Modeling the initial monolayer formation in thermally localized surface deposition

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ABSTRACT

In atomic layer deposition (ALD), thin layers of materials are deposited on a substrate with atomic layer precision in the vertical direction. The ability to control layer growth in the lateral direction as well is expected to greatly increase the potential of ALD as a path to the bottom-up additive fabrication of electronic devices like solar panels and organic light-emitting diode displays. We explore the possibility of controlling the lateral growth by modifying the temperature profile on the substrate using, for instance, pulsed lasers. This maskless technique keeps the majority of the substrate at a low temperature suppressing one of the chemical half-reactions, while in a small, localized area, the substrate is heated, which allows the reaction to proceed at a higher rate. We test this idea with coarse-grained computational models that model the control of the temperature by various illumination protocols and simulate the nucleation and growth of the initial monolayer within this inhomogeneous temperature distribution. Our results suggest that the location and the extent of deposition can, in principle, be localized and controlled and address operational regimes in which a thin conducting line may be obtained.

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I. INTRODUCTION

Atomic layer deposition (ALD) is a technique to deposit thin layers of material on a substrate. A typical ALD protocol is a two-step process (although more elaborate variants are also possible) in which a solid substrate is first exposed to a precursor; a gas at the operating conditions reacts with the substrate surface but not with itself. This is the first half-reaction. Then, the remaining precursor gas is purged from the system and the substrate is exposed to a coreactant that, in the second half-reaction, reacts with the precursor at the surface to complete the first cycle. After the coreactant is removed again, the system is ready to undergo another cycle of the same two-step process, resulting in extremely precise control over the height of the deposited material. This procedure is the standard AB-cycle.^{1,2}

Clearly, ALD allows for accurate layer-by-layer linear growth in the vertical direction but, in the standard process, accurate control in the lateral directions is lacking. Several techniques to achieve so-called area-selective ALD (AS-ALD) have been developed to control this lateral growth during AS-ALD.³ There are three main approaches in the AS-ALD toolbox: area deactivation,

area activation techniques, and intrinsically selective ALD. In all three cases, the substrate is divided into regions where growth is desired and regions where it must be inhibited. In the case of area deactivation, the nongrowth area is treated to locally inhibit deposition. One example of this approach is the use of self-assembling monolayers where the substrate first reacts with a solution of molecules that preferentially bind to the nongrowth area, obscuring it for otherwise standard AB-cycle ALD (Refs. 4 and 5) and limiting growth to the nonmonolayer-covered area. More generally, the use of inhibitors in ABC-cycle ALD processes involves an additional first step relative to the AB-process where the substrate is exposed to a vaporized inhibitor that attaches to the nongrowth area and obscures it for one cycle. The inhibitor is lost during this cycle and must therefore be replaced every cycle.⁶ In the case of area activation, the reverse happens: precursors are chosen such that nucleation occurs only on the growth area.⁷ This approach, where the substrate is locally activated, can also be implemented using physical rather than chemical treatment and without a pre-existing pattern. Two examples of such processes in which the area is activated by local addition of some form of energy to the substrate are

electron beam-induced nucleation (EBID)^{8,9} and laser-assisted ALD. An example of laser-assisted ALD, GaAs is created by photochemical excitation;^{10,11} these techniques, in general, can be used to create a seed layer: a physical pattern on the substrate, which limits further vertical ALD growth to specific areas. We note that the technique we propose here could be promising in combination with this seed layer approach: our model describes the formation of the initial layer, which as the seed layer fixes the entire subsequent pattern. In the case of intrinsically selective ALD, the differential absorptive properties of precursor molecules (which can be related to different types or phases of materials and also, for instance, to the presence of defects on the surface) in different regions on the substrate is used to achieve localization of deposition.^{12–14}

In this article, we use coarse-grained modeling to assess the potential of a mechanism for local activation by physical patterning of a substrate in ALD based on the localized heating of the substrate by a pulsed laser that moves across the substrate—writing the thermal pattern, as it were. To be clear, we do not consider situations where deposition happens on the entire substrate. We study short, localized laser pulses applied in either half-reaction to prompt the formation of a localized reactive zone to which the deposition of a layer over a single cycle remains confined. As it is presented here, our model applies to the deposition of the initial layer since we do not take surface topography into account in our modeling of laser-induced surface heating. Toward the end of this article, we will discuss the potential use of this technique in cyclic growth protocols. Most of the substrate remains at a baseline temperature which, under ideal circumstances, is too low for deposition. This does mean that the approach we propose here is not suitable for precursors that are not significantly less adsorbed below the ALD temperature window. Local heating creates areas where the temperature is higher, allowing for local growth there—see Fig. 1 for a schematic of the approach. The challenge here is that the laser must, first of all, be on for some time to reach the activation temperature threshold. Generally, the

temperature dependence of ALD reactions is weak, and the growth below the ALD temperature window is only marginally slower than inside the window. Therefore, considerable temperature differences will be needed to have an effect.¹⁵ During the time that the laser is on, however, the size of the activated area will increase beyond the typical size of the laser spot due to thermal conduction. Clearly, a combination of the thermal properties of the substrate, the physical characteristics of the laser (power and spot size), and the illumination protocol (pulse duration, off time between pulses, and translation speed) will determine the quality, dimensioning, and extent of the ultimate surface coverage. The question we seek to answer here is whether in this complex interplay of factors, it is possible to reach a lateral feature width of $1\mu\text{m}$; that is, can we write a line with a width of $1\mu\text{m}$? This particular width is chosen because a feature size of $1\mu\text{m}$ is of considerable applied interest, for instance, for the printing of electronic circuitry in large-area settings such as solar panels and organic light-emitting diode (OLED) displays. The technique proposed here has the potential to be implemented in-line using standard, existing technologies and allows freeform patterning.

We recognize that typical ALD precursors are generally not well-suited to this approach. The temperature dependence is generally weak, resulting in considerable deposition at reasonable reference temperatures and too little thermally induced differentiation between growth and nongrowth areas. The temperature dependence of some ALD systems is too weak. For instance, ZnO with precursor diethylzinc and H_2O , Al_2O_3 with precursor trimethylaluminum, and O_3 and TiO_2 with the use of Ti isopropoxide and H_2O (Refs. 15–17) are less naturally suited. Prior work suggests, however, that a disilane (Si_2H_6)-based ALD method might offer experimental proof-of-principle. A substrate is exposed to Si_2H_6 at 300°C , which leaves a monolayer of silicone atoms with hydrogen atoms as ligands. The system is purged and then heated to 500°C , which removes the hydrogen ligands and prepares the surface for the next cycle after cooling back down to 300°C .¹⁸ This ALD method of Si_2H_6 can be made into a thermal AS-ALD technique,¹⁹ when one applies the heat in the third step of the procedure only locally; in this case with an Ar+ laser with a full width at half maximum (FWHM) of $150 \pm 25\mu\text{m}$, the resulting growth rate distribution after multiple cycles has an FWHM of about $200\mu\text{m}$ and a base of $300\mu\text{m}$. This technique uses the decomposition behavior of precursors to its advantage, although care should be taken as for typical ALD precursors, this is not optimal because of the associated deterioration of the deposited material.²⁰ Another potential candidate system is MeCpPtMe_3 and O_2 , a process that has been shown to depend sensitively on temperature: At 150°C , there is no growth while the ALD window sharply starts at 250°C (Ref. 21)—a near-ideal temperature profile for the application we explore here.

Clearly, the approach has some potential. To assess this more broadly, we focus in this article on controlling the localization of nucleation on a substrate induced by localized heating. We split the problem into two parts: first, we model the evolution of temperature profiles as a function of laser properties and illumination protocol. Then, we develop a simple model for the nucleation and growth of deposition domains during either the first or the second half-cycle. We perform Monte Carlo simulations to study the conditions under which growth can be initialized and terminated thermally. Previous kinetic Monte Carlo simulation performed on ALD

FIG. 1. Schematic view of our model: a short laser pulse (heat source) is used to localize the heating (temperature profile) of the substrate, activating the area for growth (growth area) by a precursor in the gas phase, and ideally there should be no growth in the area at the reference temperature (nongrowth area).

has focused on capturing the atomistic scale during the early stages of deposition²² or has focused on larger length scales, in particular, to address the issue of conformality—the ability to deposit reliably on nonflat templates—in ALD, studying the ALD process specifically for the system with high aspect ratio features.²³ Here, we will take a coarse-grained approach suitable to address the characteristics of nucleation and growth in the intermediate regime between the atomistic scale and the models conventionally used to study conformality. Our model takes into account both the dynamics and the temperature dependence of the reaction and is, therefore, capable of modeling evolving, and partially saturated, conditions.

II. COMPUTING THE TEMPERATURE PROFILES

To begin with, let us study the temperature profile at the surface of a substrate. We assume that the substrate is only heated for a short amount of time so that the gas is not itself convectively heated via the substrate. This is described by the heat equation, supplemented with a source term to describe the effect of local heating by a laser pulse and a (Newtonian) cooling term to model the exchange of heat with the surroundings which will generally be at a lower temperature. The Newtonian cooling term is typically used to model convection but can be used as a linearized representation for other cooling mechanisms, such as radiative transfer, with use of an effective heat transfer coefficient.²⁴ We consider the specific geometry of a 3D slab, with an area A (m^2) and thickness d (m). We will assume this width to be small enough to allow the heat to become uniformly distributed in the z -direction instantaneously. The slab is insulated from its surroundings (i.e., no heat exchange) at the bottom surface. In this situation, the equation governing the evolution of the temperature profile $T(\vec{r}, t)$ in space and time is

$$\rho c_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = -\frac{h}{d}(T - T_{\text{ext}}) + \frac{I(\vec{r}, t)}{d}, \quad (1)$$

with T (K) being the temperature, T_{ext} (K) being the temperature of the surroundings, t (s) being the time, and I (W m^{-2}) being the incident power per unit area of the laser. In addition, we have the material parameters, such as the specific heat c_p ($\text{J kg}^{-1} \text{K}^{-1}$), the density ρ (kg m^{-3}), the thermal conductivity λ ($\text{W m}^{-1} \text{K}^{-1}$), and the heat transfer coefficient h ($\text{W m}^{-2} \text{K}^{-1}$). For the heat transfer coefficient, we will use a typical value of $10 \text{ W m}^{-2} \text{K}^{-1}$.²⁴ For demonstrational purposes, we will first work with the heat equation in a one-dimensional form, considering the situation in which the temperature profile changes only in the x -direction. If we then rescale time and space according to

$$T = T_{\text{ext}}(1 + \tilde{T}), \quad t = \tau \tilde{t}, \quad x = z \tilde{x}, \quad I = q \tilde{I}, \quad (2)$$

with $z = \sqrt{\lambda d/h}$, $\tau = \rho c_p d/h$, and $q = T_{\text{ext}} h$, we arrive at the dimensionless form of the heat equation (1) that we will use to illustrate our following solution procedure:

$$\frac{\partial \tilde{T}}{\partial \tilde{t}} - \frac{\partial^2 \tilde{T}}{\partial \tilde{x}^2} = -\tilde{T} + \tilde{I}(\tilde{x}, \tilde{t}). \quad (3)$$

The scaling time τ can be interpreted as the typical time it takes one unit of area of the slab to cool down by dissipation of heat into the surroundings. For the materials we consider here, we use the order-of-magnitude estimates (not intended to represent one particular material but rather to assess the effects of changing material parameters in general) for glass-type and silicon-type substrates;²⁵ τ —the thermal relaxation time for substrate cooling in a colder environment—is of the order of 0.05 s. On timescales shorter than this τ , the material will not cool appreciably by heat exchange with the surroundings. The scaling length z likewise has a direct physical interpretation. For this, it is instructive to first consider the thermal diffusivity $\alpha = \lambda/(\rho c_p)$ ($\text{m}^2 \text{s}^{-1}$), which measures the rate at which heat is diffusively transported within the material. With this quantity, we may rewrite $z = \sqrt{\alpha \tau}$ from which we conclude that z is the typical length scale heat travels by diffusion in one characteristic time τ . For the material classes, we consider (glass-type and silicon-type),²⁵ z is computed, using the formulas above, from literature material properties to be between 10^{-4} and 10^{-3} m.

The laser is modeled to have a Gaussian intensity profile with scaled width $\tilde{\sigma}$ (–), and to begin with, we will consider a single short pulse with scaled amplitude $\tilde{A}$ (–) and duration (in scaled time units) of $\tilde{D}$ [–],

$$\tilde{I}(\tilde{x}, \tilde{t}) = \begin{cases} \tilde{A} \exp(-\tilde{x}^2/\tilde{\sigma}^2), & \tilde{t} \leq \tilde{D}, \\ 0, & \tilde{t} > \tilde{D}. \end{cases} \quad (4)$$

The finite duration of the pulse, which in real-time units equals $t_p = \tau \tilde{D}$, introduces a new length scale into the problem—the length scale over which the pulse can penetrate into the layer by thermal conduction. This penetration depth is, therefore, given by $z_p = z \sqrt{\tilde{D}}$. Likewise, the finite width of the pulse introduces a second time scale $\tau_\sigma = \tau \tilde{\sigma}^2$ that measures the time it takes for the temperature profile to broaden by once the width of the laser. Equation (3) for the dimensionless temperature profile is readily solved using Green's functions²⁶ (to avoid notational clutter, we will drop the tildes from now on and work in scaled units unless explicitly noted otherwise): for a given source function $\tilde{I}$, its solution is given by

$$T(x, t) = \int_0^t d\theta \int_{-\infty}^{\infty} dy G(x, t|y, \theta) I(y, \theta), \quad (5)$$

with $G(x, t|y, \theta)$ being appropriate Green's function

$$G(x, t|y, \theta) = \frac{\exp\left(-\frac{(x-y)^2}{4(t-\theta)}\right)}{2\sqrt{\pi}\sqrt{t-\theta}}. \quad (6)$$

Applying Eq. (6) to the single-pulse profile leads to the following analytical solutions for the scaled temperature profile:

$$T(x, t) = \begin{cases} \frac{1}{4} A \sigma \sqrt{\pi} \exp\left(\frac{\sigma^2}{4} - |x|\right) \left(\operatorname{erf}\left(\frac{4t + \sigma^2 - 2|x|}{2\sqrt{4t + \sigma^2}}\right) - \operatorname{erf}\left(\frac{\sigma}{2} - \frac{|x|}{\sigma}\right) \right) \\ \quad + \frac{1}{4} A \sigma \sqrt{\pi} \exp\left(\frac{\sigma^2}{4} + |x|\right) \left(\operatorname{erf}\left(\frac{4t + \sigma^2 + 2|x|}{2\sqrt{4t + \sigma^2}}\right) - \operatorname{erf}\left(\frac{\sigma}{2} + \frac{|x|}{\sigma}\right) \right), & t \leq D, \\ \frac{1}{4} A \sigma \sqrt{\pi} \exp\left(\frac{\sigma^2}{4} - |x|\right) \left(\operatorname{erf}\left(\frac{4t + \sigma^2 - 2|x|}{2\sqrt{4t + \sigma^2}}\right) + \operatorname{erf}\left(\frac{4(D-t) - \sigma^2 + 2|x|}{2\sqrt{4(t-D) + \sigma^2}}\right) \right) \\ \quad + \frac{1}{4} A \sigma \sqrt{\pi} \exp\left(\frac{\sigma^2}{4} + |x|\right) \left(\operatorname{erf}\left(\frac{4t + \sigma^2 + 2|x|}{2\sqrt{4t + \sigma^2}}\right) + \operatorname{erf}\left(\frac{4(D-t) - \sigma^2 - 2|x|}{2\sqrt{4(t-D) + \sigma^2}}\right) \right), & t > D. \end{cases} \quad (7)$$

These solutions allow us to study the spatial and temporal evolution of the surface temperature of the substrate. To facilitate comparison, we will choose parameters such that the maximum temperature at position $x = 0$ is always 600 K. For different pulse durations D , this is achieved by adjusting the power amplitude A of the laser.

First, let us look at the scaling of the required power amplitude A to reach the target maximal temperature of 600 K at the center of the illuminated spot, as a function of the pulse duration D . As Fig. 2(a) shows, in which both the power amplitude and the time have been scaled back to real units using Eq. (4), there are three distinct regimes. In the first, short-pulse regime, for pulse times below τ_σ , there is a linear relation between the amplitude and pulse time. In the second regime, for times between τ_σ and τ , A scales as $\sqrt{D}$. In the final, long-pulse regime where pulse times are greater than τ , the amplitude levels off to its asymptotic value, corresponding to a limit where there is, effectively, constant illumination. We may intuitively understand these regimes as follows: below τ_σ , there is no significant diffusive broadening of the spot and all the energy is deposited into an area with width σ . For time scales longer than τ_σ , the spot does broaden the distribution of the injected energy over a wider area; for this reason, a higher amplitude A is needed to reach the target central temperature of 600 K compared to what would have been required if the short-time regime was extended further. In the terminal, long-time regime for times greater than τ , finally, the illuminations happen on time scales long enough to be balanced by dissipation from the cooling term and the amplitude becomes independent of D .

As the duration of the pulse is changed, the effective width of the profile changes too. As Figs. 2(b) and 2(c) show, shorter pulses lead to narrower profiles. We use the full width at half maximum (FWHM) W as a measure of the spatial width of the profile, and in Fig. 2(c), we graph it as a function of pulse duration D . Again, three regimes are visible. The first occurs for pulse times shorter than τ_σ , where the substrate heats up quickly, and the energy injected does not have time to spread diffusively. In this regime, the width of the temperature profile remains equal to the intrinsic width σ of the Gaussian laser beam, independent of D . In the second regime, for pulse times between τ_σ and τ , the width W becomes proportional to $\sqrt{D}$; this is the regime in which the width is controlled by the pulse time. In the third, long-pulse regime (pulse times larger than τ), we see a leveling off of the width as a stationary profile develops due to the balance between heating and cooling off; in this regime, the width no longer changes with D .

The reason to illuminate in the first place is to ensure that locally, in as limited a region as possible, the temperature exceeds some critical value for efficient deposition. In Fig. 2(d), we illustrate this “operational time window” as a function of pulse duration. For ultrashort pulses, the width of the profile becomes independent of D because the pulse shape does not become significantly broader due to diffusion—a fact also borne out by (c). For pulse times larger than τ_σ , the time spent above the half-max temperature becomes a linear function of the illumination time.

In summary, our analysis shows that shaping the illumination protocol involves striking a balance between time and space. If we attempt to limit width W of the nucleation zone where the temperature exceeds the threshold value, we must work at the lower end of pulse durations D . This is, however, also the regime where higher laser powers are required (although, as we shall see, these power requirements likely can be met with fairly standard technology), and potentially more challenging, the operational time window is limited; the growth must take place within a very limited amount of time, which places constraints on the surface physical-chemistry, reactions should proceed swiftly once the threshold temperature is exceeded. We will comment in the discussion and conclusion on overall feasibility but for now will turn to the second part of the process: the nucleation and growth of the surface deposition process.

III. MONTE CARLO SIMULATION OF NUCLEATION AND GROWTH

To investigate the growth of the deposited material at the surface, we use a coarse-grained kinetic Monte Carlo (MC) model.²⁷ Our model is intended to provide a general proof-of-principle to assess the feasibility of the laser-assisted technique and does not model specific chemistry. In this model, the substrate is represented as a two-dimensional square lattice whose sites may be occupied or empty to represent the local presence or the absence of a deposited atomic layer. Importantly, this is a coarse-grained representation; a single lattice site represents roughly $100 \times 100 \text{ nm}^2$ and thus a mesoscale patch of the deposited material rather than a single atom. The deposition process itself is represented in this model by three energy contributions. The first is an energy barrier for deposition ΔE_{dep} , which—together with the local temperature and the ambient concentration of the species to be deposited—determines the rate at which new domains are nucleated on the surface.²⁸ On the atomic scale, there may be some surface mobility/diffusion of, for instance, adsorbed precursor species, which allows adsorbed species to explore the surface before they are fixed. To be able to capture such effects,

FIG. 2. Spatial and temporal characteristics of the surface temperature profile after illuminating the substrate with a single pulse of a Gaussian laser profile with width $\sigma = 500$ nm and different pulse durations D . (a) Required amplitude to attain a central (i.e., at $x = 0$) temperature of 600 K for a given pulse time. (b) Temperature profiles along the x axis, shown at $t = D$ for the glass substrate. (c) Width at half max of the temperature profile as a function of the pulse time. (d) Operational time window—amount of time spent above the half max temperature at position $x = 0$.

we include the possibility of neighbor interactions between the deposited species. These interactions are included for completeness and can be switched off; the features of the deposition process we describe in the following depend quantitatively but not qualitatively on the presence of lateral interactions. A final note: in this general model, we do not explicitly choose which step of the typical two-stage ALD process is modeled here. Our nucleation model is to be understood in the spirit of the Avrami model,²⁸ frequently invoked to describe the dynamics of growth in AS-ALD settings where growth is locally promoted or, equivalently, inhibited elsewhere. The main feature we wish to capture is that in one of the two half-reactions, the surface density of reactive sites is locally elevated

through laser heating. In this same vein, the energy barrier for deposition is to be understood as an aggregate parameter representing a combination of physical and chemical aspects of the process such as the physisorption of precursor, local convection, the presence or absence of surface defects and contaminants, and other process variables.

Once the initial nucleation event has occurred, further deposition is potentially facilitated at sites adjacent to already-occupied positions on the lattice. We include this optional co-operativity in our model through nearest-neighbor (NN), next-nearest-neighbor (NNN), and next-next-nearest-neighbor (NNNN) contributions to the deposition energy. Figure 3 shows how the NN terms are

FIG. 3. Schematic view of the lattice used in the kinetic MC simulations. We show the site where a deposition event is attempted in black and already-occupied sites in gray. Each occupied nearest neighbor reduces the energy barrier for deposition by an amount ϵ_{NN} . Thus, the total energy barrier for deposition if n_1 nearest neighbors are occupied is $\Delta E_{\text{tot}} = \Delta E_{\text{dep}} - n_1 \epsilon_{NN}$. Higher order terms are included in conceptually similar fashion.

included: the bare energy barrier for addition ΔE_{dep} is reduced by an amount ϵ_{NN} for each already-occupied neighbor. Higher order terms are included in a similar fashion; the corresponding energy decreases per NNN or NNNN occupied site are $\epsilon_{NNN} = \gamma/\sqrt{2}$ and

$\epsilon_{NNNN} = \gamma/2$, respectively, and the factors $\sqrt{2}$ and 2 accounting for different distances to the respective surrounding sites. Together, the neighbor terms encode the facilitation of growth at the edges and promote the formation of compact (and round, to the extent that the lattice allows) deposited domains. The values of various energies, of course, differ from process to process but for the remainder of this article, we will set $\Delta E_{\text{dep}} = 6 \times 10^{-20}$ J, $\epsilon_{NN} = 1 \times 10^{-20}$ J, and $\gamma = 1 \times 10^{-21}$ J.

Our MC algorithm mimics deposition by attempting, at a coarse-grained attempt frequency ν_0 that reflects the ambient concentration, kinetic transport processes in the gas, and the mesoscopic dimensions of one site, to switch one site from unoccupied to occupied per MC step. We note already that one MC step does not correspond to one tick of the wall clock and will return to the issue of simulational versus real time shortly. If the site was already occupied, nothing is done. If the site is not yet occupied, we compute the total energy barrier to switching from the bare energy, and n_1 , n_2 , and n_3 are the numbers of already present NN, NNN, and NNNN: $\Delta E_{\text{tot}} = \Delta E_{\text{dep}} - n_1 \epsilon_{NN} - n_2 \epsilon_{NNN} - n_3 \epsilon_{NNNN}$. Using this energy, we compute the acceptance probability P_{acc} for flipping the site from unoccupied to occupied using the Boltzmann factor: $P_{\text{acc}} = \exp(-\beta \Delta E_{\text{tot}})$, with $\beta = 1/k_B T$ being the inverse thermal energy.²⁹ The role of local temperature is thus crucial: deposition happens with a higher probability if the local temperature is higher. This will be how we incorporate the results from Sec. II into our deposition MC model.

Although our approach is coarse-grained, the effective resolution of the model can be altered from atomistic to the coarser scales we use by adjusting the parameters. This scale-dependent remapping of parameters is achieved by ensuring that the most relevant dynamic is observable—the time to reach the end of the half-reaction (EHR) independent of cell size. In particular, the actual clock time t_M^{EHR} that it takes to cover an area that contains, say, M atoms should be the same as the clock time t_N^{EHR} that it

FIG. 4. The end of half-reaction times of the system can be mapped on each other (a) if there is no neighbor interaction shown for different coarse-grainings and (b) with neighbor interaction an additional phenomenological scaling function is used to map the coarse-grainings.

FIG. 5. Typical spot grown in our MC model (a) for a laser pulse with a width of $\sigma = 500$ nm, a pulse duration of $D = 250$ ns, and a maximum central temperature of 700 K on a glasslike substrate of $10 \times 10 \mu\text{m}^2$. The energy parameters of the deposited material were set at $\Delta E_{\text{dep}} = 6 \times 10^{-20}$ J, $\epsilon_{\text{NN}} = 1 \times 10^{-20}$ J, and $\gamma = 1 \times 10^{-21}$ J. The bare substrate is the dark area (blue), and lattice sites where deposition has occurred are shown in white. (b) Zooming into the spot of (a), the circle indicates the radius, as derived from radial density distribution, and the vertical lines are the boundaries used to determine the connectivity of the spot.

takes to fully cover the same area represented in coarse-grained fashion by N cells, that each contains q atoms (i.e., $M = qN$). Calling Δt_M the time-per-MC-move in the M system, we should, therefore, choose Δt_N such that the two times

$$t_M^{\text{EHR}} = f(M) e^{\beta \Delta E_{\text{tot}}} \Delta t_M \quad (8)$$

and

$$t_N^{\text{EHR}} \equiv f(N) e^{\beta \Delta E_{\text{tot}}} \Delta t_N \quad (9)$$

are equal. The function $f(p)$ is a numerical factor accounting for the probabilistic and combinatorial contributions to the end of half-reaction time, which is also affected by the average number of attempts needed before an actual unoccupied site (rather than one already occupied) is targeted for deposition. Now, $\Delta t_M = (M\nu_0)^{-1}$ is set by the attempt frequency defined above and the number of atoms M (since these are visited sequentially in the MC algorithm, but simultaneously in actuality, the number of sites factors into

FIG. 6. Results of a grown spot initiated by localized heating of the substrate. (a) Probability of growing a spot for different pulse times and varying maximum temperature for a laser with width $\sigma = 500$ nm. (b) Probability of growing a spot for different pulse times and varying maximum temperatures for a laser with width $\sigma = 250$ nm. (c) Diameter of successful full grown spots for a laser with width $\sigma = 500$ nm. (d) Diameter of the successful full grown spots for a laser with width $\sigma = 250$ nm.

Δt), and, therefore, if we remap times as follows:

$$\Delta t_N = \left(\frac{1}{M_{V_0}} \right) \frac{f(M)}{f(N)}, \quad (10)$$

then the end of half-reaction time should remain a constant among differently coarse-grained simulations. A big advantage of rescaling times, rather than energies, in our kinetic MC scheme is that we are able to work at the same acceptance probabilities P_{acc} in the coarse-grained system, greatly reducing simulation times while retaining accurate dynamical outcomes.

In the simplest case, without neighbor interactions, the function $f(p)$ can be analytically computed and is given by $f(p) = H_{p-1}$, with H_k being the k th so-called harmonic number, defined by $H_k = \sum_{i=1}^k (1/i)$. In Fig. 4(a), we show the results for simulations with different coarse-grained systems that are all of the same physical size at different temperatures. After rescaling time according to the procedure detailed above, the end of half-reaction times averaged over 60 simulations are, indeed, all equal. When the neighbor interactions are included, we have no analytical expression for $f(p)$ and the function of the end of half-reaction time must be further corrected relative to the system without neighbor interactions with a phenomenological scaling function $f(p) \approx (1.75 p^{0.06}) H_{p-1}$. As Fig. 4(b) shows, with this additional correction, the end of half-reaction times is independent of the resolution of the system with neighbor interactions. Figure 4(b) also shows the expected exponential dependence of the end of half-reaction time on temperature. With these conventions, we are ready to combine localized heating and coarse-grained nucleation and growth of deposition domains in one simulation.

IV. RESULTS

A. Spot deposition: Growth prompted by a single laser pulse

Because nucleation and growth, as we have seen, occur in accelerated fashion at higher temperatures, heating a localized area by means of a single laser pulse could, in principle, localize deposition to a predetermined spot on the substrate. We have tested this concept in our simulations for various illumination protocols. We simulated the evolution of the deposit for two different widths σ_0 of the laser (set to 250 and 500 nm). In addition, we vary the pulse duration D and the maximum substrate temperature reached at the center of the illuminated spot. The results of a typical simulation, as shown in Fig. 5, demonstrate that indeed a localized spot develops. Although there is some deposition in the peripheral regions as well—this is unavoidable in a stochastic process—the growth remains largely limited to the illuminated area. The parameters of interest for analyzing the growth of the spot are the spot size and a property we will refer to as connectivity. Our measure for the size of the spot is its radius r_c , which we determine from the radial distribution function of the deposited material, which maps the density of deposition relative to the center of the laser spot (details are given in the Appendix). Once we have this radius, we determine the connectivity of the spot. Since our objective is to area-selectively deposit conducting patches, it is important that a conducting path

exists from one side of the spot to the other. We quantify this by connectivity, which we determine using radius r_c : relative to the center-of-mass x_c of the spot, we draw two vertical lines that are at $x = x_c - 0.5r_c$ and $x = x_c + 0.5r_c$. If there exists a percolating (connected) path between these two lines, we label the spot as connected. We repeat this measurement for many spots, grown at same conditions, and average the results to compute the probability P_c that an individual spot is connected. P_c is a number between 0 and 1 and quantifies the connectivity of the spot.

We vary the pulse time of the laser from 1 to 750 ns, and in Figs. 6(a) and 6(b), we show the dependence of connectivity P_c on the peak temperature for a wider [500 nm (a)] and narrower [250 nm (b)] laser spot. In all cases, we see that (as expected) the probability of depositing a connected spot increases with peak temperature for all pulse lengths and approaches $P_c = 1$ at the higher end of the temperature range, doing so quicker for longer pulse durations. Still, even for ultrashort pulses of 1 ns, the connectivity probability gets up to 0.8 at 700 K. For narrower pulses with a width of 250 nm, the entire P_c curve is shifted to higher temperatures with a width of 250 nm and the probability curve is shifted to higher temperatures, and the transition from no to almost complete connectivity is flattened compared to the laser width of 500 nm.

To assess the feature size that we can reach, we also measured the diameter of the connecting spots; this is shown for peak

FIG. 7. Snapshot of the MC model where three laser pulses are used to heat the substrate, with the width of the laser $\sigma = 500$ nm, pulse time $D = 300$ ns, maximum temperature 700 K, and the distances between the pulses $\delta = 1 \mu\text{m}$ on a glasslike substrate (the dark area) of $10 \times 10 \mu\text{m}^2$. The energy parameters of the deposited material were set to $\Delta E_{dep} = 6 \times 10^{-20}$ J, $\epsilon_{NN} = 1 \times 10^{-20}$ J, and $\gamma = 1 \times 10^{-21}$ J; the growth is shown in white and the vertical lines indicate the start and end lines for testing the connectivity of the line.

temperatures above 550 K in Fig. 6(c). We work at these higher temperature because as the other results suggest, P_c is too low at lower temperatures, ruling this out as a feasible regime for the current set of typical parameters. In general, the diameter shows the expected steady increase with increasing temperature; likewise, longer pulse times lead to larger diameters. In Fig. 6(d), the results for laser width of $\sigma = 250$ nm are shown; indeed, for smaller laser spots, we see smaller diameter spots. Again, this comes at a cost—the required temperatures are higher. For temperatures below 600, P_c is, again, too low; these results are not shown.

B. Line deposition: Growth prompted by a moving, pulsed laser

In this final section, we look at the deposition of lines. To minimize the thermal load, lines are best written using multiple individual dots, where one must demand that these too are connected from one side to the other. Specifically, we illuminate the substrate with three laser pulses separated by a distance δ that we vary. We use a laser pulse with fixed width $x_0 = 500$ nm. For the timing of these three pulses, we define a duty cycle consisting of a repeating pattern of illumination for a duration of D , followed

FIG. 8. Results of growth due to three sequential laser pulses with width $\sigma = 500$ nm at a center to center distance δ for three different time patterns, the first pulse time $D = 30$ ns and waiting time $t_w = 10$ ns are shown in dots; the second pulse time $D = 30$ ns and waiting time $t_w = 100$ ns are shown in squares; and third pulse time $D = 300$ ns and waiting time $t_w = 10$ ns are shown in triangles. (a) Probability to get a connecting line between the center of the first laser pulse and the center of the third laser pulse with a maximum temperature of 600 K. (b) Probability to get a connecting line between the center of the first laser pulse and the center of the third laser pulse with a maximum temperature of 700 K. (c) Width of the line due to multiple laser pulses with a maximum temperature of 600 K. (d) Width of the line due to multiple laser pulses with a maximum temperature of 700 K.

by a refractory period (a “waiting time”) t_w , during which the center of the laser spot moves a distance δ . As before, we set the maximum temperature the substrate reaches during the first pulse to some target temperature; for subsequent pulses, we use this same intensity. To assess the effect of changing this temperature, we used maximal temperatures of 600 and 700 K (see Fig. 7).

Similar to what we assessed for single spots, we can now determine whether a line of spots is connected as a whole and how wide it is. Percolation is determined by drawing lines through the centers of the first and last spots and computing the probability (by averaging over many repeated measurements) of the connected path between the two lines. The width of the line is determined using the width at half maximum of the lateral density profile, averaged along the connecting line between the first and last spots.

We used three different pulse patterns. The first is a $D = 30$ ns pulse with a waiting time of $t_w = 10$ ns, the second is with a pulse time of $D = 30$ ns and a waiting time of $t_w = 100$ ns, and the third is with $D = 300$ ns and $t_w = 10$ ns. We vary the distances between the centers of the laser pulses between $\delta = 0.5$ and $1.5 \mu\text{m}$. We observe that within this range, if we take a maximal center temperature of 600 K, we get near-perfect conductance ($P_c \approx 1$) for pulse spacings smaller than $\delta = 0.75 \mu\text{m}$ for all pulse patterns considered. For longer pulses ($D = 300$ ns, $t_w = 10$ ns), this near-perfect conductance is retained up to a pulse distance of $\delta = 1 \mu\text{m}$ [see Fig. 8(a)]. The maximal distance allowed between pulses to still obtain a connected line increases by a further 10% if the maximal central temperature is increased to 700 K to $\delta = 1.1 \mu\text{m}$. For the longest illuminations ($D = 300$ ns and $t_w = 10$ ns), it becomes up to $1.4 \mu\text{m}$ [see Fig. 8(b)]. The width of the line is essentially the same as before and is primarily determined by the length of the pulse, with longer pulses leading to wider lines. The width is additionally influenced by the distance between pulses: The larger the distance, the narrower the line [see Figs. 8(c) and 8(d)]. For both temperatures, the probability and the width are not influenced by the waiting time between pulses, which thus appear to be sufficiently long to be able to ignore transient heating.

V. DISCUSSION AND CONCLUSION

In this work, we investigate using analytical and computational models the possibility of localizing and controlling the nucleation and growth of the initial spot by local heating of the substrate. This local heating is achieved by a short pulse from a laser with a Gaussian beam profile. We find that the effective width of the resulting temperature profile on the substrate can be controlled by modifying the pulse time of the laser and demonstrate the extent of this control for both glass and silicon substrates. Furthermore, we use the kinetic Monte Carlo method to simulate the subsequent nucleation and growth of a deposited atomic layer on the heated substrate and were able to identify model parameters and a heating protocol for which a single spot with controllable connectivity (as required for conduction through the layer) and size; control is achieved by adjusting the maximum temperature and pulse time resulting in predictable and systematic changes to spot size and properties. By firing multiple pulses at the substrate, it is also possible to deposit lines locally. Our simulations suggest that conducting lines as narrow as $1 \mu\text{m}$ should be feasible,

rendering this a technique with potential use and application for the fabrication of large-area devices such as solar panels and OLED displays. Such an application would benefit from the use of precursors that feature a sharp transition in surface coverage depending on temperature. Our work is a computational proof-of-concept; further work will be needed to fully assess the applied potential. This will involve calibrating the parameters in our current model (such as the gas density during exposure, the surface coverage as a function of temperature, and the end of half-reaction time intrinsic to the particular physical chemistry) against those in common ALD materials and chemistry settings and selecting optimal candidates for further trials. As noted in the Introduction, the technique proposed here may be useful for the deposition of an initial seed layer, templating a pattern for further regular ALD cycles. If subsequent layers are deposited using the same process however, repeated laser scans are required. For the micrometer-sized features we target here, the required precision in alignment is well within current technological possibilities, and feature functionality (conductivity) does not suffer critically from some edge roughness. For potential future applications with stricter specifications, additional modeling will be needed to accurately account for the changes in substrate topography, which may require changes to the illumination protocol as the deposited feature builds. Regardless, the micrometer-scale writing of linear patterns, we suggest, may be within current reach, and we hope that this work will invite follow-up to further explore this potentially relevant approach to area-selective atomic layer deposition.

APPENDIX

Analyzing the grown spot due to a single pulse is done in a two-step approach; the first step is to determine the radial distribution of activated sites with the origin in the center of the system. From this radial distribution, radius r_c is determined by a cutoff at the density of 0.3 (see Fig. 9); with this radius, two vertical lines are

FIG. 9. Radial density distribution from the center of the system for a single pulse, the dots, and the determined radius is shown with the line.

defined at $-0.5r_c$ and $0.5r_c$ in the system of growth (see Fig. 5). If there is a connecting path between them, the spot is labeled “connected,” and the diameter of the spot is defined as the distance between the two vertical lines.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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