Scaling of the $(\sqrt{3}\times\sqrt{3})R30°$ Domain-Size Distribution with Coverage for Ag/Si(111)

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The evolution of the $(\sqrt{3}\times\sqrt{3})R30°$ domain-size distribution with coverage for Ag on Si(111) has been studied by high-resolution low-energy electron diffraction. Scaling of the size distribution, which can be fitted by a gamma distribution, is observed. A temperature dependence of the exponent n describing a power growth law for mean size versus coverage is found where n decreases with decreasing deposition temperature. By introducing a simple relation, $q+nd=1$, where the dimensionality $d=2$ and q is an exponent describing the power law for domain density versus coverage, the behavior of n is explained in terms of the experimentally observed behavior of q.

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Thin-film growth on a solid surface is of ever increasing importance in scientific and industrial applications. Understanding the basic physics of a growth process is a challenging problem of theoretical and experimental interest.[1,2] In many growth processes the most characteristic feature is the domain-size distribution and its evolution with deposition time or coverage at a given substrate temperature and deposition rate, from which much basic physics can be drawn.[1-7] Therefore, studying the evolution of domain-size distribution with coverage is of general interest.

Recent theoretical and computer-simulation studies of growth kinetics in various systems have shown that the domain-size distribution and its moments are scale invariant.[2-5] For conserved coverage, scaling phenomena in ordered systems have been experimentally verified in two-dimensional (2D) chemisorbed systems where an overlayer with fixed coverage evolved with time after the quench from a disordered state to an ordered state.[8] Similar phenomena would also exist during a thin-film deposition where the coverage is not conserved.[3] In this Letter we report the first experimental evidence for scaling of a 2D domain-size distribution with coverage in an ordered system, Ag/Si(111)-$(\sqrt{3}\times\sqrt{3})R30°$ (or simply $\sqrt{3}$), using high-resolution low-energy electron diffraction (HRLEED). Also, a simple relation, Eq. (5), is introduced to explain the observed temperature dependence of the power growth law for mean size versus coverage.

The fundamental process of ordering during vapor deposition generally will consist of nucleation, growth, and coalescence stages.[1] In the first stage small domains are nucleated from deposited individual atoms (2D vapor). As the deposition progresses, these domains grow by direct condensation from the 2D vapor and by coarsening (Ostwald ripening) in which larger ones grow at the expense of smaller ones. When the separation between various domains decreases, they will coalesce to form larger ones which, in turn, join to form large patches of the ordered structure separated by unfilled regions. These regions gradually fill until a layer is completed. A completed layer may still consist of many equivalent domains (or degenerate ground states)[2] which are delineated by energetically favored boundaries.

For the quantitative description of a growth process, one often assumes that the mean linear size $\bar{R}$ of domains and the distribution width $\sigma\equiv\langle(R-\bar{R})^2\rangle^{1/2}$ grow with coverage θ as

$$\bar{R}\sim\theta^n \text{ and } \sigma\sim\theta^{n'}, \tag{1}$$

with all sizes in units of the lattice spacing. If scaling exists, i.e., there is only one length scale in a system during growth, the exponents n and n' in Eq. (1) should become equal, and the size distribution function $P(R,\theta)$, which describes the probability of finding a domain with linear size of R lattice spacings at a coverage θ, can be written in the form

$$P(R,\theta)=(1/\bar{R})P'(x), \tag{2}$$

where $x=R/\bar{R}$ and $P'(x)$ is the scaling function independent of θ. For a given coverage θ, particle-number conservation requires

$$M(\theta)\sum_R R^d P(R,\theta)\sim M(\theta)\bar{R}^d\sim C_T\theta, \tag{3}$$

where d is the effective dimensionality of the domains, $\bar{R}^d\sim\bar{R}^d$ upon the assumption of scaling, $M(\theta)$ is the domain density, and C_T is a quantity measuring the percentage of the deposited atoms going into the ordered structure. When the deposited atoms all go into the ordered structure, $C_T=1$, which is close to the case in our experiment.[9,10] Apparently, for a constant C_T the domain density $M(\theta)$ will also follow a power law based on Eqs. (1) and (3), i.e.,

$$M(\theta)\sim\theta^{1-nd}\sim\theta^q. \tag{4}$$

The exponents for both $\bar{R}(\theta)$ and $M(\theta)$ are related by

$$q+nd=1. \tag{5}$$

This implies that for a given d, the exponents n and q are

complementary. Equation (5) will be generally true as long as scaling exists. It is these relations [Eqs. (1)–(5)] that we have observed for the $\sqrt{3}$ domain growth of Ag on the Si(111) surface.

The measurements were conducted in a UHV chamber with a pressure routinely in the 10^{-11}-Torr range. Diffraction profiles were recorded with a HRLEED system having a transfer width of ≥ 1000 Å. An n-type Si(111) wafer was used as the substrate on which the average terrace width was measured to be equal to or larger than the HRLEED transfer width. The sample was cleaned by annealing at $\geq 1000\,^{\circ}$C with the temperature monitored by a W5%Re-W26%Re thermocouple mounted on a corner of the sample. Ag atoms were evaporated on the clean Si(111)7×7 surface at a fixed rate of ~0.15 monolayer/min from a pure (99.999%) Ag foil heated by electron bombardment from the back side. Complete condensation of Ag on Si(111) was observed up to at least 1 monolayer (ML) over a wide range of substrate temperatures[10] with formation of the $\sqrt{3}$ structure for a submonolayer of Ag deposited above ~190 °C. Depositions were performed when the substrate was held at a desired temperature T (350–450 °C), and the LEED measurements were done after interruption of the deposition and cooling the sample to near room temperature. Coverage was calibrated by measuring the Auger intensities of Ag and Si, and the total intensity of a $\sqrt{3}$ superlattice LEED beam.[11] The kinetics of the $\sqrt{3}$ domain growth are very fast (<1 min) at the deposition temperatures used; therefore the $\sqrt{3}$ domain morphology was in a very late stage of growth when each LEED measurement was made.

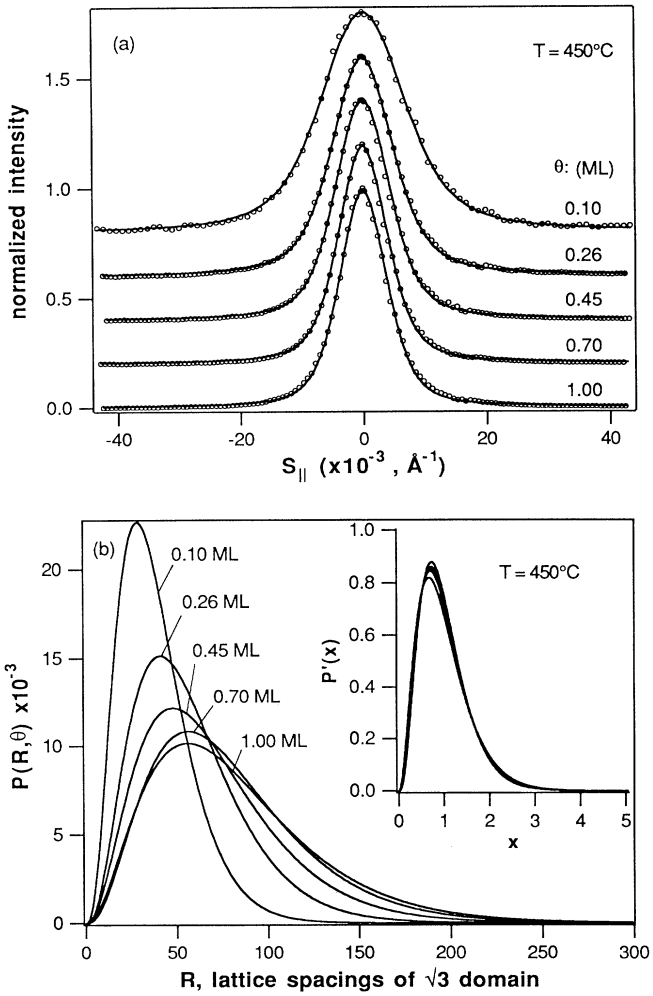

FIG. 1. (a) The angular profiles of the $(\frac{1}{3}\ \frac{1}{3})$ superlattice beam at different coverages θ for $T=450\,^{\circ}$C. The solid lines represent the best fits of Eq. (6), convoluted with the instrument response function and using the gamma distribution. (b) Gamma domain-size distributions obtained in the fits of (a) at different coverages. Inset: The scaling function $P'(x)$ vs x, which is independent of θ.

Since the line shape of a LEED beam depends on the domain-size distribution of an ordered structure, the angular profile of a $\sqrt{3}$ superlattice beam was measured as a function of coverage to monitor the $\sqrt{3}$ domain growth. The incident electron energy was chosen to be $E=84$ eV at which the intensity is highest. Figure 1(a) shows the evolution of the angular profiles of the $(\frac{1}{3}\ \frac{1}{3})$ beam with coverage at $T=450\,^{\circ}$C. The narrowing of the profile indicates the growth of the $\sqrt{3}$ domain because the full width at half maximum (FWHM) of the profile is inversely proportional to the average domain size $\bar{R}$. To see the details of the domain-size distribution, we have employed an incoherent scattering model to fit the angular profiles. The model assumes that the positions of domain boundaries are randomly distributed so that the interference among domains is negligible.[12] Then, the intensity of any superlattice beam can be expressed as

$$I(\mathbf{S},\theta)=M(\theta)\sum_{R=1}^{\infty}P(R,\theta)\frac{\sin^2[\frac{1}{2}R(\mathbf{S}_{\parallel}\cdot\mathbf{a})]}{\sin^2[\frac{1}{2}(\mathbf{S}_{\parallel}\cdot\mathbf{a})]}, \quad (6)$$

where $\mathbf{S}_{\parallel}$ and $\mathbf{a}$ are the momentum transfer parallel to the surface and the surface unit vector (6.65 Å) of the $\sqrt{3}$ structure, respectively. This assumption is expected to hold well for a system with ground-state degeneracy $Q>2$ because the larger the Q, the more complicated and random the domain-boundary structure could be. The Q for the $\sqrt{3}$ structure of Ag/Si(111) with a honeycomb geometry[9] is between 3 and 9, and thus the model should be suitable for our case. Also, since the intensity distribution of $\sqrt{3}$ superlattice beams is symmetric, implying an isotropic distribution of $\sqrt{3}$ domains, this 1D model for the 1D angular profile is appropriate for obtaining the 1D size distribution as a projection of the 2D size distribution.[13] For comparison with the experimental profiles, we have tried different distributions for $P(R,\theta)$ in Eq. (6) and found that the gamma distribu-

tion gives the best fit. The gamma distribution has the form

$$P(R,\theta)=\frac{1}{\lambda^{\alpha}\Gamma(\alpha)}R^{\alpha-1}e^{-R/\lambda} \quad (7)$$

with the mean $\bar{R}=\alpha\lambda$ and distribution width $\sigma=\lambda\sqrt{\alpha}$, where α and λ were chosen as fitting parameters which are functions of θ and T. In Fig. 1(a) the solid curves are the least-squares fits of Eq. (6) convoluted with the Gaussian instrument response function and using the gamma distribution in $P(R,\theta)$. Excellent fits give $\alpha=3.4\pm0.3$ and $\lambda=10.7$ to 26.3 for $\theta\sim0.1$ to 1 ML. The mean size $\bar{R}$ is calculated to be 38.5 to 81.4 lattice spacings, accordingly. Plotted in Fig. 1(b) are the corresponding domain-size distributions at different coverages which broaden with increasing coverage. This indicates that at $T\sim450$ °C, either domain coalescence has already occurred after $\theta\sim0.1$ ML or the larger domains grow faster than smaller ones because, independent of coarsening, the deposited atoms have a higher probability to attach to the larger domains than to the smaller ones as they migrate. The gamma distribution with $\alpha>1$ will peak at $R_p=(\alpha-1)\lambda$. The steep drop in the probability of finding domains with size $R<R_p$ may be attributed to coarsening effects, whereas the exponential decay for $R\gg R_p$ implies weak interactions among large domains. More interestingly, the similar values of the parameter α (~3.4) obtained for different coverages remind us that the gamma distribution can be written in a scaling form of Eq. (2) if we let $x=R/\bar{R}$ and $P'(x)=[\alpha^{\alpha}/\Gamma(\alpha)]x^{\alpha-1}e^{-\alpha x}$. According to Eq. (2), $P'(x)=\bar{R}P(R,\theta)$ vs x is plotted in the inset of Fig. 1(b). Remarkably, although $P(R,\theta)$ broadens and its mean increases with θ, $P'(x)$ is independent of coverage. This coverage-independent scaling behavior is also confirmed by a direct comparison of the angular profiles at different coverages. An identical line shape of $1/(S_{\parallel}^2+\kappa^2)^m$ with $m=1.5\pm0.1$ is obtained for the profiles after deconvolution to remove the instrument response function, where κ is the inverse correlation length varying with θ. In Fig. 2 we have plotted 1/FWHM of the angular profiles, mean size $\bar{R}$, and distribution width σ versus coverage θ on a ln-ln scale to see the validity of Eq. (1) and the scaling behaviors of the moments of the distribution. As seen in the figure, all three quantities versus θ follow a power law as assumed in Eq. (1) and the linear slopes give $n=n'=0.35\pm0.02$. This indicates that there is only one length scale in our growth process. Similar scaling behavior has also been observed at other deposition temperatures but the parameter α increases slightly with decreasing deposition temperature.[11]

In addition, we have found that the exponent n for $\bar{R}$ in Eq. (1) varies with the deposition temperature. In Fig. 3, 1/FWHM of the $(\frac{1}{3}\ \frac{1}{3})$ beam is plotted against coverage on a ln-ln scale for different deposition temperatures. By fitting the linear slopes of the data, n is determined to be 0.35, 0.30, 0.24, and 0.20 ± 0.02 for

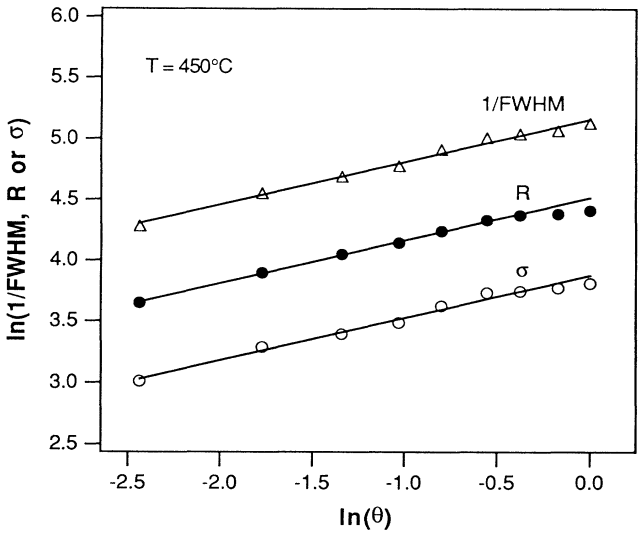

FIG. 2. 1/FWHM of the $(\frac{1}{3}\ \frac{1}{3})$ beam (after the removal of the instrument response width), the mean size $\bar{R}$, and distribution width σ obtained in the fits of Fig. 1(a) plotted against coverage θ (ML). On the ln-ln scale, all the linear slopes are fitted to give $n=n'=0.35\pm0.02$. The units are as follows: FWHM, Å^{-1}; $\bar{R}$ and σ, lattice spacing.

$T=450$, 425, 400, and 350 °C, respectively, which cannot be explained by any existing theory.[1,3,14] Since the $\sqrt{3}$ domains grow with coverage faster at high temperature than at low temperature, the domain density $M(\theta)$ must increase with coverage in an opposite way. We be-

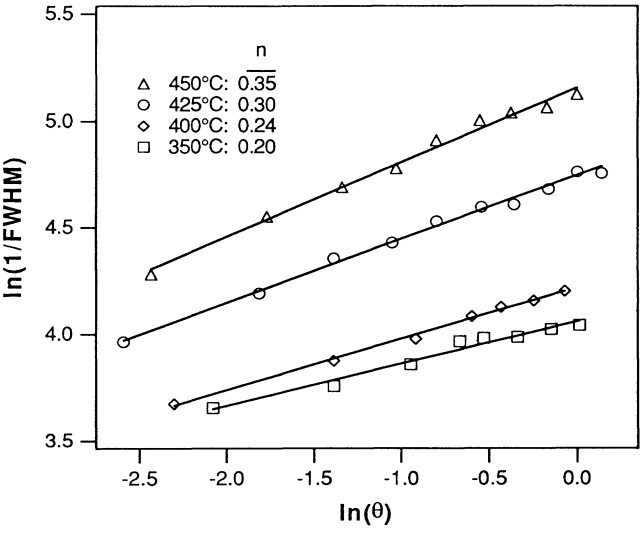

FIG. 3. A ln-ln plot of 1/FWHM vs coverage θ (ML) for the $(\frac{1}{3}\ \frac{1}{3})$ beam at different deposition temperatures, where the instrument response width has been removed and the FWHM is in units of Å^{-1}.

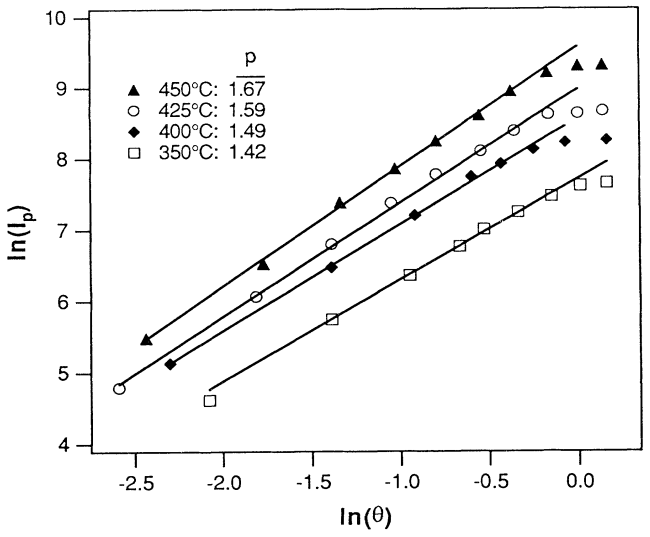

FIG. 4. A ln-ln plot of the peak intensity I_p (arbitrary units) of the $(\frac{1}{3}\ \frac{1}{3})$ beam vs coverage θ (ML) at different deposition temperatures.

lieve that with decreasing T, the observed decrease of the exponent n is associated with the increase of the exponent q for $M(\theta)$ according to Eq. (5). To check this, we have also measured the peak intensity I_p of the $(\frac{1}{3}\ \frac{1}{3})$ beam as a function of coverage at different deposition temperatures as shown in Fig. 4 with a ln-ln scale. Obviously, a power law can also be established, i.e., $I_p \sim \theta^p$, with $p=1.67$, 1.59, 1.49, and 1.42 ± 0.03 for $T=450$, 425, 400, and 350 °C, respectively. It can be shown that $I_p \sim M(\theta)\bar{R}^4$ from Eq. (6) if scaling exists, where we have considered that the peak intensity reflects the 2D domain structure. By using Eqs. (1) and (4), the peak intensity versus coverage is $I_p \sim \theta^{q+4n}$. If Eq. (5) holds, in our case ($d=2$) it can be written as $I_p \sim \theta^{1+2n}$. Using the values of n obtained in Fig. 3, $p=1+2n$ is calculated to be 1.70, 1.60, 1.48, and 1.40 for $T=450$, 425, 400, and 350 °C, respectively, which are in good agreement with the measured values of p obtained from the data in Fig. 4. This proves that the exponents n and q for $\bar{R}$ and $M(\theta)$ are complementary through Eq. (5). Using Eq. (5) and the values of n, the exponent q for $M(\theta)$ is determined to be -0.3, 0.4, 0.52, and 0.6 for $T=450$, 425, 400, and 350 °C, respectively.

In conclusion, we have presented HRLEED data of the $\sqrt{3}$ domain growth as a function of coverage for Ag deposited on a Si(111) surface. By analyzing the angular profiles of a $\sqrt{3}$ superlattice diffraction beam, it is found that the $\sqrt{3}$ domain-size distribution can be fitted by a gamma distribution which is scale invariant with coverage. A power growth law for mean size versus coverage is also established and the growth exponent n decreases with decreasing deposition temperature. By introducing a simple complementary relation, $q+nd=1$, where $d=2$ and the exponent q describes the power law for domain density versus coverage, the temperature dependence of the growth exponent n is associated with that of exponent q, which is experimentally verified.

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