PREDICTIVE CONTROL OF THIN FILM SURFACE MICROSTRUCTURE IN A COMPLEX DEPOSITION PROCESS

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Abstract: In this work, a complex deposition process including two types of molecules whose growth behaviors are very different and influenced by long range interactions is investigated. The study of this process is motivated by recent experimental results on the growth of high-κ dielectric thin films using plasma-enhanced chemical vapor deposition (PECVD). A multi-component kinetic Monte-Carlo (kMC) model is developed for the deposition. The dependence of the surface microstructure of the thin film, such as island size and surface roughness, on substrate temperature are studied. The surface morphology is found to be strongly influenced by these two factors and growth regimes governed by short and long range interactions are observed. Furthermore, a kMC model-predictive control scheme which uses the substrate temperature to control the final surface roughness of the thin film is proposed. The closed-loop simulation results demonstrate that robust deposition with controlled thin film surface roughness can be achieved under the proposed kMC model-predictive controller.

1. INTRODUCTION

The industrial demands for advanced materials having certain properties, have driven the development of thin film technology. Various deposition methods have been developed and widely used to prepare thin films, however, the dependence of the thin film properties, such as uniformity, composition and microstructure, on the deposition conditions is a severe constraint on reproducing thin film's performance. Thus, real-time feedback control of thin film deposition becomes increasingly important in order to meet the stringent requirements on the quality of thin films. Significant research efforts have been made on the feedback control of thin film deposition processes with emphasis on control of film spatial uniformity in rapid thermal processing (RTP) (Theodoropoulou *et al.*, 1999; Christofides, 2001) and plasma-enhanced chemical vapor deposition (PECVD) (Armaou and Christofides, 1999).

In addition to achieving spatially uniform deposition of thin films, one would like to control film properties that characterize film quality. While deposition uniformity control can be accomplished on the basis of continuum type distributed models, precise control of film properties requires models that predict how the film state (microscopic scale) is affected by changes in the controllable process parameters (macroscopic scale). Kinetic Monte-Carlo (kMC) simulation provides a framework for modelling the effect of macroscopic process variables on the thin film microstructure and it has been widely used to simulate CVD processes (see (Battaile and Srolovitz, 2002) for a review of kMC simulation of CVD). However, the majority of these works have focused on studying the growth kinetics or interface structure while only a few works (Reese *et al.*, 2001) have addressed the computational efficiency which strongly affects the use of such kMC models in real-time feedback control systems. Recently, a methodology for feedback control of thin film growth using kMC models was developed in (Lou and Christofides, 2003*a*) and (Lou and Christofides, 2003*b*). The method was successfully applied to control surface roughness in a *GaAs* deposition process using an experimentally determined kMC process model (Lou and Christofides, 2004). Other approaches have also been developed to: (a)

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identify linear models from outputs of kinetic Monte-Carlo simulators and perform controller design by using linear control theory (Siettos *et al.*, 2003), and (b) construct reduced-order approximations of the master equation (Gallivan and Murray, 2003).

However, among these computationally attractive models, most of them consider only single component system, and long range interactions have not been modelled explicitly. In reality, more than one species participate in the film growth in most CVD processes. Moreover, direct long range interactions (Einstein, 1996) and substrate-mediated long range interactions (Merrick *et al.*, 2003) are very important in many of these processes. For example, in the PECVD ZrO_2 process, there is a large number of different species present in the gas phase during the deposition, and many of them participate in the thin film growth, particularly, zirconium hydroxide and hydrocarbon species (see (Cho *et al.*, 2002) for detailed experimental results). Moreover, recent experimental results (Cho *et al.*, 2003) have shown that, when zirconium hydroxides are the dominant species in the gas phase, the deposited ZrO_2 thin film has a very smooth surface with a roughness value less than half ZrO_2 monolayer, which suggests that the zirconium hydroxide species tend to uniformly cover the substrate surface. On the other hand, when hydrocarbons dominate the gas phase, the deposited ZrO_2 thin film has a very rough surface characterized by big islands, which suggests that the aggregation of the hydrocarbon species on the substrate surface, as a result of long range interactions, is quite significant. It is quite obvious that a single component kMC model considering only short range interactions is inadequate to describe the thin film growth in this process. Therefore, a computationally efficient kMC model of a heterogeneous deposition process in which long range interactions are accounted for is needed.

In this work, a complex deposition process including two types of molecules whose growth behaviors are very different and influenced by long range interactions is investigated. The study of this process is motivated by recent experimental results on the growth of high-κ dielectric thin films using PECVD (Cho *et al.*, 2002; Cho *et al.*, 2003; Ni *et al.*, 2003). A multi-component kMC model is developed for the deposition. The dependence of the surface microstructure of the thin film, such as island size and surface roughness, on substrate temperature are studied. The surface morphology is found to be strongly influenced by these two factors and growth regimes governed by short and long range interactions are observed. Furthermore, a kMC model-predictive control scheme which uses the substrate temperature to control the final surface roughness of the thin film is proposed. The closed-loop simulation results demonstrate that robust deposition with controlled thin film surface roughness can be achieved under the proposed kMC model-predictive controller.

2. SURFACE MICROSTRUCTURE MODEL FOR THIN FILM GROWTH

Deposition processes such as PECVD, often involve large numbers of participating species with heterogeneous growth behaviors. Here, we consider a heterogeneous deposition process in which two types of molecules, type *A* and type *B*, which behave very different from each other are considered. Type *A* molecule is significantly affected by long range attractions and tends to aggregate with other *A* molecules into clusters, i.e., favors Volmer-Weber (VW) growth mode. Hydrocarbon molecules generated from the decomposition of metal-organic (MO) precursors in a PECVD process are good examples of such type. Type *B* molecule favors surface sites of local minimum height, which usually results in Frank-van der Merwe (FM) type of film growth. Metal oxides or hydroxides originated from the MO precursors may behave similar to molecules of type *B* as discussed in the introduction.

The geometry of the deposition process is shown in Fig. 1. The gas flux is perpendicular to the substrate surface. Flux composition, i.e., flux of *A* and *B*, in terms of the number of molecules encountered per unit time per surface site, are taken as macro scale process parameters, that can be measured in real-time (via mass spectrometer for example). Both *A* and *B* can diffuse from the gas phase onto the substrate, however, *B* type molecules settle to surface sites of local minimum height simultaneously during adsorption. Surface migration and desorption processes are ignored, while hopping of *A* type molecules is allowed. Surface reactions are not explicitly considered in this process, however, the long range behavior of *A* and the local minimum adsorption behavior of *B* could be consequences of surface reactions (i.e., surface mediated).

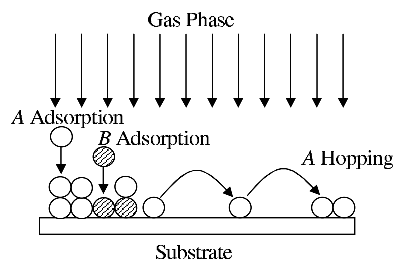

Fig. 1. Thin film growth process.

The growth micro-process model is constructed based on a standard kMC scheme (Gillespie, 1976) which assumes the growth process to be a Poisson process and its dynamics to be governed by the master equation which describes the evolution of transitions between the probabilities of the surface being in specific micro-configurations. Monte-Carlo simulation is used to obtain unbiased realizations of the master equation numerically. A simple cubic lattice structure is used and the simulated surface domain is a square grid of 100 lattice points by 100 lattice points. To improve computational efficiency, the solid-on-solid assumption is made.

Table 1. Model parameters.

Hopping Freq. Const.	k_{h0}^A	10^{13}	s^{-1}
Hopping Energy (bottom)	E_s^A	0.8	eV
Hopping Energy (side)	E_n^A	0.2	eV
Attraction Range	l_a	20	units

We consider multilayer growth and assumed that the adsorption rates of A (w_a^A) and B (w_a^B) can be obtained through real-time measurements as discussed above. Considering only the interactions of the first nearest neighbors (4 side neighbors and 1 bottom neighbor) to determine the hopping rate at a specific site, the hopping rate of a molecule of type A on the surface with n first nearest neighbors is given by

$$w_h^A(n) = k_{h0}^A \exp\left(-\frac{E_s^A + nE_n^A}{kT}\right) \quad (1)$$

where k_{h0}^A is the hopping event frequency constant, E_s^A and E_n^A are the energy barriers associated with surface hopping of A for bottom and side neighbors respectively (we note that for simplicity we do not distinguish the neighboring molecules of different types).

To incorporate different growth behaviors into the kMC simulation, we set up two rules for A type molecule aggregation and B type molecule local minimum adsorption, respectively. For A type molecules, we enforce a rule on the hopping process, specifically, the hopping direction of a specific A molecule is determined by comparing the distance-weighted sum of all the A molecules in each direction and pick the one with largest value of the sum so that A molecules will aggregate from long range. Specifically, the weighted sum, for example, the weighted sum in the positive x direction of an A located at surface lattice point (x_0, y_0), $N_{h,+x}^A(x_0, y_0)$, is computed as follows:

$$N_{h,+x}^A(x_0, y_0) = \sum_{x=1}^{l_a} \sum_{y=-x}^{x} S_{(x_0+x, y_0+y)}^A \left(1 - \frac{\sqrt{x^2+y^2}}{l_a}\right) (2)$$

where l_a is the maximum range of attraction, and the value of the occupancy factor $S_{(i,j)}^A$ is unity when the surface site (i, j) is occupied by an A and zero otherwise.

For B type molecules, we enforce a rule on the adsorption process. When the target site does not have the local minimum height, a B type molecule will be adsorbed onto one of the neighboring sites that has the local minimum height. In this work, only the 4 first nearest neighbor sites and 4 second nearest neighbor sites are considered. In addition, the sticking probability of type B molecule on surface site occupied by type A molecules is considered very small (5% in this study). This is because when this sticking probability is close to unity, the surface would be smoothened by type B molecules independently of the presence of type A molecules, and thus, the dynamics of the two-component deposition would not be observable. All other sticking probabilities are considered to be unity for simplicity.

The parameters, k_{h0}^A, E_s^A, E_n^A and l_a in the model can be determined by experiments. The parameters of the process studied in this work are shown in Table 1. When the lattice is set and the rates of the three events (A adsorption, B adsorption, A hopping) are determined based on measurements or its corresponding rate expression (1), a kinetic Monte-Carlo simulation is executed following the algorithm reported in (Reese *et al.*, 2001). First, the surface A molecules are grouped into five classes based on the number of side neighbors (from 0 to 4 side neighbors); in each class, the molecules have the same hopping rates and the A and B adsorption rates are site independent. Then, a random number is generated to select an event to be run based on the rates; if the event is A hopping, the class in which the event will happen is also selected. After that, a second random number is generated to select the site where the event will be executed; if the event is A or B adsorption, the site is randomly picked from sites in the entire lattice; if the event is A hopping, the site is randomly picked from the list of the sites in the selected class. After the site is selected, the MC event is executed. If the event is adsorption, it is executed by adding one molecule on the selected site (B adsorption rule is applied if the event is B adsorption); if the event is A hopping, the A type molecule on the site is moved to the next site in the direction selected by the hopping rule. Upon an executed event, a time increment τ computed based on Eq. 2 is added to the process time t. The lattice is set to be periodic to satisfy the mass balance of the hopping molecules.

3. SIMULATION RESULTS AND DISCUSSION

We simulate the multi-component complex deposition using the proposed process model (see (Ni and Christofides, 2004) for results of single-component deposition). Both A and B types of molecules are present in the gas phase and the relative ratio of the two species is set for simplicity to be unity in the simulated case. The effect of substrate temperature (in the range of 300 K to 440K) on the surface microstructure of the deposited thin films is investigated. The root-mean-square (RMS) roughness definition is used to evaluate roughness of the thin film surface in this work.

Figs. 2 and 3 show the surface morphologies of thin films obtained by depositions at low ($T = 320$ K) and high ($T = 440$ K) substrate temperatures, respectively. The thin film deposited under low substrate temperature has a high island density but a small lateral island size, while the thin film deposited under high substrate temperature has a low island density but a large lateral island size. Such difference in surface morphology between the two thin films is similar to the single component scenario in which only A type of molecules are present in the gas phase (see (Ni and Christofides, 2004) for detailed explanation).

Fig. 4 shows the surface roughnesses of thin films deposited at different substrate temperatures. It can be clearly seen that there are two temperature regimes

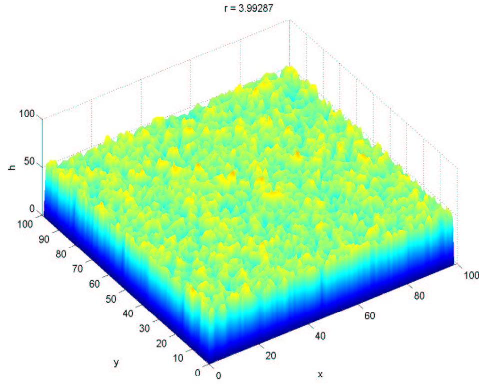

Fig. 2. Surface of a thin film deposited with $w_a^A = 0.05s^{-1}$, $w_a^B = 0.05s^{-1}$ and $T = 320K$ - $t = 900s$.

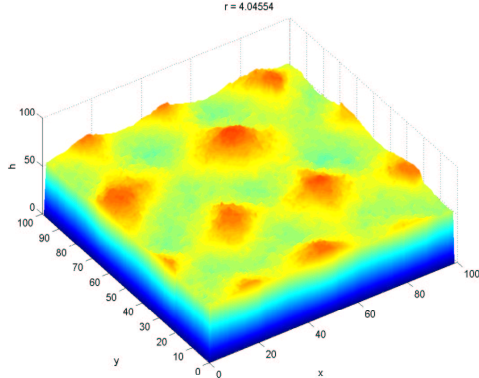

Fig. 3. Surface of a thin film deposited with $w_a^A = 0.05s^{-1}$, $w_a^B = 0.05s^{-1}$ and $T = 440K$ - $t = 900s$.

in which thin film growth is quite different. In the low temperature regime, the surface roughness drops with increasing temperature, in the high temperature regime, the surface roughness rises with increasing temperature (however, the surface roughness drops again when the substrate temperature is very high when stable surface islands start to coalesce and form islands with lateral dimension larger than the range of attraction). The transition from the low temperature regime to the high temperature regime corresponds to the change in growth process from short range interaction dominant to long range attraction dominant.

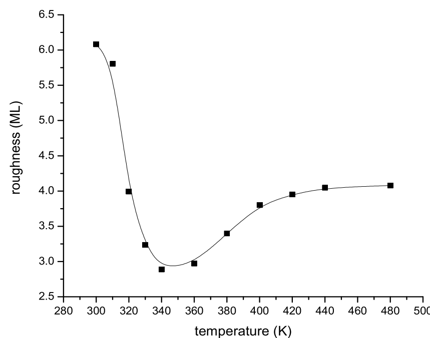

Fig. 4. Surface roughness of thin films deposited with $w_a^A = 0.05s^{-1}$, $w_a^B = 0.05s^{-1}$ for different substrate temperature - $t = 900s$.

4. FEEDBACK CONTROL

To obtain thin films of desired and reproducible surface microstructure, it is necessary to operate the deposition processes under feedback control. In this process, since there are two temperature regimes for which thin film surface morphologies are quite different, control of surface roughness in these two regimes is considered separately. Here, we only focus on the high temperature regime (see (Ni and Christofides, 2004) for results on feedback control in the low temperature regime), in which long range interactions are significant, and traditional control strategies such as proportional integral (PI) control lead to poor closed-loop performance. The final surface roughness of the thin film is selected as the controlled variable and the manipulated variable is chosen to be the substrate temperature T, which is restricted within the range of 340 K $\sim$ 420 K. The major disturbance to the deposition process is the variation of the gas phase composition.

4.1 *Open-loop response*

Fig. 5 shows the response profile of the surface roughness with respect to step changes in substrate temperature at time $t = 400$ s. We can see that the value of the surface roughness at the end of the deposition can be controlled by manipulating the substrate temperature, however, the responses to step changes in substrate temperature are in fact dependant on the surface microstructure of the thin film, i.e. instantaneous surface roughness. Fig. 6 shows the response profiles of surface roughness, with respect to step changes in substrate temperature at time $t = 200$ s and $t = 800$ s, when the surface of the thin film is relatively smooth and rough, respectively. It can be seen that the increase in substrate temperature corresponds to increasing final surface roughness when the surface is smooth and decreasing final surface roughness when the surface is rough. This result suggests that a more advanced controller may be needed to control the surface roughness in the high temperature regime.

Fig. 7 shows the profiles of surface roughness with respect to disturbances in the gas phase composition (i.e., gas flux pattern). It can be seen that the effect of the disturbance in the gas phase composition on the surface roughness is significant and very complex (i.e., it can not be described by a low order analytical model), and thus, the proposed growth model is needed to predict the evolution of the surface roughness.

4.2 *Controller design*

In order to achieve robust closed-loop operation in the high temperature regime, a kMC model-based predictive control scheme is proposed. Fig. 8 shows the block diagram of the closed-loop system. A reference trajectory of the instantaneous surface roughness of the thin film is selected based on off-line optimization, and in this work for simplicity, the profile of the surface roughness of the thin film in a ideal open-loop deposition (no disturbance during the process and the final surface roughness is just the desired value) is chosen. Using such a reference trajectory, instead of solving the receding horizon optimization problem of minimizing the difference between the final surface roughness and the desired value with multiple

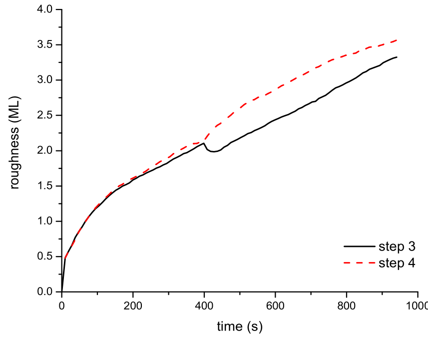

Fig. 5. Response of surface roughness with respect to step changes in substrate temperature: a. T changes from 185 K to 205 K at t=400 s (step 3); b. T changes from 185 K to 165K at t=400 s (step 4).

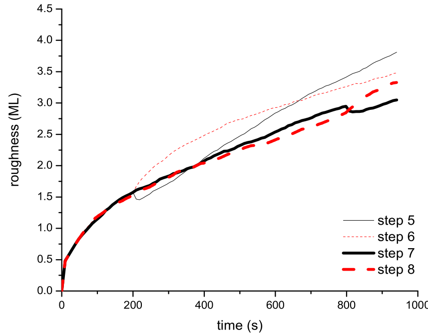

Fig. 6. Response of surface roughness with respect to step changes in substrate temperature: a. T changes from 185 K to 205 K at t=200 s (step 5); b. T changes from 185 K to 165K at t=200 s (step 6); c. T changes from 185 K to 205 K at t=800 s (step 7); d. T changes from 185 K to 165K at t=800 s (step 8).

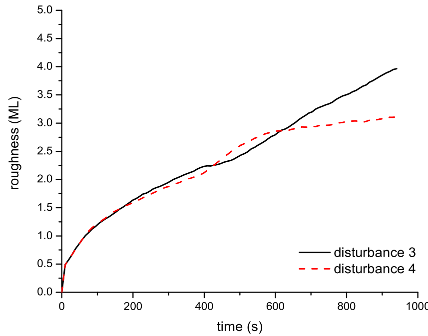

Fig. 7. Response of surface roughness with respect to step disturbance in gas phase composition: a. gas phase composition changed from $50\%A+50\%B$ to $20\%A+80\%B$ (disturbance 3); b. gas phase composition changed from $50\%A+50\%B$ to $80\%A+20\%B$ (disturbance 4).

decision variables, we only need to solve the fixed short horizon optimization problem of minimizing the difference between the instantaneous surface roughness and the reference value with a decision variable. Therefore, the computation time of each optimization is greatly reduced, since the kMC simulation duration is reduced from the scale of the total deposition time to the controller turnover time. This is very important since kMC simulation is relatively time consuming and large scale numerical optimization using kMC model is almost impossible to solve in real-time.

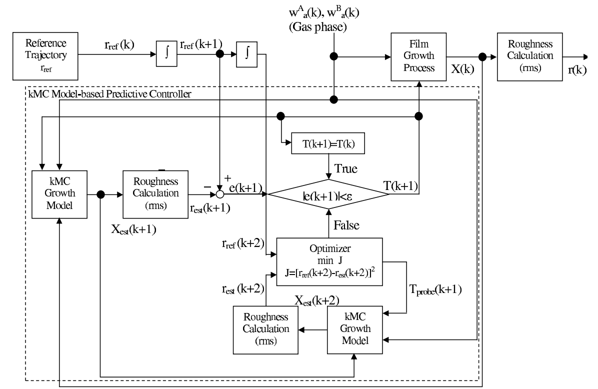

Fig. 8. Block diagram of the closed-loop system with the kMC model-predictive controller.

During each control cycle, the surface configuration $X(k)$ is first measured, an estimate of the surface configuration at the next control action time $X_{est}(k+1)$ is computed based on current process conditions using the proposed kMC model, and the estimated surface roughness value $r_{est}(k+1)$ is compared with the reference value $r_{ref}(k+1)$. If the error is less than ε ($\varepsilon = 0.05$ in this work), the next controller output $T(k+1)$ is set to be the same as the current output $T(k)$. If the error is larger than ε, the optimizer is called to compute the output value of the next control action $T(k+1)$ so that the error between the surface roughness after the next control action $r(k+2)$ and the reference value $r_{ref}(k+2)$ is minimized.

The optimizer uses direct search to find the optimal solution since the kMC model does not have a closed-form expression. The estimate of the surface roughness after the next control action $r_{est}(k+1)$ is computed using the proposed kMC model based on the estimated surface configuration before the next control action $X_{est}(k+1)$, the probe output value $T_{probe}(k+1)$ and current process conditions. The search precision specified in this work is 1 K, and since the proposed kMC model is highly computationally efficient, the optimization problem can be solved by an entry level personal computer within the controller turnover time (10 s). Furthermore, the speed and the precision of the direct search optimization algorithm can be substantially improved by parallel computing.

Fig.9 shows the profile of a closed-loop deposition with final surface roughness set-point value of $3.2ML$. It can be seen that the surface roughness value of the thin film follows the reference trajectory closely and the final surface roughness has been controlled at the desired value. Fig. 10 shows the profile of a closed-loop deposition with final surface roughness set-point value of $3.2ML$. A disturbance in the gas phase composition is introduced in this simulation in terms of a change in the adsorption rates at $t = 400s$ to $t = 500s$, specifically, w_a^A changed from $0.05s^{-1}$ to $0.1s^{-1}$ and

w_a^B changed from $0.05s^{-1}$ to $0s^{-1}$ at $t = 400s$, while at $t = 500s$, w_a^A and w_a^B both changed back to $0.05s^{-1}$. It can be seen that the surface roughness follows closely with the reference trajectory and final surface roughness has been controlled at the desired value which is 13.5% lower than open-loop. Compared to the failure of the PI controller on the same closed-loop simulation scenario (see detailed comparison with PI scheme in (Ni and Christofides, 2004)), kMC model-based predictive controller delivers substantially improved and robust closed-loop performance.

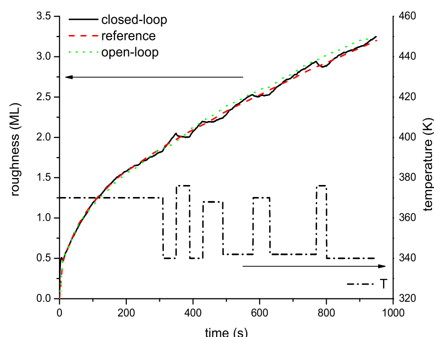

Fig. 9. Profiles of a closed-loop deposition with surface roughness set-point of $3.2ML$: a. closed-loop surface roughness (solid line, left scale); b. reference surface roughness (dashed line, left scale); c. open-loop surface roughness (dotted line, left scale); d. substrate temperature (dashed-dotted line, right scale).

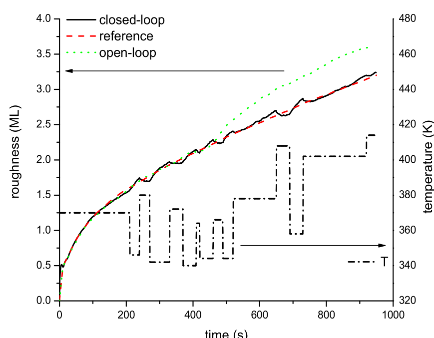

Fig. 10. Profiles of a closed-loop deposition with surface roughness set-point of $3.2ML$: a. closed-loop surface roughness (solid line, left scale); b. reference surface roughness (dashed line, left scale); c. open-loop surface roughness (dotted line, left scale); d. substrate temperature (dashed-dotted line, right scale).

REFERENCES

Armaou, A. and P. D. Christofides (1999). Plasma-enhanced chemical vapor deposition: Modeling and control. *Chem. Eng. Sci.* **54**, 3305–3314.

Battaile, C. C. and D. J. Srolovitz (2002). Kinetic-monte carlo simulation of chemical vapor deposition. *Annu. Rev. Mater. Res.* **32**, 297–319.

Cho, B., J. P. Chang, J. Min, S. H. Moon, Y. W. Kim and I. Levin (2003). Material characteristics of electrically tunable zirconium oxide thin films. *J. Appl. Phys.* **93**, 745–749.

Cho, B., J. Wang and J. P. Chang (2002). Metalorganic precursor decomposition and oxidation mechanisms in plasma-enhanced ZrO_2 deposition. *J. Appl. Phys.* **92**(8), 4238.

Christofides, P. D. (2001). *Nonlinear and Robust Control of Partial Differential Equation Systems: Methods and Applications to Transport-Reaction Processes*. Birkhäuser. Boston.

Einstein, T. L. (1996). *Handbook of Surface Science*. Chap. 11, pp. 577–650. Vol. 1. Elsevier. Amsterdam.

Gallivan, M. A. and R. M. Murray (2003). Model reduction and system identification of master equation control systems. In: *Proceedings of American Control Conference*. Denver, Colorado. pp. 3561–3566.

Gillespie, D. T. (1976). A general method for numerically simulating the stochastic time evolution of coupled chemical reactions. *J. Comp. Phys.* **22**, 403–434.

Lou, Y. and P. D. Christofides (2003*a*). Estimation and control of surface roughness in thin film growth using kinetic Monte-Carlo models. *Chem. Eng. Sci.* **58**, 3115–3129.

Lou, Y. and P. D. Christofides (2003*b*). Feedback control of growth rate and surface roughness in thin film growth. *A.I.Ch.E J.* **49**, 2099–2113.

Lou, Y. and P. D. Christofides (2004). Feedback control of surface roughness of *gaas* (001) thin films using kinetic Monte-Carlo models. *Comp. & Chem. Eng.,* to appear.

Merrick, M. L., W. Luo and K. A. Fichthorn (2003). Substrate-mediated interactions on solid surfaces: theory, experiment, and consequences for thin-film morphology. *Prog. Surf. Sci.* **72**, 117–134.

Ni, D. and P. D. Christofides (2004). Dynamics and control of thin film surface microstructure in a complex deposition process. *Chem. Eng. Sci.,* submitted.

Ni, D., Y. Lou, P. D. Christofides, L. Sha, S. Lao and J. P. Chang (2003). A method for real-time control of thin film composition using OES and XPS. *Proceedings of American Control Conference* pp. 1320–1327, To appear in *IEEE Trans. Semiconduct. Manufact.*

Reese, J. S., S. Raimondeau and D. G. Vlachos (2001). Monte Carlo algorithms for complex surface reaction mechanisms: Efficiency and accuracy. *Journal of Computational Physics* **173**, 302–321.

Siettos, C. I., A. Armaou, A. G. Makeev and I. G. Kevrekidis (2003). Microscopic/stochastic timesteppers and "coarse" control: a kMC example. *A.I.Ch.E J.* **49**, 1922–1926.

Theodoropoulou, A., R. A. Adomaitis and E. Zafiriou (1999). Inverse model based real-time control for temperature uniformity of RTCVD. *IEEE Trans. Semiconduct. Manufact.* **12**, 87.