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Micropatterning of small molecular weight organic semiconductor thin films using organic vapor phase deposition

Max Shtein

Department of Chemical Engineering, Center for Photonics and Optoelectronic Materials (POEM),
Princeton University, Princeton, New Jersey 08544

Peter Peumans

Department of Electrical Engineering, Center for Photonics and Optoelectronic Materials (POEM),
Princeton University, Princeton, New Jersey 08544

Jay B. Benziger

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

Stephen R. Forrest^{a)}

Department of Electrical Engineering, Center for Photonics and Optoelectronic Materials (POEM),
Princeton University, Princeton, New Jersey 08544

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Using both analytical and experimental methods, we show that micron scale patterned growth of small molecular weight organic semiconductor thin films can be achieved by the recently demonstrated process of organic vapor phase deposition (OVPD). In contrast to the conventional process of vacuum thermal evaporation, the background gas pressure during OVPD is typically 0.1–10 Torr, resulting in a molecular mean free path (mfp) of from 100 to 1 μm , respectively. Monte Carlo simulations of film growth through apertures at these gas densities indicate that when the mfp is on the order of the mask-to-substrate separation, deposit edges can become diffuse. The simulations and deposition experiments discussed here indicate that the deposited feature shape is controlled by the mfp, the aperture geometry, and the mask-to-substrate separation. Carefully selected process conditions and mask geometries can result in features as small as 1 μm . Furthermore, based on continuum and stochastic models of molecular transport in confined geometries, we propose the *in situ* direct patterning growth technique of organic vapor jet printing. The high pattern definition obtained by OVPD makes this process attractive for the growth of a wide range of structures employed in modern organic electronic devices. © 2003 American Institute of Physics. [DOI: 10.1063/1.1557783]

I. INTRODUCTION

Organic-based electronic devices such as organic light emitting diodes (OLEDs), thin film transistors, and photovoltaic cells, have gained tremendous attention of researchers during the last decade.^{1–4} These devices typically consist of thin (<100 nm) films of either conjugated polymers⁴ or aromatic molecules,^{2,3} each requiring a different deposition method.^{1,4–6} In many device applications, the films are deposited on substrate surfaces 1–100 cm across, while the active device area must be patterned with a lateral resolution ranging from the nano- to the micrometer scales. Generally, for simple devices such as small monochromatic active and passive matrix displays, only the metal contacts need to be patterned, since the lateral electrical conductivity of the organic films is low.⁷ However, for more complex device structures such as full-color displays, the active organic layers must be patterned as well.

Polymer-based devices have been fabricated using several different techniques.^{4,8–14} The polymer solution can be spin-coated onto the substrate and patterned after the

deposition.⁴ Conventional photolithography may be used, but the active polymer layer should be insoluble in the photoresist solvent.^{9,11} The patterning of polymers has also been demonstrated using a variety of stamp and transfer methods,^{15–17} as well as *in situ* patterning of polymer-based devices by ink-jet printing.^{9,10,14} Furthermore, in deposition of multilayer structures, the same solubility considerations apply.

Since small-molecule organics often have poor solubility in common solvents, different thin-film deposition methods are generally employed,^{5,18,19} the most common being vacuum thermal evaporation (VTE). Here, the prepurified organic source materials are evaporated from heated containers in vacuum onto substrates placed directly above the sources, allowing for precise control of the deposition of multilayer structures.³ Vacuum deposition can also follow the processes described above to obtain hybrid polymer–small molecule structures. To pattern the active organic layers, a shadow mask is placed in close proximity to the substrate.¹⁸ Because the process is carried out in vacuum, the organic molecules do not suffer collisions *en route* to the substrate, resulting in the line-of-sight deposition of sharply defined features.

^{a)} Author to whom correspondence should be addressed; electronic mail: forrest@ee.princeton.edu

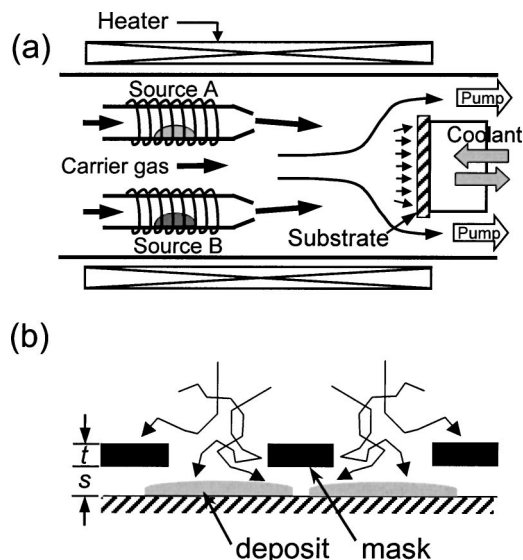


FIG. 1. (a) Conceptual schematic of the OVPD process. The individually heated organic vapors are transported by a carrier gas through a hot wall chamber toward a cooled substrate, where selective physisorption of the organic molecular species occurs. (b) The diffusive transport of organic molecules through a background of the carrier gas results in diffuse deposition profiles, when transported through a mask of thickness t at a distance s from the substrate.

Recently, the technique of organic vapor phase deposition (OVPD) was introduced as an alternative to VTE growth of small-molecular weight organic thin films, heterostructures, and devices.^{20–24} In OVPD, a hot, nonreactive carrier gas is used to transport an organic vapor toward a cooled substrate onto which the organic materials condense, as shown in Fig. 1(a). The method affords precise control over the layer thickness and dopant concentration, while increasing the materials use efficiency over that obtained by VTE.²³ Dilution of the organic in an inert carrier gas results in molecules suffering many collisions before reaching the substrate, reducing the molecular mean free path (mfp) limiting both pattern size and resolution. Since these collisions may lead to the deposition of patterns with diffusely-defined edges [see Fig. 1(b)], molecular transport through small apertures must be understood to control film patterning for advanced, micron or sub-micron scale electronic device applications.

This work reports experiments together with computer simulations to examine patterned organic thin film deposition with micron-scale resolution. A connection is made between continuum-based models of OVPD on the size scale of the reactor vessel, and the particle-based models for deposition of micron-scale features. We find that resolutions of $\sim 1\ \mu\text{m}$ can be achieved, with the deposit shape controlled by the mask-to-substrate separation, mask aperture shape, and reactor pressure during deposition. Based on our understanding of OVPD, we propose a *in situ* direct patterning approach—organic vapor jet printing (OVJP)—wherein jets of hot carrier gas containing organic vapors impinge on cooled substrates, resulting in deposit shapes similar to those obtained by OVPD through apertures.

This article is organized as follows: In Sec. II we summarize our previous analysis of material transport during OVPD growth of unpatterned thin films. Then, the transport mechanisms of VTE and OVPD are contrasted in the context of *in situ* patterning of films by evaporation through apertures. Section III describes Monte Carlo simulations of OVPD growth of organic films through apertures. Pattern evolution is considered as a function of molecular mean free path and aperture geometry, with the simulation results discussed in Sec. IV. Patterned film deposition experiments are described in Sec. V, with the results compared to simulations in Sec. VI. OVJP is discussed in Sec. VII, along with a preliminary analysis of the process using Monte-Carlo simulations and finite element techniques. We conclude with a summary of our findings in Sec. VIII.

II. THEORY

A. Transport regimes for organic film growth

The process of OVPD is illustrated schematically in Fig. 1(a). This technique proceeds by evaporation of a molecular organic source material into a stream of a hot inert carrier gas, which transports the molecules toward a cooled substrate where selective physisorption occurs.^{20,21,23} The deposition chamber is maintained above the equilibrium condensation temperature of the organics, while the substrate temperature is kept low to produce amorphous thin films,^{21,23} or is elevated for the growth of crystalline films.^{20,24} Layer thickness control can be achieved either by means of a mechanical shutter positioned over the substrate, by regulating carrier gas flow, or by a combination of both. By maintaining all surfaces of the deposition system except the substrate above the condensation temperature, organic materials are not deposited onto the reactor wall, and hence materials use efficiency is kept high.

The rate of organic film growth, the doping concentration, and film uniformity depend on the deposition conditions used.²³ Film growth can be limited by the supply of organics into the deposition chamber, or by the rate of physisorption on the substrate. To efficiently transport the vapor out of the source region, a minimum pressure drop of ~ 0.1 Torr from the source to the substrate is necessary. Below this value convective flow cannot be established, resulting in poorly regulated Knudsen-type diffusion of organics from the source to the substrate.^{25,26} By increasing the source pressure, the carrier gas velocity increases and the transport from the evaporation to the deposition regions becomes faster, regulated more precisely by the volumetric carrier gas flow rate $\dot{V}$. If the convective flow of the carrier gas is preserved in the deposition zone, a stagnant boundary layer of thickness δ is established, across which the organic molecules diffuse prior to physisorption. As shown previously, in this flow regime the film deposition rate, r_{dep} , is diffusion-limited²³

$$r_{\text{dep}} = D_{\text{org}} \frac{C_{\text{org}}}{\delta}, \quad (1)$$

where C_{org} is the concentration of the organic species, D_{org} is its gas phase diffusivity, and δ is the boundary layer thick-

ness. However, the variation of r_{dep} with deposition conditions is nontrivial, with the parameters in Eq. (1) depending on the hydrodynamics inside the deposition chamber. For example, D_{org} varies inversely with the total chamber pressure P_{dep} ,²⁷ while δ varies inversely with the square root of the carrier gas flow rate.²⁸ Typically, if the supply rate of organics into the deposition chamber is constant, decreasing P_{dep} (<10 Torr) helps maintain a reasonably high r_{dep} (e.g., $1-10 \text{ \AA/s}$).

To further investigate the hydrodynamics of the deposition process, the flow patterns in the experimental OVPD reactor were modeled using finite element methods.²⁹ The Navier–Stokes equations for flow were solved numerically for the simplified deposition geometry shown in Fig. 2(a). The pressure drop from the source to the substrate is sufficiently small ($<10\%$) to assume incompressible flow, while the concentration of the organic species ($<1\%$) is insignificant in affecting the hydrodynamics of the carrier gas. The physical parameters and boundary conditions were matched to those encountered in previous deposition experiments.²³ Figure 2(b) shows a map of the flow streamlines and a temperature color map in the deposition chamber for a simulation using a Reynolds number of $\text{Re} \sim 10$, similar to deposition conditions considered in this study. The distribution of the organic species in the flow field is shown as a concentration color map in Fig. 2(c). Both images help to visualize the existence of the hydrodynamic and the concentration boundary layers near the substrate. The boundary layer in Fig. 2(b) leads to diffusion-limited transport of organics to the substrate, where the deposition driving force is the concentration gradient apparent in Fig. 2(c).

This diffusion-limited deposition implies that the molecular velocities are completely randomized near the substrate. As will be discussed below, this mode of transport is dramatically different from vacuum thermal evaporation, where the molecular source-to-substrate transport is ballistic. This also implies a difference between VTE and OVPD in the film patterning mechanism. The distinction is due to the scale of the molecular mean free path

$$\text{mfp} = \frac{k_B T}{\sqrt{2} \cdot \pi d^2 \cdot P_{\text{dep}}}, \quad (2)$$

where k_B is the Boltzmann constant, T is the gas temperature, and πd^2 is the effective collision area for two molecules, each having a diameter d . At 25°C and a typical VTE chamber pressure of 10^{-6} Torr, the $\text{mfp} > 50 \text{ cm}$ for nitrogen ($d = 3.25 \text{ \AA}$), while in OVPD at $P_{\text{dep}} = 0.1-10$ Torr, $\text{mfp} \sim 100-1 \text{ }\mu\text{m}$. Thus, while the continuum analysis helps visualize transport on the scale of the chamber dimension, to predict the OVPD growth of patterns whose size and resolution are on the order of the mfp, the molecular nature of transport near the substrate must be considered.

The Knudsen number Kn , is frequently used to characterize different transport regimes in terms of the ratio of the mfp to the critical apparatus dimension, L ($\text{Kn} = \text{mfp}/L$).³⁰ The dimension L is typically chosen such that Kn represents the ratio of intermolecular to molecule-wall collision frequencies. In OVPD of nonpatterned films, $L \approx 1-100 \text{ cm}$

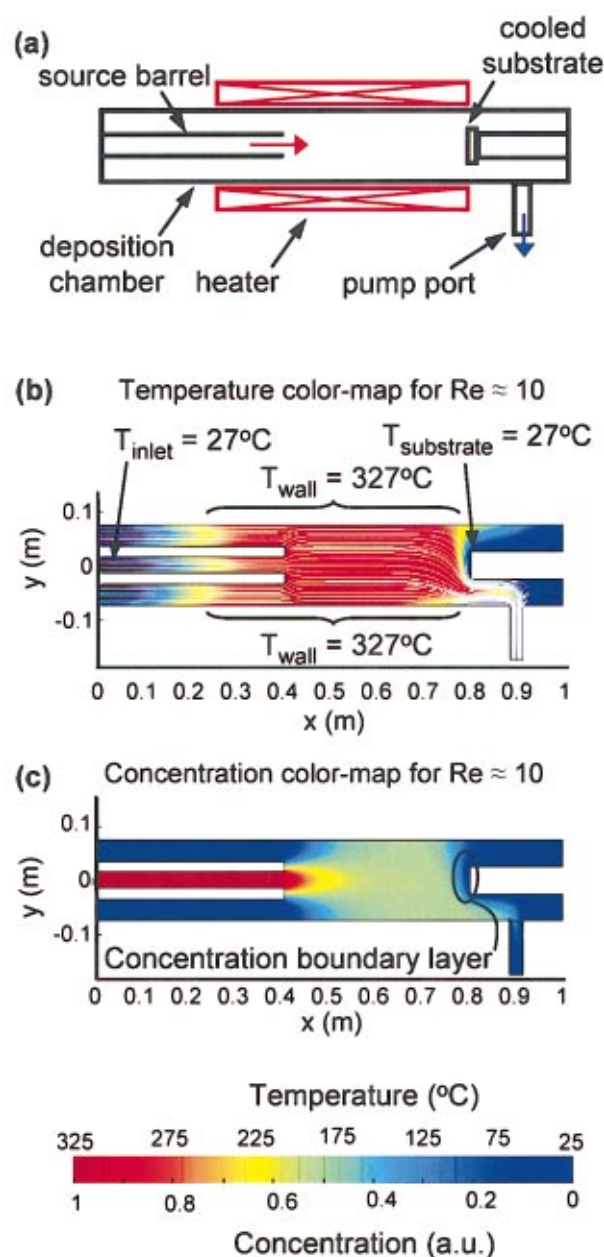


FIG. 2. (Color) (a) Geometry of an OVPD reactor used in the numerical modeling of flow, temperature and deposition using methods discussed. (b) Results of numerical solution of the Navier–Stokes equations for the geometry in (a), where carrier gas is introduced in the barrel at a Reynolds number of $\text{Re} \sim 10$; the flow field is indicated by the streamlines, while the temperature distribution is shown by the color-map. The flow of the gas around the substrate creates a stagnant boundary layer, evidenced by the flow field. (c) Concentration distribution color-map of the organic species carried by N_2 from (b). The concentration boundary layer near the substrate follows the hydrodynamic boundary layer from (b).

(approximately that of the chamber diameter), while $\text{mfp} \approx 1-10^3 \text{ }\mu\text{m}$. Thus, for OVPD, $\text{Kn} \ll 1$, and continuum models can be used to understand film deposition. However, when film patterning is considered, the apparatus dimension must account for the aperture geometry. In this case, L is $1-100 \text{ }\mu\text{m}$, and $0.1 < \text{Kn} < 10$ for much of the useful deposition pressure range. In this case, the discrete molecular nature of the gas flow cannot be ignored.^{25,26}

Molecular flow through small channels has been previ-

ously studied using several techniques. For example, Guevremont and co-workers³¹ experimentally analyzed the shape of molecular fluxes from collimated effusive beam sources and the nature of gas transport within small-diameter capillary arrays. The beam shape was obtained by translating the beam across a skimmer, behind which a mass spectrometer collected the molecular flux. Channel conductance was studied for a range of Kn. The sources consisted of arrays of capillaries, whose individual diameters were as small as 10 μm . Although the mfp in their experiments ranged from 1 to $10^4 \mu\text{m}$, thereby covering a wide range of Kn, the overall diameter of the source array and hence, the beam width, was $>1 \text{ mm}$. Furthermore, no substrate was present to affect the beam, leading to more collimated fluxes than are possible with the isotropic velocity distribution present in pure diffusion through apertures. Thus, although the beam profiles resemble the pattern shapes obtained by OVPD, those results are not strictly applicable.

In contrast to the case where collimated beams are employed, transport of species to the substrate is often diffusive during reactive ion etching and physical vapor deposition. Semiconductor electronic device processing typically involves etching of, and deposition in holes and trenches of submicron dimensions.³² The processing pressure, however, is typically such that $\text{Kn} \approx 1$, similar to OVPD growth of patterned films. Studies reveal that Monte Carlo type simulations can accurately predict deposition and etch rates when coupled with the proper surface reaction models,^{33,34} suggesting their applicability to micropatterning of thin film deposits by OVPD. Models of OVPD growth, however, are greatly simplified by the absence of gas-phase and surface reactions, and re-evaporation of adsorbed species that must be considered for reactive deposition or etching.³⁵

B. Film patterning by vacuum thermal evaporation through a shadow mask

Vacuum thermal evaporation has traditionally been used to deposit molecular organic layers for electronic device applications. A typical deposition geometry is illustrated in Fig. 3(a). Here, the organic material is evaporated from a resistively heated cell onto a substrate positioned directly above it. In deposition of doped films, two or more materials are co-evaporated with the sources separated by a baffle, as shown in the figure. The substrate is placed within a distance less than mfp from the source, and the transport of organic molecules from the source to the substrate is ballistic.

For patterned film deposition, a shadow mask is placed at a distance s in front of the substrate [see Fig. 3(b)]. For a mask aperture with straight walls, thickness, t , and using a source of width l centered on the aperture axis, the shape of the deposit is approximately trapezoidal, with the width of the edge taper and, hence, the resolution limit ρ given by

$$\rho \approx \frac{(s+2t)l}{2h}. \quad (3)$$

Here, w is the aperture width, and h is the source-to-mask separation [see Fig. 3(b)]. Typical values for s , t , and w might be 10, 70, and 100 μm , respectively, while l is 1 cm, and h is 50 cm, yielding $\rho \approx 2 \mu\text{m}$.

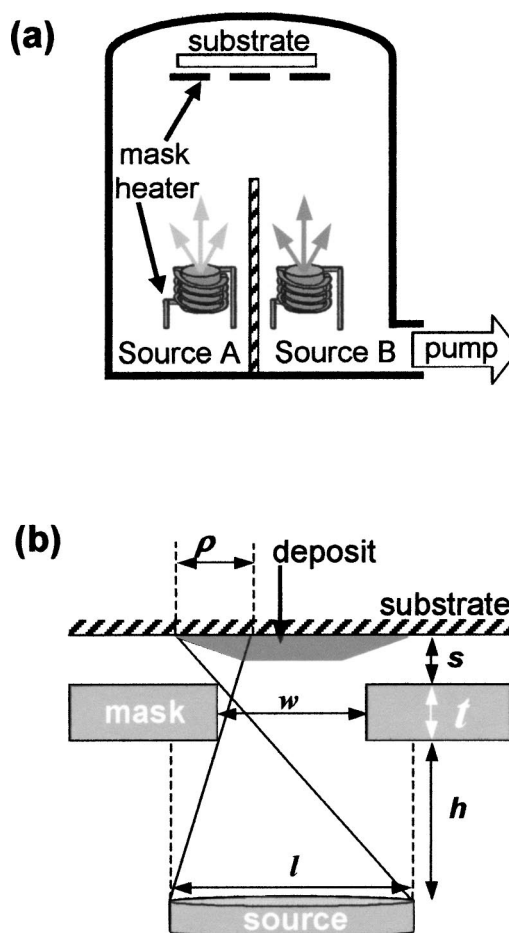


FIG. 3. (a) Vacuum thermal evaporation involves subliming the organic source material in a vacuum, ejecting the molecules along ballistic paths to the substrate positioned directly above. At 10^{-6} Torr, the molecular mean free path is $\sim 1 \text{ m}$, setting the limit of the ballistic trajectories. (b) Schematic of vacuum deposition through a shadow mask. Due to the finite thickness of the mask, t , mask-to-substrate separation, s , and the diameter of the source, l , the resulting deposit has a trapezoidal profile, with the width of the edge taper, ρ , setting the pattern resolution limit.

Layer thickness control is achieved using a mechanical shutter positioned between the source and the substrate. The thickness control generally decreases with the film deposition rate, which is proportional to the evaporation rate r_v , given by

$$r_v = A \cdot \exp\left(\frac{-\Delta H^{\text{evap}}}{RT_{\text{source}}}\right). \quad (4)$$

Here, A depends on the source shape and other system geometry-dependent factors, ΔH^{vap} is the enthalpy of evaporation, and R is the universal gas constant. When simultaneously depositing two or more materials, small fluctuations in the individual source temperatures T_{source} can result in substantial variations of the component ratios in the deposited film.

C. Film patterning by OVPD

As discussed in Sec. II A, the carrier gas flow in OVPD creates a hydrodynamic boundary layer at the substrate ranging from 1 mm to $\sim 5 \text{ cm}$ in depth, across which the organic

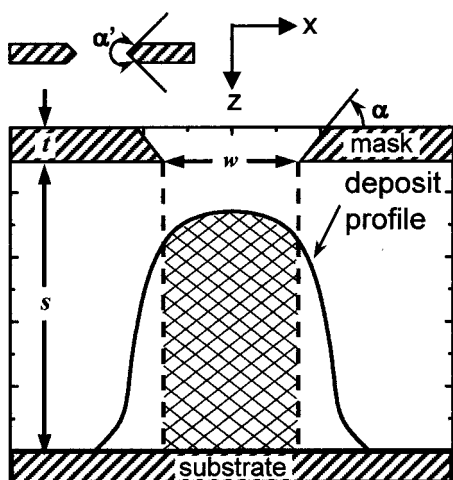


FIG. 4. The bell-shaped profile of a deposit obtained by OVPD through a shadow mask. The mask aperture width, mask thickness, and mask-to-substrate separation are denoted by w , t , and s , respectively. The deposit shape factor, η , is the ratio of the shaded area of the deposit to its total cross section. The aperture wall profile is characterized by the angle α (or α' for biconical apertures).

species diffuse prior to condensation. The organics are a minority species ($< 1\%$ molar concentration) and collide with the carrier gas molecules en route to the substrate, as indicated in Fig. 1(b). The resulting deposition pattern is bell-shaped, substantially different from the trapezoidal pattern typically obtained by VTE.

Continuum-based analysis is not accurate in this transport regime, since the intermolecular collision frequency is on the order of that between the molecules and aperture walls. Understanding diffusion within the boundary layer provides insight into why patterned deposition should be modeled stochastically. Consider the geometry depicted in Fig. 4, where the mask of thickness t and aperture of width w is separated from the substrate by distance s . For isotropic diffusion, the width of the deposit base will increase with s . That is, the longer it takes for a molecule to diffuse to the substrate, the longer it will take (by the same amount) for it to diffuse laterally. The mutual cancellation of these rates will result in identical patterns at different pressures, which is not the observed experimental trend. Moreover, in the continuum assumption, the pattern formation does not depend on the shape of the aperture above the edge closest to the substrate, which is again contrary to experiment. Due to the discrete nature of transport at very low pressure, some collimation of flux through the aperture must occur when the organic molecules condense on the aperture sidewall.

As a means for quantifying pattern shape, we define the shape factor η , which is equal to the area bound by $-w/2 < x < w/2$ (the cross-hatched region in Fig. 4) divided by the total deposit cross-sectional area. Then $\eta = 1$ for a rectangular deposit, decreasing as the deposit becomes increasingly bell shaped. For example, a deposit shaped as a Gaussian distribution, with half width $w/2$, will have $\eta \approx 0.67$. In analyzing the effects of aperture geometry on the deposited feature shape, we also consider the fraction, f , of molecules lost by deposition on the side of the mask facing the substrate,

and on the aperture walls. Then, the deposition efficiency is simply $\varepsilon = 1 - f$.

III. MONTE CARLO SIMULATION OF DEPOSITION THROUGH APERTURES

To avoid the shortcomings of the continuum approximation, we have modeled the dynamical deposition process employing Monte Carlo (MC) simulations. The objective of the simulations was to examine the trends in deposit shape as functions of process parameters such as the deposition pressure, temperature, molecular diffusivity, mask geometry, and mask-to-substrate spacing. The MC model allows the variation of the mfp directly, tracking the random path of a molecule as it diffuses through a background of carrier gas in the vicinity of the substrate. For simplicity, the molecular sticking probability on the substrate and mask surfaces is assumed to be unity, which is usually valid for typical multi-ring aromatic semiconductor molecules and substrate temperatures ~ 300 K. Generally, under OVPD growth at $T = 250^\circ\text{C}$, the vapor pressure of the organics is in the milli-Torr range,^{23,36,37} while the background carrier gas pressure is on the order of 0.01–10 Torr, allowing for a gradient in the organic vapor concentration at a relatively constant total pressure. In this case, organic–organic collisions are rare except at very high deposition rates where gas phase nucleation can occur.²³ Hence the model is valid only for low-to-moderate (50 Å/s) film deposition rates.

The rate of molecular transport in gases due to a concentration gradient is characterized by the diffusivity D ²⁵

$$D = \frac{1}{3} \bar{u} \cdot \text{mfp}, \quad (5)$$

where $\bar{u}$ is the molecular mean thermal velocity. Since the organic vapors consist of molecules that have collision diameters greater than 10 Å and are geometrically and energetically more complex than the hard sphere atoms of kinetic theory, molecular dynamics simulations should be used for an accurate estimation of the mfp. However, since this study is concerned with the dependence of trends in pattern evolution on process parameters, simple kinetic theory equations are sufficient for the analysis.

The Monte Carlo simulation proceeds as follows. The computational space is divided into an $x-z$ grid extending infinitely in the y direction (see Fig. 4 for definition of the coordinate space). The purpose of the grid is to locate the substrate and mask surfaces, and track changes in the thickness of the deposits. A spherical “test organic molecule” is assigned a random initial location (x_0, y_0, z_0) inside the boundary layer and above the mask. A random initial direction is then chosen, and the molecule travels a distance $r = [(x_1 - x_0)^2 + (y_1 - y_0)^2 + (z_1 - z_0)^2]^{1/2}$, where (x_1, y_1, z_1) is its new location. Molecules escaping the boundary layer are reflected back toward the substrate. The distance r is the minimum of the grid size, or $\text{mfp}/10$. The probability of collision, P_{coll} , with a carrier gas molecule is equal to r/mfp , which is checked against a random number, rn , between 0 and 1. If $P_{\text{coll}} < rn$, the molecule is again allowed to proceed in the same direction for another step of distance r .

If $P_{\text{coll}} > rn$, the particle is assumed to collide with a carrier gas molecule having a velocity chosen randomly from a Maxwell–Boltzmann distribution. The collision causes the molecule to be deflected with a velocity and an angle consistent with momentum and energy conservation in the elastic collision of two hard spheres. If the path of the particle crosses the substrate plane or the aperture wall, the particle is assumed to stick to the surface with unity efficiency. A single aperture is simulated, with periodic boundary conditions imposed in the x direction. Effects of aperture geometry on deposited pattern formation are modeled by assigning different aperture sidewall angles, $\alpha = 45^\circ, 90^\circ, 135^\circ$, and $\alpha' = 270^\circ$ (see Fig. 4).

IV. MONTE CARLO SIMULATION RESULTS AND DISCUSSION

We consider the growth of films of the archetype molecule, *tris*(8-hydroxyquinoline) (Alq_3), having $d \sim 10 \text{ \AA}$. The mean free path is calculated using Eq. (2), assuming that the collision diameter for a mixture of Alq_3 in a N_2 carrier gas is the average of the respective diameters of the two species in self diffusion viz.: $d = 1/2(d_{\text{Alq}_3} + d_{\text{N}_2})$.

Figure 5(a) shows a gray-scale map of the organic species concentration from a simulated deposition of 10^5 particles, with $s = 7 \mu\text{m}$, $t = 3 \mu\text{m}$, and $\alpha = 135^\circ$, and $\text{mfp} = 100 \mu\text{m}$, corresponding to a total deposition pressure of $P_{\text{dep}} \sim 0.1 \text{ Torr}$ at $T = 500 \text{ K}$. While the simulated particle diameter was $10 \text{ \AA}$, it was enlarged in the figure to better illustrate the deposited profile. The initial particle velocities were assigned from a random thermal distribution, and are superimposed onto a z -directed velocity vector with a magnitude of 10 m/s . By decreasing the mfp by a factor of 10, a more diffuse pattern is obtained, shown in Fig. 5(b). Note that the films shown in Fig. 5 are unrealistically thick and t is unrealistically thin for conventional OVPD conditions; a film thickness of $\sim 1000 \text{ \AA}$ and $t \sim 50 \mu\text{m}$ are more practical. The figure nevertheless illustrates the increased parasitic deposition on the mask and aperture walls when the mfp is reduced. For clarity, subsequent simulation results will provide only the thickness profile without the shadow mask shown. The total number of Alq_3 molecules was also increased to 10^6 to obtain smoother, more accurate thickness profiles.

The effects of deposition pressure on pattern resolution were investigated by varying mfp . Growth through an aperture with $w = 80 \mu\text{m}$, $t = 70 \mu\text{m}$, and with the substrate separated from the lower mask edge by $s = 20 \mu\text{m}$ was considered. The choices for s and t are consistent with deposition of high resolution display picture elements (pixels) by VTE, where the substrate facing downward evaporation geometry causes the mask to bow away from the substrate under gravity, leading to $s \sim 20 \mu\text{m}$. To stiffen the mask and minimize s , usually $t > 70 \mu\text{m}$ is required for VTE. Considerably thinner masks (e.g. $t \sim 50 \mu\text{m}$) can be used with OVPD due to the possibility of top-down deposition. Figure 6 shows that the shape factor η increases only weakly as mfp varies over 4 orders of magnitude ($1 \mu\text{m} \leq \text{mfp} \leq 1000 \mu\text{m}$, corresponding approximately to $10 \text{ Torr} \geq P_{\text{dep}} \geq 0.01 \text{ Torr}$), as would be expected for a system approaching the Knudsen transport

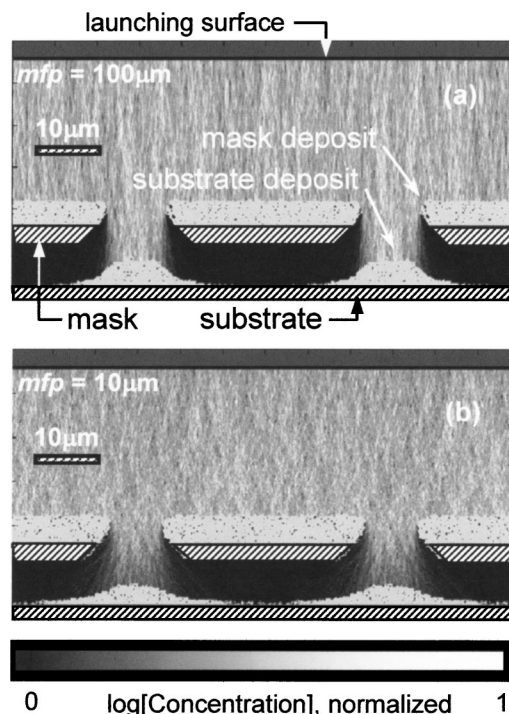


FIG. 5. (a) Normalized spatial concentration profile and deposited film obtained from a Monte Carlo simulation using 10^5 particles, $\text{mfp} = 100 \mu\text{m}$, $s = 7 \mu\text{m}$, $t = 3 \mu\text{m}$, and $\alpha = 135^\circ$. (b) Normalized spatial concentration profile using 10^5 particles, $\text{mfp} = 10 \mu\text{m}$, $s = 7 \mu\text{m}$, $t = 3 \mu\text{m}$, and $\alpha = 135^\circ$. Decreasing the mfp results in a more diffuse species flux and a correspondingly more diffuse pattern on the substrate. Also note the increased parasitic deposition on the mask and aperture walls when the mfp is reduced. The organic molecular diameter and the mask dimensions are not to scale to emphasize the deposition profiles of the films. The white streaks represent molecular trajectories.

regime. However, η does not reach unity (corresponding to a rectangular deposit profile) due to parasitic deposition on the sidewalls of the almost square aperture. As expected, the highest pattern edge resolution (and hence, highest η) is achieved for the largest mfp , i.e., the lowest P_{dep} . However, as discussed below, the pattern profile exhibits a dome-like shape due to a relatively large t/w .

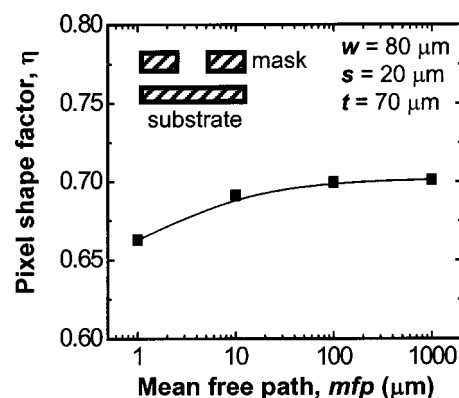


FIG. 6. Deposit shape factor, η , as a function of the molecular mean free path, mfp . Here, η approaches a maximum value of 0.7, in contrast to vacuum deposition from a point source where $\eta \rightarrow 1$, due to the distributed nature of the molecular source (i.e., the well-mixed boundary layer) in OVPD.

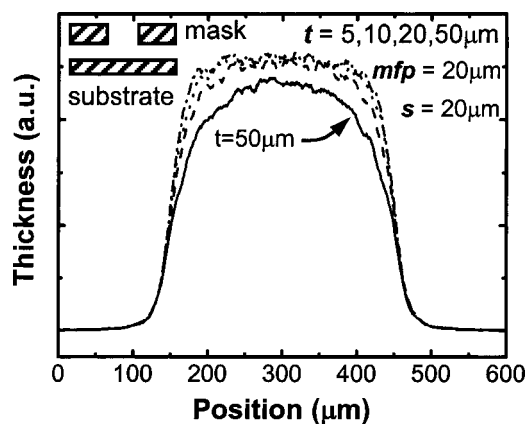


FIG. 7. Deposit profile as a function of mask thickness, t , obtained from the Monte Carlo simulation discussed in the text, using 10^6 Alq_3 molecules in N_2 background carrier gas with $\text{mfp}=s=20\text{ }\mu\text{m}$. The aperture dimensions are listed on the plot. The pixel shape factor η decreases weakly with s for this set of parameters.

Increasing the aperture thickness can improve collimation of the molecular flux toward the substrate due to the condensation on the walls of the aperture. However, as Fig. 7 shows, increasing t from 5 to $50\text{ }\mu\text{m}$ for $s=\text{mfp}=20\text{ }\mu\text{m}$ and $w=300\text{ }\mu\text{m}$, has no effect on the spreading of the lower edge of the deposit. However, as t/w increases, the deposited pattern becomes significantly more domed due to the scavenging of the organic molecules by the upper edges of the aperture. The shape factor decreases by less than 5% over the range $1\text{ }\mu\text{m}<t<100\text{ }\mu\text{m}$.

The mask separation s can vary due to bowing under gravity (in VTE), or possibly heating during the deposition process. Figure 8 shows profiles for depositions where $s=2, 10, 22$, and $50\text{ }\mu\text{m}$, and $t=20\text{ }\mu\text{m}$, $w=300\text{ }\mu\text{m}$, and $\text{mfp}=20\text{ }\mu\text{m}$. Appreciable edge broadening arises due to collisions in the mask-substrate gap for $s>\text{mfp}$. In addition, for large s the dome in the middle of the deposit is pronounced and, in contrast to the case of large t/w , the profile is also broadened at the edges. The inset of Fig. 8 shows a linear decrease in η with s for this series of depositions. Thus, optimal pattern resolution leading to a rectangular deposit is achieved for the smallest values of s and t , as expected. Since OVPD can, in principle, be carried out with the mask positioned above the substrate, thin masks can be used while s is kept small, contrary to the case in VTE. By using thinner masks, the pattern deposition efficiency ε is also increased, because less material will be deposited on the aperture sidewall, as will be shown later. The drawback of thin masks is that they are more susceptible to thermally and mechanically induced stresses. Nevertheless, in a “top-down” configuration of OVPD, smaller values of s and t are possible, potentially leading to higher resolution patterns than are achievable using conventional VTE deposition.

It is also possible to minimize t at the aperture edge while keeping the mask thick elsewhere. The variation in η with the aperture shape was investigated by varying the aperture side-wall angle $\alpha=45^\circ, 90^\circ, 135^\circ$, and $\alpha'=270^\circ$ (see Fig. 4). The pattern profiles for these aperture shapes are shown in Fig. 9. The aperture with $\alpha=135^\circ$ results in the

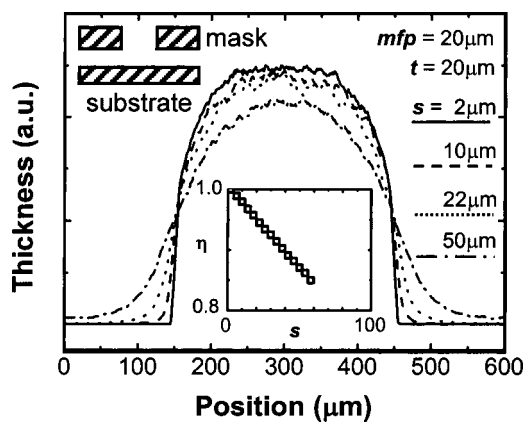


FIG. 8. Simulated deposit profiles for a cylindrical aperture mask at various separation distances, s , with dimensions and details of the simulation listed on the plot. The pattern edge becomes more diffuse, while the deposition efficiency decreases with increasing t due to parasitic deposition on the aperture sidewall, as discussed in the text. (Inset) The deposit shape factor decreases approximately linearly with s . (Legend: $s=[-]$ 2, $[- - -]$ 10, $[\cdots]$ 22, $[- \cdot -]$ 50 μm .)

most diffuse edge of the deposit (smallest η) due to the lack of collimation of the approach angle of the molecules. This occurs to a lesser extent with the biconical aperture ($\alpha'=270^\circ$), but the sharpest patterns are achieved with $\alpha=90^\circ$ and $\alpha=45^\circ$. The variation of the shape factor η versus t is plotted in Fig. 10(a) for all four aperture geometries. While apertures with $\alpha=90^\circ$ and 45° show a minimal decrease in η with t , curves for $\alpha'=270^\circ$ and $\alpha=135^\circ$ drop significantly with t , consistent with the profiles in Fig. 9.

In addition to allowing deposition of sharper patterns, it is desirable to maximize the material flux to the substrate. The pattern deposition efficiency ε normalized to that of the

$s=10\text{ }\mu\text{m}$; $\text{mfp}=20\text{ }\mu\text{m}$; $t=5\text{--}75\text{ }\mu\text{m}$

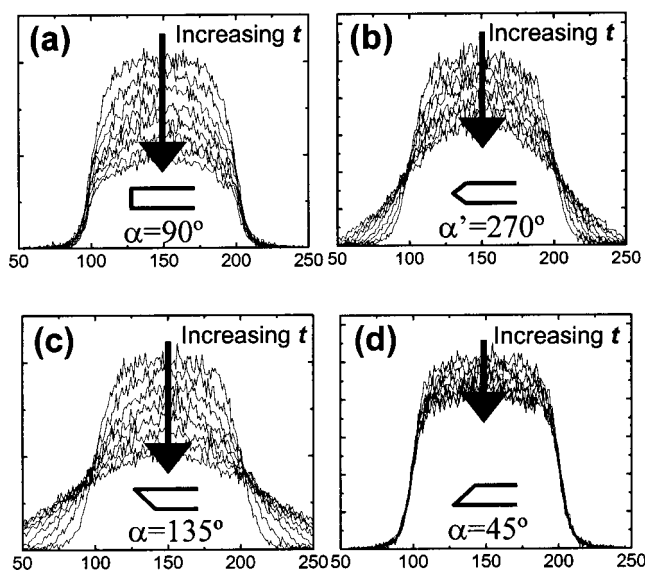


FIG. 9. (a)–(d) Effects of aperture wall profile (and mask thickness t) on deposit cross section. In each part, the mask thickness increases from $5\text{ }\mu\text{m}$ (upper curve) to $75\text{ }\mu\text{m}$ (lower curve) in $10\text{ }\mu\text{m}$ increments. The mask-to-substrate separation, s , and mfp are held constant at 10 and $20\text{ }\mu\text{m}$, respectively.

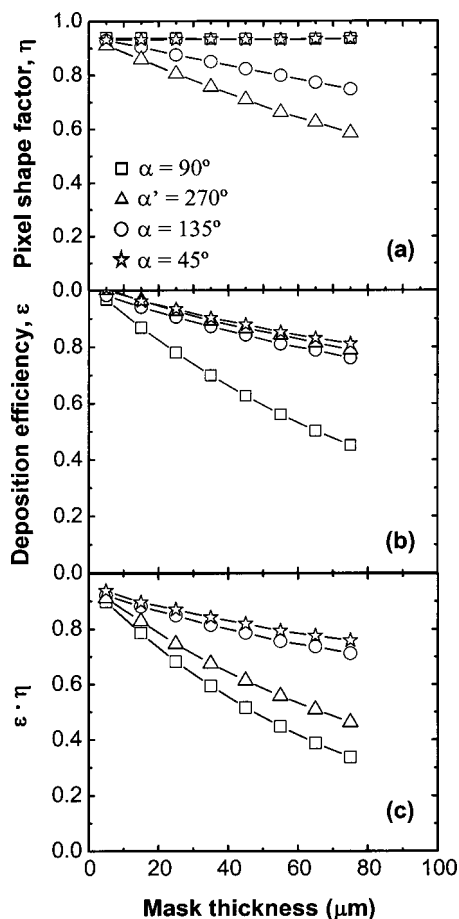


FIG. 10. (a) Deposit shape factor, η , as a function of the mask thickness, t , for the simulated depositions in Fig. 9. (b) Plot of the deposition efficiency, ε vs t for various aperture shapes. The efficiency for $\alpha = 90^\circ$ is lowest due to parasitic deposition on the aperture walls. (c) The figure of merit, $\varepsilon \cdot \eta$, represents the combined effects of pattern sharpness and deposition efficiency using a particular aperture configuration. Apertures with $\alpha = 45^\circ$ yield the highest $\varepsilon \cdot \eta$.

aperture with $\alpha = 45^\circ$ and $t = 2 \mu\text{m}$, is plotted versus t in Fig. 10(b). For all four aperture shapes, ε decreases for larger t , the effect being most pronounced for $\alpha = 90^\circ$. By plotting the product $\varepsilon \cdot \eta$ versus t , the cumulative effect of aperture shape on the deposited pattern can be seen. While the aperture with $\alpha = 90^\circ$ yields sharp deposit edges, the drop in ε with t for this shape makes it less desirable than the aperture with $\alpha = 45^\circ$ for depositing well-defined patterns with the least amount of material wasted on coating the mask. However, since ε includes all material deposited on the substrate, $\varepsilon \cdot \eta$ for $\alpha = 135^\circ$ is greater than for $\alpha' = 270^\circ$ and $\alpha = 90^\circ$, although the pattern edges are significantly more spread out.

V. EXPERIMENT

The deposition of thin films of Alq_3 was carried out using a multibarrel horizontal reactor described previously.²³ The deposition system consists of an 11 cm diam by 150 cm long quartz cylinder, fitted at the upstream end with four evaporation cells housed in separate, 2.5 cm diam by 100 cm long quartz barrels. The main reactor tube is heated by

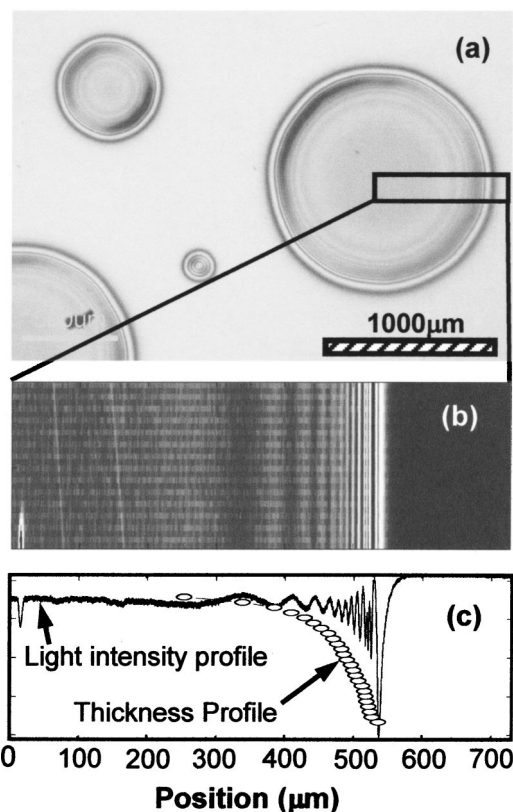


FIG. 11. (a) Micrograph showing circular Alq_3 patterns deposited on Si using OVPD. The interference fringes observed for each deposit indicate a variation in the thickness near its edge. Here, a cylindrical mask was used with $t = 50 \mu\text{m}$, $s = 0$, and $w = 100, 300$, and $1000 \mu\text{m}$. (b) Digitized image of a deposit showing the interference fringes near the edge of the deposit. (c) Plot of the light intensity along the radius of the deposit, and the corresponding thickness profile calculated from the interference pattern similar to the one shown in (a).

means of a three-zone furnace enabling source temperature control via positioning of each cell along the temperature gradient within the tube. Carrier gas flows on the inside of the main tube as well as in each of the barrels, and is regulated by mass flow controllers while the deposition pressure is controlled by adjusting the exhaust vacuum pump throttle valve and the total carrier flow rate from 10 to 100 sccm. Organic molecules from the vapor phase physisorb onto a rotating water-cooled substrate, positioned behind a mechanically operated shutter. Film thickness and growth rate are monitored by a quartz crystal microbalance calibrated using *ex situ* ellipsometry.

The deposition profiles of organic thin films obtained using OVPD were compared with those prepared by VTE. The VTE source-to-substrate distance was approximately 30 cm and the deposition base pressure was maintained at 10^{-6} Torr.

Three types of shadow-masks were used. One (Mask A) was a 60 μm thick, 1 cm $\times$ 1 cm Mo mask with circular openings having diameters of 1000, 300, and 100 μm . The aperture profile in this mask was cylindrical ($\alpha = 90^\circ$). A second mask (Mask B) was a 75 μm thick Mo sheet with circular apertures having the same nominal diameters as in Mask A. The openings in this mask had a double-beveled edge, forming a biconical aperture ($\alpha' = 270^\circ$). The third

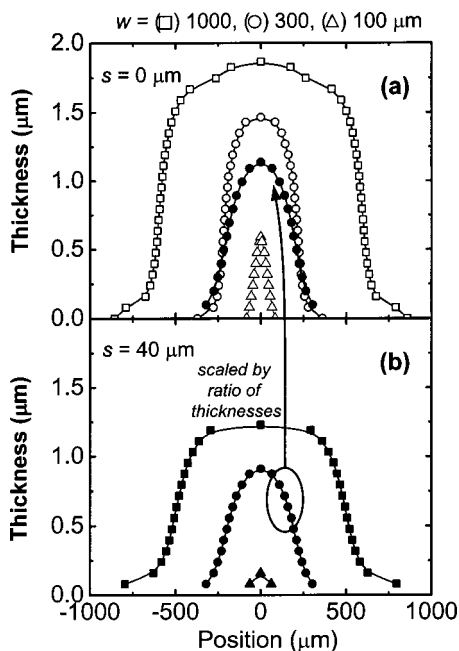


FIG. 12. Experimental pixel profile for Mask A with a mask-to-substrate separation of (a) $s=0$ and (b) $s=40$ μm , respectively. The nominal film thicknesses were: (a) 2 μm and (b) 1.6 μm . The thickness profile was obtained for the larger diameter deposits by scanning from the center of the deposit outward, and reflecting the resulting thickness profile about the origin. For smaller deposits, the entire deposit was scanned. Both (a) and (b) indicate that the pixel deposition efficiency decreases with the aperture aspect ratio, t/w , where t and w are the mask thickness and aperture width, respectively. The profiles from both runs for the $w=300$ μm aperture are scaled by their thicknesses and compared in Fig. 13(a) (open and solid circles). The experimental comparison shows that greater mask-to-substrate distance results in a more diffuse deposit and lower pattern deposition efficiency.

mask (Mask C) was a Ni mesh, 3.5 ± 0.5 μm thick, with nominally 7.5 and 12.5 μm square openings separated by equally wide lines. The masks were fixed to silicon substrates using a retainer ring. The mask-to-substrate separation was controlled by shims of multiple layers of the Ni mesh placed between the Si substrate and the Mo mask bottom surface. In depositions through the Ni meshes, 1 cm $\times$ 1 cm mesh sheets were fixed to the substrate by sandwiching them between the substrate and the first or second type of mask, and then were clamped to the holder by the retainer. Due to the profile of the Ni mesh, the smallest effective separation was 1.0 ± 0.5 μm .

Analysis of the deposited pattern profiles was performed using scanning electron microscopy (SEM) and atomic force microscopy (AFM) for the smallest pattern sizes, and interference microscopy for the larger patterns. The latter method entailed illuminating the substrates with a monochromatic source (with wavelength $\lambda = 540 \pm 10$ nm) and observing the interference fringes formed at the sloping edge of the bell-shaped deposit [see Fig. 11(a)]. The thickness profile was extracted from the digitized pattern image [Fig. 11(b)] by counting the number of fringes from the edge [Fig. 11(c)] and using $H = m\lambda/2n$, where H is the pattern thickness, $m = 0, 1, 2, 3$, etc. is the fringe order, and $n = 1.74$ is the refractive index of Alq_3 .

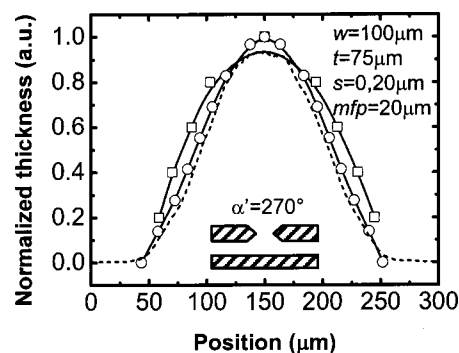


FIG. 13. Thickness profile of an Alq_3 film grown by OVPD through a shadow mask with an aperture width $w=100$ μm and mask thickness $t=75$ μm . The simulation (dashed line) was performed with 10^6 Alq_3 molecules assuming $s=20$ μm and $\text{mfp}=20$ μm for $\alpha'=270^\circ$ mask. Experimental depositions employed the same type of mask, but without spacers, to obtain Alq_3 patterns having 0.9 μm (squares) and 2.1 μm (circles) maximum thicknesses for $w=100$ μm . The presence of pattern dispersion in both runs, and a close resemblance to the simulated result indicate inadequate control of the parameter s in the experiment.

VI. EXPERIMENTAL RESULTS AND DISCUSSION

A micrograph with circular pixels deposited by OVPD through Mask A ($\alpha=90^\circ$) is shown in Fig. 11(a). In Fig. 12(a), the measured pattern profiles for $s=0$ μm are plotted (open circles), while those for $s=40$ μm are shown in Fig. 12(b). The open circles in Fig. 12(a) correspond to films nominally 2 μm thick, while those in Fig. 12(b) were 1.6 μm thick. Both plots indicate that the pattern deposition efficiency (inferred from the area under each profile) decreases with the aperture aspect ratio t/w . The dome in the center of each pattern, which is particularly pronounced for large t , is similar to that obtained in the simulation (see Fig. 8). Also plotted in Fig. 12(a) is the profile for $w=300$ μm and $s=40$ μm from Fig. 12(b) (filled circles). It is evident that increasing s decreases the efficiency of pattern deposition (due to condensation on the mask) and edge sharpness, as predicted in Fig. 10. As discussed in Sec. II D, this result is not obtained using the simple continuum diffusion model.

Experimental deposition profiles for Mask B with $\alpha'=270^\circ$, $w=100$ μm , $t=75$ μm , and $s \approx 0$ μm are compared to simulations in Fig. 13. The simulation assumes $\text{mfp}=20$ μm and diffusive deposition (i.e., no bulk flow in the z direction) at $P_{\text{dep}} \approx 0.2$ Torr, as used in the experiment. The simulated aperture geometry matches the experimental setup, but s was adjusted to 20 μm to match the profile of the deposited pattern. The discrepancy is possibly due to lack of control of mask-to-substrate separation used in the experiment. Using microscopic analysis we find that the mask with $t=75$ μm and $\alpha'=270^\circ$ has surface irregularities on the order of several microns in height such that $s > 0$, contrary to assumptions used in the simulations. Furthermore, uneven clamping of the mask to the substrate may lead to warping of the mask, and hence to a larger s .

The highest resolution patterns achieved by OVPD used Mask C with the bottom of the Ni mesh in close contact with the substrate, resulting in $s \approx 1$ μm , due to the profile of the mesh wires. A patterned Alq_3 film deposited by OVPD at $P_{\text{dep}}=0.1$ Torr was imaged using AFM as shown in Fig.

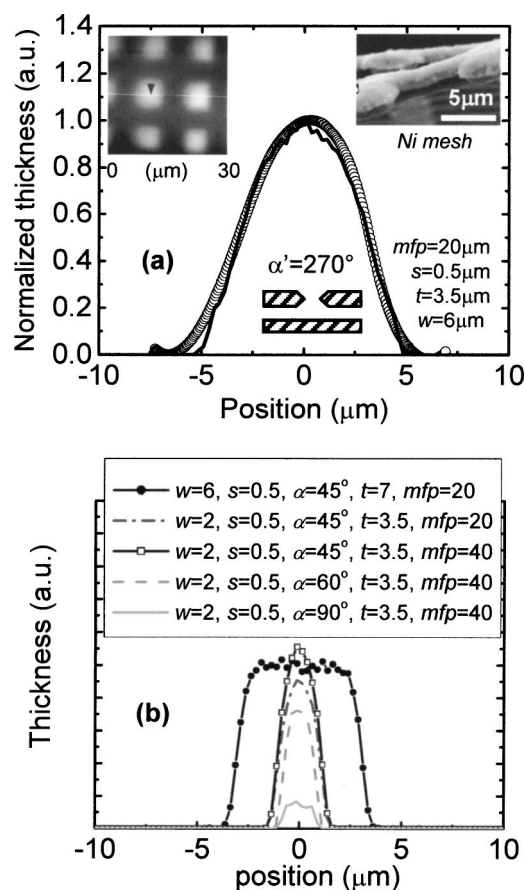


FIG. 14. (a) Comparison of the experimental (circles) and simulated (line) pattern profiles of a patterned Alq_3 film, where the edge sharpness was approximately $1\text{--}3\text{ }\mu\text{m}$. (Left inset) An AFM image of a patterned Alq_3 film deposited by OVPD at 0.1 Torr through a nickel mesh with an aperture width, $w=6\text{ }\mu\text{m}$ and mask thickness, $t=3.5\text{ }\mu\text{m}$, with $s<1\text{ }\mu\text{m}$. (Right inset) SEM side view of the Ni mesh. (b) Simulation results for higher resolution patterns that are predicted for OVPD at the conditions listed.

14(a). The edge sharpness is $\sim 3\text{ }\mu\text{m}$, obtained from the thickness profile extracted from the image in the left inset of Fig. 14(a). Simulation of these deposition conditions is also shown in Fig. 14(a) as a solid line. The experimental deposit profile is fit assuming $w=6.0\text{ }\mu\text{m}$, $t=3.5\text{ }\mu\text{m}$, $s=0.5\text{ }\mu\text{m}$, $\text{mfp}=20\text{ }\mu\text{m}$, and $\alpha'=270^\circ$. The simulated and experimental dimensions are nearly identical, suggesting that the stochastic simulation accurately describes the patterned deposition mechanism. Similar patterns have been obtained for depositions at pressures of from 0.1 to 2 Torr, with the lower pressures increasing pattern definition, as expected. Fig. 14(b) shows simulation results for several other deposition conditions. One curve (solid circles) is for an aperture with $\alpha=45^\circ$ and $s=0.5\text{ }\mu\text{m}$, showing improved pattern edge sharpness compared to that in Fig. 14(a). Rectangular patterns with $\eta>90\%$ can be achieved for $w=2\text{ }\mu\text{m}$ and $\alpha=90^\circ$.

Two instances of micron-scale resolution patterning are illustrated by the SEMs in Fig. 15: (a) Alq_3 patterns deposited on Si by VTE through Ni meshes at $P_{\text{dep}}=10^{-6}$ Torr and $s\approx 1\text{ }\mu\text{m}$ without substrate rotation, and (b) analogous patterns deposited by OVPD at $P_{\text{dep}}=2$ Torr. The vacuum-deposited patterns show the trapezoidal profile discussed in

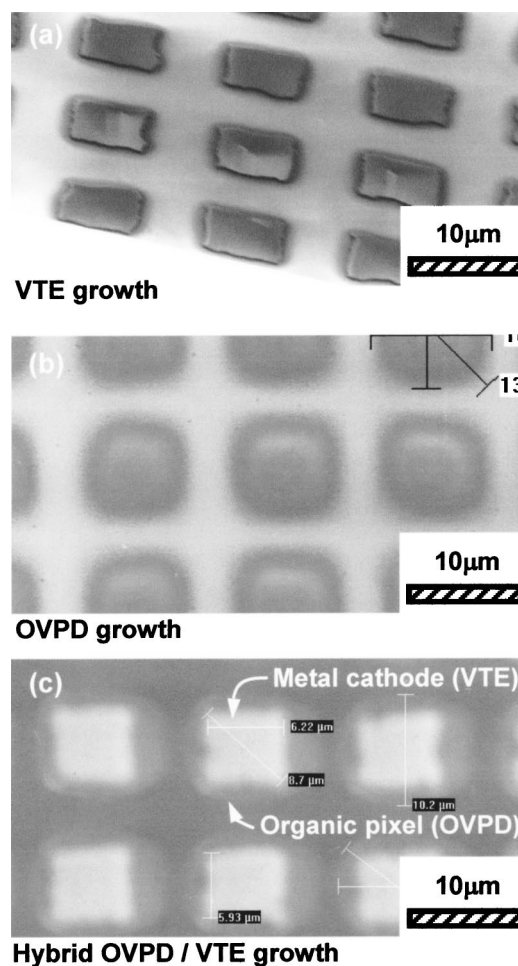


FIG. 15. (a) SEM of an Alq_3 film deposited by vacuum thermal evaporation on Si through a mesh with an aperture width, $w=7.5\text{ }\mu\text{m}$ and mask-to-substrate separation, $s\sim 0\text{ }\mu\text{m}$ at 10^{-6} Torr. (b) SEM showing Alq_3 patterns deposited on Si using OVPD at 0.1 Torr through a nickel mesh with $t=3.5\text{ }\mu\text{m}$, $w=7.5\text{ }\mu\text{m}$, and $s<1\text{ }\mu\text{m}$. (c) SEM of hybrid OVPD-VTE deposition showing Alq_3 patterns deposited on Si by OVPD at 1 Torr, with Ag caps subsequently deposited by VTE at 10^{-6} Torr, without shifting the shadow-mask between depositions.

Sec. II where $\rho<1\text{ }\mu\text{m}$, while OVPD patterns have edge dispersion on the order of $1\text{--}3\text{ }\mu\text{m}$. Simulations in Fig. 14(b) indicate that if apertures with $\alpha=45^\circ$ and minimal s are used, submicron resolution is achievable using this growth technique.

Finally, fabrication of OLED-based full-color displays entails the deposition of an array of pixels with one color emissive layer followed by the deposition of a second and third array of different color pixels, forming the red-green-blue full-color triad.^{18,19} The deposition of organic layers is followed by metal deposition to form the cathode contacts to the OLEDs. To confine the metal cathode to coat only the organic films, and hence prevent shorting of the cathode to the anode contacts, an “integrated” polymer shadow mask consisting of photoresist walls is pre-patterned onto the substrate.¹⁹ The integrated shadow mask can be eliminated by OVPD at moderate pressure through a conventional shadow mask, yielding slightly broadened deposits. This is followed by the deposition of a well-defined metal contact in vacuum without moving the mask between the growth steps.

The controlled dispersion of the organic coating, therefore, prevents electrical shorts around the edge of the organic film, since VTE of the electrode will automatically yield a smaller size “cap” over the organic pixel. A SEM image of the resulting confined electrode structure from such hybrid deposition is shown in Fig. 14(c). Clearly, in a passive-matrix architecture the confined individual electrode squares are replaced by stripe electrodes. A second set of pixels may be deposited by simply translating the mask laterally (possibly *in situ*), avoiding the realignment of the mask to a previously deposited pattern.

VII. ORGANIC VAPOR JET PRINTING

The ability to form well-defined, high resolution patterns by growth through apertures suggests that OVPD may be modified to allow for direct printing of individual pixel patterns, analogous to ink jet printing of polymer devices.^{8,9,12,14} That is, under certain conditions, the diffusive transport in the boundary layer can be replaced by relatively high velocity carrier gas jets, depositing the organic species on the substrate in a highly directional process. Thus, we modeled a jet of carrier gas delivered through a small-diameter capillary, or nozzle, onto a cooled substrate. In the Monte Carlo simulation, the z -directed carrier gas velocity u_z can be increased to simulate a jet that broadens only by the isotropic random molecular velocities superimposed onto this flow field. Figure 16(a) shows the spatial concentration profile for a simulated jet of N_2 carrying Alq_3 , with $mfp=10\ \mu m$, $t=50\ \mu m$, and $u_z=100\ m/s$, while the mean thermal speed, $u=500\ m/s$. Since the flow field was not known in this regime, the simulation assumes $du_z/dz=0$ for simplicity. The figure shows that the collimated jet can result in a deposit with well-defined edges even for $s \gg mfp$. The flow field used for this simulation, however, is only approximate, neglecting the influence of the substrate in close proximity to the nozzle. Alternatively, the flow from the nozzle can be modeled using the Navier–Stokes equations, as was done for the OVPD chamber in Sec. II. Simulating the flow of rarified N_2 at $Re \approx 10$ through a nozzle heated to $225\ ^\circ C$ results in the flow field shown in Fig. 16(b). Deposition of organic species from this jet onto the substrate produces the pattern shown in Fig. 16(c). While the flow velocity does not appear to have a significant influence on the deposit shape (not shown), changing the shape of the nozzle itself has a dramatic effect [see Fig. 16(c)].

The foregoing results have modeled the jet deposition process using two extreme assumptions—one modeled only individual collisions of the organic molecules with the carrier gas, while the other ignored the molecular nature of the flow altogether. The hydrodynamics of high-velocity, rarified flow through a small channel are likely to be intermediate between these two regimes, which requires the simulation of simultaneous n -body interactions ($n \geq 2$),²⁶ which is currently under investigation. The preliminary simulation results, however, suggest that careful selection of (u_x, u_y, u_z) , P_{dep} , α , and s may thus enable direct printing of molecular organic thin films analogous to ink-jet printing for polymers, where the liquid solvent is replaced by a jet of a highly

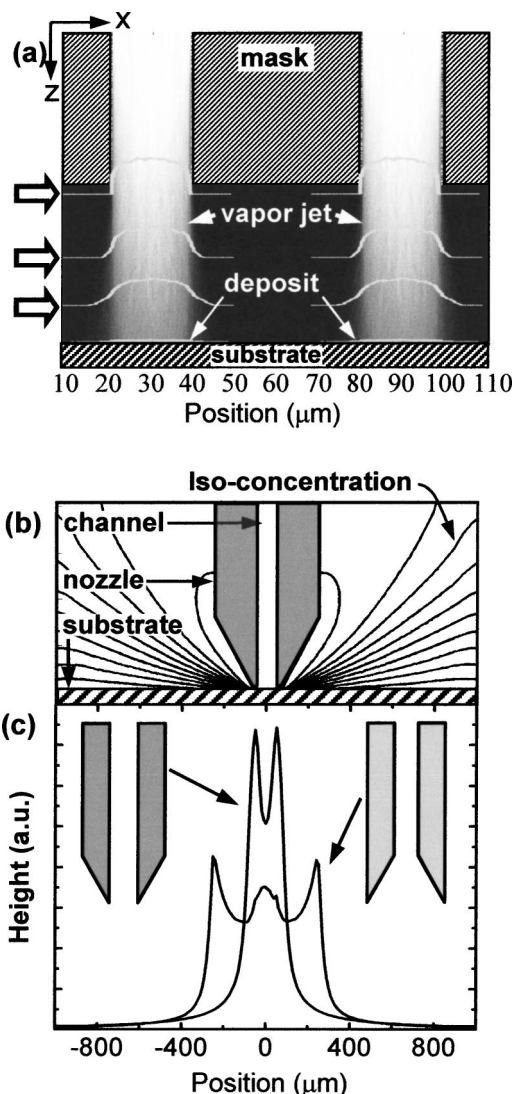


FIG. 16. (a) Spatial concentration profile for a simulation of OVJP of Alq_3 molecules in a N_2 gas stream, with molecular mean free path $mfp=10\ \mu m$, nozzle-to-substrate distance, $s=50\ \mu m$, and z directed velocity component $u_z=100\ m/s$ held constant along z . The widening of the vapor jet is indicated by the concentration profiles taken along the x direction at positions indicated by the arrows. (b) Continuum-based simulation of a hot jet of N_2 impinging on a cooled substrate. The nitrogen is transporting the organic species to the substrate, where they selectively physisorb. (c) Effect of nozzle shape on the deposit profile.

volatile inert carrier gas. Advantages over conventional shadow-masked deposition include further economy of the source material, reduction of complexity associated with manipulation and cleaning of large masks, elimination of pre-deposition substrate patterning (e.g., the integrated shadow-mask), and the ability to conformally coat nonplanar substrates.

VIII. CONCLUSIONS

We have shown that OVPD can be used for patterned deposition of organic thin films with micrometer scale resolution. Due to the background pressure of the carrier gas used in OVPD, the molecular mean free paths are frequently on the order of the mask dimensions, suggesting that molecular level Monte Carlo simulations can accurately model

TABLE I. Effects of masking geometry and process parameters on pattern shape.

Parameter ^a	Pixel shape factor	Deposition efficiency	Figure of merit
	η	ε	$\eta \cdot \varepsilon$
$s \uparrow$	$\downarrow$	$\downarrow$	$\downarrow$
$\alpha \uparrow$	$\downarrow$	-	$\downarrow$
$t \uparrow$	$\downarrow^b$	$\downarrow$	$\downarrow$
mfp $\uparrow$	$\downarrow$	$\downarrow$	$\downarrow$

^aHere $\uparrow$ indicates an increase in the parameter, $\downarrow$ a decrease.

^bFor $\alpha \leq 90^\circ$, η was insensitive to t .

the growth process. Table I summarizes the effects of variations in masking geometry and process conditions, in order of decreasing strength of influence, on the resulting pattern shape represented by η , ε , and $\eta \cdot \varepsilon$. The mask-to-substrate separation (s) strongly affects the deposit shape, with $s < \text{mfp}$ being favorable for sharper pattern edges. Thinner masks increase the molecular flux transmission efficiency through the apertures, but must be coupled with small s to increase the pattern resolution and quality. As the deposition pressure decreases, the mean free path increases, resulting in sharper edges for the deposited pattern. By depositing at the lower end of the pressure range (<1 Torr) and using appropriate aperture shapes (e.g., $\alpha < 90^\circ$) it is possible to achieve submicron pattern resolution, ultimately limited by control of the mask-to-substrate separation distance, s . The possibility of a top-down deposition geometry in OVPD, contrasted to bottom-up deposition in VTE, can allow for further decreases in the mask thickness and s for finer pattern resolution. Increasing the carrier gas momentum in the z direction may improve edge sharpness when transport by bulk flow dominates, suggesting the possibility of local patterning by organic vapor jet printing.

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