A Novel Predictive Tool in Nanoengineering: Straightforward Estimation of Superconformal Filling Efficiency

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It is shown that the superconformal filling (SCF) efficiency ($\epsilon_{SCF}$) of nanoscale cavities can be rationalized in terms of relevant physical and geometric parameters. Based on extensive numerical simulations and using the dynamic scaling theory of interface growth, it is concluded that the relevant quantity for the evaluation of $\epsilon_{SCF}$ is the so-called physical aspect ratio $S_p = L/M^\beta$, where $\alpha$ ($\beta$) is the roughness (growth) exponent that governs the dynamic evolution of the system and $L$ ($M$) is the typical depth (width) of the cavity. The theoretical predictions are in excellent agreement with recently reported experimental data for the SCF of electrodeposited copper and chemically deposited silver in confined geometries, thus giving the basis of a new tool to manage nanoengineering-related problems not completely resolved so far.

Modern trends in technology require the development of straightforward routes to the fabrication of ultrasmall devices with complex architectures [1]. At present one of the most efficient procedures appears to be the filling of molds having nanometer sized patterns with a depositing material [2,3]. This method is a promising strategy for nanofabrication in several technological fields such as nanowire production, information storage, nanoelectronics, nanoelectromechanical systems, etc.. A crucial point for the application of this strategy is that the complete filling [4,5] of nanometer sized complex cavities present in the mold, i.e., the so-called superconformal filling (SCF), is required [6]. This is a non-trivial problem of increased complexity as the aspect ratio $S = L/M$ increases, where $L$ ($M$) is the typical depth (width) of the structure to be filled. Significant advances towards highly efficient SCF have been achieved in both electrochemical deposition (ECD) [7] and chemical vapor deposition (CVD) [8,9], which are techniques widely employed in serial fabrication of microdevices. In contrast to the progress in the development of experimental and technical aspects of this subject, a theoretical framework to understand the mechanisms involved in SCF is still lacking. This theoretical knowledge would be the starting point of new tools in nanoengineering design.

Recently, interface evolution upon both CVD and ECD growth, has successfully been accounted for the so-called Kardar-Parisi-Zhang (KPZ) growth mode [10]. Thus, KPZ has been used for modeling conformal growth [11,12] in complex architectures, i.e., a technique closely related to SCF. These results open the possibility of exploring the SCF problem with the aid of the framework already established for the study of interface dynamics [13]. In this letter we develop quantitative relationships between relevant interface dynamic parameters, the aspect ratio of the architecture to be filled, and the SCF efficiency. Thus, for a given dynamic behavior of a growing system under nanoscale confinement, the SCF efficiency for each architecture can be predicted.

Metal particles are deposited in narrow cavities of depth $L$ and width $M$ (see figures 1(a-b)) according to both the KPZ [10] and the EW [14] growth modes by means of Monte Carlo simulations of a two-dimensional lattice model [15] (three-dimensional simulations are limited to small system sizes) [8]. The formation of a bcc crystal is considered and the cavity dimensions are measured in lattice units (l.u.). So, the ranges $20 \leq L \leq 1600$, $20 \leq M \leq 1600$, and $1 \leq S \leq 8$, where $S = L/M$ is the aspect ratio of the cavity, are considered.

Figure 1 shows typical growth regimes obtained assuming the KPZ mechanism. The deposition process starts at the surface of the cavity and the development of a rough growing interface, which runs essentially parallel to the substrates, can be observed, as expected for a conformal filling process (figure 1(a)). During these early time stages, the width of the interface, defined as the r.m.s. of average deposit height (figure 1(b)), increases according to $W(t) \sim t^\beta$, where $\beta > 0$ is the growth exponent. As the system evolves the correlation length in the direction parallel to the growing interface increases as $\xi \sim t^{1/z}$, where $z$ is the dynamic exponent. If the development of the interface is not interrupted by the collision among growing interfaces within the cavity, eventually the correlation length reaches the size of the system, e.g. $\xi \approx L$ since the depth is the relevant length scale in this case. At this long-time regime the interface width saturates at some constant value $W_{sat} \sim L^\alpha$, where $\alpha$ is the roughness exponent. This type of behavior is known as the Family-Vicsek scaling approach [16] that has proved to be very successful for the description of the dynamic evolution of growing interfaces, namely

$$W(L,t) \sim L^\alpha f\left(\frac{t}{L^z}\right),$$

where $f(u)$ is a suitable scaling function that behaves as follows: (i) $f(u) = constant$ for $u \gg 1$ so that the interface width saturates for a long enough time and (ii) $f(u) \sim u^\beta$ for $u \ll 1$. The former condition implies that
$W(t) \sim t^\beta$ holds during the short-time regime. A scaling relationship can easily be derived so that $z = \frac{\alpha}{\beta}$ and only two independent exponents remain.

![Diagram of cavity filling](image)

FIG. 1. Typical configurations obtained upon cavity filling according to the KPZ growth mode. Black points show the location of the growing interfaces. Relevant quantities such as the depth ($L$) and the width ($M$) of the cavity, as well as the width ($W$) of the interface and the distance from the lowest inaccessible site to the bottom of the cavity ($H$), are shown.

As the SCF process further develops, the topmost sites of the longest interfaces, running in the direction parallel to $M$, eventually collide. Notice that figure 1(c) has been selected in order to show the first collision event. Since the collision occurs before in-accessible sites below the collision point become inaccessible and can no longer be filled. Collision events and the consequent generation of inaccessible sites are due to stochastic fluctuations of the interface width and take place during the latest stages of the SCF process.

Finally, a number $N_I$ of inaccessible sites along the center of the cavity remains empty (figure 1(d)) limiting the quality of the deposit, [2]. Also at this stage, the depletion of the interface close to the center of the cavity is observed (figure 1(d)) as experimentally observed [4].

So, the SCF efficiency ($\epsilon_{SCF}$) can be defined as

$$\epsilon_{SCF} = 1 - \left( \frac{N_I}{LM} \right)$$  

(2)

Figure 2(a) shows plots of $\epsilon_{SCF}$ vs $S$ obtained by filling cavities of different size. Values of $\epsilon_{SCF}$ corresponding to various experiments, estimated after proper digitalization of the published images, which have also been included in figure 2(a), indicate an excellent qualitative agreement with the simulation results. As follows from figure 2, the filling efficiency not only depends on the aspect ratio but also on the dimensions of the cavity. Such a dependence can be derived using equation (1) and heuristic arguments. In fact, at the final stage of deposition one has

$$N_I \approx 2W(M - H),$$  

(3)

where $H$ is the average height of the lowest inaccessible site (see figure 1(c)). Furthermore, the height of the deposit as measured from the bottom of the cavity is of the order of $M/2$, so that $H = BM/2$, where $B$ is a constant close to unity. At this point one has to consider two possible scenarios, namely: [ii] the collision of the interfaces occurs after (before) the saturation of the interface width. So, defining $\chi = 1 - \epsilon_{SCF}$ and using equation (1) within the interface saturation regime, for the case [ii] one gets

$$\chi^i = 2AL^\alpha(L - BM/2)/LM = 2ASL^{\alpha-1}[1 - B/2S],$$  

(4)

where $A$ is a constant of the order of unity.

![Graphs showing cavity filling efficiency](image)

FIG. 2. (a) Cavity filling efficiency $\epsilon_{SCF}$ vs the aspect ratio $S$ obtained for cavities of different width $M$ as listed in the figure and assuming both KPZ and EW growth modes. $\triangle$, $\nabla$, and $\bigcirc$ correspond to experimental results on copper electrodeposition ([2] and [6]), and on silver chemical vapor deposition [9], respectively. (b) $\chi = 1 - \epsilon_{SCF}$ vs the depth of the cavity $L$, for $S = 1$. The dotted lines have slopes $\alpha - 1 = -0.5$, and dashed lines have slopes $\beta - 1 = -0.66$ (KPZ) and $\beta - 1 = -0.75$ (EW), respectively. Inset: relative increase of the SCF efficiency $\Delta \epsilon$ vs $S$ for different values of the width $M$.

On the other hand, if the collision occurs before interface saturation (case [ii]), replacing $W(t) \sim t^\beta_{coll}$ with a collision time $t_{coll} \sim M/2$ in equations (2) and (3), it follows that

$$\chi^{ii} = CM^{\beta-1}[1 - B/2S],$$  

(5)
where $C$ is a constant of the order of unity.

Figure 2(b) shows log-log plots of $\chi$ vs $L$. For the KPZ growth mode the crossover between two different regimes can clearly be observed at a certain crossover length $L_c$. In fact, for $L < L_c \approx 280$, which corresponds to the collision of saturated interfaces (case [i]), the obtained straight line has slope $\alpha - 1 = -0.5$ (see equation (4)), in excellent agreement with the well-known (exact) value $\alpha = 1/2$ of the KPZ growth mode [13]. Furthermore, for $L > L_c$ the regime of non-saturated interface collision is observed and the straight line has slope $\beta - 1 = -0.66$ (see equation (5)), also in excellent agreement with the exact value $\beta = 1/3$ for KPZ [13]. The same trend is also observed for the EW growth mode and the lines corresponding to the different regimes have slopes $\alpha - 1 = -0.5$ and $\beta - 1 = -0.75$, respectively, also in excellent agreement with $\alpha = 1/2$ and $\beta = 1/4$ expected for the EW model.

Figures 2(a) and (b) also show that for the EW process the values of $\varepsilon_{SCF}$ are higher than those of the KPZ growth mode. This finding is in agreement with the well known fact that KPZ interfaces are rougher than the EW ones. The inset in figure 2(b) shows, for different values of $S$, the relative increase in $\varepsilon_{SCF}$ for both growth modes, defined as $\Delta \varepsilon \equiv (\varepsilon_{EW} - \varepsilon_{KPZ})/\varepsilon_{KPZ}$. Furthermore, it is interesting to note that the growth mode upon metal electrodeposition can be modified by placing suitable additives into the plating bath. In this way unstable interfaces turn into smoother ones [7,17]. For this reason the presence of additives has been found to be an essential requirement for the achievement of high SCF efficiency [5]. It should be remarked that this scenario is fully consistent with our theoretical predictions.

At the crossover length the values of $\chi$ given by equations (4) and (5) must be the same, so it follows that

$$L_c = D M^{2/\alpha} = D M^{1/z},$$  

(6)

where $D$ is a constant. This relationship is consistent with the fact that the dynamic exponent $z$ sets the crossover length scales upon self-affine interface growth [13]. Furthermore, equation (6) strongly suggests that the physical aspect ratio $S_P = L/M^{1/z}$ is the relevant magnitude for the evaluation of the cavity filling efficiency, instead of the geometric one $S = L/M$. In fact, $S_P$ actually accounts for the two different regimes that may dominate SCF efficiency: for $S_P \ll 1$ the filling efficiency is greater, but decreases upon increasing the depth of the cavity, since the colliding interfaces have no longer fully developed their maximum roughness. Furthermore, for $S_P \gg 1$ the filling efficiency is smaller and decreases faster when the depth of the cavity is increased, due to the fact that the colliding interfaces exhibit their maximum roughness.

Finally it should be noted that we are dealing with a two-dimensional model. Three-dimensional simulations are more realistic but are limited to small systems sizes and experiment long crossovers that would turn unreliable the interpretation of the interface dynamic parameters [15]. It can be also argued that a three-dimensional model would give different results; however, our model predictions are in well agreement with data taken from cross-section images of systems grown in three dimensions, as shown in figure 2(a).

In conclusion, based on a well-established scaling approach for the description of growing interfaces, a powerful predictive tool for a straightforward estimation of the SCF efficiency has been developed. Only the knowledge of the dynamic $z = \frac{1}{d}$ exponent is required to predict the ability of a given process to fill nanocavities. Therefore, all the experimental information obtained during the last years on growing dynamics using planar substrates [18] can be managed in order to predict the processing conditions of complex nano-architectures.

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