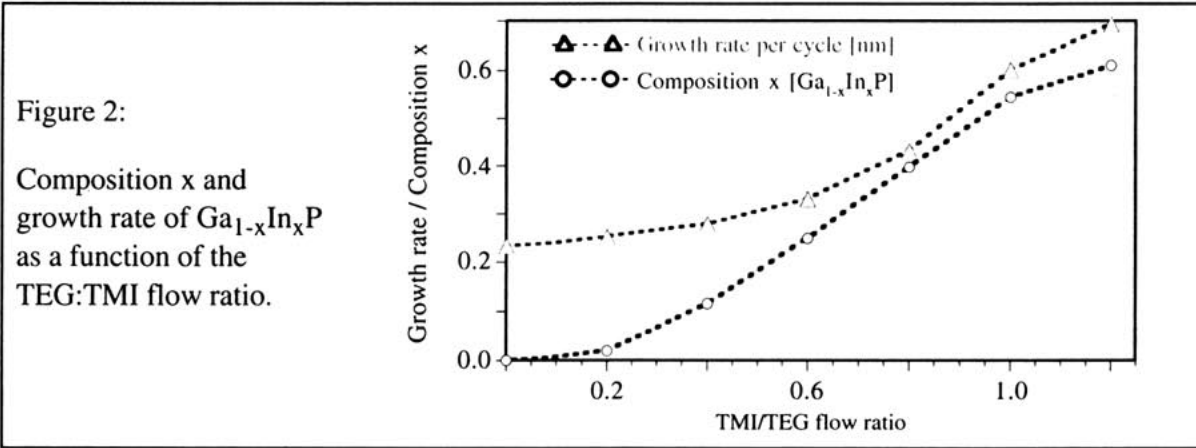
$$n_{GaP}^+ = e^{-C_{TEG}^k} \left(n_{GaP}^c - S_{GaP} u_{TEG}^k \right) + S_{GaP} u_{TEG}^k$$

$$n_{InP}^+ = e^{-C_{TMI}^k} \left(n_{InP}^c - S_{InP} u_{TMI}^k \right) + S_{InP} u_{TMI}^k, \quad (12)$$

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.

III. Open- and closed-loop control results

From a series of experiments we established the correlation of composition and growth rate dependency as a function of flow-ratio. For this, epilayers with thick constant composition x in $Ga_{1-x}In_xP$ were grown and analyzed by XRD to obtain the compositional relationship with the established flow-ratio TMI:TEG. The growth rates were calculated from the interference fringes obtained in the PR signals. Figure 2 shows the results of these ex-situ analysis, clearly indicating the nonlinear correlation between growth rate and composition as a function of an established flow ratio TMI:TEG. The established correlation between growth rate and composition x with the TMI:TEG flow ratio is used next to estimate the growth parameter for compositionally graded heterostructures under open-loop control conditions. The correlation is also used as initial data base for closed-loop control.



For the growth of a parabolic $Ga_{1-x}In_xP$ heterostructure under open-loop control, a predetermined time-wise flow profile was employed in which the flow of TEG is kept constant and the flow of TMI is varied to match desired composition and thickness. The target profile is shown in Figure 3a together with the calculated time-wise precursor flux profile for TEG and TMI. The grown parabolic $Ga_{1-x}In_xP$ heterostructure is analyzed by secondary mass ion spectroscopy (SIMS), the depth profile of which is shown in Figure 3c. The instrumental broadening of approximately 50\AA and a depth integration of typically 40\AA to 50\AA leads to two errors in the SIMS analysis: (a) a compositional smear-out of profiles over 100\AA to 150\AA and (b) the compositional dependency of the sputtering rate, which leads to an accumulative error in the depth estimate. Even though the SIMS analysis contains large error margins, it is clear that the open-loop control algorithm has a large discrepancy between the target profile and measured profile.

The closed-loop control algorithm contains the same initial start values as for the open-loop control. However, the precursor flux values are updated in real-time integrating the real-time estimate of the optical PR-signals as described in section II. The real-time updated closed-loop control flow profile is shown in Figure 4b. During closed-loop control, variation of the flow of TMI is employed to control composition x while variation in the flow of TEG is used to control the growth rate. A SIMS depth profile analysis for the such grown $\text{Ga}_{1-x}\text{In}_x\text{P}$ heterostructure is shown in Figure 4b. The results clearly displays superior tracking ability under closed-loop control, particularly in maintaining a constant composition before and after the parabolic heterostructure.

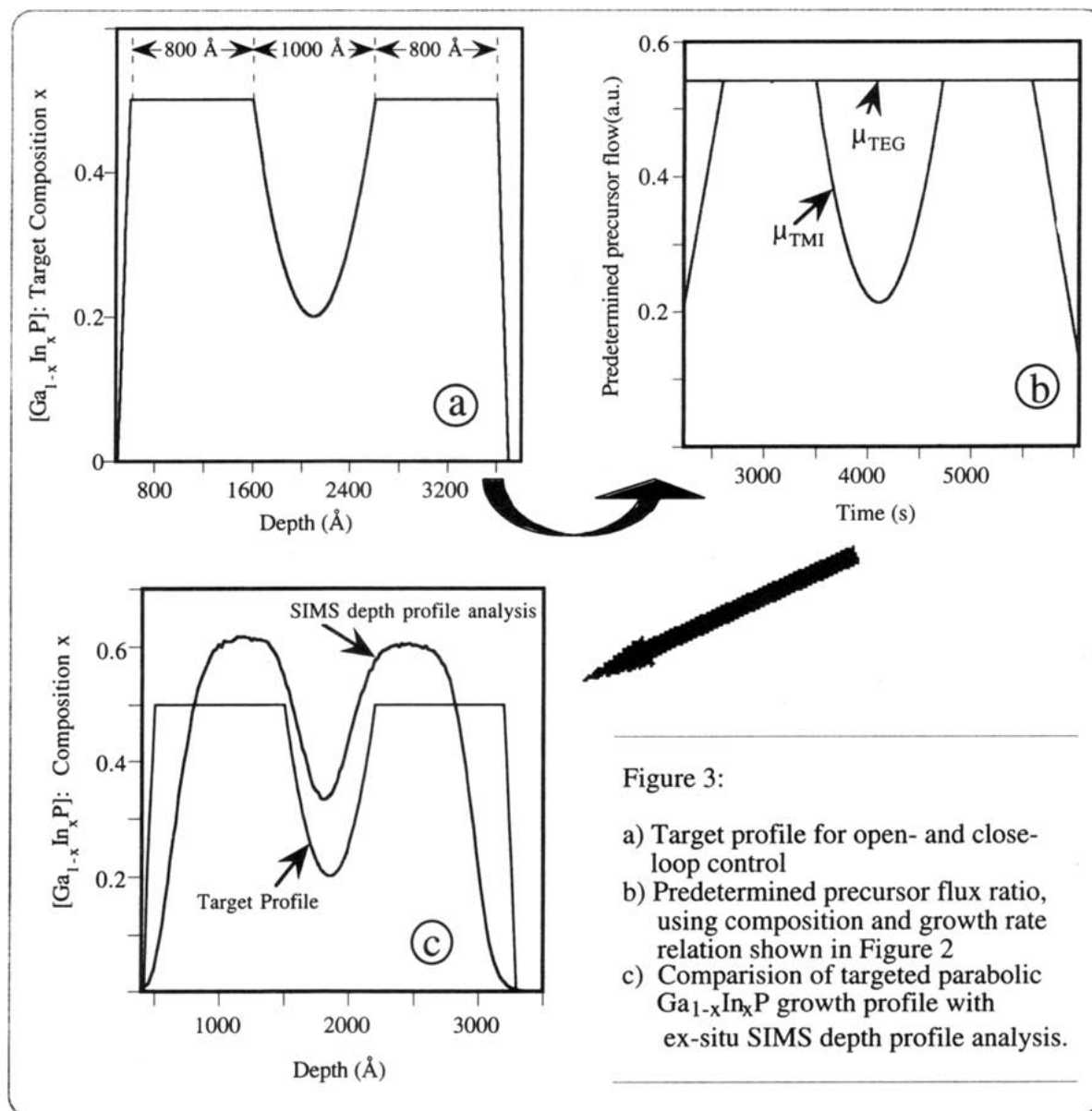


Figure 3:

- a) Target profile for open- and close-loop control
- b) Predetermined precursor flux ratio, using composition and growth rate relation shown in Figure 2
- c) Comparison of targeted parabolic $\text{Ga}_{1-x}\text{In}_x\text{P}$ growth profile with ex-situ SIMS depth profile analysis.

IV. CONCLUSION

We described the compositional and thickness controlled growth of parabolically graded $\text{Ga}_x\text{In}_{1-x}\text{P}$ heterostructures on Si, using a reduced order surface kinetics model that links the optical sensor to nonlinear filtering algorithm that estimates the optimal flow rates of the source vapors to achieve the desired composition and growth per cycle in real time. Parabolically graded

$\text{Ga}_{1-x}\text{In}_x\text{P}$ heterostructure wells grown under open- and closed-loop conditions were analyzed by SIMS, demonstrating that the on-line estimate of growth rate and composition provided by the PR probe adjusts to the non-linearity in growth kinetics present in our system and provide better tracking to the desired profile.

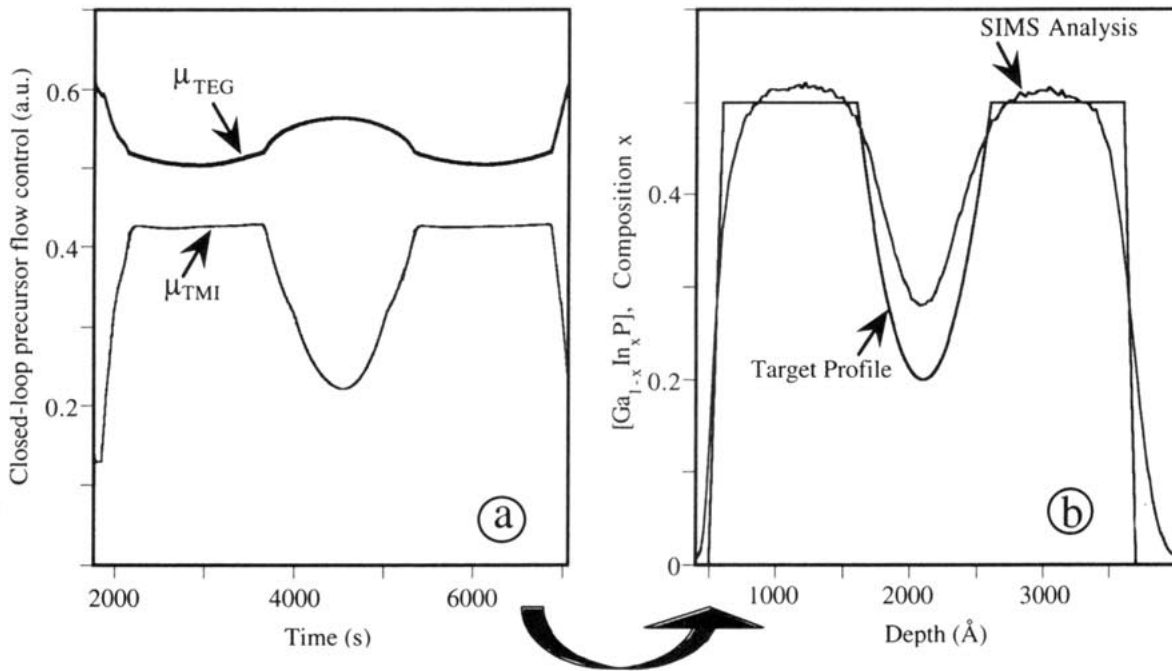


Figure 4: a) Adjustment of precursor flux during close-loop control to achieve composition and thickness target. b) Ex-situ SIMS depth profile analysis for a parabolic graded $\text{Ga}_{1-x}\text{In}_x\text{P}$ heterostructure grown under close-loop control.

V. Acknowledgment

This work has been supported by the DOD-MURI Grant F49620-95-1-0447.

VI. References

1. M. Yoshimoto, T. Hashimoto, P. Vaccaro and H. Matsunami, *Appl. Surf. Sci.* **79**, 227 (1994).
2. D.E. Aspnes, J.P. Harbison, A.A. Studna and L.T. Florez, *Appl. Phys. Lett.* **52**, 957 (1988).
3. N. Kobayashi and Y. Horikoshi, *Jpn. J. Appl. Phys.* **29**, L702 (1990).
4. N. Dietz and K. J. Bachmann, *MRS Bull.* **20**, 49 (1995).
5. M. Ebert, K. A. Bell, S. D. Yoo, K. Flock and D. E. Aspnes, "In-situ monitoring of MOVPE growth by combined spectroscopic ellipsometry and reflectance difference spectroscopy", *Thin Solid Films*, accepted (2000).
6. N. Dietz and K. J. Bachmann, *Vacuum* **47**, pp. 133-140 (1996).
7. N. Dietz, V. Woods, K. Ito and I. Lauko, *J. Vac. Sci. Technol. A* **17**(4), 1300 (1999).
8. D. E. Aspnes, *J. Vac. Sci. Technol. A* **14**, 960 (1996).
9. D. E. Aspnes, *IEEE Journal on Selected Topics in Quantum Electronics* **1**, 1054 (1995).
10. K. Ito and K. Xiong, "New Gaussian filter for nonlinear filtering problems", *IEEE, Trans. Automatic Control*, accepted for publication (1999).