NUCLEATION AND GROWTH OF SILICON MICROSTRUCTURES BY DIRECT-LASER WRITING

David E. Kotecki* and Irving P. Herman**
* Physics Department, Lawrence Livermore National Laboratory, Livermore CA. 94550 and Department of Applied Science, University of California, Davis/Livermore, Livermore, CA. 94550
** Department of Applied Physics, Columbia University, New York, N.Y. 10027

ABSTRACT

This paper reports on a study of the nucleation phase of thin film growth during pyrolytic deposition by direct-laser writing. A Monte Carlo computer simulation is used to model the initial surface dynamics occurring during the deposition of silicon from silane (SiH_4) on strongly binding substrates such as silicon, and on weakly binding substrates such as silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). Results show that for high peak temperatures ($\geq$ 1200 K) and weakly binding substrates, the most probable location for the initiation of thin film growth is radialy displaced from the center of the locally laser-heated region of the surface. At low peak temperatures, thin film nucleation is found to begin at the center of the locally laser-heated surface for all substrates.

INTRODUCTION

Direct-laser writing (DLW) has become an important process for the direct fabrication of microstructures [1–4]. One critical element in thin film deposition is the nucleation phase, in which a supersaturated concentration of adatoms on the surface combine to form stable nuclei from which nucleus coalescence and growth proceeds. Practical application of DLW requires understanding the role of nucleation during thin film formation. The morphology and internal structure of deposited material, such as whether it is crystalline, polycrystalline, or amorphous, is strongly influenced by the nucleation phase of the growth process. In polycrystalline materials, the resulting grain size and grain boundaries influence the optical and electrical properties of the material. Also, when depositing materials onto weakly binding substrates, such as silicon onto substrates of silicon dioxide, (SiO_2), and silicon nitride, (Si_3N_4), the nucleation phase may be the rate limiting step in the deposition process.

During DLW, the physical conditions which prevail are radically different from those encountered during other thin film deposition processes such as sputtering, evaporation, molecular beam epitaxy and large-area chemical vapor deposition (CVD). In pyrolytic deposition by DLW, a focussed laser induces a temperature gradient across the surface with a spatial variation on the order of one micron. Parent molecules adsorbed onto the surface thermally dissociate into the atom being deposited plus a volatile product which eventually leaves the surface. Since the probability of molecular dissociation is temperature dependent, the formation of deposited atoms is also spatially varying over this one micron-dimension region.

The most notable differences in thin films produced by DLW compared to those made by other deposition processes are the localized nature of the deposit and the large vertical growth rates which occur in DLW. Vertical growth rates in excess of 10^7Å/s have been observed during pyrolytic deposition of polysilicon from silanes [5] using DLW. This can be compared to vertical growth rates [6] of less than 1000Å/s during large area CVD; less than 100Å/s during sputtering and evaporation; and less than 10Å/s during molecular beam epitaxy.

The primary purpose of this study is to gain insight into the dynamics which govern the initial thin film formation for the conditions encountered in pyrolytic deposition by DLW. The initial stages of thin film growth involve impingement of molecules onto a

Mat. Res. Soc. Symp. Proc. Vol. 75.

surface; formation of adatoms from parent molecules; migration of the adsorbed atoms resulting in the formation of stable clusters; the possible migration of small clusters of adatoms; and the desorption of single adatoms and possibly clusters of adatoms. A Monte Carlo computer simulation [7] mimics these processes in real time and thereby produces a representation of the initial thin film formation as a function of time.

In this study, the pyrolytic deposition of silicon from silane (SiH_4) on strongly binding substrates, such as silicon, and weakly binding substrates, such as silicon dioxide (SiO_2) and silicon nitride (Si_3N_4), was examined. Predictions of the dwell time before nucleation commences and the time dependence of the nucleation rate were obtained for the various regions of the laser–heated surface. Additional information about the density of clusters is also presented. Silicon deposition was investigated because of existing experimental data for the pyrolysis of silane as a function of temperature, the previous experimental results of nucleation during large–area CVD [8,9] which forms a good basis for comparison, and also because of the technological importance of silicon deposition for applications in microelectronics.

ADATOM SURFACE DYNAMICS

Consider the case when the parent gas is at low pressure ($<$ 10 Torr) so that the mean free path in the gas phase is comparable or larger than the laser heated region of the surface. Under this condition, rarefied gas dynamics can be used to describe the flux of reactant molecules onto the surface, simplifying the more general case where diffusion will eventually limit the flux of parent gas molecules to the surface. Molecules of the parent gas are incident onto the surface at a rate given by:

$$R_P = \frac{3.51 \times 10^{22} \, P}{(MT_g)^{\frac{1}{2}}} \tag{1}$$

where R_P has the units of $cm^{-2}s^{-1}$, P is the pressure in Torr, M is the molecular mass, and T_g is the temperature of the gas. For SiH_4 at 300 K incident onto a surface which has 1.36×10^{15} atomic sites per cm^2 (such as silicon), equation 1 reduces to:

$$R_{SiH_4} = 2.63 \times 10^5 \, P \tag{2}$$

where R_{SiH_4} is now the rate of impingement in units of $(\text{atomic site})^{-1}\ s^{-1}$, and P is again the pressure in Torr.

The dissociation rate of SiH_4 into a silicon atom and two hydrogen molecules ($SiH_4 \rightarrow Si + 2H_2$) has been experimentally determined by a number of investigators; see [10,11] and references contained within. Farrow [11] measured the probability of molecular dissociation of silane, $\alpha(T)$, on a silicon surface over the temperature range of 700 K to 1100 K and over a pressure range from 10^{-5} to 0.2 Torr, arriving at:

$$\alpha(T) = 5.45 e^{-\frac{1.7 \times 10^4}{RT}} \tag{3}$$

where R is the molar gas constant (1.98 cal $mole^{-1}$ deg^{-1}), and T is the substrate temperature. Even though equation 3 has been shown to be valid only from 700 K to 1100 K, it was extended in this study to the entire temperature range surveyed from 600 K to 1600 K and assumed to be independent of the surface. Combining equations 1 and 3, the net rate of silicon atom formation on the surface as a function of substrate temperature T and SiH_4 pressure P is given by:

$$R_{Si}(P,T) = 1.43 \times 10^6 e^{-\frac{1.7 \times 10^4}{RT}} \, P \tag{4}$$

It should be noted that any effects of adsorbed quantities of SiH_2 or H on the deposition kinetics are ignored; the consequence of this is discussed in reference [12].

In addition to the atomic formation rate, two other important physical processes strongly influence the nucleation process: adatom desorption and adatom migration [13]. The mean residence time, τ_a, of a single adsorbed atom before desorbing from the substrate is given by:

$$\tau_a = \nu_0^{-1} e^{\frac{E_a}{kT}} \tag{5}$$

where E_a is the average adsorption energy, which is assumed here to be independent of position and temperature on the substrate, and ν_0 is the rate constant for desorption which is taken to be 10^{12} sec^{-1}, and also assumed to be independent of temperature. For the purpose of this study, a range of adsorption energies from 0.8 to 1.2 eV was surveyed.

The mean time between migrations across adjacent sites on the substrate is given by:

$$\tau_m = \nu_1^{-1} e^{\frac{E_m}{kT}} \tag{6}$$

where E_m is the average activation energy required for a migration of a single adatom on the substrate to an adjacent site and is assumed to be independent of position and temperature; ν_1 is the rate constant for migrations and is taken to be equal to ν_0 (10^{12} sec^{-1}). For a large number of material systems, the migration energy E_m is between 0.3 and 0.6 times the adsorption energy E_a [13]. For the purpose of this study, the ratio of E_m to E_a was set equal to 0.5.

For a single adatom on the bare surface, it is useful to define the quantity Λ which is equal to the average distance an adatom migrates before desorbing. From a random walk treatment, the average distance migrated is the distance travelled during each migration times the square root of the number of actual migrations. Since the average number of migrations made before desorbing is the ratio of residence time to the mean time between migrations, the average distance migrated by a single adatom before desorbing (assuming the surface is free of clusters) is given by:

$$\Lambda = \left(\frac{\tau_a}{\tau_m}\right)^{\frac{1}{2}} d = e^{\frac{E_a - E_m}{2kT}} d = e^{\frac{E_m}{2kT}} d \tag{7}$$

where d is the unit distance from site to site on the surface. For the migration energies and range of temperatures of interest in this study, Λ ranges from a minimum of 4.3 d for $E_m = 0.4$ eV and 1600 K, to a maximum of 331 d for $E_m = 0.6$ eV and 600 K. For silicon $d = 2.72$ Å.

Once nucleation initiates and clusters begin to form, the residence time τ_a, the average time between migrations τ_m, and the mean distance an adatom migrates before desorbing Λ, will decrease due to the possibility of capture of adsorbed atoms by clusters.

MONTE CARLO COMPUTER SIMULATION

The details of the Monte Carlo simulation are described in references [12,14]. A three dimensional grid, ($55 \times 55 \times 10$) is used to represent the possible positions of atoms. (For a silicon substrate, this corresponds to a surface area of 150Å × 150Å.) The lowest layer of the grid consists of a square array of surface atoms which are stationary and do not change. The dynamics of each adatom are determined by its surroundings which consists of a sub–cube of 26 atoms; nine on the plane below the atom, nine of the plane above the atom, and eight on the same plane with the atom. Even for amorphous SiO_2 and Si_3N_4 surfaces, a substrate with cubic symmetry is used to represent the available surface sites.

The rate at which silicon atoms are generated on the substrate associates a real value of time to the simulation process. An important quantity needed in the model of adsorbed atom dynamics and the nucleation process is Φ, the number of attempted events (migrations + desorptions) of each adsorbed atom that occur between successive formations of deposited atoms per site. This equals the total rate of adatom events, divided by the adatom formation rate per site:

$$\Phi = \frac{6.98 \times 10^5 \, e^{\frac{8.59 \times 10^3}{T}} \left(e^{-\frac{E_m}{kT}} + e^{-\frac{E_a}{kT}}\right)}{P} \tag{8}$$

Random boundary conditions are imposed in the computer simulation. Any adatom migrating across a boundary edge is automatically reinserted at a randomly determined position along the boundary.

General Sequence

The general sequence of the simulation process consists cf the following steps:

1. Initial conditions and growth parameters including the pressure, binding energies, and temperature are established.
2. An atom is placed on a randomly chosen site.
3. The "relaxation" process is simulated:
    (a) An adatom is randomly choosen.
    (b) Probabilities for all possible events (adatom migrations and desorptions, dimer and trimer migrations and desorptions) are computed.
    (c) A random number is obtained which determines which possible event, if any, takes place.
    (d) The grid representing the locations of atoms is updated to reflect the latest move.
4. The relaxation process (step # 3) is repeated until each adatom has on the average attempted the required number of relaxations Φ given by equation 8. If a desorption took place during the previous relaxation step, the value of Φ is updated by considering the average number of relaxations per adatom up to that point.
5. Steps #2 - #4 are repeated until the desired surface coverage is obtained.

The relaxation process listed above is a general representation of the possible events that might be taken into account in a simulation program. In the simulation results presented below, only single adatoms are allowed to migrate and desorb. Single adatoms may migrate and desorb from clusters of adatoms, but entire clusters themselves are stationary.

Evaluation of Activation Energy

To calculate the activation energy for a particluar move, a binding energy E_{as} is associated with a single bond between an adsorbed atom and the surface, and a binding energy E_{aa} is associated with each single bond between adatoms. All bond energies are assumed to be additive. All adatoms are treated equally and can migrate into any of the 26 adjacent sites which are vacant in the sub-cube. The bond strengths of the nearest-neighbor, next-nearest-neighbor and the next-next-nearest-neighbor atoms are assumed to follow a van der Waals attraction relation so that the normalized bond energies (b_{s_1}, b_{s_2}, and b_{s_3}) are 1, 0.125, and 0.037 respectively for the cubic structure.

The energy for a migration from the initial position of an atom to another position within the sub-cube is determined by the number of bonds which are broken. If the particular bond becomes stronger in the process of the move, it does not contribute to the total energy of the move; if the bond becomes broken in the process of the move, the total bond energy is added to the activation energy; if the bond is stretched ($b_{s_1} \rightarrow b_{s_2}$, $b_{s_1} \rightarrow b_{s_3}$ or $b_{s_2} \rightarrow b_{s_3}$) and thereby becomes weaker, the energy expended is the initial bond strength times a factor f, which is set to obtain the desired ratio of migration to desorption energy for a single adatom on the surface.

If the atom is no longer attached to any other atoms after the migration (*i.e.* a migration straight up with no other atoms surrounding it) or if the atom is attached with a total binding energy less than $E_{\min}$ where ($E_{\min} < E_{aa}, E_{as}$) the atom is desorbed. In this model, migration and desorption are treated equally. A desorption is a migration to a position in which the total binding energy is less than $E_{\min}$.

The probability of each move is determined by Boltzmann statistics and is given by:

$$P = \frac{\nu_0 e^{-\frac{E}{kT}}}{q} \tag{9}$$

where E is the energy of a particular move, and q is the normalization factor that represents the total energy for all possible migrations and desorptions for a single adatom on the substrate. It is given by:

$$q = e^{-4E_{me}-4E_{mc}-9E_a} \tag{10}$$

where E_{mc} is the migration energy in the direction along the diagonal, E_{me} is the migration energy in the direction parallel to an edge of the cubic lattice, and E_a is the adsorption (and therefore desorption) energy of a single atom on the substrate as used in equation 5. Due to the nature of the bond breaking model used to compute the energy of a particluar move, E_{mc} is slightly greater than E_{me} for the cubic structure. Due to the near equality of E_{mc} and E_{me}, the approximation $E_{mc} \sim E_{me} \sim E_m$ is used.

RELATION TO DIRECT-LASER WRITING

In order to relate the results of the Monte Carlo simulation to the conditions encountered during DLW, a given laser intensity and beam diameter at the surface must first be chosen. The laser modified surface temperature profile must next be determined. One way of accomplishing this is to compute the temperature profile from known laser parameters (power, beam profile, and beam diameter at the surface) and material thermal properties.

A finite difference solution to the heat equation was used to calculate a typical surface temperature profile [1,12]. The material system consisted of a silicon substrate covered with a 500Å layer of SiO_2. Only the silicon appreciably absorbs the laser light. Silicon was characterized by a temperature–dependent thermal conductivity, absorption coefficient, and index of refraction. The overlying layer of SiO_2 was characterized by a constant thermal conductivity and a constant index of refraction. Figure 1 shows the resulting surface temperature profile produced by a Gaussian TEM_{00} laser beam with a wavelength of 514.5 nm and a 2.5 μm FWHM intensity beam waist at the surface for integrated power levels ranging from 200 mW to 450 mW.

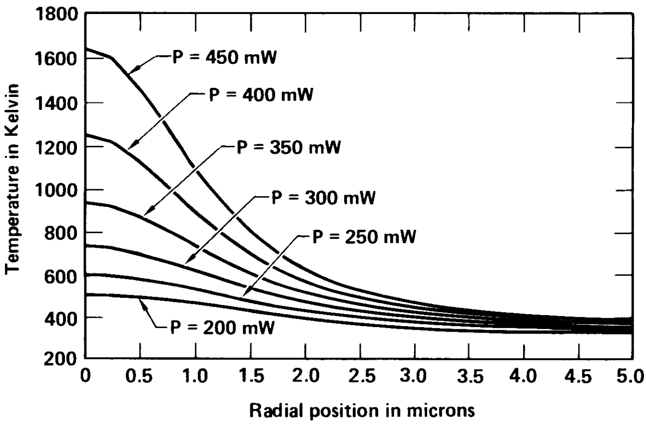

Figure 1: Calculated laser induced surface temperature profile produced by a Gaussian laser beam at a wavelength of 514.5 nm, a beam waist at the surface of 2.5 μm, and the powers specified when incident onto a 0.05 μm layer of SiO_2 on a silicon substrate.

The temperature used during the Monte Carlo simulation may now be compared to the surface temperature profile for a given laser power and beam diameter to obtain the corresponding physical location on the surface. The nucleation rate and the cluster density are thus determined as a function of time for various locations within the laser irradiated region of the surface. In essence, the Monte Carlo simulation samples a small area of the laser heated region of the surface and the thermal calculation produces the connection between the specific temperature and its corresponding location on the surface. This sampling procedure is valid as long as the average migration distance before desorption, Λ, is small compared to the size of the grid used for the Monte Carlo simulation. As can be seen, only at low temperatures < 800 K, and for large migration energies $E_m \geq 0.6$ eV, does Λ become equal or larger than the grid size used in the simulation. Fortunately, under these conditions the formation of clusters occurs almost immediately, as will be seen in the next section, and the number of atoms that migrate outside of the simulation grid is no larger than for cases when Λ is smaller than the simulation grid size.

COMPUTER SIMULATION RESULTS

For all calculations conducted, the gas pressure was taken to be 10 Torr. The migration energy E_m was set equal to 0.40, 0.45, 0.50, and 0.60 eV. $E_m \leq 0.5$ eV was used to simulate nucleation on weakly binding substrates, while $E_m = 0.6$ eV was used to represent nucleation on strongly binding substrates where nucleation does not represent much of a hindrance to thin film formation. The temperature range examined was from 600 to 1600 K, which represents typical temperatures encountered during DLW of silicon from SiH_4. Below 600 K, the dissociation rate of SiH_4 becomes so negligibly small that it need not be considered.

Figures 2 – 4 show the number of deposited atoms as a fraction of surface coverge as a function of time for various migration energies and temperatures. In Figure 2 where $E_m = 0.60$ eV, nucleation commences almost immediately and the initial thin film growth rate is limited only by the rate of silane dissociation for all T. The rate of silicon growth is seen to increase with higher temperatures in accordance with the increase in probability with which silicon atoms are generated at the surface. Under these conditions the initial thin film formation during pyrolytic deposition by DLW will commence at the center of the laser heated region of the surface where the the temperature is a maximum.

Figure 3 shows the nucleation characteristics for a migration energy of $E_m = 0.50$ eV. Here, nucleation begins rapidly for $T \leq 1200$ K. But, for $T > 1200$ K, the desorption rate of silicon adatoms dominates over the silicon adatom formation rate causing a delay in the onset of nucleation. Two plots of the nucleation characteristics at 1600 K are shown to give an indication of the statistical uncertainty in the time at which the first nucleus forms. For this migration energy, the delay in nucleation is not substantial, and the increased silicon generation rate with increasing temperature will quickly cause most of the deposited material to form at the center of the locally heated region once nucleation begins.

At even lower migration energies, such as $E_m = 0.45$ eV, the delays before nucleation commences become more pronounced even at lower temperatures, as shown in Figure 4. Under these conditions, nucleation may strongly alter the morphology of the growing film. The initial deposit of material during pyrolytic deposition by DLW with sufficiently high peak temperatures would take the shape of a volcano, where the material is deposited in a ring about the center of the laser heated region of the surface. At a migration energy $E_m = 0.40$ eV, no nucleation is observed after 10 ms of laser irradiation.

The general trend observed in this data is as follows: At and below a critical migration energy E_c (which is a function of pressure) the initial thin film formation of silicon from silane deviates from one in which an increase in the nucleation rate is associated with increased temperature, to one in which the nucleation rate is a maximum at a specific temperature, T_c. During the nucleation process, there is a constant competition between the desorption of single adatoms from the surface and the combining of adatoms

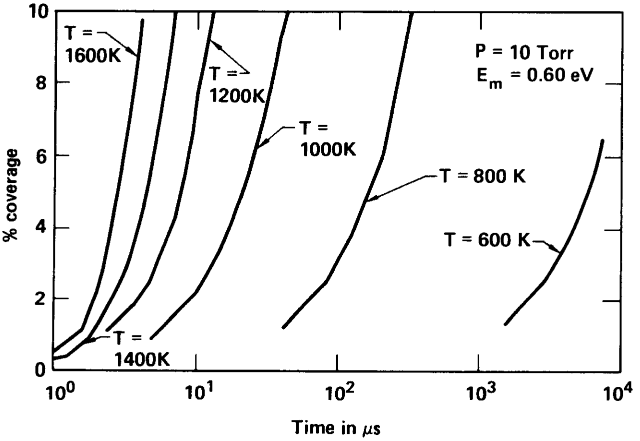

Figure 2: Surface coverage as a function of time for a migration energy $E_m = 0.60$ eV and the specified temperatures.

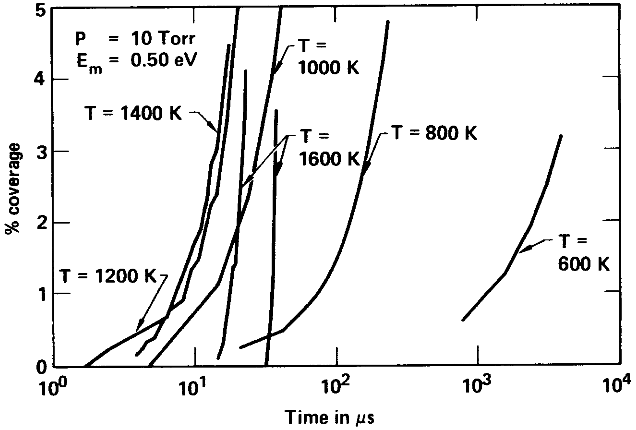

Figure 3: Surface coverage as a function of time for a migration energy $E_m = 0.50$ eV and the specified temperatures.

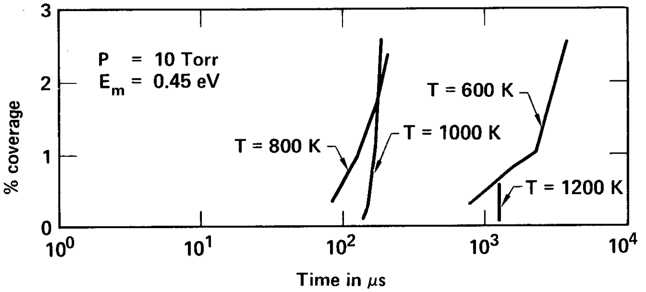

Figure 4: Surface coverage as a function of time for a migration energy $E_m = 0.45$ eV and the specified temperatures.

by migrations to form clusters. For $E_m > E_c$, adatom migration very quickly leads to cluster formation and continued growth. The cluster density is relatively large as clusters form with ease over the entire surface. For $E_m < E_c$, the competition between adatom desorption and cluster formation results in adatom desorption being dominant. This leads to a low density of growing clusters on the surface and a statistical uncertainty in the time at which cluster formation will occur. Once a nucleus does form however, the nucleus growth rate will be a maximum at the highest temperature where the flux of adatoms which can supply the growing nucleus is greatest.

During DLW, if the peak temperature of the locally heated region of the surface is greater than T_c, and $E_m \leq E_c$, the initial morphology of the deposited material will take the shape of a ring about the center of the laser heated region of the surface. Under all other conditions, ($E_m > E_c$ or both $E_m \leq E_c$ and $T_{peak} < T_c$) the initiation of the deposited material will be greatest at the center of the laser heated region of the surface.

For the cases studied, with the silane pressure is 10 Torr, the critical migration energy E_c was found to equal 0.50 eV. The migration energy of silicon on SiO_2 and Si_3N_4 is $\leq$ 0.40 eV [8], while the migration energy of silicon on silicon is $>$ 0.60 eV. Using these simulations along with the thermal profiles in Figure 1, it can be concluded that for a laser power of 450 mW and a beam waist at the surface of 2.5 μm FWHM incident onto 500Å of SiO_2 on silicon, the peak surface temperature will be near the melting temperature of silicon and initiation of the silicon deposit should produce an annulus pattern centered with respect to the incident laser beam with an inner radius of $> 1.0\,\mu$m. For the deposition of silicon onto a strongly binding surface such as silicon, the initiation of the silicon deposit should occur at the center of the laser heated region of the silicon.

CONCLUDING REMARKS

The spatial dependence of the nucleation rate and the density of growing clusters within the localized laser heated region of the surface may strongly influence the resulting morphology of silicon microstructures deposited pyrolytically by DLW. Current modeling work is further investigating the effects of the nucleation phase and subsequent growth stages on the resulting morphological structures obtained during pyrolytic deposition by DLW.

Additional work in progress is aimed toward experimentally examining the nucleation process during DLW of silicon on surfaces of Si, SiO_2 and Si_3N_4. Ultra–high vacuum conditions (2×10^{-10} Torr) are being used to prepare atomically clean surfaces of silicon. The oxidized and nitrided surfaces are then prepared *in situ*. Timed exposures of focussed Ar^+ laser radiation is directed onto the surface in the presence of silane. Resulting deposits of silicon will be subsequently examined by scanning electron microscopy and transmission electron microscopy.

ACKNOWLEDGMENTS

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

REFERENCES

[1] I.P. Herman, in Photochemical Materials Processing, edited by K.G. Ibbs and R.M. Osgood (Cambridge University Press, 1987).

[2] Y. Rytz-Froidevaux, R.P. Salathé, and H.H. Gilgen, Appl. Phys. A. 37, 121 (1985).

[3] R.M. Osgood and T.F. Deutsch, Science 227 709 (1985).

[4] D.J. Ehrlich and J.Y. Tsao, in VLSI Electronics: Microstructure Science, edited by N. Einspruch (Academic Press, New York, 1983) p.129.

[5] B.M. McWilliams, H.W. Chin, I.P. Herman, R.A. Hyde, F. Mitlitsky, J.C. Whitehead, and L.L. Wood, in Proceedings of the SPIE, edited by S. Allen (SPIE, Bellingham, Washington, 1984) 459, p. 49.

[6] L.I. Maissel and R. Glang, Handbook of Thin Film Technology, (McGraw-Hill, New York, 1970).

[7] H. Müller-Krumbhaar in Monte Carlo Methods, edited by K. Binder (Springer-Verlag, New York, 1979).

[8] W. A. P. Claassen and J. Bloem, J. Electrochem. Soc. 127, 194 (1980).

[9] J. Bloem and W.A.P. Claassen, Phillips Tech. Rev. 41 60 (1983/1984).

[10] M.K. Farnaam, PhD thesis, University of California, Berkeley, 1983.

[11] R.R.C. Farrow, J. Electrochem. Soc. 121 899 (1974).

[12] D.E. Kotecki and I.P. Herman, (to be published).

[13] B. Lewis and J.C. Anderson, Nucleation and Growth of Thin Films, (Academic Press, New York, 1978).

[14] I.P. Herman, F. Magnotta, and D.E. Kotecki, J. Vac. Sci. Technol. B. 4 659 (1986).