Dynamics of Rough Interfaces in Chemical Vapor Deposition: Experiments and a Model for Silica Films

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We study the surface dynamics of silica films grown by low pressure chemical vapor deposition. Atomic force microscopy measurements show that the surface reaches a scale invariant stationary state compatible with the Kardar-Parisi-Zhang (KPZ) equation in three dimensions. At intermediate times the surface undergoes an unstable transient due to shadowing effects. By varying growth conditions and using spectroscopic techniques, we determine the physical origin of KPZ scaling to be a low value of the surface sticking probability, related to the surface concentration of reactive groups. We propose a stochastic equation that describes the qualitative behavior of our experimental system.

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The dynamics of growing interfaces has become of increasing interest in order to understand the physical processes that determine film quality [1]. In the absence of morphological instabilities, many surfaces evolving out of equilibrium display time and space scale invariance, i.e., such surfaces are *rough*. A successful framework for the study of rough interface dynamics has been the formulation of stochastic differential equations for the surface height $h(\boldsymbol{r}, t)$, where $\boldsymbol{r}$ denotes a site of a two-dimensional substrate, and t is time. A prominent example is the Kardar-Parisi-Zhang (KPZ) equation [2]

$$\partial_t h = \nu \nabla^2 h + (\lambda/2)(\nabla h)^2 + \eta(\boldsymbol{r}, t), \qquad (1)$$

expected to describe the large length scale dynamics of any rough surface growing in the absence of specific conservation laws. In Eq. (1), ν and λ are constants. The first term on the right-hand side (rhs) is sometimes called a surface tension term, as it tends to smooth the interface through evaporation-condensation processes [1]. The nonlinear term accounts for growth along the local normal direction (lateral growth), and $\eta(\boldsymbol{r}, t)$ is a Gaussian white noise of constant strength $2D$, accounting for microscopic fluctuations, e.g., in a deposition beam.

One of the techniques for thin film production which might be expected to lead to surfaces described by (1) is chemical vapor deposition (CVD). CVD is very widely used for technological applications and industrial devices [3]. It is also very interesting from the fundamental point of view due to its conceptual similarities with other growth techniques such as electrodeposition. Thus, a considerable effort has been made to model CVD growth [4–6] using partial differential equations. These models predict the development of unstable morphologies within the time ranges studied, contradicting the above expectation of KPZ scale invariant behavior. Let us note that, to date, very few experimental systems are known whose scaling is described by KPZ in three dimensions [7]. Moreover, on the fundamental level there are no experiments addressing the long time behavior of the surface morphologies produced by CVD, and the identification of the determining physicochemical mechanisms.

In this Letter we study the interface dynamics of low pressure SiO_2 CVD films by atomic force microscopy (AFM), Raman and infrared spectroscopies, and numerical simulations. SiO_2 films were studied because of their amorphous nature, to avoid Schwoebel barrier effects on the surface dynamics [8], and to prevent formation of facets that can also alter the scaling behavior [6]. Our experimental system displays a transient unstable behavior related to the gas phase transport character of CVD growth [4–6], but a stationary state is achieved which, rather, is compatible with KPZ scaling. The surface dynamics is well described, over a wide spatial and temporal range (up to 2 days of deposition time), by a stochastic differential equation in which surface diffusion, shadowing effects, and lateral growth are allowed for.

Amorphous SiO_2 films were grown at a temperature $T = 723$ K on Si (100) substrates in a hot wall, horizontal, low pressure tubular CVD reactor. The precursor gases were silane (diluted at 2% in nitrogen, 99.999% purity) and oxygen (99.9992% purity), with an oxygen/silane ratio equal to 20 and a total gas flow rate of 50 SCCM (SCCM denotes cubic centimeter per minute at STP). The chamber pressure was 1.4 Torr. The film thickness increases linearly with deposition time at a constant growth rate of 20 nm/min. Films were deposited in the range $5\ \text{min} \leq t \leq 2$ days. The surface morphology was characterized by AFM (Nanoscope III from Digital Instruments, CA) operating in tapping mode at ambient conditions up to a scale of 50 μm using silicon cantilevers.

AFM imaging of our silica films shows (Fig. 1) a deposit formed initially by small rounded grains 30–60 nm in size.

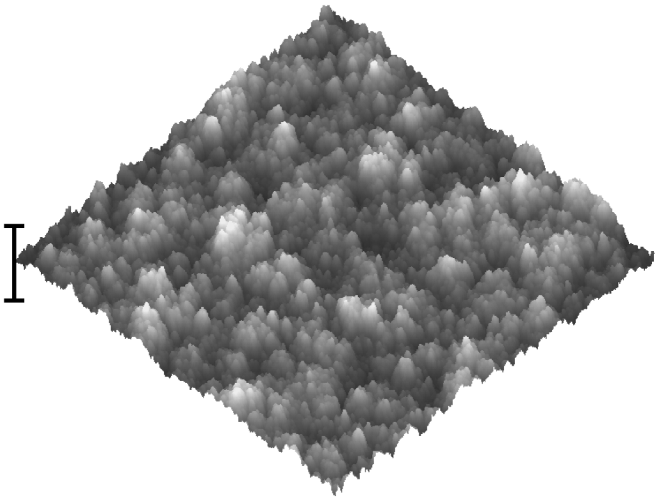

FIG. 1. AFM 3 × 3 μm^2 image of amorphous SiO$_2$ films deposited at $T = 723$ K for $t = 75$ min. The vertical bar represents 400 nm.

A similar morphology has been reported on amorphous silicon films deposited by thermal evaporation [9]. As deposition proceeds, structures resembling mountains and valleys appear at larger length scales increasing in size, until a stationary regime is attained in the 15–30 h range.

Power spectral density (PSD) (or surface power spectrum) plots of the surface morphology at different times are displayed in Fig. 2. For $t < 35$ min and small enough wave vector k, the PSD follows that of the initial substrate, while for $t > 35$ min and $k < k_c$ it takes a constant k-independent value, interface portions separated by distances $r > 1/k_c$ being uncorrelated. For a rough interface [1], the value of k_c decreases with time as $k_c \sim t^{-1/z}$, where z is the *dynamic* exponent. Indeed, from the log-log plot of k_c vs t (Fig. 3), a slope value $z = 1.6 \pm 0.1$ is obtained. Therefore, the time behavior of our CVD growth process is well described by that of a self-affine rough surface. The same conclusion is obtained from the spatial behavior of the surface morphology. Specifically, for a two-dimensional rough interface the PSD behaves as [1] PSD$(k) \sim 1/k^{2\alpha+2}$, with α the *roughness* exponent. In Fig. 2, as time proceeds, up to three spatial regions can be observed.

(i) For $t < 50$ min we can distinguish two regions: Region I, for $k > k_0$, features $\alpha_{\rm I} = 0.99 \pm 0.04$; k_0 initially decreases from 0.04 nm^{-1} for $t = 20$ min to a constant value of 0.02 nm^{-1} for $t \geq 50$ min. Region II with $\alpha_{\rm II} = 0.75 \pm 0.03$ is observed for $k_1 < k < k_0$, where k_1 changes from 0.025 nm^{-1} for $t = 20$ min to 0.0034 nm^{-1} for $t = 50$ min.

(ii) For $t > 50$ min a new region III appears for $k_c < k < k_1$, with $\alpha_{\rm III} = 0.42 \pm 0.03$; as noted above, k_c decreases with time. Regions I and II are still observed.

The above behavior of the PSD is compatible with that of the surface width, $W^2(t) = \langle \overline{[h(\boldsymbol{r},t) - \bar{h}(t)]^2} \rangle$, which we measure independently (Fig. 3). The bar denotes spatial average. For a rough interface, initially $W(t) \sim t^{\alpha/z} = t^{\beta}$, as long as $t \ll L^z$, with L a measure of the spatial extent of the system. For $t \gg L^z$, the interface saturates into a stationary state for which $W \sim L^{\alpha}$. As a difference with the PSD, we observe only two temporal behaviors in $W(t)$, corresponding to regions II and III of the PSD. For $t < 50$ min, the width is described by the growth exponent $\beta_{\rm II} = 0.42 \pm 0.04$, while for 50 min $\leq t \leq$ 15–30 h, $W(t)$ data are consistent with $\beta_{\rm III} = \alpha_{\rm III}/z = 0.26 \pm 0.03$ as obtained from the PSD data. For $t >$ 15–30 h, the width $W(t)$ saturates to a constant value. Note that the contribution of the short length scales (region I) to the surface width is masked by the spatial region II. However, despite the few data points for $t \leq 50$ min, an attempt to estimate $\beta_{\rm I}$

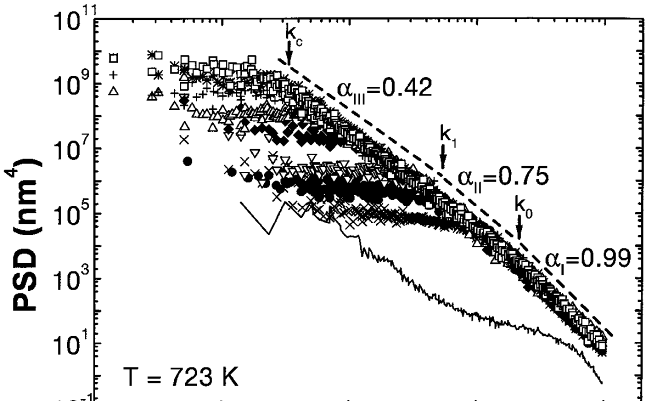

FIG. 2. PSD curves from AFM images of the SiO$_2$ surface at different times: substrate (solid line), 5 min (×), 20 min (●), 50 min (▽), 180 min (◆), 480 min (△), 900 min (+), 1800 min (∗), and 2880 min (□). Wave vectors k_0, k_1, and k_c separating the scaling regions are shown for $t = 2880$ min. The slopes of the dashed lines are $\alpha_{\rm III} = 0.42$ (for $k_c < k < k_1$), $\alpha_{\rm II} = 0.75$ (for $k_1 < k < k_0$), and $\alpha_{\rm I} = 0.99$ (for $k > k_0$).

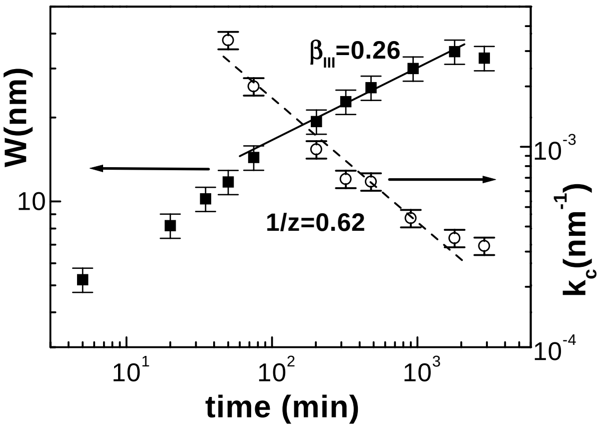

FIG. 3. Plot of $W(t)$ (■, left axis) and $k_c(t)$ (○, right axis). The slopes of the solid and dashed lines are, respectively, $\beta_{\rm III} = 0.26$ and $1/z = 0.62$.

from the PSD curves [10] leads to $\beta_{\rm I} = 0.28 \pm 0.09$. Regarding the long distance properties of our system, the observed $\alpha_{\rm III} = 0.42 \pm 0.03$, $z = 1.6 \pm 0.1$, and $\beta_{\rm III} = 0.26 \pm 0.03$ are close, within experimental errors, to the approximate exponents for the KPZ universality class in three dimensions, namely [1], $\alpha_{\rm KPZ} = 0.39$, $z_{\rm KPZ} = 1.63$, and $\beta_{\rm KPZ} = 0.24$. Thus, the asymptotic scaling behavior of the growing CVD surface is of the KPZ class, an experimental result very rarely found in three dimensions [7].

It is important to understand the origin of the KPZ regime under our experimental conditions. It is known [11] that, for CVD systems with a low surface reaction kinetics (low sticking probability s), lateral growth, which is the fingerprint of KPZ behavior, is promoted leading to the so-called conformal growth. The mechanism inducing conformal growth is the reemission of the precursor (i.e., depositing) species due to a low sticking probability. For our experimental conditions s has actually been reported [12] to decrease with temperature from $s = 0.5$ at 573 K down to $s = 0.08$ at 723 K. Also, the growth conformality of submicron trenches by SiO_2 films has been reported [12,13] to improve as T increases. Physically, s can be related to the concentration of reactive sites at the growing film surface, which for our system are mainly associated with hydrogenated groups, such as Si-OH and Si-H, and with strained siloxane (Si-O-Si) groups, rather than with the less reactive relaxed siloxane groups [14].

To study the role played by the sticking probability on our film morphology, we have grown SiO_2 films at lower $T = 611$ K (higher s) with the *same growth rate* ($\approx$20 nm/min). Analysis of our films by Raman and infrared spectroscopies shows [15] that the 611 K films indeed present a significantly higher concentration of reactive groups than the 723 K films, in agreement with the higher sticking probability expected for the low temperature growth. Moreover, regarding the surface dynamics of the low T films, neither the KPZ nor the saturation regimes were found after 2 days of deposition. In Fig. 4 we plot the PSD of a film grown at 611 K after 2 days. The KPZ region does not appear but only regions I and II do. In Fig. 4 (inset) we plot $W(t)$ for the same set of films. Again, only unstable growth is obtained for long times. From the point of view of Eq. (1), these experiments suggest that when T is reduced the effective λ coefficient of the KPZ term decreases. These results are analogous to the crossover found between diffusion-limited aggregation and Eden growth when tuning the sticking probability [16], and allow us to identify region II in the scaling behavior at the high temperature value ($T = 723$ K) as an unstable transient.

The above results suggest that the KPZ equation might be a good starting point to describe the observed behavior. However, in our system we expect the first term in Eq. (1) to be negligible, since the SiO_2 vapor pressure is extremely low (i.e., ν is very small) in our temperature range, whereas surface stabilization by surface diffusion seems to be relevant [9]. In fact, $\alpha_{\rm I} \approx 0.99$ and $\beta_{\rm I} \approx 0.28$ are consistent within experimental errors with the linear theory of surface diffusion [17]. On the other hand, due to the large values of the effective exponents $\alpha_{\rm II}$ and $\beta_{\rm II}$ and in view of the discussion above, we believe region II corresponds to unstable growth. This instability can be related to shadowing effects which occur in CVD [4–6] due to the random walk motion of the depositing particles. Nonlinear surface diffusion [18] can be discarded as the origin of the unstable behavior in region II since it leads to anomalous scaling [1], not present in our measurements. Similarly, the unstable equation for h derived in [6] can be ruled out as a description of the unstable behavior in region II because it leads to a nonconstant growth rate, incompatible with our experimental setup. Thus, we propose the following continuum equation to describe the silica CVD growth:

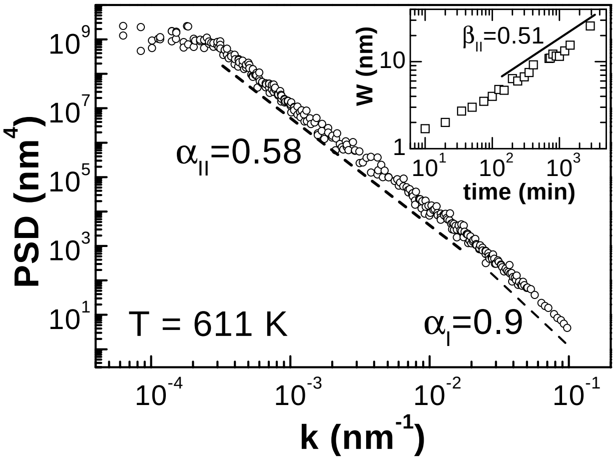

FIG. 4. PSD of a SiO_2 film grown for 2 days at 611 K. Slopes of the dashed lines are $\alpha_{\rm II} = 0.58$, $\alpha_{\rm I} = 0.9$. Inset: $W(t)$ for the same system. Slope of the solid line is $\beta_{\rm II} = 0.51$.

$$\partial_t h = -K\nabla^4 h + \varepsilon\, \theta/\overline{\theta} + (\lambda/2)(\nabla h)^2 + \eta(\mathbf{r}, t). \quad (2)$$

In Eq. (2), K and ε are positive constants; the first term on the rhs represents relaxation by surface diffusion and the second term represents geometric shadowing effects, θ being the local exposure angle and $\overline{\theta}$ being the spatial average of θ [19]. In order to check the validity of (2) we have performed numerical simulations in two dimensions (three-dimensional simulations are limited to small system sizes [20]). In Fig. 5 we plot the time evolution of the PSD for $K = D = 1$, $\varepsilon = 1/2$, and two values of the strength of the KPZ nonlinearity $\lambda = 0.2, 3$. For these sets of parameters we have employed system sizes up to $L = 8192$ in order to reliably identify the different scaling regimes. For $\lambda = 3$ (solid line in Fig. 5), and as experimentally observed at high T (Fig. 2), the surface PSD evolves from a scaling regime dominated by surface diffusion at short distances to KPZ scaling at large length scales, through an unstable transient due to the

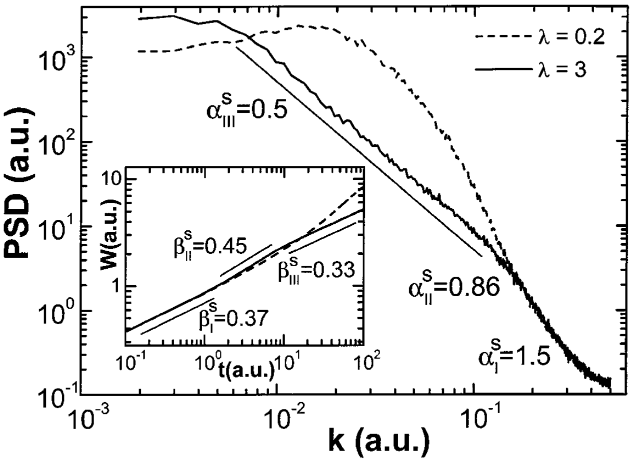

FIG. 5. PSD from numerical integrations of Eq. (2) for $K = D = 1$, $\varepsilon = 1/2$, $L = 1024$, $t = 100$, averaged over 250 realizations, for $\lambda = 0.2$ (dashed line) and $\lambda = 3$ (solid line). Slope of the straight solid line is $\alpha^s_{\mathrm{III}} = 0.5$. For $\lambda = 3$, the values $\alpha^s_{\mathrm{I}} = 1.5$, $\alpha^s_{\mathrm{II}} = 0.86$ give the best fit to the PSD behavior in each region. Data curvature at large k is due to discretization effects. Inset: $W(t)$ for the same parameters. Slopes of the straight solid lines are $\beta^s_{\mathrm{I}} = 0.37$, $\beta^s_{\mathrm{II}} = 0.45$, and $\beta^s_{\mathrm{III}} = 0.33$.

shadowing effects [21]. Also in agreement with the experimental data, after a certain growth time both k_0 and k_1 are frozen, and no anomalous scaling is observed. The time evolution of the surface width is shown in the inset of Fig. 5 for the same parameters. Again, for $\lambda = 3$, it resembles quite closely that shown in Fig. 3 [21] since, as t increases, the behavior changes from surface diffusion to unstable growth and finally to KPZ scaling. For smaller $\lambda = 0.2$ (dashed lines in Fig. 5), corresponding experimentally to low T (Fig. 4), we observe from the PSD and $W(t)$ behaviors that the crossover from the unstable region II to KPZ behavior takes place, if at all, at longer time and larger length scales. Similar behaviors to those in Fig. 5 are obtained for other parameter sets [15], provided that the relative weight of the different contributions is preserved.

In summary, we have found that low pressure CVD growth of silica films is governed by the relative balance between surface diffusion, shadowing, and lateral (KPZ) growth. Our experimental system is well described by a differential continuum stochastic equation in which these three mechanisms are allowed for. Moreover, our study allows one to link the value of the effective KPZ nonlinearity to the physical and chemical properties of the growing interface. Thus, we conclude that the observation of asymptotic KPZ scaling is favored under growth conditions (e.g., high temperatures) which promote a low sticking probability of the depositing species.

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[1] A.-L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, 1995); J. Krug, Adv. Phys. **46**, 139 (1997).
[2] M. Kardar, G. Parisi, and Y.-C. Zhang, Phys. Rev. Lett. **56**, 889 (1986).
[3] K. F. Jensen and W. Kern, in *Thin Film Processes II*, edited by J. L. Vossen and W. Kern (Academic, Boston, 1991).
[4] C. H. J. Van den Brekel and A. K. Jansen, J. Cryst. Growth **43**, 364 (1977).
[5] B. J. Palmer and R. G. Gordon, Thin Solid Films **158**, 313 (1988).
[6] G. S. Bales, A. C. Redfield, and A. Zangwill, Phys. Rev. Lett. **62**, 776 (1989).
[7] J. Chevrier *et al.*, Europhys. Lett. **16**, 737 (1991); E. A. Eklund *et al.*, Phys. Rev. Lett. **67**, 1759 (1991); R. Paniago *et al.*, Phys. Rev. B **56**, 13 442 (1997).
[8] R. L. Schwoebel, J. Appl. Phys. **40**, 614 (1968).
[9] H.-N. Yang *et al.*, Phys. Rev. Lett. **76**, 3774 (1996).
[10] By integrating the PSD curves from the maximum k available down to k_0.
[11] M. J. Cooke and G. Harris, J. Vac. Sci. Technol. A **7**, 3217 (1989).
[12] K. Watanabe and H. Komiyama, J. Electrochem. Soc. **137**, 1222 (1990).
[13] M. Ikegawa and J. Kobayashi, J. Electrochem. Soc. **136**, 2982 (1989); D. G. Coronell and K. F. Jensen, *ibid.* **141**, 2545 (1994).
[14] R. K. Iler, *The Chemistry of Silica* (J. Wiley & Sons, New York, 1979); T. A. Michalske and B. C. Bunker, J. Appl. Phys. **56**, 2686 (1984); Q. Sun *et al.*, Europhys. Lett. **43**, 47 (1998).
[15] F. Ojeda *et al.* (to be published).
[16] P. Meakin, *Fractals, Scaling and Growth far from Equilibrium* (Cambridge University Press, Cambridge, 1998).
[17] J. Villain, J. Phys. I (France) **1**, 19 (1991); Z.-W. Lai and S. Das Sarma, Phys. Rev. Lett. **66**, 2348 (1991).
[18] F. Family and J. Amar, Fractals **1**, 753 (1993).
[19] Related equations have been studied by R. P. U. Karunasiri, R. Bruinsma, and J. Rudnick, Phys. Rev. Lett. **62**, 788 (1989); J. H. Yao, C. Roland, and H. Guo, Phys. Rev. A **45**, 3903 (1992).
[20] J. H. Yao and H. Guo, Phys. Rev. E **47**, 1007 (1993).
[21] The values of α and z depend on dimensionality, and thus differ in the experiments and in our numerical simulations. However, the qualitative behaviors are the same: for Fig. 5 we obtain for the $\lambda = 3$ case $\alpha^s_{\mathrm{I}} = 1.5 \pm 0.1$ ($\beta^s_{\mathrm{I}} = 0.37 \pm 0.01$), $\alpha^s_{\mathrm{II}} = 0.86 \pm 0.04$ ($\beta^s_{\mathrm{II}} = 0.45 \pm 0.02$), and $\alpha^s_{\mathrm{III}} = 0.5 \pm 0.01$ ($\beta^s_{\mathrm{III}} = 0.33 \pm 0.02$), consistent, respectively, with linear surface diffusion, unstable growth, and KPZ scaling in two dimensions.