Measurement of Growth Kinetics in a Heteroepitaxial System: Pb on Cu(100)

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The kinetically driven low temperature growth of Pb on Cu(100) has been investigated using helium beam scattering. Up to 16 equivalent layers (monolayers, ML), a complex growth pattern is the result of the non-negligible Pb mobility, the large lattice mismatch, and the square symmetry substrate. Subsequently, growth shows characteristics of dynamical scaling. The growth and roughness exponents are measured to be $\beta \simeq 0.3$ and $\alpha \simeq 1$. The growth of the interface width saturates at about 40 ML due to the influence of the typical size of the mosaic of Pb(100) domains.

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Molecular beam epitaxy (MBE) is a widely used deposition technique for the study of the growth of materials. While in homoepitaxial systems the growth process is mostly determined by kinetic parameters, in heteroepitaxial systems it is also influenced by misfits of geometric and electronic nature [1,2]. During the past few years a large number of measurements have been done on molecular beam epitaxial systems using reflection high energy electron diffraction (RHEED) and atomic beam scattering (ABS), but few have yielded a complete picture of the entire growth process from monolayer to hundreds of layers [3]. Recently, dynamical scaling theories [4] have been applied to describe the growth front undergoing roughening for various systems [5–11]. The measured exponents have a range of values ($\alpha \simeq 0.4 \sim 1.0$, $\beta \simeq 0.2 \sim 0.3, 1$) which have not yet been fully understood and unequivocally associated with specific theoretical models or computer simulations. No measurement of both exponents has been done, to the best of our knowledge, for a heteroepitaxial system with large lattice mismatch.

The characteristic of growth kinetics in a heteroepitaxial system with large lattice mismatch might offer unique opportunities not only to understand basic growth processes but also to address a type of growth which is clearly of importance to many fields of materials and surface science [12] and which might uncover unusual phenomena. For example, in the heteroepitaxial case the role of different processes or properties in determining the morphological characteristic of the film, such as diffusion, and local structural and chemical environments, might change with time as the growth proceeds away from the substrate. It is conceivable that available models of growth, which were developed for homoepitaxial systems, might have to be modified to accommodate this richer case. As we will see, the presence of the substrate leads to the development of a morphology which influences the characteristics of the evolution of the growth.

In this work, we have studied the kinetics of growth of Pb on Cu(100). At high temperature, and presumably in conditions of local equilibrium, Pb grows in the Stranski-Krastanov mode (one layer followed by three-dimensional clusters) [13]. At extreme low temperature, when the mobility of Pb atoms is negligible, atoms should stick near where they land, as in models of ballistic growth, and the presence of the mismatched interface would count little. This is the case of nonconservative growth. At 150 K, however, because of the significant (but limited) mobility of Pb atoms [13], we expect the growth to be the result of the interplay of kinetics and of the lattice-mismatched interface. The desorption of Pb atoms and formation of overhangs and voids should be negligibly small, and the mass and volume conservation laws should play an important role in the growth.

We have observed that growth in the very early stage is strongly influenced by the Pb/Cu interface, evolving from ordered growth (first layer) to disordered growth (second and third layer) and ordered growth again (from four to sixteen layers). However, the long-range growth of Pb on Cu(100) at 150 K is still kinetically driven and can be described by dynamical scaling theory; the growth (β) and roughness exponent (α) are measured to be $\sim$0.3 and $\sim$1, respectively. The large α value is as expected for conservative growth. The growing interface roughens faster (i.e., with a larger β) than would have been expected for the growth of a homoepitaxial system described by a linear diffusion equation; at $\sim$40 ML the growth of interface width saturates ($\beta \simeq 0.05$, $\alpha \simeq 1$).

The experiments were performed with a helium beam scattering apparatus [14] in which a supersonic helium beam was used to probe the growing interface. The copper sample was cleaned prior to each run by Ar^+ sputtering at 620 K and then annealing at 850 K. The average terrace width of the Cu(100) surface is about 450–500 Å. Pb of 99.999% purity was deposited from a liquid-nitrogen shielded Knudsen evaporation source onto the Cu(100) surface at a temperature of 150 K. The base pressure of the UHV chamber was at low 10^{-10} Torr. The depositon rate used in this study was usually 1 monolayer (ML) per 10 or 20 s [1].

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Pb film grows on Cu(100) at 150 K in a rather complicated form, as seen from Fig. 1. Previous studies [14] have shown that the first layer (corresponding to the first oscillation) is a high-order commensurate $(5 \times 5)R\tan^{-1}(3/4)$ phase with 16 atoms per unit supercell. This phase disorders around 2 to 3 ML and is replaced, starting from the fourth layer, by the Pb(111) phase; the low energy electron diffraction pattern consists of 12 spots with hexagonal symmetry. The influence of the square symmetry substrate/monolayer is reflected in the two main domains rotated by 90° [1].

The sharp and narrow diffraction peak of the first layer [inset (a) of Fig. 1] indicates a flat surface. The diffraction profiles under antiphase condition at 1.5 ML show two sidebands, suggesting that the second layer grows by islands [insets (b) and (c) of Fig. 1]. Around 2 ML, the sidebands move closer toward the specular due to the coalescence of islands; the diffraction profiles are much wider compared with the first layer, revealing a high density of steps. The subsequent layers (up to 16 layers) grow in a quasi-layer-by-layer fashion, and analysis of the envelope of the scattered helium beam intensities shows evidence of quantum size effects [1].

Steps at the surface produce a broad diffuse component of the diffraction profile which is superimposed to the central narrow peak [15]. The FWHM's of the diffuse part were plotted as a function of incident angle for 2 ML and 50 ML films in Fig. 2. The FWHM oscillation arises from alternating constructive and destructive interference conditions of the He beam interacting with a system containing many steps and terrace structures. The

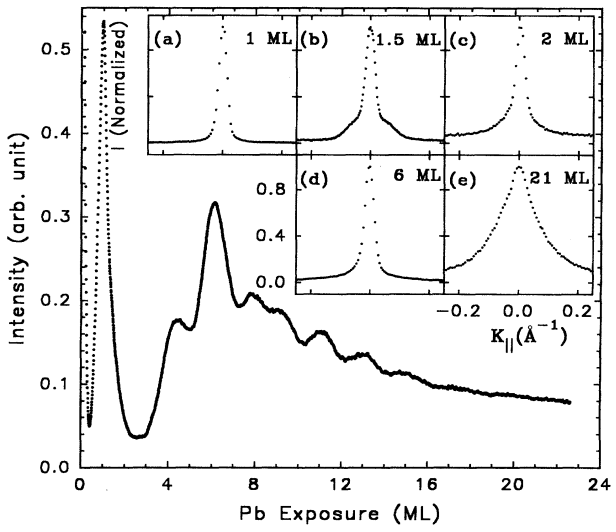

FIG. 1. Specularly reflected intensity of He beam off Cu(100) vs exposure to Pb at 150 K. The He beam energy is 18.4 meV and the incident angle is 62° (antiphase to Pb multilayer). In the inset are the diffraction peak profiles (intensity versus scattering vector $K_{\|}$) at various coverages. Insets (a) and (d) were taken under in-phase, while (e) antiphase conditions for Pb multilayer. Insets (b) and (c) were taken under antiphase condition for 1.5 to 2 ML films.

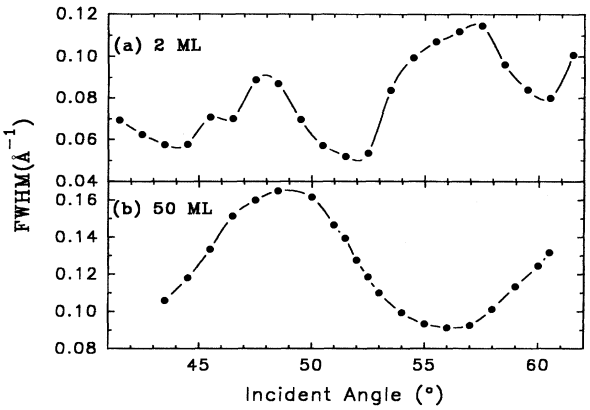

FIG. 2. FWHM of diffuse part of the specular beam versus incident angle for 2 ML (a) and 50 ML (b) Pb/Cu(100) films.

minima are obtained at the Bragg in-phase conditions by $2hk\cos(\theta_i) = 2n\pi$ with n an integer. h is the overlayer height, θ_i is the incident beam angle, and k is the beam wave vector. The analysis of data in Fig. 2 gives a value of 4.87 ± 0.15 Å for 2 ML and 2.86 ± 0.10 Å for multilayer. while 2.86 Å is exactly the vertical lattice spacing of Pb(111), 4.87 Å is much smaller than twice this value; rather, it is close to 4.95 Å, which is twice the (001) interplanar distance of Pb. This suggests that for the first few layers Pb grows in ⟨001⟩ direction due to the influence of a square symmetry substrate and monolayer. At any rate, the changeover from double steps at 1.5–2 ML to single atomic step from 6.5 ML on is undoubtly observed.

The first Pb layer is a highly corrugated $(5 \times 5)R\tan^{-1}(3/4)$ phase with square symmetry. Influenced by this buckled monolayer, the second and third ML Pb follow a disordered growth with many domains along the Pb⟨001⟩ direction; the average terrace width is estimated to be around 60 Å. From 6 ML on, the FWHM's of the in-phase diffraction peak profiles are observed to increase with deposition time. We think this occurs because mosaic-like surface structures develop when deposition proceeds from the disordered many-domain surface at 2–3 ML, resulting in the broadening of the diffraction angular profiles due to finite domain size.

As deposition proceeds beyond 16 ML, the intensity of the diffraction peak decays with Pb exposure, and the FWHM broadens dramatically at antiphase condition, indicating roughening of the growth front. As shown in inset (d) of Fig. 1, the line shape of in-phase diffraction peak at 6 ML is a Gaussian-like narrow peak of the specularly scattered beam from a relatively flat surface. As the film grows thicker and thicker, the peak profiles become wider due to roughening, as seen at 21 ML [inset (e) of Fig. 1].

According to dynamical scaling, the scaling of the interface width $w(L,t)$ on length scale L at time t is expected to be of the form, $w(L,t) \sim L^{\alpha} f(t/L^{\alpha/\beta})$ with $f(x) \sim x^{\beta}$ for $x \ll 1$ and $f(x) \sim$ const for $x \gg 1$

where α is the roughness exponent and β is the growth exponent. For $L^{\alpha/\beta} \gg t$, the interface width, a measure of vertical roughness, grows with time in the form of power law, $w \sim t^{\beta}$, while for $L^{\alpha/\beta} \ll t$, $w \sim L^{\alpha}$, showing that the interface morphology has a stationary self-affine form. Another quantity, the lateral correlation length ξ, is a measure of the size of the lateral coarsening. It also grows with time in a power law, $\xi \sim t^{\beta/\alpha}$. The exact values of α and β depend on the growth mechanism and dimensions of the interface.

The structure factor of diffraction from a multilevel interface can be separated into two parts [4], the so-called δ peak and a broad diffuse component:

$$I(K_{\parallel}, K_{\perp}, t) \sim e^{-[\phi]^2 w^2} \delta(K_{\parallel}) + I_{\mathrm{diff}}(K_{\parallel}, K_{\perp}, t) \quad (1)$$

where $[\phi]$ means $2K_{\perp}c$ modulo 2π such that $-\pi < [\phi] < \pi$ and c is the vertical lattice spacing [$c = 2.86$ Å for Pb(111)]. $K_{\parallel}$ and $K_{\perp}$ are the parallel and perpendicular momentum transfer with respect to the substrate. $[\phi/\pi] = 1$ corresponds to the out-of-phase condition while $[\phi/\pi] = 0$ corresponds to the in-phase condition. The δ-peak intensity is a function of interface w which is defined as the asymptotic value of $w(L, t)$ for infinite length scales, $w(t) = w(L \to \infty, t)$, and therefore contains the information on exponent β. The diffuse part reflects properties of the interface on a local scale and contains information on exponent α.

To determine the two exponents, the diffraction profiles are decomposed into a Gaussian (whose half-width is determined by instrumental resolution) representing the δ peak and a Lorentzian representing the broad diffuse part. The exponent α can be extracted from diffraction line shape of the diffuse component measured at different phase conditions [4]. In particular, the FWHM of the diffuse component away from in-phase condition has the form of power law in $[\phi]$, FWHM $\sim 2[\phi]^{1/\alpha}/\eta$. The FWHM's of the diffuse part are shown as a function of $[\phi/\pi]$ in the inset of Fig. 3. From 16 to 450 ML, the diffuse part of the structure factor appears to be time invariant and the FWHM vs $[\phi/\pi]$ curves coincide for different coverages. Therefore, the average terrace width η seems to be time-independent during 16 ML to 450 ML within our experimental sensitivity. A power-law fit of the FWHM vs $[\phi/\pi]$ gives $\alpha \simeq 1$ and $\eta = 33 \pm 6$ Å.

The growth exponent can be derived from δ-peak intensity decay with coverage. Under close to in-phase condition, the δ intensity can be approximated as $I_{\delta}(K_{\parallel}, K_{\perp}, t) \sim I_0 e^{-w^2(t)[\phi]^2}$ [5,6] where I_0 is the δ intensity at the beginning of the growth when the interface is flat, which corresponds to 6 ML in this case. In Fig. 4, $\ln[-\ln(I_{\delta}/I_0)]$ is plotted as a function of ln(coverage). The growth undergoes two stages with different growth exponents. The interface grows as t^{β} with $\beta \sim 0.3$ until about 40 ML. After that β becomes small ($\sim$0.05), suggesting a logarithmic growth of the interface width. This means that the film hardly increases its roughness after the initial stage.

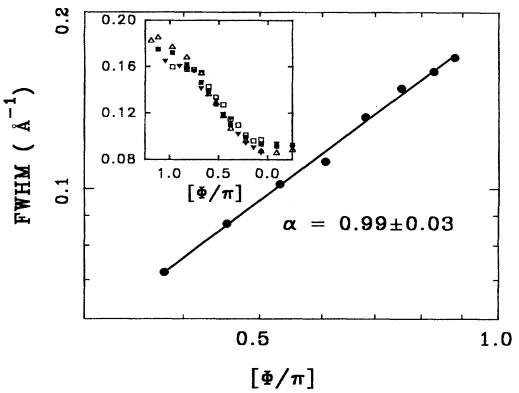

FIG. 3. The FWHM of diffuse part of the specular beam as a function of $[\phi/\pi]$ at 93 ML. In the inset, the FWHM of diffusive part is displayed as a function of $[\phi/\pi]$ in linear scale for Pb coverages of 27 ML (open squares), 49 ML (filled triangles), 93 ML (open triangles), and 450 ML (filled squares). An in-phase broadening of 0.08 Å is introduced to account for broadening due to finite resolution, finite domain size, inelastic processes, and scattering from isolated defects.

Growth models for MBE processes at intermediate to high temperature have been classified as conservative. Lai and Das Sarma [16] have proposed the following for ideal MBE growth:

$$\frac{\delta h}{\delta t} = -\gamma_1 \nabla^4 h + \lambda_1 \nabla^2 (\nabla h)^2 + \gamma \quad (2)$$

where γ is the noise term and the term $\lambda_1 \nabla^2 (\nabla h)^2$ is believed to correspond to "high-temperature" regime where the surface atoms at the kink sites can break bonds and hop with larger probability to steps with smaller height. A number of reports on the atomistic growth model [17] and continuum growth equation [18] have pointed out that the simple linear diffusion equation model $\frac{\delta h}{\delta t} = -\gamma_1 \nabla^4 h + \gamma$ is adequate to describe the early stage MBE growth at low temperature, although there

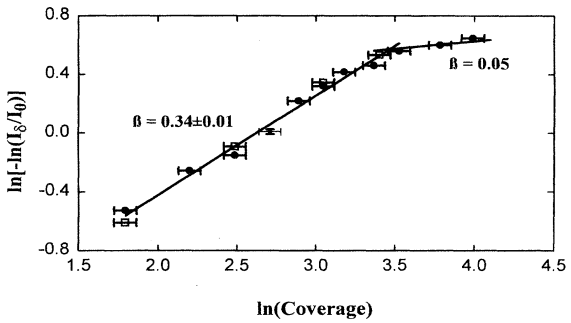

FIG. 4. Plot of $\ln[-\ln(I_{\delta}/I_0)]$, as a function of ln(coverage), at close to in-phase condition for Pb multilayer. The linear fit for Pb exposure less than 40 ML gives $\beta = 0.34 \pm 0.01$. A very small β of $\sim$0.05 is found thereafter. The error bars for x axis are shown for all the data points, while the error bar for y axis is shown. The data points of filled circles and open squares were taken in two separate runs under exactly the same conditions.

are controversial views in recent studies [19] in which the long-time process is shown to be still governed by the Kardar-Parisi-Zhang dynamics. The linear diffusion equation in three-dimension predicts $\alpha = 1$ and $\beta = 1/4$.

There seems to be consistent experimental evidence that the interface width scales as $t^{1/4}$ and the roughness exponent α is close to 1 for early-time MBE growth regime at temperatures where surface diffusion is significant [5,9–11]. The lower value of α observed in Refs. [5], [10], and [21] might be due to the fact that the growth processes of these systems are crossing over to the one governed by Eq. (2) with a significant λ_1 ($\lambda_1 \neq 0$); the λ_1 nonlinear term prevents the formation of high steps, substantially reducing the value of α.

Our measurements agree best with the linear diffusion equation. The value for the static scaling exponent α is, within the experimental uncertainty, equal to 1, indicating that surface diffusion processes are very important in this growth. The value of β we measured is larger than expected, and this might be due to the influence of mosaic surface structures caused by the interface of a heterogeneous system. From 6 ML on, the increase in in-phase FWHM indicates that the typical size of the mosaic structures shrinks due to increasing disorder. The finite size of the domain structures imposes an overall maximum length scale. We speculate that at saturation single grooves with typical size of the maximum length might be developed as predicted in Ref. [22]; $\alpha \simeq 1$ at saturation would consist with the groove profile in which the local essentially scales linearly. The existence of a groove instability at saturation is a consequence of the fact that a self-affine surface cannot exist with roughness exponent $\alpha \geq 1$ [22]. No diffraction caused by faceting has been found within our experimental sensitivity.

In conclusion, the evolution of growth front has been measured in a heteroepitaxial system with large lattice mismatch, Pb/Cu(100). We found that the interface between a Pb film and Cu(100) strongly influences the film growth at the very early stage (up to 16 layers). However, the long-range growth is still kinetically driven and shows characteristics of dynamical scaling. The measured exponents suggest that the growth of Pb on Cu(100) at 150 K is conservative and the relaxation mechanism is dominated by surface diffusion. The change in the value of β has been related to the saturation of the interface width. The mismatch at the film/substrate interface makes it possible to develop a mosaic of Pb(111) domains. Eventually the finite size of the domains sets a limit length in the dynamical scaling.

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Note added.—Most recently, a new class of growth models has been introduced based on a different driving force, i.e., the asymmetric diffusion barrier at step edges. Our results ($\alpha \sim 1$, a time-invariant η) are consistent with some predictions of this type of growth. The detailed discussion is presented in Ref. [23].

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