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# Simulation of a triode plasma-assisted chemical vapour deposition system

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## Abstract

The behaviour of a triode plasma-assisted chemical vapour deposition (PACVD) system was studied with a newly developed simulation program based upon a one-dimensional particle (cloud in cell) model. The simulations were performed with argon as process gas to focus on the behaviour of the system without having to deal with complicated plasma chemistry. The simulations show that it is possible to control the production (and transport) of reactive species and the ion bombardment independently using the freedom to choose the total pressure, the r.f. amplitude and the d.c. voltage. In combination with these simulations a number of experiments were done where TiN was deposited on molybdenum substrates. The surface topology of these coatings, as analysed with atomic force microscopy, changes with increasing pressure from 'egg'-like to columnar.

**Keywords:** PACVD; PIC; CIC; TiN; AFM

## 1. Introduction

The role of a plasma in plasma-assisted chemical vapour deposition (PACVD) can be divided into three parts, namely (1) production of reactive species (radicals and ions), (2) transport of these species to the substrate and (3) assistance to surface reactions. In an r.f. system it is in principle possible to control these three tasks by varying the pressure, the r.f. power and the frequency [1]. It is, however, not simple to change the frequency, so we are left with only two parameters to control three phenomena. Changing the standard diode r.f. parallel plate configuration to a triode system by adding a d.c. electrode yields an extra degree of freedom to influence the deposition conditions. Results on the deposition of TiN and Al<sub>2</sub>O<sub>3</sub> with a triode system have already been reported [2], showing excellent adhesion of the layer on the substrate.

We have modelled a parallel plate r.f.-d.c. triode plasma with a one-dimensional particle (cloud in cell (CIC)) model to study the behaviour of our experimental triode PACVD system. Argon was used as the processing gas since we were interested in the behaviour of the system itself and not in plasma chemistry. The set-up of the simulated system corresponds to our experimental triode PACVD system. Fig. 1 shows schematic drawings of the PACVD system and of the one-dimensional model of the simulations. The difference in area of the driven electrodes and grounded electrode in the experimental scheme is not taken into account in the model.

## 2. Particle model

Electrostatic one-dimensional particle models are a proven technique to simulate low density r.f. plasmas [3,4]. In a particle model the Boltzmann transport equation and the Poisson equation are solved by following trajectories in  $v-x$  phase space. A set of so-called 'superparticles', representing all charged particles of the plasma, are followed with a timestep loop.

The numerical cycle starts with collecting the charge  $q$  of the particles. In the CIC approach the particles are assumed to be clouds of width  $\Delta x$  and height  $q/\Delta x$ . The charge of the particle is assigned to its two nearest gridpoints corresponding to the overlap of the gridcell and the cloud. The collected charge is used to calculate the electric field which in turn is used to move the particles. The field at the position of the particles is interpolated from the nearest gridpoints using the CIC procedure. This prevents the occurrence of self forces [5]. The CIC procedure has a smoothing effect and reduces fluctuations that arise due to the discretization. After each timestep the particles are assumed to collide if their collision probability is larger than a random number  $z$ ,  $z \in [0,1]$ .

## 3. Simulations

The simulated parallel plate triode system has a capacitively coupled middle r.f. electrode, a top d.c. and

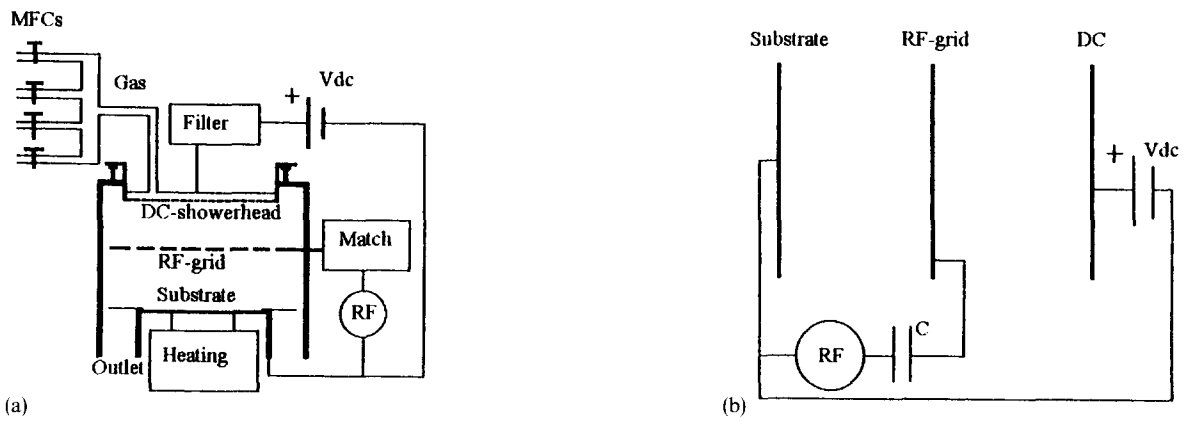


Fig. 1. (a) A schematic drawing of the PACVD system used. The upper electrode is biased with a positive d.c. voltage. The r.f. source is capacitively coupled to the middle electrode. (b) A schematic drawing of the one-dimensional model of the simulations.

a lower grounded electrode. The distance between the outer electrodes is 6 cm and their area is 26 cm<sup>2</sup>. The collision cross-sections for electron-neutral (elastic, excitation and ionizing collisions) and ion-neutral collisions (scattering and charge exchange) used in the simulations are plotted in Fig. 2.

After an ionizing collision a new electron and ion are introduced. The energy of the neutral and the ionizing

electron minus the ionization energy (15.7 eV) is divided over the three particles. In the case of excitation the electron energy is reduced by the excitation energy (11.6 eV) and a factor  $\Delta E(\chi) = 2E(1 - \cos(\chi)m_e/m_a)$  where  $\chi$ ,  $m_e$  and  $m_a$  are the scattering angle and the electron and neutral mass respectively. The energy of an electron after an elastic collision is reduced by  $\Delta E(\chi)$  and of a scattering ion by  $\frac{1}{2}E(1 - \cos(\chi))$ . Charge

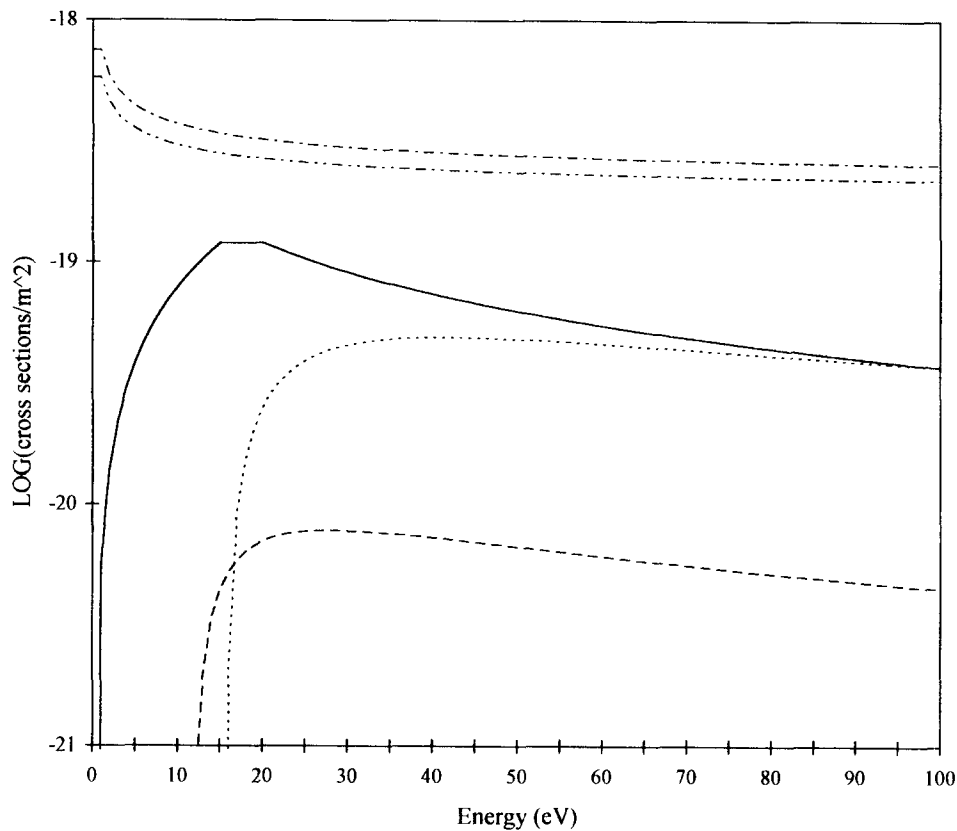


Fig. 2. Cross-sections for binary collisions used in the simulations. — Scattering; --- excitation; ... ionizing; -.-.- scattering ions; - - - charge exchange.

exchange collisions are included by choosing an energy from a 400 K thermal distribution for the colliding ion. Secondary electrons are released from the electrodes due to arriving ions with a probability of 0.1.

The calculations were done for pressures from 13 to 133 Pa. The amplitude of the 13.56 MHz r.f. supply was varied from 100 to 150 V and the d.c. voltage from 0 to 300 V.

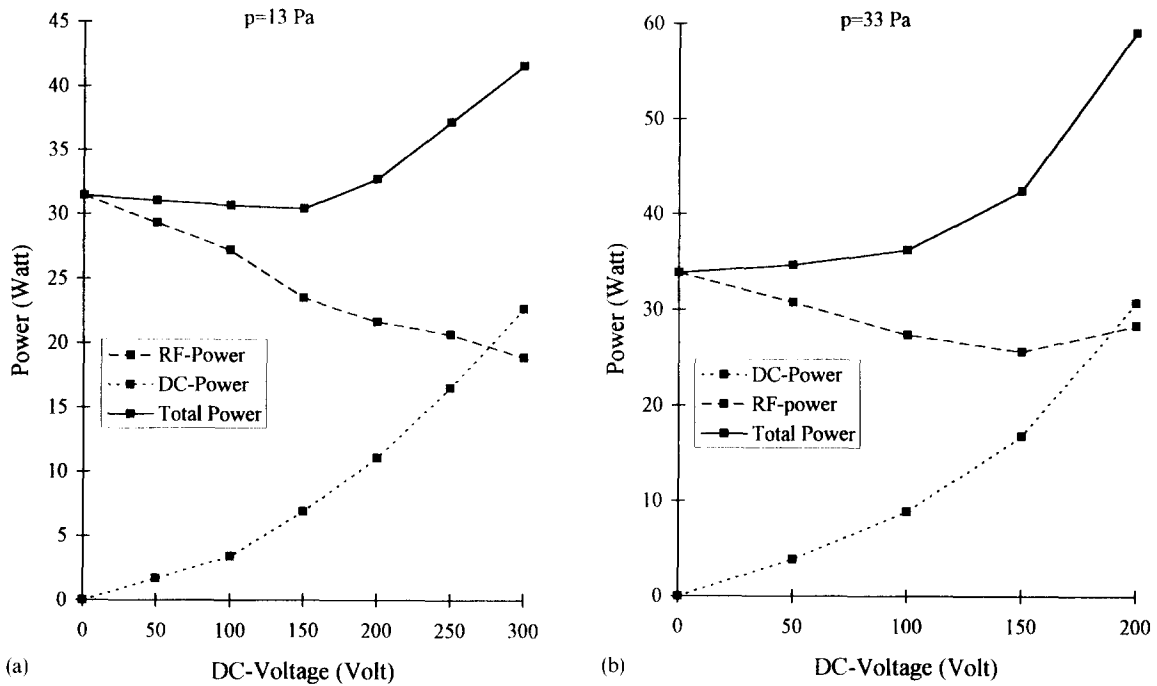


Fig. 3. The absorbed r.f., d.c. and total power as a function of the applied d.c. voltage at an r.f. amplitude of 125 V and a pressure of (a) 13 Pa and (b) 33 Pa.

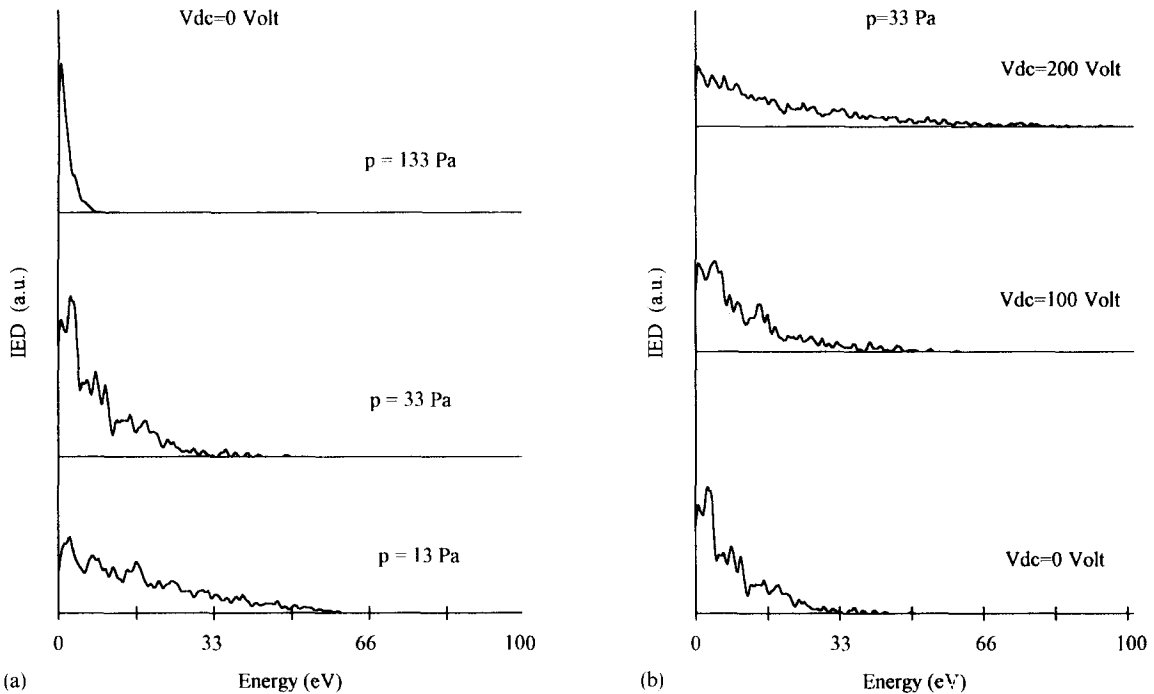


Fig. 4. The calculated ion energy distributions at the grounded electrode. (a) From bottom to top:  $p = 13, 33$  and  $133$  Pa with an r.f. amplitude of 125 V and zero d.c. voltage. (b) From bottom to top:  $V_{dc} = 0, 100$  and  $200$  V with an r.f. amplitude of 125 V and pressure of 13 Pa.

**4. Deposition experiments**

TiN coatings were deposited on polished molybdenum with a substrate temperature of 500 °C monitored by thermocouples. The gas mixture used was H<sub>2</sub>/N<sub>2</sub>=1/4 and 1% TiCl<sub>4</sub>. Argon was used as carrier gas for the

TiCl<sub>4</sub>. The coating process consisted of three steps. First the samples were cleaned for 1 h with an argon-hydrogen plasma with a gas ratio H<sub>2</sub>/Ar=1/3, 250 W r.f. power, 200 V d.c. voltage and a total pressure of 13 Pa. During the second 'nitriding' step the samples were exposed to the coating conditions without TiCl<sub>4</sub> at a pressure of

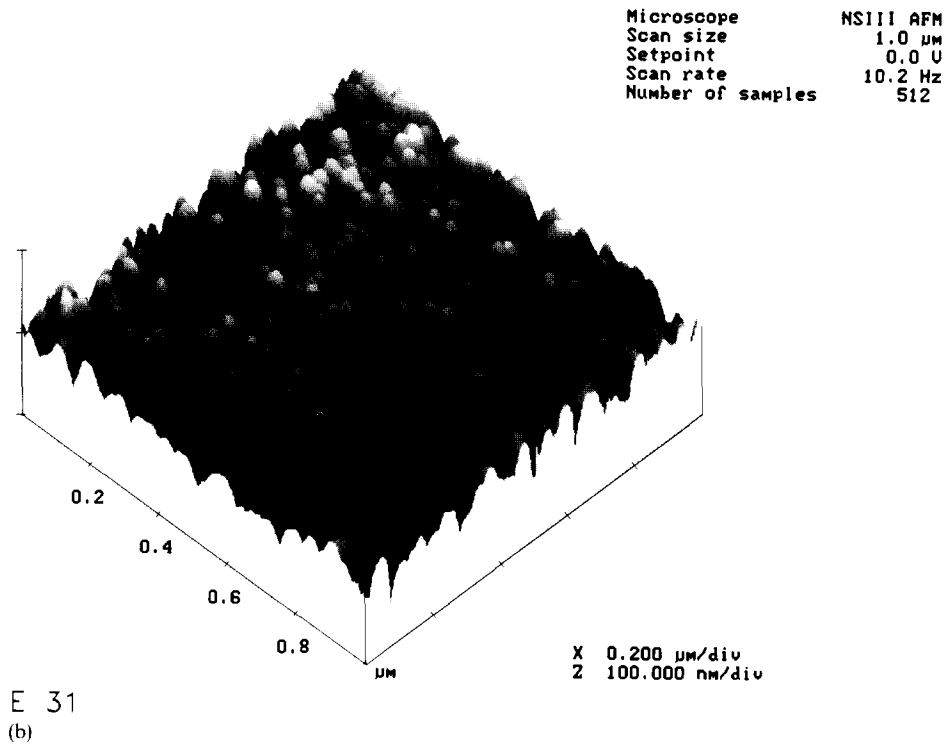
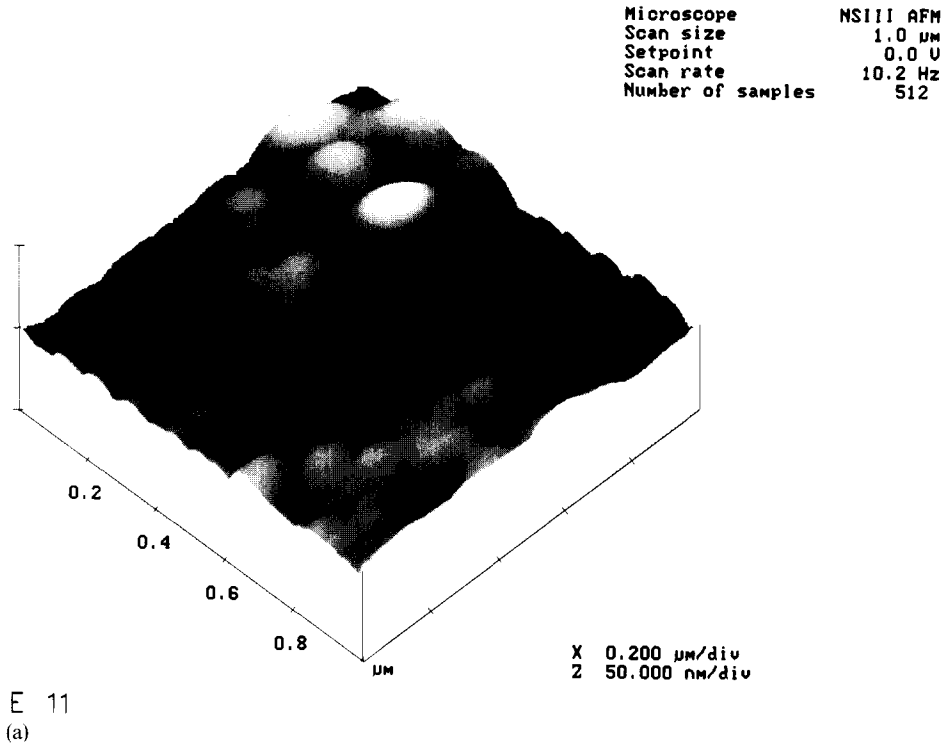
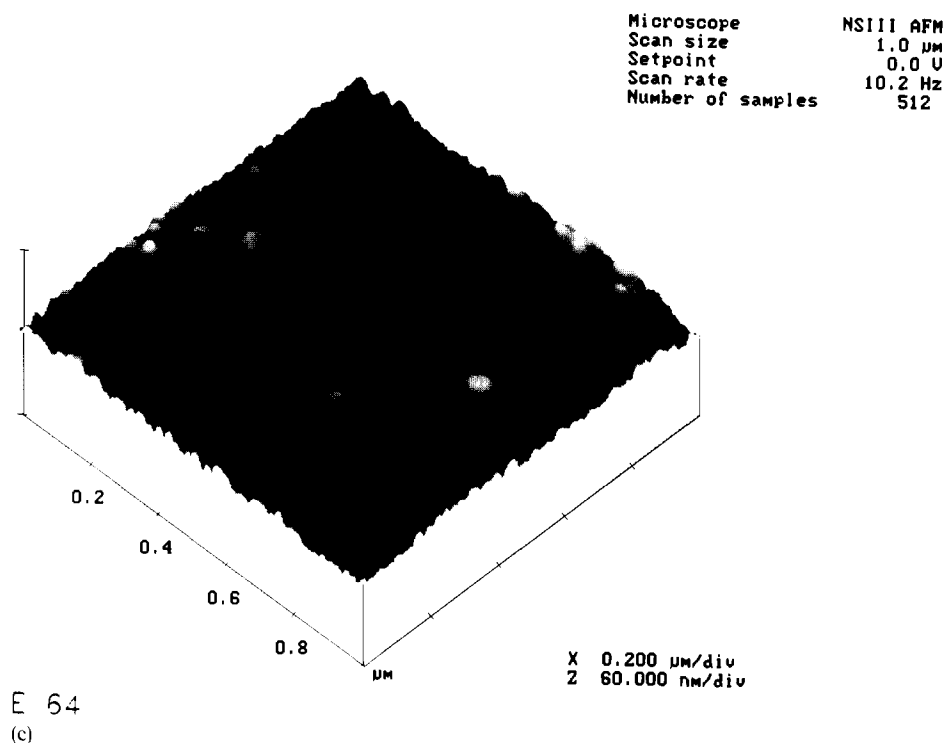


Fig. 5. Atomic force microscopy pictures of the surface of TiN layers deposited on molybdenum at pressures of (a) 13, (b) 33 and (c) 67 Pa.



13–266 Pa and an r.f. power of 200 W. The coating process started when after 1 h of nitriding the  $\text{TiCl}_4$  was introduced. The d.c. voltage was adjusted (50–100 V) to keep the average r.f. voltage (bias) zero. After 3 h the plasma was shut off. The samples were cooled down under vacuum.

## 5. Simulation results

The dependence of the absorbed power as a function of the applied d.c. voltage is plotted in Fig. 3(a) and (b) for pressures of 13 Pa and 33 Pa respectively. The r.f. amplitude was 125 V. Two regimes can be identified, namely at a d.c. voltage below and above the r.f. amplitude. Below the r.f. amplitude an increase in the d.c. voltage leads to an increase in the d.c. power and a corresponding decrease in the r.f. power; the total absorbed power is constant. The increase in the total power above the r.f. amplitude becomes more important at higher pressures (up to 133 Pa) but the two regimes continue to exist. In the first regime the plasma can be considered as an r.f. plasma. The d.c. voltage changes the plasma potential but not the production of ions and excited species considering the constant total power.

The calculated ion energy distribution functions (IEDF) depend on the potential difference between the electrode and the plasma and the total pressure. Fig. 4 shows six IEDFs calculated at (a) different pressures and (b) different d.c. voltages. An increase in the pressure or

a decrease in the d.c. voltage leads to a decrease in the energy of the arriving ions.

From this effect and the absorbed power behaviour we conclude that it is possible to control the production (and transport) of reactive species and the ion bombardment on the substrate by choosing a correct setting of the triplet pressure, r.f. amplitude and d.c. voltage.

## 6. Deposition results

The surface topology of the TiN coatings was analysed using atomic force microscopy (AFM). Fig. 5 shows three AFM pictures of the surface of TiN coatings deposited at pressures of 13, 33 and 67 Pa. The pictures indicate that the size of the surface structures increases with decreasing pressure. At 13 Pa the surface contains 'egg'-like structures while at 67 Pa columnar structures are observed.

The increase in structure size with decreasing pressure can be understood as an ion bombardment-induced surface diffusion effect assuming that the growing process itself is pressure independent in the applied pressure range. This interpretation is supported by the observed strong dependence of the calculated IEDF on the pressure.

## 7. Conclusions

From the simulation results it is clear that with the described triode system the production (and transport)

of reactive species and the ion bombardment on the substrate can be controlled independently by choosing a certain setting of the total pressure, r.f. amplitude and d.c. voltage. The importance of this possibility is underlined by the experimental results where the surface topology of the deposited layers showed significant modifications when the pressure is changed. Since the structure of a coating is a combined result of growth and diffusion mechanisms this control is a necessary key to 'engineer' the deposited layer.

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