Height Fluctuations and Intermittency of $V_2O_5$ Films by Atomic Force Microscopy

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The spatial scaling law and intermittency of the $V_2O_5$ surface roughness by atomic force microscopy has been investigated. The intermittency of the height fluctuations has been checked by two different methods, first, by measuring scaling exponent of q-th moment of height-difference fluctuations i.e. $C_q = \langle |h(x_1) - h(x_2)|^q \rangle >$ and the second, by defining generating function $Z(q,N)$ and generalized multi-fractal dimension $D_q$. These methods predict that there is no intermittency in the height fluctuations. The observed roughness and dynamical exponents can be explained by the numerical simulation on the basis of forced Kuramoto-Sivashinsky equation.

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I. INTRODUCTION

Due to the technical importance and fundamental interest, a great deal of effort has been devoted to understanding the mechanism of thin-film growth and the kinetic roughening of growing surfaces in various growth techniques. Analytical and numerical treatments of simple growth models suggest, quite generally, the height fluctuations have a self-similar character and their average correlations exhibit a dynamic scaling form [1-6].

Vanadium pentoxide, $V_2O_5$, has been the subject of intense work because of its diverse applications in catalytic oxidation reactions, cathodic electrode in solid state micro-batteries, windows and electrochromic devices as well as gas sensors and to be of interest for state micro-batteries, windows and electrochromic analytical oxidation reactions, cathodic electrode in solid intense work because of its diverse applications in catalytic oxidation reactions.

This work aims to study the roughness and dynamical exponents ($\chi$ and $z$) and the intermittency of the $V_2O_5$ films by the atomic force microscopy. We measure the height-difference moments $C_q(l = |x_1 - x_2|) = \langle |h(x_1) - h(x_2)|^q \rangle >$ and show that they behave as $\sim |x_1 - x_2|^\xi_q$. The obtained $\xi_q$ is a linear function of $q$. We also introduce the generating function $Z(q,N)$ and generalized multifractal dimension $D_q$ and show that $D_q$ behave also as a linear function of $q$. These observations indicate that the height fluctuations are not intermittent. It is also argued that the measured roughness and dynamical exponents belong to early-time scaling regime of the noisy Kuramoto-Sivashinsky equation.

II. EXPERIMENTS

$V_2O_5$ layers were grown on the polished Si(100) substrate by resistive evaporation method in a high vacuum chamber. The pressure during evaporation was $10^{-5}$ torr. The thickness of the growing films was measured in situ by a quartz crystal thickness monitor. We performed all deposition at room temperature, with deposition rate about $10 - 15$nm/min. However, during the film deposition the substrate temperature raised to $T \sim 60\,$C, due to the radiation effect of alunina boat. The substrate temperature was determined using chromel/alumel thermocouple mounted in close proximity of samples. Surface composition of samples was measured by Auger electron spectroscopy (AES) using a 3 keV electron beam and a cylindrical mirror analyzer (Varian model 981-2607).

The surface topography of the films was investigated using Park Scientific Instruments model Autoprobe CP. The images are collected in a constant force mode and digitized into $256 \times 256$ pixels with scanning frequency of 0.6 Hz. The cantilever of 0.05 $N\,m^{-1}$ spring constant with a commercial standard pyramidal $Si_3N_4$ tips has been used. A variety of scans, each with size $L$ were recorded at random locations on the $V_2O_5$ film surface. In order to determine the structure of the deposited $V_2O_5$ films, we have performed XRD measurements of samples. The spectra for the as-deposited $V_2O_5$ films grown showed that the $V_2O_5$ thin films are amorphous. For thick films ($d > 200nm$) two very broad weak peaks were observed representing the growth of (001) and (002) peaks of the $V_2O_5$ orthorombic structure[7]. The yellow color of deposited oxide films and their optical transmission spectra indicates the existence of $V_2O_5$ structure rather than other vanadium oxide phases[8]. AES analysis of the $V_2O_5$ samples showed $V$ and $O$ peaks at the surface of the deposited films. The stoichiometry of the vanadium oxide films was calculated from the ratio of $O$
to V Auger peak heights by considering the elemental sensitivity factors. The O/V ratio was 2.5 ± 0.1 indicating the formation of stoichiometric vanadium pentoxide at the surface of the thin film (see Fig. 1). With these observations we conclude the film composition is nearly stochiometric[9].

III. RESULTS

Figure 2 shows the variation of the surface morphology for different growth times (or thickness) of processed samples by AFM. As deposition proceeds, the size of mountains and valleys grows until the system approaches to a stationary state in which the thickness is about 150nm.

The quantitative information of the surface morphology can be derived by considering a sample of size $L$, and defining the mean height of growing film $\bar{h}$ and, its roughness $w$ through [10]:

$$\bar{h}(L, t) = \frac{1}{L} \int_{-L/2}^{L/2} dxh(x, t)$$

and

$$w(L, t) = \langle (h - \bar{h})^2 \rangle^{1/2}.$$  

$\langle \cdots \rangle$ denotes an averaging over different realization (samples). Starting from a flat interface (one of the possible initial conditions), it was conjectured by Family and Vicsek [11] that a scaling of space by factor $b$ and of time by a factor $b^z$ ($z$ is the dynamical scaling exponent), re-scales the roughness $w$ by factor $b^\chi$ as follows: $w(bL, b^zt) = b^\chi w(L, t)$, which implies that

$$w(L, t) = L^\chi f(t/L^z).$$

If for large $t$ and fixed $L$ ($t/L^z \to \infty$), $w$ saturates then $f(x) \to const.$, as $x \to \infty$. However, for a fixed large
$L$ and $1 << t << L^z$, one expects that correlations of the height fluctuations are set up only within a distance $t^{1/z}$ and thus must be independent of $L$. This implies that for $x << 1$, $f(x) \sim x^\beta$ with $\beta = \chi/z$. Thus dynamic scaling postulates that, $w(L,t) \sim t^\delta$ for $1 << t << L^z$ and $\sim L^x$ for $t >> L^z$. The roughness exponent $\chi$ and the dynamic exponent $z$ characterize the self-affine geometry of the surface and its dynamics, respectively. We measure the exponent $\chi$ from equal-time height-height correlation function defined as $C_2(l = |x_1 - x_2|) = \langle |h(x_1) - h(x_2)|^2 \rangle$. Here $h(x)$ is the surface height at position $x$ on the surface relative to the mean surface height.

In order to determine the roughness exponent $\chi = \xi_2/2$, we consider the roughness of the samples with thickness 20nm, 100nm and 260nm. Fig.3 shows that, for the thickness 20nm and 100nm, the scaling behavior exists only for the scaling region $\sim 4nm$ to $20nm$, but for the stationary state sample, $<h> = 260nm$, there is a cross over for the stationary exponent $\chi = \xi_2/2$ in $l = l^* \approx 22nm$. The exponent is $\xi_2$ for the length scales $4nm$ to the scale $l^*$, and for the length scales $25nm \leq l \leq 50nm$, the fluctuation is determined by another exponent $\xi_{22}$. The measured values for the exponents $\xi_2$ and $\xi_{22}$ are $1.64 \pm 0.06$ ($\chi_1 = 0.83 \pm 0.03$) and $0.58 \pm 0.08$ ($\chi_2 = 0.29 \pm 0.04$) respectively. The measured roughness exponent $\chi$ of the samples 20nm, 100nm and 150nm are $0.71 \pm 0.04$, $0.77 \pm 0.03$ and $0.82 \pm 0.03$, respectively. As shown in Figs. 4 and 5, we note that the correlation length $l^*$ is about $22nm$. Therefore, we are dealing with the statistical properties of the correlated scaling surfaces. As discussed in [22], such systems exhibit the sampling-induced hidden cycles (log-periodic fluctuations [23]). Such oscillatory behavior will diminish when the sampling size is sufficiently large. The oscillation amplitude approaches zero to within an order of $\delta = \sqrt{l^*/ML}$, where $L$ and $M$ are the sampling size and the number of independent curves which are averaged. We have determined each exponents by averaging on the eight AFM images. In our averaging it appears that there is no log-periodic property for the height-height correlation function. Therefore the surfaces of $V_2O_5$ are self-affine.

The existence of the cross over scale $l^*$ in the stationary state is not observed only in the second moment $C_2$. In Fig.4 log-log plot of $C_3$ vs $l$ for the three samples are presented. It is evident that for the stationary state sample, the scaling exponent of the third moment $C_3$ has also a cross over in $l^*$. The measurement shows that in the stationary state the exponents $\xi_3$, behave as $\xi_3 = 3/2\xi_{2i}$ with $i = 1, 2$.

We also examine the scaling behaviour of the $q$-th moment of the height-difference $C_q = \langle |h(x_1) - h(x_2)|^q \rangle$ and show that all of the moments at least up to $q = 20$ behave as $|x_1 - x_2|^\xi$. Fig.5 shows $\xi_q$ vs $q$ for 260nm sample in $25nm \leq l \leq 50nm$ scaling region.

![FIG. 3. Log-log plot of the second moment of height-difference vs $l$, which shows that for samples with thickness 20nm and 100nm the scaling region is $4nm < l < 20nm$ and for the sample with thickness 260nm there is a cross over scale $l^* \approx 22nm$. The upper and lower parts of height-height correlation function have the roughness exponent $0.29 \pm 0.04$ and $0.83 \pm 0.03$, respectively.](image)
Our measurement for $H_q$ shows that the $H_q$ is independent of $q$ and this means that $D_{eff} = D_q = D_0$. Let us discuss the origin of the $D_{eff}$ in eq.(6). To evaluate the $C_q$ we should calculate the summation

$$\frac{1}{N} \sum_{i=1}^{N} |h(x_i) - h(x_i + l)|^q,$$

where $N$ is the number of points over which the average is taken. Normally small $l$ is meant by $l \sim 1/N$. The authors of Ref.[20] assumed that, in evaluation of $C_q$, $l$ and $N$ may be related in a way different from $l \sim 1/N$. That is $N \sim l^{-D_{eff}}$ ($D_{eff}$ could be considered here as a fractal dimension of the effective support of the process). The choice of a particular partition has no effect on the $H_q$ spectrum. However, $D_{eff}$ enters the relation between $H_q$ and generalized dimension $D_q$ as expressed in eq.(6).

**IV. DISCUSSION AND GROWTH MODEL**

In our experiments we obtain a region in which the growth exponents of $V_2O_5$ are consistent with early-scaling regime of forced Kuramoto-Sivashinsky (KS) equation in 2+1 dimensions [19]. The forced Kuramoto-Sivashinsky has the following form [14-19],

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h - k \nabla^4 h + (\lambda/2)(\nabla h)^2 + \eta(x,t)$$

where the $\nu, k$ and $\lambda$ are the surface tension, surface diffusion and non-linear factor, respectively. The force $\eta$ is a noise term reflecting spatial and temporal fluctuation in the incoming flux of material and has a Gaussian distribution and uncorrelated in space and time. In the limit $k = 0$ and for $\nu > 0$ the forced KS equation reduces to
the Kardar-Parisi-Zhang (KPZ) equation. The KS equation with \( \lambda = 0 \) is a linear equation and can be exactly solved by the standard methods \([19,22]\). For some Gaussian noise term, because of the linearity the probability distribution function (PDF) of \( h - \bar{h} \) is also Gaussian. It is discussed in \([22]\) that for \( \lambda = 0 \) and \( \nu/k < 0 \) the KS equation generates a mound surface and for \( \nu/k > 0 \) gives a self-affine surface, with a roughness exponent \( \approx 1. \) For \( \lambda \neq 0 \) the nonlinear term breaks the symmetry under transformation \( h \to -h \). Therefore the PDF of \( h - \bar{h} \) must be skewed. Our measured value for the PDF of \( h - \bar{h} \) shows that the PDF has positive skewness. We will report the skewness and kurtosis of the PDF of the \( V_2O_5 \) films elsewhere \([12]\).

Recent simulation of KS equation reveals the presence of the early and long scaling regimes \([19]\). The initial-time values for the growth exponent \( \beta \) and the roughness exponent \( \chi \) are found to be 0.22 − 0.25 and 0.75 − 0.80 respectively. The long time scaling regime is determined by the exponents \( \beta = 0.16 − 0.21 \) and \( \chi = 0.25 − 0.28 \). The scaling exponents are notably less than the exponents of KPZ equation \([19]\). The long-time behavior of the KS-equation has an interesting feature. For long-times the height-height correlation function exhibits a bifractal structure with two different roughness exponents (see Fig.11 in ref. \([19]\)). For \( \lambda = 2.0, \nu = -0.2 \) and \( k = 2.0, \) the upper and lower parts of height-height correlation function have the roughness exponent 0.27 and 0.71, respectively.

Now let us compare our results with the numerical simulation of KS equation. Using the numerical results of ref. \([19]\) in table II, one can observe that for early-scaling regime of the Kuramoto-Sivashinsky equation the exponents \( \chi \) and \( z \) satisfy the exponent-identity \( \chi + z \approx 4. \) Using the time dependence of roughness of the samples with thickness 20\( \text{nm} \), 50\( \text{nm} \), 100\( \text{nm} \), 120\( \text{nm} \) and 150\( \text{nm} \) we find that \( \beta = 0.29 \pm 0.04 \) (see Fig.7) and therefore \( \chi + z = 3.7 \pm 0.4 \), which satisfies the exponent-identity within the experimental errors. We also observe the similar bifractal structure of the height-height correlation function in our samples with thickness 260\( \text{nm} \) (see Fig.11 in \([19]\)). To relate the cross over scale \( l* \) to the the surface morphology, we have measured average distance of nearest local maxima \( \bar{d}_{max} \), and obtain that the \( \bar{d}_{max} \) is in the same order of magnitude of \( l* \). This means that, in the stationary state, in average, if the distance between the points \( x_1 \) and \( x_2 \) lies between the two local maxima of \( h(x) \), the dynamics is determined by the roughness exponent \( \chi_1 \). Also for the points that the relative distance lies between the next neighbor maximums ( \( \sim 20 - 40\text{nm} \) ), the dynamics is given by another exponent \( \chi_2 \) which is less than the KPZ roughness exponent. Our measurements show that the roughness exponent \( \chi_2 = 0.29 \pm 0.04 \) is less than the the KPZ roughness exponent in \( 2 + 1 \) dimensions i.e. 0.38.

In summary we have checked the intermittency of
height fluctuation of $V_2O_5$ via two different methods. These methods predict that the statistics of height fluctuations is not intermittent. We measure the scaling exponents of height-difference moments, $C_{q}(l = |x_1 - x_2|)$, and show that for small $l$, they behave as $|x_1 - x_2|^{\xi_q}$. The obtained $\xi_q$’s are linear function of $q$. The observation can be explained with the recent numerical simulation on the basis of nonlinear KS equation. However, one should note that for very early stages, when $\nu$ term dominates $k$ term, instability arises in $x$ or $y$ direction causing the ripple structure with corresponding wave vector in $x$ or $y$ direction in KS equation. When the ripple structure is formed, there exists slope asymmetry that activates the nonlinear effect. Therefore, in the early-stage of the process, the ripple structure transforms to symmetric mounds. In our experiments we were not able to detect the ripple structure for the samples with $<h> \ll 20nm$. It could mean that the polished Si(100) substrate may have an initial roughness which may destroy the ripple structure of the film for very early-stages of the growth. We measure the roughness exponent of the silicon substrate and find that the $\chi_{si} = 0.47 \pm 0.03$ (see Figs.8 and 9).

Finally we note that the measured roughness exponents $\chi$ and $\beta$ can be higher than the true values because of the tip effect [21]. Aue et al. showed that the surface fractal dimension (fractal dimension $d_f$ for 2+1 interface is related to $\chi$ by $d_f = 3 - \chi$ ) determined with a scanning probe technique will always lead to an underestimate of the actual fractal dimension, due to the convolutions of tip and surface. Their analysis included tips with different shapes and aspect ratios. For a tip similar to what we have used, it is suggested that our true $\chi_1$ and $\chi_2$ should be around $\sim 0.75$ and $\sim 0.25$, respectively. We note that the corrected exponents also satisfy the exponent identity.

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