Pulsed laser deposition-type growth kinetics: control by moderate-sized mobile clusters

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Abstract. The nonequilibrium growth kinetics of pulsed laser deposition (PLD) is investigated using a realistic set of rate equations. Our results indicate that growth from a supersaturated pulsed flux of kinetically hyperthermal species is ruled by the kinetics of moderate-sized mobile clusters. On vicinal surfaces (e.g., oxide surfaces), whose high corrugations hinder large-scale diffusions at the moderate temperatures commonly used in PLD, direct impingement and transient mobility play a key role in the nucleation of such mobile clusters. Based on these insights, we propose a new description of the growth kinetics of PLD that should prove valuable in the development of oxide-based nanoscale devices.

Two decades after the first successful preparation of functional oxides with complex stoichiometry in epitaxial thin film form [1, 2], pulsed laser deposition (PLD), the method mainly responsible for this breakthrough, is a well-established technique. PLD is widely used to prepare high quality films in various frontier fields, for example the preparation of materials with giant/colossal magneto resistive properties [2], the heteroepitaxy of atomically perfect layers and heterostructures of dielectric oxides on massive semiconductors [3], and oxide nanostructuration by self-organization [4]. However, the application of PLD is typically guided by an intuitive empirical approach, and the physical mechanisms underlying the growth kinetics during PLD are poorly understood. This knowledge gap represents a serious hindrance to the use of PLD in outstanding applications such as nanoengineering, which demand nanoscale control of the operating atomic mechanisms.

Only a few studies have examined the PLD-type growth kinetics; most of them have focused on the nucleation regime [5], which has distinctive characteristics due to the pulsed
nature of the incoming flux. However, the real degree of pulse supersaturation (as large as 0.05 ML/pulse), the nature and energy of the impinging species including potential phenomena of transient mobility, the lifetime and the kinetics of surface species generated in nonequilibrium amounts, and related processes are phenomena regularly omitted in previous models [6, 7]. Such omissions mean that these models cannot be used to elucidate the mechanisms underlying ubiquitous experimental findings such as: (i) under optimized conditions, the surface roughness of PLD-grown films is lower than that of the corresponding films prepared by quasi-equilibrium techniques such as molecular beam epitaxy or thermal evaporation [8, 9]. This is explained as a result of nonequilibrium transports [10, 11], which promote an efficient layer completion prior to the nucleation of top layers happens. (ii) The surfaces of PLD-grown films exhibit lateral correlation lengths larger than those expected for highly corrugated (several eV) oxide surfaces at the moderate temperatures commonly used [7]. From these evidences, the effective diffusion coefficients [7, 9] (∼10⁻¹⁰ cm² s⁻¹) by PLD are estimated to be three orders of magnitude larger than those obtained by sputtering and co-evaporation ([9] and references there in). (iii) The temperatures at which epitaxy occurs in PLD are lower than those required by other vapour deposition techniques [7]. All of these observations suggest that the growth kinetics of oxides during PLD is enhanced with respect to other energetic (e.g., sputtering) and thermal (evaporation) deposition techniques [7]–[11].

In this paper, we describe the PLD-type growth kinetics on a highly corrugated vicinal surface by means of a realistic set of rate equations. From their numerical solutions, we elucidate the origin, nature, stability and underlying mechanisms that govern the kinetics of the nonequilibrium mobile species in this system and demonstrate that the growth process is controlled by moderate-sized clusters. Finally, we discuss the implications of these findings in the light of the above observations.

A realistic rate equation (considering first and second order contributions) that describes the growth in a step-flow regime from a supersaturated pulsed flux of kinetically hyperthermal (hereafter ‘hot’) heterogeneous species on the highly corrugated vicinal surface of an oxide substrate (i.e., PLD-type growth) is the following:

\[ \frac{\partial \rho_n}{\partial t} = \tilde{F}(t) \sum_{i=1}^{n} \alpha_i(t) A_{n-i} \rho_{n-i} - \tilde{F}(t) A_n \rho_n - \tilde{F}(t) \alpha_n(t) A_s \rho_s + \sum_{i=1}^{n-1} (D_i \sigma_{n-i} + D_{n-i} \sigma_i) \rho_i \rho_{n-i} \\
- \sum_{i=1}^{\infty} (D_i \sigma_n + D_n \sigma_i) \rho_i \rho_n - D_n \rho_n \sigma_n \rho_s - \rho_n \sum_{i=1}^{n/2} \Gamma_i^n + \sum_{i=n+1}^{n^*} (\Gamma_i^n + \Gamma_i^{n-n}) \\
+ \Gamma_s^n \rho_s - \epsilon_n \rho_n - \frac{\partial}{\partial \vec{r}} \left( D_n \frac{\partial}{\partial \vec{r}} \rho_n \right), \]

(1)

where \( \rho_n, \rho_0 = 1 - \sum_{i=1}^{\infty} \rho_i \) and \( \rho_s \) are the density of clusters of size \( n \), the fraction of uncovered surface and the density of step sites, respectively. \( \tilde{F}(t) \) corresponds to the pulsed flux of incoming particles belonging to the minority chemical species (other than oxygen under PLD conditions) in the system, which limits the growth kinetics. \( \tilde{F}(t) \) is related to the continuous deposition flux (\( F \) in ML s⁻¹) according to the relation \( \tilde{F}(t) = (Ft_0/t_p)U(t_p - t') \), where \( t_p \) and \( 1/t_0 \) are the pulse width and repetition rate, respectively; \( U(x) \) is the unit step function; and \( t' \) is the time lapsed from the beginning of the previous pulse, which is computed as the remainder of the division \( t/t_0 \). The pulsed flux is composed of species whose sizes are distributed according to the function \( \alpha(n, t) \),
The relationship between the evaporation rate of an $n$-sized cluster, $\sigma_n$, and the flux, $\Phi_1(n, m)$, can be described by the following equation:

$$\sigma_n = \frac{2 \sqrt{n \pi}}{\Gamma_1(n, \infty)} \cdot \Phi_1(n, \infty)$$

where $\Gamma_1(n, \infty)$ is the capture number of an $n$-sized cluster (a step), $\Phi_1(n, \infty)$ is the capture area by a step, and $\Phi_1(n, m)$ is the capture area by a step of $m$ (with $m > n$).

The capture area by an $n$-sized cluster, $A_n$, is defined as:

$$A_n(R) = \pi \left( \sqrt{\frac{R}{n}} + R \right)^d$$

except $A_0 = 1$ for any $R$.

The capture number of an $n$-sized cluster (a step) is given by:

$$\sigma_n = 2 \sqrt{n \pi}, \quad \left( \sigma_x = \left(1 + \frac{D_n^{S-E}}{D_n} \right)/2 \right)$$

Table 1. Empirical size-scaling relationships [15]. $R$ denotes the capture radius, which is taken as $R = 0$ for direct impingement and $R > 0$ for captures by transient mobility of the impinging hot particles. $D_n$ and $D_n^{S-E}$ correspond to the intra- and inter-terrace diffusion coefficients, respectively, and thus $D_n^{S-E}/D_n \propto \exp[-E_n^{S-E}/k_B T]$ (where $E_n^{S-E}$ is the step-edge barrier) indicates the anisotropy degree of the mass transport across the step. $v_0 = k_B T/\hbar$ is the attempt frequency, where $h$ denotes Planck’s constant. $E_1^{d}$ and $\Delta E_1 (E_b$ and $\Delta E_b)$ correspond to the intra-terrace diffusion barrier for monomers and its increasing rate with $n$ for larger clusters (the effective binding energy of the edge atoms and its attenuation as the atom coordination increases), respectively. $E_n^e$ is the barrier to evaporate an $n$-sized cluster as a whole. $\Phi(n, m) = (n/m - 1)U(n - 2m) + 1$ describes the multiplicity of the binary dissociation phenomenon occurring through $\Phi(n, m)$ independent ways. $U(x)$ and $\delta_{x,y}$ are the unit step and Dirac delta functions, respectively. $\delta_{1,y}$ was used in the dissociation and evaporation size-scaling relationships to simplify the calculation on the basis of considering the dissociation into monomers and their later evaporation as energetically more favourable than the dissociation into larger clusters and their evaporation as a whole. This assumption, which implies $\Gamma_1(n)/\Gamma_1(1) \ll 1$ and $\epsilon_n/\epsilon_1 + \epsilon_n \sum_{j=2}^{n} 1/\Gamma_j^0 \ll 1$ for any $n < 8$ and $1 < i \leq n/2$, was verified for the set of characteristic parameters of the system investigated here.

**Geometric scaling**

Capture area by an $n$-sized cluster: $A_n(R) = \pi \left( \sqrt{\frac{R}{n}} + R \right)^d$ except $A_0 = 1$ for any $R$

Capture area by a step: $A_n^x = R \left( 1 + \frac{D_n^{S-E}}{D_n} \right)$

Capture number of an $n$-sized cluster (a step): $\sigma_n = 2 \sqrt{n \pi}$, $\left( \sigma_x = \left(1 + \frac{D_n^{S-E}}{D_n} \right)/2 \right)$

**Kinetic scaling**

Diffusion coefficient of an $n$-sized cluster (with $n < 10$): $D_n = v_0 \exp \left[ - \frac{E_1^{d} + (n - 1)\Delta E_1}{k_B T} \right]$.

Binary dissociation rate: $\Gamma_1^n = v_0 \Phi(n, m) \exp \left[ - \frac{E_1^{d} + (m - 1)\Delta E_1 + m(n - m)\Delta E_b}{k_B T} \right] \delta_{1,m}$

Evaporation rate of an $n$-sized cluster: $\epsilon_n = v_0 \exp[-E_n^e/k_B T] \cdot \delta_{1,n}$

and hence $\alpha_n(t) = \int_{n-1/2}^{n+1} n \left( \alpha(n', t) / \tilde{F} \right) dn'$ represents the contribution (in percent) of $n$-sized species of a common chemical nature (chemical reactions within the vapour phase are ignored) to the flux. $A_n$ ($A_{n'}$) denotes the capture area of impinging species by $n$-sized clusters (step sites), capture that takes place instantaneously either by direct impingement or by transient mobility of hot species. The transient mobility is understood as the lateral ballistic motion of incident hot species on the growing surface prior to thermalization with the substrate. During this motion, the hot species undergo successive collisions with prominent features on the potential energy surface (PES) of the growing surface, thereby progressively transferring their excess translational energy to the substrate. The travelled ballistic path allows the hot species to be captured by neighbouring clusters within an area $R^2$ around the impinging sites. $R$ depends on the energy and nature of the incident species, the PES landscape and the thermodynamic properties of the substrate. It is expected that $R$ increases as the kinetic energy (size) of the hot species increases (decreases), and/or both the PES corrugation and the capability of the substrate to dissipate surface overheating decrease [12]. The relationship between $A_n$ and $R$ is defined in table 1.
Thus, $A_n$ collects the dependence of $\rho_n$ on the excess energy of the incident species considering transient mobility as an instantaneous phenomenon since its timescale (~picoseconds) ([13] and references there in) is several orders of magnitude lower than the characteristic times of thermally activated processes such as the diffusion, dissociation and evaporation. $D_n$, $\sigma_n$ ($\sigma_n$ for step sites) and $\varepsilon_n$ are the random walk diffusion coefficient, the coverage-independent capture number and the evaporation rate of whole clusters of size $n$, respectively. $\Gamma'_n$ is the binary dissociation rate of an $n$-sized cluster into a pair of clusters of sizes $j$ and $(n - j)$, with $j \leq n - j$. $\Gamma'_n$ represents the detachment rate of a $j$-sized cluster from a step. $n^*$ (critical size) denotes the size of the largest cluster whose dissociation rate is non-negligible at the growth timescale.

The terms in equation (1) describe the contributions of the pulsed random incidence (first to third), the random diffusive walk (fourth to sixth), dissociation (seventh to ninth), and evaporation (tenth) to the evolution of the density of $n$-sized clusters $\rho_n(t)$. Third, sixth and ninth terms take into account the fact that the growth takes place on a vicinal surface. The last term accounts for the coverage dependence of the diffusion capture numbers through the uniform depletion model [14]. Non-binary dissociations and/or those in which only part of a cluster evaporates can be addressed as a series of binary processes. Equation (1) is valid for subcritical mobile clusters (i.e., $n \leq n^*$ and $n \leq \hat{n}$, where $\hat{n}$ is the size of the largest mobile cluster). To describe the evolution of the density of subcritical immobile clusters (termed as ‘islands’ hereafter) ($\rho_m = \sum_{i=\hat{n}+1}^{\infty} \rho_i$), equation (1) is modified as follows: (i) the capture-by-step terms are omitted and (ii) the fifth term is replaced with $-\langle \sigma_m \rangle \rho_m^{df} \sum_{i=1}^{\hat{n}} (iD_i \rho_i)$, which considers the decay in $\rho_m$ due to island coalescence; here, $df$ is the island fractal dimension.

The system of $\hat{n} + 1$ partial differential equations $\partial\rho_i/\partial t, \ldots, \partial\rho_{\hat{n}}/\partial t, \partial\rho_m/\partial t$ with $\hat{n} = 7$ and $n^* \rightarrow \infty$ was solved numerically using the standard method of the lines to discretize the 2D space, and then integrating with respect to its temporal variable using the Runge–Kutta method. Initial conditions $\rho_n(\vec{r}, t = 0) = 0$ and periodic boundary conditions with $\rho_n(\vec{r} = \vec{r}_{\text{step}}, t) = 0$ which consider cluster capture by steps to be the main depletion mechanism, are assumed. The system solution requires a consistent set of parameters for clusters of any size. These parameters are estimated using empirical size-scaling relationships [15] (table 1) from their known values for monomers, which were chosen within the typical range for the 2D epitaxial growth of perovskite oxides—in particular, those reported [9] for YBa$_2$Cu$_3$O$_{7-\delta}$ on SrTiO$_3$. Once computed, $\rho_m(\vec{r}, t)$ is averaged over the surface and its time evolution ($\rho_m(t)$) is a key characteristic of the system considered in this study. The calculation was performed for vicinal surfaces formed by terraces of width $l_i$ with non-straight line steps. In particular, the steps considered here had periodic in-phase meandering profiles—similar to envelopes of two-miscut angle steps or induced by Bales–Zangwill instabilities—with $\rho_s = 10\sqrt{(1 + B^2)/\pi^2I_0}\Psi[B^2/1 + B^2]$, where $\Psi[x]$ and $B$ denote the complete elliptic integral and the meandering amplitude, respectively.

Figure 1(a) shows the time evolution of $\rho_n$ for a 1 Hz pulsed flux of monomers starting at $t = 0$ s. As the growth progresses, the $\rho_n$ maxima of the pulses tend to steady values (note, for instance, as $\rho_1$ (black curve) maxima decrease slightly down to reach a steady value after five pulses). This behaviour defines two regimes: a transient regime (magnified in figure 1(b)) and a stationary step-flow regime (figure 1(c)). In both regimes, the pulsed flux gives rise to a pulsed time-dependence of $\rho_n$. Each pulse $\rho_n(t')$, as depicted in figures 1(b) and (c) is comprised of a rising front of $\rho_n$ with increasing time until the flux stops (case of $\rho_1$) or a maximum value is reached for each $\rho_n$ (with $1 < n \leq n^*$), and then, a dropping front occurs until the next pulse. Figure 1(b) (transient regime) reveals that the rising front $\rho_n(t')$ for $t' \leq t_p$ follows a power-law dependence $\rho_n = (P_{l_0}/t_p)^\alpha(\prod_{i=1}^{n-1} A_i)t'^\alpha/n!$. Such a dependence is the analytical
solution of equation (1) under the following conditions: (1) $\rho_i\rho_j \approx 0$, (2) $\rho_i \ll \rho_{i-1}$ and (3) $\nabla \rho_i \approx 0$ for any $i$ and $j$. These conditions correspond to the growth stage (first stage) in which cluster formation by direct impingement and/or transient mobility prevails over other mechanisms, i.e., equation (1) is mostly controlled by the first three terms. For longer times, the conditions are progressively released. Thus initially, condition 1 is relaxed to $\rho_i\rho_j \approx 0$ only for $i > 1$ and $j > 1$, and the time-dependence of $\rho_n$, $\rho_n = (Ft_0/t_p)^n D_i^{n-1}(\prod_{i=1}^{n-1} \sigma/(2i + 1))t^{2n-1}$,
becomes consistent with cluster formation ruled by monomer diffusion (second stage: fourth to sixth terms). Later on, \( \rho_i\rho_j \approx 0 \) just for \( i \gg 1 \) or \( j \gg 1 \) describing new contributions of arising mechanisms (such as aggregation of mobile small clusters and the dissociation of \( n \)-sized clusters, fourth to seventh terms) to the evolution of \( \rho_n(t') \) and so on. In this second stage, \( \rho_n(t') \) ceases to follow a power-law as a result of the competition among the several activated mechanisms.

The crossover between the first stage and the second one \( t_n^{cross} \approx \Xi_n/nD_1 \) (with \( \Xi_n = (\prod_{i=1}^{n-1} (2 - 1/i)(A_i/\sigma_i))^{1/n-1} \) estimated from the continuity condition for \( \rho_n(t') \) at \( t' = t_n^{cross} \)) is flux-independent and shifts to longer times as the capture area by transient mobility \( A_n \) increases. The high surface corrugation causes—even in absence of transient mobility, note that \( \rho_n(t) \) displayed in figure 1 were computed for \( R = 0 \)—\( t_n^{cross} \geq t_p \) for \( n > 1 \) (see solid line in figure 1(b)). This implies that for highly corrugated oxide surfaces, on which diffusion is partially hindered at moderate temperatures, the cluster formation during the arrival of a supersaturated pulse of hot particles (with \( R > 0 \) and then \( A_n > n \), see table 1) takes place almost exclusively by direct impingement and/or transient mobility. As it could be expected for \( t_n^{cross} > t_p \) the first stage vanishes as soon as the flux stops (shown as a change of the slope \( \partial \rho_n/\partial t \) at \( t_p \) in figure 1(b)). It is straightforward to explain because this first stage is preferably controlled by mechanisms related to the incidence process and the surface relaxation of the impinging species at timescale of transient mobility.

Similar behaviour to that described above (shown in figure 1(b)) is observed in the step-flow regime (figure 1(c)) for clusters with a negligible memory effect between pulses (here, those smaller than tetramers). This memory effect appears when the next pulse starts before the dropping front of the previous one has reached its saturation value. For clusters with larger memory effects, \( \rho_n(t') \) ceases to follow a power-law at shorter times. The results indicate that in all cases (both regimes), direct impingement and transient mobility are the main responsible mechanisms for the nucleation of small and moderated-sized clusters in this system.

In quasi-equilibrium growths, the critical size has a dynamic meaning: the size above which further growth of the cluster will cause a lowering of the Gibbs free energy of the system. Thus the critical size represents a crossover size towards a growth regime characterized by increasing cluster stability as the clusters coarsen. However, this definition of \( n^* \) is unsuitable for far-from-equilibrium growths, such as the case considered here where a kinetic interpretation of \( n^* \) is required. The kinetic critical size \( \hat{n}^* \) is defined through the condition \( (D_1\rho_n)^{n^*-n^*} = \prod_{i=n^*+1}^{n^*+10} \Gamma_i/\sigma_i \) as the size of the largest cluster that cannot be stabilized by diffusion of the fastest surface species (here, the monomers). \( n^* \) is thus-understood as the size at which the destabilizing (dissociation) and stabilizing (coarsening by diffusion, transient mobility, etc.) processes are balanced. Since the dissociation of a kinetic supercritical cluster results unlikely, so if \( \Gamma_{n^*<n<10} = 0 \) are arbitrarily nullified, the system statistics should not change. The system statistics was inspected by calculating the standard deviation (\( \Sigma \)) of \( \rho_n(t) \) computed for \( n^* = n^* (\rho_n^m; \text{considering all the dissociations}) \) and \( n^* < n^* (\rho_n^m; \text{neglecting the dissociations of the kinetic supercritical clusters}) \) as \( \Sigma_n^2(t) = \sqrt{(\hat{n} + 1)^{-1} \sum_{i=n^*}^{n^*+10} (\rho_i^n(t) - \rho_i^m(t))^2 + (\rho_m^n(t) - \rho_m^m(t))^2} \). The thus calculated \( \Sigma_n^2(t) \) were normalized and plotted in figure 2(a) for \( n^* \) ranging between one and \( \hat{n} \). The region enclosed in the dashed box on the lefthand side of figure 2(a) is magnified in figure 2(b). An arbitrary standard deviation of \( \xi = 10% \) is taken as the threshold of an unchanged system statistics. Thus, values of \( \Sigma_n^2(t) \) larger than \( \xi \) mean that the system statistics changes because the chosen \( n^* \) for the calculation is smaller than the real one. The kinetic lifetime \( (\tau_n^*) \) calculated according to the condition \( \Sigma_n^2(\tau_n^*) = \xi \) and averaged over the first ten pulses is used to estimate the time dependence of \( n^* \) (figure 2(c)). As shown in figure 2(c), \( n^* \) drops suddenly.
to one during the pulse as a result of the flux supersaturation that gives rise to a nonequilibrium extremely high density of mobile species. The so-generated small and moderate-sized clusters are kinetically stable during the pulse. Once the flux is stopped and the fastest diffusing species are captured by the slower ones, $n^+$ rises progressively at a rate that depends on the capacity of the
smaller clusters to stabilize the larger ones. For example, whereas the excess of dimers decreases by dissociation (for $n^+ = 2$), the resulting monomers stabilize the trimer population that is also in excess, and so on. It is only when the densities of the smaller clusters tend to their equilibrium values that the larger clusters become kinetically unstable. This process allows moderate-sized clusters to survive for long times—on the order of the pulse period $t_0$—under conditions of high temperature and no flux. Since this lifetime in the step-flow regime is only slightly dependent on the pulse repetition rate, the moderate-sized clusters remain stable throughout the entire growth process carried out using high-frequency pulsed fluxes (e.g., see in figure 2(d) that sextamers become stable for a 4 Hz pulsed flux, and tetramers are expected to be stable at the standard experimental rate of 10 Hz).

The increase in the density of small- and moderate-sized clusters induced by the flux supersaturation, the high energy of the incident particles, and the long cluster survival times gives rise to an inversion of the surface species population with respect to the size distribution for a continuous flux. This population inversion is evaluated as the ratio of the density of mobile clusters larger than monomers to the density of monomers plus islands (i.e., $\omega(t) = \sum_{i=2}^{n} \rho_i(t)/[\rho_{m}(t) + \rho_m(t)]$). The behaviour of $\omega(t)$ for pulsed and continuous fluxes on vicinal and singular ($l_i \to \infty$) surfaces is illustrated in figure 3(a). The population inversion ratio for a pulsed flux is four times that obtained for a continuous flux (figure 3(b)). This difference
becomes even larger (up to five times) during growth on vicinal surfaces with preferential capture of monomers by steps, with a further increase as the population of clusters within the incident flux (heterogeneous flux) rises; e.g., for a flux comprising 10% of dimer \( (\alpha_2 \approx 0.17) \) and 5% of trimer \( (\alpha_3 \approx 0.12) \), \( \max(\omega_{\text{pulsed}}/\omega_{\text{cont}}) \approx 6.2 \) (not shown here). The results confirm the key role played by the direct impingement and the transient mobility—distinctive features of the PLD-type growth kinetics due to the flux supersaturation and nonthermal energies of incident species, respectively—on the formation of the mobile stable clusters.

Considering the nucleation of moderate-sized clusters by direct impingement and/or transient mobility as quasi-instantaneous events (discussed above), a non-negligible fraction of the excess energy carried by the incident particles is transferred to the resulting clusters, which may cause these clusters to exhibit transient mobility in their turn. This latter transient mobility would be presumably responsible for the nonequilibrium transport invoked \([11]\) to account for the extremely low surface roughness of PLD-grown films. Remarkably, the massive formation of hot moderate-sized clusters on the growing surface without associated erosion phenomena due to, for example, the use of sources of accelerated clusters, ion beams or assisting plasmas is an exclusive key feature of PLD. Nevertheless, it is improbable that transient mobility of moderate-sized clusters alone accounts for all of the experimental findings outlined above, given that this process occurs on a picosecond timescale and hence could move the hot cluster only a few tens of atomic positions from its formation site \([13]\). A recent report \([16]\) on the diffusion of clusters on oxide surfaces proposed a complementary viewpoint: it predicts anomalies in the size-scaling relationship in table 1 for the diffusion of clusters with certain sizes; for example, Pd tetramers diffuse via a ‘rolling’ mechanism that allows them to move faster than the monomers by an order of magnitude on a (100) MgO surface \([16]\). Both pieces of information (i.e., a feasible transient mobility and diffusivity anomalies) point to a two-stage process underlying the PLD-type growth kinetics: an initial stage ruled by transient mobility of hot clusters, and once released the excess energy but not the phenomenon of population inversion; a later stage controlled by the thermal diffusion of the fastest moderate-sized clusters, which continues until the next pulse. This indicates that the enhancement of growth kinetics observed under PLD-type conditions is related to the kinetics of the moderated-sized clusters, whose density is larger than the equilibrium one. In this sense, new experimental findings and theoretical insights considering the size-scaled diffusivity anomalies are required.

In conclusion, we have investigated the PLD-type growth kinetics through a set of realistic rate equations comprised of terms modelling various mechanisms involved in the far-from-equilibrium growth that occurs when a supersaturated pulsed flux of hot particles is directed at a vicinal surface. From this study, the following picture emerges revealing the PLD key features: the PLD-type growth kinetics is distinctively controlled by the density and kinetics of moderate-sized clusters, which (i) are generated in huge amounts by direct impingement and/or transient mobility, (ii) are kinetically stable during the entire growth, and (iii) retain a fraction of the excess energy of the incident hot particles.

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