

## X-Ray Reflectivity and Adsorption Isotherm Study of Fractal Scaling in Vapor-Deposited Films

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We have carried out x-ray reflectivity and adsorption measurements on thermally evaporated silver and gold films deposited onto substrates held at 80, 300, and 500 K to investigate whether the surfaces of such films are fractal in nature. Both techniques indicate self-affine fractal scaling for Ag films deposited at near-normal incidence onto substrates held at 80 K.

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This paper reports a comparison of adsorption and x-ray reflectivity measurements which investigate the physical origins of fractal growth in vapor-deposited films. Our study focuses on films with self-affine fractal surfaces [1,2], since much theory and computer simulation has been devoted to a fundamental understanding of the mechanisms which underlie the growth of such films [3]. Our purpose is twofold: to assess the ability of these techniques to distinguish fractal growth and to provide insight concerning the origins of such growth. We have studied films prepared under conditions which approach those of the self-affine surface deposition models (Ag deposited on 80-K substrates) and two other categories of films which are not expected to have fractal surfaces (Fig. 1). Both adsorption and reflectivity single out the first category as self-affine, and are in general agreement concerning the surface dimension.

Profiles of self-affine surfaces are depicted in Figs. 1(a)–1(c) [4]. Each is a vertical cross section of a single-valued Gaussian rough surface  $h(x,y)$  with average height  $h$ , and root-mean-square (rms) width  $\sigma = \langle [z(x,y)]^2 \rangle^{1/2}$ , where  $z(x,y) = h(x,y) - h$ . Such surfaces are self-affine if  $\sigma$  increases with the horizontal length  $L$  sampled according to  $\sigma \sim L^H$ , where  $0 < H < 1$  is a parameter reflecting the degree of height-height correlation. Small  $H$  values are associated with jagged surfaces (anticorrelation), while large values are associated with well-correlated, smooth-textured surfaces. Self-affine fractals are distinguished from self-similar (“genuine”) fractals by an asymmetry in the scaling behavior perpendicular to the surface, generally manifested by an absence of surface overhangs [5]. A “local” regime may, however, be present where below a certain crossover length, the surface is indistinguishable from a self-similar fractal whose dimension is  $D = 3 - H$  (three spatial dimensions are assumed throughout this paper). Regardless of whether this regime actually exists, it is commonplace in the literature to refer to self-affine surfaces by their local ( $D = 3 - H$ ), rather than “global” ( $D = 2$ ) dimension [2,6,7].

Many classes of vapor-deposited films are expected to have self-affine surfaces with a universal scaling exponent  $H$  [8]. Large-scale atomistic simulations of nonequilibrium deposition onto two-dimensional substrates suggest

that  $0.33 \leq H \leq 0.40$  for normal incidence deposition [9]. Continuum deposition models allowing for the surface relaxation of particles obtain  $H = 0.67$  [10].

Previous experimental reports of microscopic fractal scaling of deposited film surfaces include three scanning tunneling microscopy (STM) reports [6,7,11] and one adsorption isotherm study [12]. All reported  $D = 2.3$  ( $H = 0.7$ ): Whether these results are directly comparable to theory is uncertain. In all cases the samples were exposed to air, and in some cases the details of sample preparation were lacking [11,12]. Further complications include the fact that STM measurements are unable to detect overhangs and are sensitive to tip curvature effects. Adsorption measurements meanwhile suffer from multiple interpretations [12–18].

X-ray reflectivity measurements have not previously been utilized for measurements of fractal scaling in film surfaces. Specular reflectivity is, however, a common technique for  $\sigma$  measurements [19,20], while diffuse reflectivity, which is sensitive to surface height-height correlations, has recently been suggested as a viable probe of the parameter  $H$  [20].

X-ray reflectivity and adsorption measurements can be simultaneously achieved if the films are deposited onto a

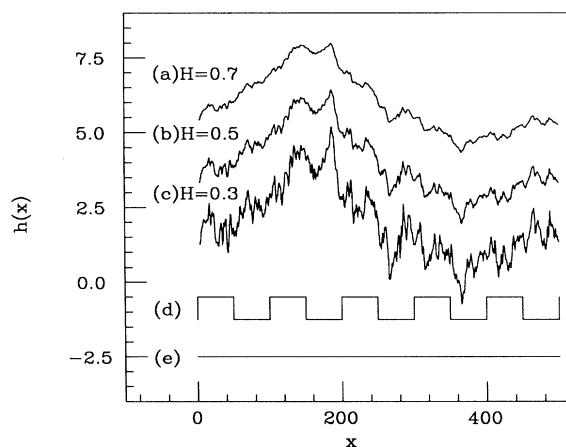


FIG. 1. Profiles of the three characteristic surface types: (a)–(c) self-affine, (d) nonfractally rough, and (e) planar, discussed in this paper. The self-affine profiles all have the same rms width  $\sigma = 1.1 \pm 0.1$ .

quartz crystal microbalance [21]. We produced Ag films by collimated thermal evaporation at  $10^{-9}$ – $10^{-8}$  torr onto  $\frac{1}{4}$ -in.-diam, optically polished quartz crystals [22] held 50 cm above a boat evaporation source. Au films were thermally evaporated at  $10^{-9}$  torr onto identical crystals held 12 cm above a tungsten wire basket source.

Adsorption isotherms were carried out by transferring the sample, within the vacuum chamber, to a tip which could be cooled to 77.4 K.  $N_2$  gas was then admitted to the chamber, and the quantity adsorbed (proportional to oscillator frequency shift) was monitored as a function of pressure under equilibrium conditions. Data were recorded on films prepared under three general types of conditions which were anticipated to produce "planar," self-affine, and nonfractally rough surfaces.

In order to produce planar surfaces, thin (500–750 Å) Au films were deposited at 0.5 Å/s and normal incidence onto quartz substrates held at room temperature, "Au(300 K)." The surfaces of such films are gentle rolling hills rather than planes [23], but the increase in surface area (relative to that of a plane) is below the detection threshold ( $\sim 10\%$ ) for adsorption. Adsorption data for a 750-Å-thick Au(300 K) sample are displayed in Fig. 2. For  $N_2$  film thicknesses ranging from 6 to 60 Å, the data match theoretical predictions [24] for adsorption on a planar substrate [Eq. (1), with  $N_2$ /Au parameters taken from Ref. [24]], with *no* adjustable parameters;

$$\ln(P_0/P) = \gamma(a)/k_B T a^n, \quad n=3. \quad (1)$$

The coefficient  $\gamma(a)$  [25] in Eq. (1) reflects substrate-adsorbate and adsorbate-adsorbate van der Waals interactions;  $T$  is the temperature,  $a$  is the quantity adsorbed, and  $P/P_0$  is the pressure relative to bulk saturation.

Adsorption on a fractal surface (with a continuous

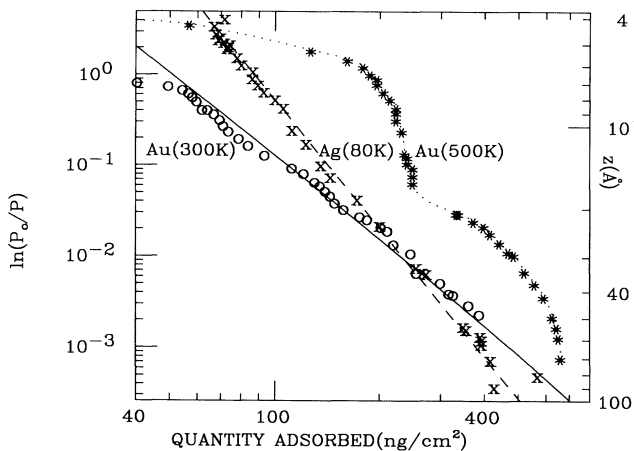


FIG. 2. Liquid nitrogen adsorption data for Au(300 K), Ag(80 K), and Au(500 K) surfaces. The right-hand axis shows film thicknesses for adsorption on a flat surface. The solid line depicts theory for nitrogen adsorption on a planar Au surface, where  $n=3$ . The dashed line corresponds to  $n=4.7$ .

roughness spectrum [26]) is predicted to be of the same form as Eq. (1), except for a different exponent  $n$ . To produce such a surface, silver films were deposited at near-normal incidence onto a substrate held at 80 K, "Ag(80 K)." Our motivation was to imitate the conditions of vapor-deposition models [27] and also those of a previous experiment which indicated such films might possess the desired type of roughness [28]. Adsorption data for a 1100-Å-thick Ag(80 K) sample, which was deposited at 0.5 Å/s and  $5^\circ$  off normal incidence, are displayed in Fig. 2 (deposition at normal incidence produced no detectable increase in area). The data for this sample, whose surface area was nearly twice that of a flat surface, are well fitted by  $n=4.7$ , at pressures where  $N_2$  films adsorbed on a flat surface range from 4 to 70 Å thick. Neglecting nitrogen surface-tension effects [29], the data are consistent with a self-similar,  $D=2.36$  [12, 13], and self-affine,  $H=0.64$ , [14] surface. Including such effects, the data are consistent with  $D=2.79$ , [15–17] and  $H=0.35$  [15].

Deposition of Au onto substrates held at elevated temperatures produces flat-topped column structures characterized by a single length scale [30], that is, nonfractal rough surfaces. To produce such a surface, 1500 Å of Au was deposited at 0.5 Å/s and normal incidence onto a quartz substrate held at 500 K, "Au(500 K)." Adsorption data for a Au(500 K) sample, whose surface area was over 4 times that of a flat surface, is shown in Fig. 2. These data cannot be fitted by the form of Eq. (1). They are, however, quite similar to the curves obtained by Robbins, Andelman, and Joanny [18], who modeled nitrogen adsorption on corrugated surfaces characterized by a single length scale.

The x-ray measurements were performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. All samples were transported to NSLS within a portable vacuum chamber equipped with beryllium windows. With the exception of the Au(500 K) sample, data were recorded in vacuum at x-ray-scattering beam line X16B with wavelength  $\lambda=1.692$  Å. The Au(500 K) data were recorded in air at beam line X20A with wavelength  $\lambda=1.375$  Å. Receiving slit geometry defined a scattering resolution relative to the diffractometer center of  $\approx 0.02^\circ$ . The resolution transverse to the scattering plane was  $\approx 0.5^\circ$ – $0.75^\circ$ . The footprint of the sample due to the finite width of the incoming beam corresponded to beam spillover at angles of  $1.3^\circ$  or less.

Specular reflectivity profiles (not shown) were measured for the film samples and the bare quartz substrates onto which they were evaporated. After correcting for beam spillover and background, the data were fitted using an analysis involving homogeneous stratified layers [31], where layer thicknesses and interfacial (Gaussian) widths are fit parameters. The film thickness obtained for each sample was within 10% of that measured by the deposition rate monitor. This implied that within experimental resolution, the film densities were equal to the bulk value.

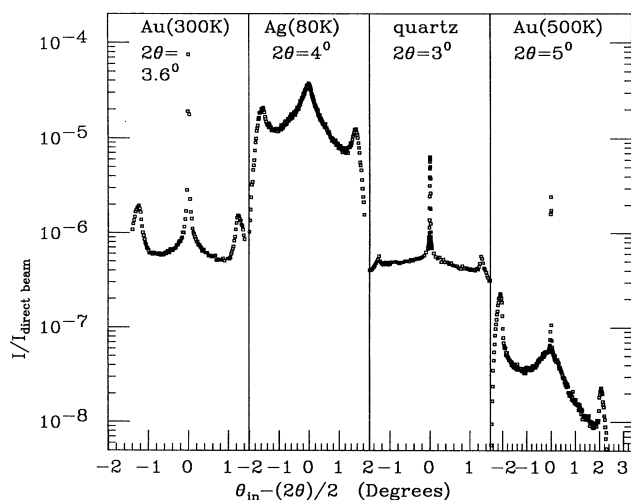


FIG. 3. Rocking curve data for the Ag(80 K), Au(500 K), Au(300 K), and bare quartz samples.

Further evidence for the compact nature of all of the films studied was provided by the location of the scattering critical angle and also by the film density profile determined from the fit parameters. A compact film is consistent with the presence of a self-affine more than with a self-similar surface, due to the absence of overhangs. Combining this evidence with the fact that vapor-deposition models consistently obtain self-affine surfaces, we continued our data analysis assuming the surfaces, if fractal, would be self-affine in nature.

In order to probe potential self-affine scaling, diffuse scattering measurements were recorded. Figure 3 shows rocking curve scattering data, including those for the bare quartz substrate for the Ag(80 K) sample. The detector ( $2\theta$ ) is fixed and the sample rocked about the specular condition (angle of incidence  $\theta_{in}$  equal to angle of reflection). The central peak in the scans corresponds to a beam which is specularly reflected off the film-vacuum and film-substrate interfaces. For the two Au samples and the bare quartz, this peak is sharp, rising well out of the adjacent diffuse scattering. Diffuse scattering is extremely bright in the case of the Ag(80 K) sample, almost completely masking the presence of its specular peak.

Both rocking curve and "off-specular" diffuse data (where the sample is offset from the specular condition so as to gather diffuse data under conditions close to specu-

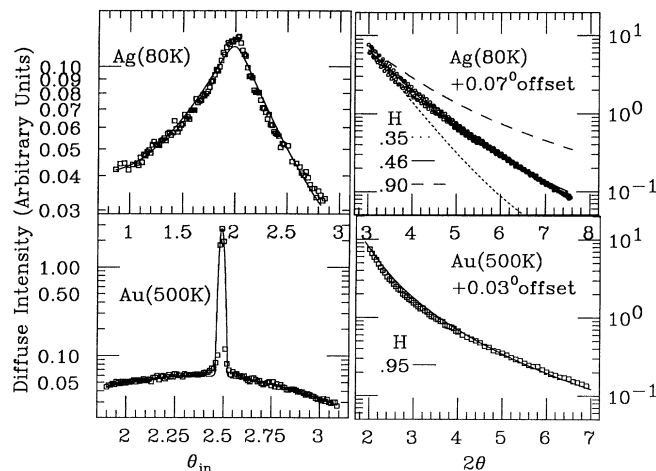


FIG. 4. Fits to the rocking curve and off-specular reflectivity data for the Au(500 K) and Ag(80 K) samples.

lar) were fitted utilizing a height-height correlation function  $C(R) = \langle z(R)z(0) \rangle$ ;  $R = (x^2 + y^2)^{1/2}$ , and "interfacial width function" [32]  $g(R) \equiv g(X, Y) = \langle [z(x', y') - z(x, y)]^2 \rangle$ ;  $(X, Y) \equiv (x' - x, y' - y)$  appropriate for a self-affine surface with a finite horizontal cutoff  $\xi$  [2,20]:

$$C(R) = \sigma^2 \exp[-(R/\xi)^{2H}]; \quad (2)$$

$$g(R) = 2\sigma^2 \{1 - \exp[-(R/\xi)^{2H}]\}.$$

The value  $\sigma$  in Eq. (2) is the maximum value which the rms width attains at the horizontal coherence length  $\xi$ . Diffuse data were fitted for  $H$  and  $\xi$ , employing the  $\sigma$  values obtained from the specular fits (Table I), and the form for the diffuse scattering intensity [Eqs. (4.41) and (4.42) in Ref. [20]] suggested by Sinha *et al.* [20]. The Ag(80 K) data were fitted by  $H=0.46$ , and the Au(500 K) data were fitted by  $H=0.95$  (which is within experimental error of a nonfractal surface value,  $H=1$ ) (Fig. 4), for perpendicular scattering length scales ranging from 11 to 33 Å. The Au(300 K) data could not be fitted by any value of  $H$ , implying the self-affine analysis approach was inappropriate for this sample. A single surface, rather than multiple interfaces, was considered in the diffuse data analysis. Quantitative comparison of the diffuse scattering from the sample surfaces to that obtained from the bare quartz substrates indicated this approach to be quite well founded for the Au(300 K) and Ag(80 K) samples, and reasonably well founded for the Au(500 K) sample.

TABLE I. Comparison of x-ray reflectivity and adsorption.

	$h$ (Å)	Adsorption $H = 3 - D$	$\sigma$ (Å)	Reflectivity $\xi$ (Å)	$H$
Au(300 K)	700	Planar	11	7000	Not fractal
Ag(80 K)	1100	0.35 <sup>a</sup> , 0.64 <sup>b</sup>	8.5	1450	0.46
Au(500 K)	1500	Not fractal	22	3300	0.95
Error	$\pm 50$	$\pm 0.1$	10%	10%	$\pm 0.1$

<sup>a</sup>Reference [15].

<sup>b</sup>References [12-14].

Adsorption and x-ray results are compared in Table I. The techniques are in complete agreement concerning which sample type, Ag(80 K), exhibits self-affine scaling. Less agreement is obtained concerning the value of the scaling parameter  $H$ . (The ranges  $0.36 \leq H \leq 0.45$  and  $0.54 \leq H \leq 0.56$  are consistent with both the x-ray and adsorption results.) Although each technique is fairly limited in terms of the perpendicular length scale probed ( $\approx 5\text{--}50 \text{ \AA}$ ), x-ray rocking curve data provide values for  $\xi$ , the upper horizontal cutoff length. This length was relatively large in general, consistent with steps perpendicular to the surface being smaller than corresponding horizontal step sizes (similar to the profiles depicted in Fig. 1).

In terms of overall comparisons, adsorption provides a measure of surface area, while x-ray reflectivity provides a measure of the rms surface width. Adsorption reveals whether discrete or continuous length scales are present in the composition of the outer surface topology, while x rays are sensitive to the inner film density profile.

Films deposited on the warmer substrates showed no evidence of self-affine scaling at the length scales probed by our measurements. The value of  $H$  measured for Ag(80 K) is, however, consistent with that predicted by the deposition models for nonequilibrium growth on a cold substrate. Since a cold-deposited Ag film may become smoother when warmed to room temperature [28], the  $H$  which we have measured is an upper limit on the "low-temperature" value. Future studies of films which have not been warmed after deposition should allow direct experimental investigations of the various details of the surface deposition models.

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