Scaling of Island Growth in Pb Overlayers on Cu(001)

Wei Li(1,1), Gianfranco Vidali(1) and Ofer Biham(1,2)

(1) Department of Physics, Syracuse University, Syracuse, NY 13244-1130
(2) Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853

The growth and ordering of a Pb layer deposited on Cu(001) at 150 K has been studied using atom beam scattering. At low coverage, ordered Pb islands with \((\sqrt{61} \times \sqrt{61})\) symmetry are formed. This is a high order commensurate phase with 30 atoms in the unit cell. From the measurement of the island diffraction peak profiles we find a power law for the mean island size versus coverage with an exponent \(n = 0.54 \pm 0.03\). A scaling behavior of growth is confirmed and a simple model describing island growth is presented. Due to the high degeneracy of the monolayer phase, different islands do not diffract coherently. Therefore, when islands merge they still diffract as separate islands and coalescence effects are thus negligible. From the result for \(n\) we conclude that the island density is approximately a constant in the coverage range \(0.1 < \Theta < 0.5\) where the ordered islands are observed. We thus conclude that most islands nucleate at \(\Theta < 0.1\) and then grow in an approximately self similar fashion as \(\Theta\) increases.
I. INTRODUCTION

The study of growth and ordering of overlayers deposited on cold single crystal substrates poses special challenges. Recent experimental and computational work on growth of metal overlayers on metal substrates has shown that our understanding of the interplay of kinetic, dynamic and energetic processes during growth is inadequate. Useful insight may be obtained from studies of the dynamics of nucleation, growth and coarsening in first order phase transitions of bulk systems. In these studies, a system in thermal equilibrium is quenched into a nonequilibrium state in which two different phases A and B coexist. As a result the system develops spatial inhomogeneities and finally separates into domains of phase A and domains of phase B. The domains of the minority phase typically form isolated droplets inside the majority phase. According to Lifshits and Slyozov, in systems with a constant order parameter the average droplet size increases as a function of time like

$$R \sim t^{x},$$

and $x = 1/3$ during the late stages of the growth process. During this process large droplets tend to grow while small droplets evaporate and shrink. The atoms propagate between droplets by diffusion. Similar phenomena on surfaces have recently been studied in the context of adsorbed monolayers. In these experiments it was found that $x = 1/3$ in agreement with the theory. In other dynamical phenomena, which occur in systems with a nonconserved order parameter, the growth exponent is $x = 1/2$.

Related studies of growth have been done for liquid droplets deposited on a surface at a constant rate. It was found that the growth is dominated by two processes. One is the creation of new droplets, while the other is the coalescence of two or more droplets into one larger droplet. The droplets generally extend into the third dimension, and can be approximated as having a spherical shape independent of the size. As a result, when two droplets coalesce into one, the surface area it covers is smaller than the sum of the areas covered by the two droplets. The liquid density on the surface is given by $\rho = r \cdot t$ where $r$
is the deposition rate and \( t \) is the time. As the deposition proceeds the mean droplet radius increases according to \( \overline{R} \sim \rho^n \). However, in the limit of completely flat droplets which do not extend into the third dimension, the power law is modified. This is due to the fact that for flat droplets, the area occupied by a droplet created after coalescence is equal to the sum of the areas of its components, and not smaller. As a result, the mean droplet size increases faster than a power law of \( \rho \). This result also applies to monolayer islands with no internal order. However, as we later show, it does not apply for ordered monolayer phases with high degeneracy (and a large unit cell).

The scaling of island growth in surface adsorption for submonolayer coverage has been studied theoretically and numerically by Bartlet, Evans and Tringides [11,12]. They used a simple lattice model in which atoms are deposited at a constant rate \( r \) and then hop between empty sites as random walkers at a constant rate \( h \). An island is created when an atom reaches a site adjacent to another atom. They then nucleate into a stable island of size two. These islands grow when more atoms reach sites adjacent to them and thus aggregate. Each island in this model, no matter how many atoms it contains, occupies a single site on the lattice. Therefore, this model applies only to the limit of low coverage, where islands are small and isolated. Using numerical simulations of the model and a rate equation which is derived from it Bartlet, Evans and Tringides [11,12] find that

\[
\overline{S} \sim \Theta^{2/3} \cdot D^{1/3}
\]

(2)

where \( \overline{S} \) is the average number of atoms in an island and \( D = h/r \) is the ratio between hopping rate and deposition rate. If we identify the linear size of an island as \( \overline{R} = (\overline{S})^{1/2} \), this result is equivalent to

\[
\overline{R} \sim \Theta^{n} \cdot D^{\chi},
\]

(3)

where \( n = 1/3 \) and \( \chi = 1/6 \). The dependence of the average island size on \( D \) turns out to be in agreement with the result obtained in Ref. [13] from a completely different approach. The simulations in [11,12] were done for low coverage of up to 0.15 monolayer (ML). This
model does not describe the regime of higher coverage, where a large fraction of the atoms are deposited directly on top of existing islands which cover a significant portion of the substrate area. Also, coalescence effects are not included in the model. The experimental results in the present paper were obtained for higher coverage, outside the regime studied in [11,12]. Experimental studies of the very low coverage limit are difficult due to the fact that the islands are very small and the diffraction signal is too weak.

The growth of ordered islands of Ag on Si(111) was studied by Zuo and Wendelken using high resolution low energy electron diffraction (HRLEED) [14]. They found that the size distribution of islands is self-similar. From the analysis of peak profiles they found that the mean linear size $R$ of islands exhibits a power law dependence on the coverage $\Theta$ of the form

$$R \sim \Theta^n,$$

where $n$ changes between 0.2 to 0.35 as the substrate temperature is varied from 350 °C to 450 °C.

In this paper we present a study of island growth in Pb on Cu(001) at 150 K. This system was chosen since it has very intriguing characteristics. First, there is a considerable lattice mismatch (the bulk lattice constant of Cu is 3.6 Å, compared to 4.5 Å for Pb). Second, although for deposition at high temperature ($\sim 400$ K) Pb orders in submonolayer structures where most of the atoms are in registry with the substrate, at low deposition temperature ($\sim 150$ K) completely different phases are obtained. At low coverage we observe islands of the $(\sqrt{61} \times \sqrt{61})R\tan^{-1}\left(\frac{5}{6}\right)$ phase. This is a high order commensurate phase with 30 atoms in the unit cell. The supercell is square, while the proposed internal structure is nearly hexagonal. This phase results from frustration effects, between the adlayer that typically prefers the hexagonal symmetry (which has the largest coordination number) and the underlying square Cu(001) substrate which tends to induce the square symmetry. Near one layer coverage the $(\sqrt{61} \times \sqrt{61})R\tan^{-1}\left(\frac{5}{6}\right)$ phase disorders and is replaced by a denser monolayer phase with symmetry $(5 \times 5)R\tan^{-1}\left(\frac{3}{4}\right)$, which is a square phase with 16 atoms in the unit cell [15].
From the analysis of the diffraction peak profile we find that for slow deposition rate, islands of an ordered phase are formed and grow according to (4) with \( n = 0.54 \pm 0.03 \). Note that this exponent \( n \) is different from the dynamical exponent \( x \) of Eq. (1), which is obtained as a function of time, for a fixed coverage. We propose a growth model consistent with these results. We find that due to the large degeneracy, coalescence effects are negligible, while from the measured exponents we conclude that the island density does not change within the range of coverage that we have explored. The paper is organized as follows. The experimental set-up is described in Section 2. In Section 3 we describe how the Pb layer is characterized and present the results of atom beam scattering experiments. These results are discussed and interpreted in Section 4, and summarized in Section 5.

II. EXPERIMENTAL

The apparatus consists of a helium beam line which is coupled to an ultra high vacuum (UHV) chamber [10]. We used a supersonic helium beam of 18.4 meV incident energy, with \( \delta v/v \sim 1\% \) velocity resolution with the beam source at 85 K and 1200 psi helium gas pressure. In the UHV chamber there are located: a liquid nitrogen cooled Knudsen evaporation source, a 4-grid low energy electron diffraction (LEED)-Auger optics and a helium beam detector, which is a differentially pumped quadrupole mass spectrometer with an aperture of 0.5°. This spectrometer can be rotated around the axis of the sample manipulator and can be positioned to measure the reflected helium beam during Pb deposition [10].

The sample is fixed on a VG long-travel manipulator with X,Y, and Z translation, and polar and azimuthal rotation. The thoroughly desulfurized copper sample was cleaned prior to each run by Ar ion sputtering first at room temperature and then at 350°C. The sample was then annealed at 580°C and slowly cooled. Helium beam scattering was used to assess the quality of the prepared surface as in previous studies [3-10].

Pb of 99.999% purity was deposited from a liquid nitrogen shielded Knudsen evaporation source. The deposition time for one monolayer of Pb was typically about 38 minutes. The
exposure calibration was obtained from Auger Pb and Cu signals and from the analysis of ABS “adsorption curves” (Fig. 1). Somewhat faster deposition rates did not affect the results. Although the layers deposited at 150 K were found to be metastable (see below), there was no indication from atom beam scattering (ABS), LEED or Auger of a rearrangement within the layer during measurements.

There is no indication that Pb atoms are incorporated in the Cu crystal. The original Cu(001) surface could be recovered by heating the sample above 580 °C until no trace of Pb was left as determined by Auger electron spectroscopy. Furthermore, Pb is virtually immiscible with Cu [17].

III. RESULTS

A. Characterization of the Pb Overlayer

In a previous study [15], we have used ABS to monitor Pb growth on Cu(001) at low temperature. Here we will describe in more detail how ABS data are used to characterize the growth of a Pb layer. Specifically, we show how the “ABS adsorption curve” (Fig. 1) and the “rocking curve” (Fig. 2) can be used to obtain precise coverage calibration, the average height of Pb adatoms above Cu(001) and the in-phase/out-of-phase scattering conditions.

We fit the ABS adsorption curve (Fig. 1) to the equation [18]:

\[
\frac{I}{I_0} = (1 - m\Theta) \frac{S_{pbn}}{m} + (m\Theta) \frac{S_{nbn}}{m} + 2 \left( \frac{A_1}{A_0} \right) cos\varphi (1 - m\Theta) \frac{S_{pbn}}{2m} (m\Theta) \frac{S_{nbn}}{2m}. \tag{5}
\]

The first and the second terms represent scattering from the uncovered parts of the surface and from the adsorbate covered parts, respectively. The last term describes the interference between these contributions. \(I_0\) is the specular peak intensity of the clean surface. The coefficients \(A_0\) and \(A_1\) represent the specular scattering amplitudes: \(A_0\) is from the clean surface while \(A_1\) is the specular peak amplitude at one monolayer completion coverage. The parameter \(m=\frac{1}{0.64}\) is the inverse of the ideal coverage for the monolayer completion phase, which is \(\Theta = 0.64\) for \((5\times5)R\tan^{-1}(\frac{3}{4})\) phase (see Fig. 3). The coverage \(\Theta\) is defined as the
ratio between the number of Pb adlayer atoms and the number of Cu substrate atoms. Thus Fig. 1 can be used to calibrate exposure into coverages. The quantities \( \Sigma_{Pb} \) and \( \Sigma_v \) are cross sections of the He atom scattering from isolated Pb atoms and vacancies in the monolayer, respectively. Fig. 1 shows the fitting result (solid line) to the ABS adsorption curve up to one monolayer coverage. From fitting we have \( \Sigma_{Pb} = 58 \text{Å}^2 \) and \( \Sigma_v = 23 \text{Å}^2 \), respectively. The \( \Sigma_{Pb} \) value obtained here is slightly smaller than the 62 \( \text{Å}^2 \) obtained from fitting to the initial slope of the ABS adsorption curve. The fitted interference factor, \( \cos \varphi = 0.99 \), gives the phase difference \( \varphi \) between beams reflected from uncovered surface and the adsorbate overlayer. It is related to the overlayer height by \[ \varphi = 2hk \cos \theta_i + 2n\pi, \quad (n, \text{integer}). \] (6)

Here \( h \) is the overlayer height, \( \theta_i \) is the incident beam angle and \( k \) is the beam wave vector which can be obtained by measuring the beam temperature. We obtain that the Pb overlayer height is \( 2.0 \pm 0.1 \text{Å} \) above the Cu plane.

Alternatively, we can obtain the Pb overlayer height by taking a rocking curve, i.e., ABS specular peak intensity vs. incident angle. Fig. 2 shows such a rocking curve taken with half layer of the \((\sqrt{61} \times \sqrt{61})R\tan^{-1}\left(\frac{5}{6}\right)\) structure (the full layer coverage is 0.49 Pb/Cu atom ratio). The intensity oscillation in Fig. 2 is due to the interference of the scattering from the substrate and Pb layer. Prior to Pb deposition a similar measurement was taken for the clean Cu(001) surface and no oscillations were detected. We have maxima at the in-phase condition and minima at out-of-phase condition. The following formula

\[ 2hk \cos \theta_i = 2n\pi \]

(7)

where \( n \) is an integer, gives the in-phase condition. For half integer \( n \) we have the out-of-phase condition. By analyzing the data in Fig. 2 we obtain that the Pb layer is \( 2.1 \pm 0.1 \text{Å} \) above the Cu(001) surface. This value is in good agreement with the one obtained above by fitting the ABS absorption curve. The above results demonstrate the equivalence of these two methods. Actually, one can see that they are all based on the interference between specular
beams: the reflection from the bare surface and from the deposited overlayer. We have used this information to select the in-phase and out-of-phase conditions for the measurements described in Section C.

B. Low Temperature Phases

In Fig. 3 we present a sketch of the phase diagram. The two phases below 0°C have not been reported by other groups before [20,21]. We have presented the (5×5)Rtan⁻¹(3/4) phase structure elsewhere [2,15]. Here we concentrate on the submonolayer (√61×√61)Rtan⁻¹(5/6) phase. This phase, as we show in Fig. 3, starts to appear at very low coverage around Θ = 0.1 and continues up to about 0.5. The LEED pattern of (√61×√61)Rtan⁻¹(5/6) turns out to be quite similar to that of (5×5)Rtan⁻¹(3/4) [15], and consists of contributions from two types of reciprocal nets. In Fig. 4 the reciprocal lattice nets and proposed structure of (√61×√61)Rtan⁻¹(5/6) are presented. The two types of reciprocal nets are from two kinds of real space domains as illustrated by two big squares in Fig. 4(b), and are rotated by tan⁻¹(5/6) and tan⁻¹(6/5) from the Cu < 110 > direction. The LEED spots actually observed are indicated in Fig. 4(a) with dark points, and many of these are from two domains and too close to be resolved. Since the observed LEED pattern is rather faint, the ABS diffraction from this phase (Fig. 5) has played an important role to determine the superstructure. Within the perimeter of the superstructure we propose a compact pseudo-hexagonal arrangement with an ideal coverage of 0.49. A similar kind of structure has been proposed before for Bi on Cu(001) [22].

The two low temperature ordered phases are obtained after deposition at 150K and are likely to be metastable. Upon heating them above about 0°C they convert into the phases obtained by depositing Pb at 400 K, and they cannot be reached by cooling the overlayer deposited at room temperature. These high temperature phases are equilibrium phases, since they can be melted and recrystallized [2,21]. The low temperature phases are high order commensurate structures with only one atom in 16 for the (5×5)Rtan⁻¹(3/4) or three
atoms in 30 for the \((\sqrt{61} \times \sqrt{61})R\tan^{-1}\left(\frac{\pi}{6}\right)\) in registry with the substrate. This suggests that they are the result of limited diffusion and of a delicate competition between Pb-Pb and Pb-Cu interactions. It is unusual to find commensurate structures with so few atoms in registry with the substrate; in fact, in most cases the overlayer structure becomes incommensurate with a hexagonal unit cell. A general procedure for classification of these phases has been proposed [23], while a calculation of their energetics is in progress [24].

C. Self-similar growth of Pb islands

As one can see from Fig. 3, the \((\sqrt{61} \times \sqrt{61})R\tan^{-1}\left(\frac{\pi}{6}\right)\) phase exists at coverages well below its ideal coverage of 0.49, which is an indication of island growth. In Fig. 6, specular peak profiles taken in the nearly in-phase condition are plotted at a few representative Pb coverages. Basically, each peak is composed of two parts: one is the sharp and narrow top peak which is reflection from uncovered Cu substrate; and the other is the broaden and shoulder-like tail part which is due to reflection from Pb islands. In the out-of-phase condition, only a broad peak is observed. Although it is possible to extract information on island growth from this measurement, in reality the analysis is complicated by the fact that the ABS specular peak has contributions both from the substrate and islands. In this instance it is far more advantageous to use the ABS diffraction peak due to ordering within Pb islands to investigate how islands grow since there is no interference from the substrate. Fig. 7 shows the evolution of the profiles of \((0,-1)\) peak [25]. The decreasing of the peak width with the increasing of the Pb coverage indicates the growth of islands.

The measured peak profiles \(I_M(\vec{k}_\parallel)\) are actually convolutions of the instrument response function \(T(\vec{k}_\parallel)\) with the "true" peak shape \(I_s(\vec{k}_\parallel)\) of the system we are investigating. Two procedures have been applied to extract "true" peak shapes from:

\[
I_M(\vec{k}_\parallel) = \int T(\vec{k}_\parallel - \vec{S}_\parallel)I_s(\vec{S}_\parallel)d\vec{S}_\parallel.
\]  

First we performed an analysis of the diffraction beam shapes by deconvolving the instrument response function using Fourier analysis. For our ABS system, the instrument response
function can be measured by positioning the detector facing the direct incident beam. A small correction, to take into account velocity broadening, has been applied when fitting diffraction peaks. For the best prepared Cu(001) surfaces there is hardly any broadening in the specularly reflected peak. Essentially, what we do is to Fourier transform the measured peaks and the instrument response function (which is a Gaussian). Using the convolution theorem we find that

\[
\hat{I}_M(\vec{k}_\parallel) = \hat{T}(\vec{k}_\parallel) \cdot \hat{I}_s(\vec{k}_\parallel)
\]

where \(\hat{I}_M, \hat{T}\) and \(\hat{I}_s\) are the Fourier transforms of \(I_M, T\) and \(I_s\) respectively. From this we obtain \(\hat{I}_s(\vec{k}_\parallel) = \hat{I}_M(\vec{k}_\parallel) / \hat{T}(\vec{k}_\parallel)\) and then we perform an inverse Fourier transform to get "true" peak profiles \(I_s(k_\parallel)\). The advantage of this process is that these deconvolved data have been obtained without assuming any functional form for the "true" signal. In Fig. 8 we present deconvolved peak profiles from three representative coverages after normalizing intensities and scaling the horizontal axis. The oscillations in the wings of the peaks are due to the deconvolution procedures; in fact, they are not present in the original data (see Fig. 7). The diffraction profiles represent the structure factor of the physical system. Through our measurement, the different peak profiles coincide with each other after scaling as shown in Fig. 8. This indicates that the structure factor for our system is a scaling function and is independent of Pb coverages. We conclude that growth of Pb islands is self-similar in the range of coverage investigated.

Comparing Fig. 8 with Fig. 6 one can see that some additional noise is introduced in the deconvolved data due to the deconvolution procedure. Using this method it is hard to determine the analytical form of the "true" peak shape from the curves in Fig. 8 especially when there is a considerable amount of noise. We used another procedure to analyze peak profiles analytically. The measured peak profiles are fitted directly by the convolution of the instrument response function (Gaussian) with a chosen function, which is supposed to be the "true" diffraction peak shape. Following analyses of island growth studied by HRLEED, we tried Gaussian, Lorentzian and power Lorentzian as fitting functions. In Fig. 7,
fits using a power Lorentzian:

\[ I(\Delta K_{||}) \propto \frac{A}{(\xi^2 + \Delta K_{||}^2)^m} \]  

(10)

with \( m=5 \) are presented for three different coverages. The same fitting function was used for all coverages, from about \( \Theta = 0.1 \) to 0.5. The fact that an identical function fits well all the line shapes is again a confirmation of the scaling behavior. However, since there is no theoretical reason to use Eq. (10), it should be considered at this stage only as a convenient fitting function.

The inverse width of the deconvolved peak (FWHM of Eq. (10)) is displayed as a function of coverage in Fig. 9. The growth of the mean island size \( R \) versus coverage can be well described by the equation [14]:

\[ R \sim \frac{1}{FWHM} \propto \Theta^n \]  

(11)

We find that the best fit for the data in Fig. 9 is obtained with \( n = 0.54 \pm 0.03 \). We estimate that the average size of ordered islands goes from about 30\( \text{Å} \) to 100\( \text{Å} \). For the case of growth of two-dimensional islands, we are not aware of any theory that makes a prediction about the exponent in Eq. (11). The value of the exponent we obtain is different from the experiment of Zuo and Wendelken [14] where \( n \) was found to vary between 0.2 at \( T = 340^\circ C \) and 0.35 at \( T = 450^\circ C \). The difference between these two results are discussed in the next Section. The temperature dependence of \( n \) might indicate that different processes are present at different temperatures.

Fig. 10 presents our result of the (0,-1) peak intensity as a function of Pb exposure plotted in a ln-ln scale. We can establish a power law by fitting the data in Fig. 10 to:

\[ I_{01} \sim \Theta^{\tilde{p}}. \]  

(12)

The solid line in Fig. 10 is the best-fit result, with \( \tilde{p} = 1.89 \pm 0.04 \).

Note that after a given amount of Pb is deposited we find that the diffraction on specular intensities didn’t change during data taking (from a few minutes to tens of minutes). This is indicating that the layer has stopped evolving before measurements are taken.
IV. DISCUSSION AND INTERPRETATION

To understand the scaling behavior of the islands we first define the island density \( N(\Theta) \) which is expected to exhibit a power law dependence on the coverage:

\[
N(\Theta) \sim \Theta^q.
\]  

(13)

Since the coverage provides the average density of adlayer atoms, which are distributed between islands of various sizes

\[
\Theta \sim N(\Theta) \cdot \overline{S}(\Theta)
\]  

(14)

where \( S(\Theta) = (\overline{R^2}) \) is the average island area. Using the scaling assumption we can write

\[
P(R(\Theta), \Theta) = \frac{1}{\overline{R(\Theta)}} P'(x)
\]  

(15)

where \( P(R(\Theta), \Theta) \) is the probability, at coverage \( \Theta \), of finding an island of size \( R \), \( P'(x) \) is a scaling function independent of \( \Theta \) and \( x = R/\overline{R} \). As a result, we obtain \( (\overline{R^2}) = (\overline{R})^2 \). In this case one can replace equation (14) by

\[
\Theta \sim N(\Theta) \cdot (\overline{R})^2 \sim \Theta^{q+2n}.
\]  

(16)

The scaling assumption thus leads to the relation [14]

\[
q + 2n = 1.
\]  

(17)

Submonolayer island growth generally involves two processes in addition to the growth of existing islands: the creation of new islands by nucleation of atoms as the coverage increases and the coalescence of two or more islands into one larger island. The first process tends to increase the island density while the second process decreases it. Typically, in the early stages of growth the islands are very small and isolated, and coalescence is rare. On the other hand, during later growth stages, at relatively high temperature and low deposition rates, very few new islands form, since mobility is high enough for atoms to aggregate into
existing islands. We can thus use Eq. (17) to identify two general regimes of $q$ and $n$. In systems where islands do not coalesce, their density can only increase, and therefore $q \geq 0$ and $n \leq 1/2$. On the other hand in cases where islands coalesce but no new islands appear, $q \leq 0$ and $n \geq 1/2$. In systems where both processes occur simultaneously, the values of $q$ and $n$ will be determined by the balance between them.

We will now show that due to the structure of the $(\sqrt{61} \times \sqrt{61})R\tan^{-1}\left(\frac{\pi}{6}\right)$ phase, coalescence is practically negligible in our system. The phase $(\sqrt{61} \times \sqrt{61})R\tan^{-1}\left(\frac{\pi}{6}\right)$ has a large unit cell with 30 atoms, only three of them are in perfect registry with the substrate. It thus exhibits a high degeneracy due to both rotations and translations. The supercell can appear with two rotation angles with respect to the substrate: $\theta = \tan^{-1}(5/6)$ or $\theta = \tan^{-1}(6/5)$ (see Fig. 4) and therefore is doubly degenerate. In addition the internal structure of the unit cell can appear in two degenerate states rotated by 90° with respect to each other. The translational degeneracy is due to the large unit cell and the fact that only three atoms are in perfect registry with the substrate. Careful analysis of the proposed unit cell structure, which covers 61 lattice sites of the substrate shows that there are 21 translationally degenerate state. We thus conclude that the total degeneracy in the system is 84-fold. The high degeneracy has a substantial effect on the island growth. When two islands start growing into each other and merge it is very unlikely that they will match properly. Since they are degenerate and not in phase they will not diffract coherently. As a result, for our diffraction experiments they behave like separate islands even if physically connected. Therefore, there is practically no coalescence in the system as far as diffraction measurements are concerned. The only process that may occur, in addition to the growth of existing island, is the creation of new islands. Therefore, the range of values available for $q$ and $n$ is $q \geq 0$ and $n \leq 1/2$.

In our experiment $n = 0.54 \pm 0.03$, which is very close to 1/2. From Eq. (17) we obtain that $q = -0.08 \pm 0.06$, which is close to zero, but negative and may indicate a slight decrease in the island density between $\Theta = 0.1$ and $\Theta = 0.5$. Since we know that there is practically no coalescence in our system we conclude that as the coverage increases between $0.1 < \Theta < 0.5$ no new islands are created and it is thus very close to the marginal case of
\( q = 0 \) and \( n = 1/2 \). From the relation \( \widehat{R} \sim \Theta^n \) we obtain

\[
\frac{d\widehat{R}}{d\Theta} \sim \Theta^{n-1} \sim \frac{\Theta^{(n-1)/n}}{n}
\]

for the average radius and

\[
\frac{dS}{d\Theta} \sim \Theta^{2n-1} \sim \frac{S^{(2n-1)/2}}{n}
\]

for the average area. For \( n = 1/2 \) we find that \( dS/d\Theta = C \) and \( C \) is a constant. This is consistent with a growth model in which the islands are randomly distributed on the surface and each island has an area around it from which it collects the adsorbed atoms.

According to this picture the islands are created in the limit of low coverage of \( \Theta < 0.1 \). The dominant mechanism for the creation of new islands seems to occur when two or more atoms meet and nucleate together after deposition [11,12]. Additional islands may appear when atoms nucleate on defects, steps or impurities on the surface. However, these can account for a small number of islands.

A simple model that may describe the growth process in this system is based on the Voronoi construction [29]. In this construction one first defines a set of random points, or centers, on the surface. One then draws the perpendicular bisecting lines to the lines joining any two centers. The smallest convex polygon around each center will contain all the points which are closest to this center. In this model one assumes that a random distribution of islands is initially created at very low coverage. As more atoms are deposited, they diffuse and aggregate into existing islands which then grow. Assuming that each atom tends to aggregate into the nearest island, each island attracts the atoms that fall in the Voronoi polygon around it. The size of each island will thus be proportional to the size of the Voronoi polygon around it, at all stages of the growth process. Therefore, within the assumptions of this model, the growth will be self similar. In reality things are more complicated. The initial seeds of islands may not be completely random. Not all deposited atoms aggregate into the nearest island, and most importantly, at larger coverage the important distance is between the deposited atom and the boundary of the island rather than to its initial seed.
However, we believe that the island size is proportional to the size of its Voronoi polygon even for high coverage.

This model may also provide a clue for why no new islands seem to appear above some low coverage. A rough estimate shows that an island which nucleates at $\Theta = 0.18$ may reach a size which is only about 10% of an island created at $\Theta = 0$ \[24\]. This results from two reasons: first, at $\Theta = 0.18$ the new island has negligibly small size, compared to the finite existing islands. Then, the domain from which it attracts more atoms is much smaller since it should be drawn by bisecting the distance between its seed and the boundaries of the existing islands. Therefore, it will grow much more slowly than islands which were created earlier. This is a particularly important effect in our system which has a very large unit cell. Islands that nucleate late may not reach the minimal size needed for diffraction. Islands that nucleate in the late stages of the deposition process thus seem to be ”shadowed” by the existing islands. We plan to explore these ideas both analytically and using computer simulations in order to obtain quantitative predictions \[24\].

Zuo and Wendelken observed that the diffraction peak intensity in their experiment increases like $I \sim \Theta^p$ and also obtained a relation between the exponents $n$ and $p$ with a Gamma domain-size distribution. As long as the scaling growth exists, the following relation should be satisfied \[14\]:

$$p = 1 + 2n.$$ \quad (20)

In our experiment we use a linear slit detector which, in fact, integrates over one dimension in $k$ space while the scan is done over the perpendicular direction. Using our power Lorentzian fits we find that the FWHM of our integrated peak scales with $\Theta$ exactly like the original peak. However, the integrated peak intensity $I_{01}(k_x)$ scales like the product of the original peak intensity $I_{01}(k_x, k_y)$ and its width (FWHM). Since the width scales like $\Theta^{-n}$ we conclude that $\tilde{p} = p - n = 1 + n$. Our result, $\tilde{p} = 1.89 \pm 0.04$ is much larger than $1 + n = 1.54 \pm 0.03$. This may be due to the fact that the slit detector is not very sensitive near its ends and thus does not provide a complete integration.
V. SUMMARY

Using ABS, we have studied Pb growth on Cu(001) substrate at 150 K. Two high order commensurate phases have been discovered. The \((\sqrt{61} \times \sqrt{61})\tan^{-1}\left(\frac{5}{\sqrt{11}}\right)\) phase has a square unit cell with a proposed quasi-hexagonal internal structure. This structure seems to be energetically favored since it provides a compromise between the adlayer-adlayer interactions which favor the hexagonal structure and the substrate that tends to induce the square symmetry. We found that the Pb layer grows in \((\sqrt{61} \times \sqrt{61})\tan^{-1}\left(\frac{5}{\sqrt{11}}\right)\) islands before forming the \((5 \times 5)\tan^{-1}\left(\frac{3}{\sqrt{11}}\right)\) phase which is a square phase. By analyzing line shapes, we are able to show that island growth is self-similar. Power growth laws for mean island size and diffraction peak intensity are established. Due to the high degeneracy of the monolayer phase, when islands merge they form a boundary line. They also do not diffract coherently and therefore coalescence effects are negligible in our diffraction experiments. From the experimental results we conclude that in this particular system, ordered islands tend to form at very low coverage and then to grow in an approximately self similar fashion as the coverage increases. In the future we plan to explore the temperature dependence of the exponents \(n\) and \(\tilde{p}\), and to examine how the initial island density is determined.

VI. ACKNOWLEDGEMENTS

This work was supported by NSF grants DMR-9119735 (G.V) and DMR-9217284 (O.B). The work at Cornell (O.B) was supported by NSF grants DMR-9118065 and DMR-9012974. We thank J.-S. Lin and H. Zeng for technical assistance and B. Cooper, T. Curcic, J. Evans, V. Elser, J. Sethna and M. Tringides for helpful discussions.

(a) Present address: The James Franck Institute, University of Chicago, Chicago, IL 60637.
REFERENCES

[1] R. Kunkel, B. Poelsema, L. K. Verheij and G. Comsa, Phys. Rev. Lett. 65, 733 (1990); W.F. Egelhoff, Jr and I. Jacob, Phys. Rev. Lett. 62, 921 (1989).

[2] Wei Li, J.-S. Lin, M. Karimi, C. Moses and G. Vidali, J. Vac. Sci. Technol. A9, 1707 (1991).

[3] D.E. Sanders and A.E. DePristo, Surf. Sci. 254, 341 (1991).

[4] J.D. Gunton, M.S. Miguel and P.S. Sahni, Phase Transitions and Critical Phenomena, edited by C. Domb and J.L. Lebowitz, Vol. 8, p. 267 (Academic Press, 1983).

[5] P.C. Hohenberg and B.I. Halperin, Rev. Mod. Phys. 49, 435 (1977).

[6] I.M. Lifshits and V.V. Slyozov, J. Phys. Chem. Solids 19, 35 (1961); C. Wagner, Z. Electrochem 65, 581 (1961).

[7] M.C. Tringides, Phys. Rev. Lett. 65, 1372 (1990).

[8] H.-J. Ernst, F. Fabre and J. Lapujoulade, Phys. Rev. Lett. 69, 458 (1992).

[9] F. Family and P. Meakin, Phys. Rev. Lett. 61, 428 (1988).

[10] P. Meakin, Rep. Prog. Phys. 55, 157 (1992).

[11] M.C. Bartlet and J.W. Evans, Phys. Rev. B46, 12675 (1992).

[12] M.C. Bartlet, M.C. Tringides and J.W. Evans, unpublished.

[13] J. Villain, A. Pimpinelli and D. Wolf, Comments Cond. Mat. Phys. 16, 1 (1992).

[14] J.-K. Zuo and J.F. Wendelken, it Phys. Rev. Lett. 66, 2227 (1991).

[15] W. Li, J.-S. Lin, M. Karimi, C. Moses and G. Vidali, Appl. Surf. Sci. 48/49, 160 (1991).

[16] G. Vidali, W. Li, J.-S. Lin, and C. Moses, Mat. Res. Soc. Symp. Proc. 208, 99 (1991).

[17] M. Hansen and K. Anderko, Constitutions of Binary Alloys, (McGraw Hill, New York,
1958).

[18] B. Poelsema and G. Comsa, in *Springer Tracts in Modern Physics* Vol. 115, edited by G. Höhler (Springer, Berlin, 1989).

[19] W. Li, J.-S. Lin, M. Karimi, P.A. Dowben and G. Vidali, *Phys. Rev.* **B45**, 3708 (1992).

[20] A. Sepulveda and G.E. Rhead, *Surf. Sci.* **66**, 436 (1977).

[21] A. Sánchez and S. Ferrer, *Phys. Rev.* **B39**, 5778 (1989).

[22] F. Delamare and G.E. Rhead, *Surf. Sci.* **35**, 172 (1973).

[23] O. Biham, L.-W. Chen and G. Vidali, *Surface Science*, in press.

[24] O. Biham, W. Li and G. Vidali, to be published.

[25] Diffraction peaks are labeled according to Fig. 4a. ABS is sensitive to the top layer only, so there is no contribution from underlying Cu atoms. However, there could be a contribution from clean Cu(001) areas. In reality, recently we observed that, when Pb is adsorbed at 400K at low coverage ($\Theta \simeq 0.15$), randomly adsorbed Pb atoms produce a change in the composition of the electronic charge density profile of neighboring Cu atoms yielding a small (0,-1) diffraction peak [28]. Without Pb adsorption the Cu(001) surface is so flat that no diffraction peaks are seen. In the present case this effect is small and confined to the smallest coverages ($\Theta < 0.1$). Thus the (0,−1) diffraction peak is overwhelmingly due to Pb islands. Strong fractional order peaks have been observed, but were not used in the fitting because they were too close to the tails of the dominant (0,0) peak.

[26] I.N. Sneddon, *Fourier Transforms* (McGraw-Hill, New York, 1951).

[27] J.-K. Zuo, Y.-L. He, G.C. Wang, and T.E. Felter, *J. Vac. Sci. Technol.* **A8**, 2474 (1992).

[28] W. Li and G. Vidali, *Phys. Rev.* **B46**, 4356 (1992).
[29] See e.g., D. Weaire and N. Rivier, *Contemp. Phys.* 25, 59 (1984).
FIGURES

FIG. 1. Pb low temperature ABS adsorption curve: I(0,0) vs. Pb coverage. Surface at 150 K, \( \theta_i = 60^\circ \). Solid line is a fit to Eq. (3).

FIG. 2. ABS specular peak intensity vs. incident angle, half layer Pb deposited. The substrate temperature is \( T_s = 150K \).

FIG. 3. Sketch of phase diagram of Pb on Cu(001) obtained by ABS and LEED data. Crossed region: disordered; cross-hatched region: phases coexist.

FIG. 4. (a) Reciprocal space: solid and dashed lines are from two domains; (b) proposed real space structure of \((\sqrt{6}I \times \sqrt{6}I)\) \( R\tan^{-1} \left( \frac{5}{6} \right) \). The unit cell which is square contains 30 atoms which are arranged in a pseudo hexagonal structure.

FIG. 5. ABS diffraction scan from \((\sqrt{6}I \times \sqrt{6}I)\) \( R\tan^{-1} \left( \frac{5}{6} \right) \), \( \theta_i = 60^\circ \) for full coverage of \( \Theta = 0.49 \). The substrate temperature is \( T_s = 150K \). We identify the labelling of the peaks as (A) \((36/61, 30/61)\), \((36/61, 31/61)\); (B) \((30/61, 25/61)\), \((31/61, 25/61)\); (C) \((24/61, 20/61)\); (D) \((18/61, 15/61)\); (E) \((12/61, 10/61)\); and (F) \((6/61, 5/61)\), \((5/61, 6/61)\). Note that peaks A, B and F are double peaks due to overlap between peaks of the two grids.

FIG. 6. ABS specular peak profiles at surfave temperature of 150 K, \( \theta_i = 60^\circ \) and different coverages. Notice the emergence of wings indicating island growth.

FIG. 7. (0,-1) ABS diffraction peaks from \((\sqrt{6}I \times \sqrt{6}I)\) \( R\tan^{-1} \left( \frac{5}{6} \right) \) islands at representative coverages; Solid lines are the fitting results of the convolution of the instrument response function with the function in Eq. (10). \( \theta_i = 60^\circ \). From the full width at half maximum (FWHM) of such peaks we obtain the scaling of the island size as a function of coverage.

FIG. 8. ABS diffraction data from islands after deconvolution of the instrument response function. Data from three representative coverages have been rescaled and plot in the same graph. \( \theta_i = 60^\circ \). w is the full width at half maximum (FWHM) of a peak.
FIG. 9. ln(Inverse FWHM) vs. ln(coverage) obtained from an analysis of diffraction peaks as in Fig. 7. The line is the best-fit through the data, see Eq. (11). The slope is $n = 0.54 \pm 0.03$ for coverage between 0.1 and 0.5.

FIG. 10. A ln-ln plot of the (0,-1) peak intensity vs Pb coverage. The solid line is the best-fit to Eq. (12). The slope is $\tilde{p} = 1.89 \pm 0.04$. 