# Step Height Oscillations during Layer-by-Layer Growth of Pb on Ge(001)

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Heteroepitaxial growth of Pb on the Ge(001) surface has been studied by He atom scattering. For low substrate temperatures, Pb is found to grow layer by layer with (111) orientation. A detailed analysis of the specular peak profile as a function of the He wave vector reveals that the step height of the growing monatomic terraces oscillates with the film thickness. This variation, initially as large as $\pm 15\%$ around the value of the Pb(111) bulk interlayer spacing, gradually dampens out after the deposition of a dozen monolayers. This is direct evidence of quantum size effects affecting the interlayer distance of a growing metal film. [S0031-9007(97)03899-4]

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The electronic properties of thin metallic films grown on insulating substrates deviate from those of the metal bulk, and the phenomenon is frequently termed as quantum size effects (QSE). According to the early calculations by Schulte [1], QSE, such as variations of the work function and electron density, are expected to be observed when the Fermi wavelength $\lambda_F$ of the electron gas is comparable with the film thickness $D$. Deviations from the bulk electronic properties should be particularly strong when the film thickness reaches an odd multiple of $\lambda_F/4$, whereas they disappear for $D = n\frac{\lambda_F}{2}$ ($n$ integer). Thus, cyclic variations of the film electronic properties should be observed with increasing film thickness. QSE were experimentally observed by measurements of electron tunneling current [2], electrical resistivity [3], and UV photoemission [4], and the experiments put in evidence the variation of the electronic properties due to the vertical confinement of the electron gas of the metal film.

Structural variation due to QSE is also to be expected. Indeed, Feibelman [5,6] performed theoretical calculations for an Al(111) slab and argued that the variations of the electron density and work function are related to the relaxation of the outermost interlayer distances in order to minimize the total energy. The structural variations of the film thus partly counteract the extent of the electronic property variations. Later on calculations by Ciraci and Batra [7,8] for the same system suggested that all the interlayers spacing within the slab can be affected by relaxation due to QSE. Hinch *et al.* [9] investigated the Pb growth mode on Cu(111) by means of He atom scattering (HAS). They reported that for certain Pb film thicknesses (2–3 monolayers), a double layer growth is favored over the single layer one and attributed this behavior to the fact that layer-by-layer growth is suppressed for film thicknesses close to an odd multiple of $\frac{\lambda_F}{4}$. Studies of Pb growth on Cu(100) by HAS [10] and on Si(111) by x-ray diffraction [11] and reflection high-energy electron diffraction (RHEED) [3] all reported an unusual disordering in the initial stages of growth, but no direct measurement of the interlayer separation as a function of film thickness was performed. Therefore a direct evidence of the structure relaxation due to QSE during the initial stages of metal growth was still lacking.

Here we present a HAS study of Pb growth on Ge(001) at low temperature (130 K). After the initial Ge(001)-pseudomorphic growth [12–15], the Pb film structure switches to Pb(111) and a layer-by-layer growth sets in. For different deposition stages a detailed analysis of the growing terrace heights is performed by measuring the specular peak profile as a function of the He wave vector. The step height is found to oscillate around the value of the Pb(111) bulk interlayer separation with a gradually decreasing amplitude. The origin of this oscillating layer relaxation is attributed to QSE, and the matching between the total film thickness and $\frac{\lambda_F}{2}$ is discussed.

The experiments were performed in an ultrahigh vacuum chamber equipped with a HAS apparatus described in detail in Ref. [16]. The diffraction pattern is collected by rotating the sample, which is mounted on a 6 degrees of freedom manipulator. The beam energy can be selected between 19 and 65 meV ($k_{\mathrm{He}} = 6$ and 11.3 $\text{Å}^{-1}$, respectively). Elastic scattering measurements have been performed with a continuous beam, while the beam energy was measured via insertion of a chopper into the He beam path and time of flight (TOF) detection. The Ge(001) sample was prepared by $Ar^+$ sputtering and annealing to 1000 K (melting temperature = 1211 K). Well ordered surfaces were obtained with terrace width exceeding 1000 Å, as judged from the diffracted peak widths. The $c(4 \times 2)$ ground state symmetry of the Ge(001) surface was found consistent with the antiferromagneticlike ordering of the dimers [17] formed by the topmost Ge atom pairing [18]. In fact, an order-disorder phase transition was observed at $T_c = 240$ K, in agreement with the recent structural determination performed at room temperature by Ferrer *et al.* [19]. Lead was deposited from a crucible placed at 20 cm from the sample and at 50° relative to the sample normal. The evaporation cell was typically operated at temperatures of ~770 K, which resulted in deposition fluxes of ca. 0.5 ML/min.

  

Figure 1 shows the specular reflectivity as a function of Pb deposition time, as measured for the He beam energy of 19 meV ($k_{\mathrm{He}} = 6$ Å$^{-1}$) and substrate temperature of 130 ± 5 K. The initial He specular intensity is rather low since the corrugation of the $c(4 \times 2)$-Ge(001) is quite high and there are several strong diffraction channels. With the onset of Pb deposition the specular intensity drops by 2 orders of magnitude due to the disorder induced by Pb random deposition. The first peak in the He reflectivity corresponds to the formation of an ordered overlayer structure which has been identified by diffraction measurements as $(4 \times 1)$-Pb/Ge(001). For this structure, as well as for the bare Ge surface, the Bragg peak intensities by far exceed that of the specular one, that is, a common fingerprint of a semiconductor surface. This agrees with the structural studies of the Pb/Ge(001) growth by STM [12], EELS [13], Auger spectroscopy, and LEED [14], which indicate that in the submonolayer regime Pb partially intermixes with the Ge substrate.

By continuing the deposition, the film changes from the highly disordered $(4 \times 1)$-Pb/Ge(001)-pseudomorphic structure to the hexagonal Pb(111) with the principal in-plane symmetry directions rotated by 45° relative to the substrate [20] [see label Pb(111) in Fig. 1]. At the same time the specular-to-diffracted He intensity ratio increases by at least 1 order of magnitude indicating that the overlayer film becomes notably flatter, reflecting the film transition to the metallic state [21]. Hricovini *et al.* studied the Pb/Ge(001) interface as a function of Pb coverage and observed an increasing asymmetry in the shape of the Pb $5d$ 3/2 photoemission peak which gradually becomes of the Doniach-Sunjic form as the interface metallicity develops [15].

The quite pronounced specular oscillations, which persist for several dozens of layers and eventually dampen out, are typical of interference among the waves scattered by adjacent surface terraces in out-of-phase conditions [22]. In the present case the specular intensity oscillations are initially quite asymmetric and irregularly spaced, but eventually reach an almost regular oscillatory behavior, similar to that detected for Pb/Pb(111) growth at 140 K by Hinch *et al.* [9]. The apparent anomalies in the first 6–7 oscillations systematically reproduce even for different deposition rates.

We have performed a detailed analysis of the low temperature growth by interrupting the Pb flux at various deposition stages (as labeled in Fig. 1) and measuring the specular peak profile $[I(\Delta K_{\parallel})]$ as a function of the He wave vector $k_{\mathrm{He}}$. Intensity and peak width variations occur as different interference conditions are met. In-phase and out-of-phase scattering from adjacent terraces separated by monatomic step give rise to minimal width (maximal intensity) and maximal width (minimal intensity), respectively. The monatomic step height $h$ is thus reflected in the position of the observed maxima and minima [23], and it was found to vary substantially with the Pb film thickness.

In order to extract the specular peak broadening, all peaks have been fitted to a Voigt line shape where the Gaussian width has been kept constant (just below the narrowest observed profile) and the Lorentzian represents the broadening due to the roughness variations during Pb deposition [24]. The Lorentzian width variation as a function of $k_{\mathrm{He}}$ is shown in Fig. 2 for a few deposition stages. It may be noted that the specular peak width of the stages *5* and *6* is mostly unaffected, indicating that the surface is essentially flat [25]. On the other hand, quite pronounced width and intensity oscillations are observed for the deposition stages *4.5* and *5.5*, meaning that the surface is locally quite rough. Of course, a flat morphology is detected close to the completion of a full

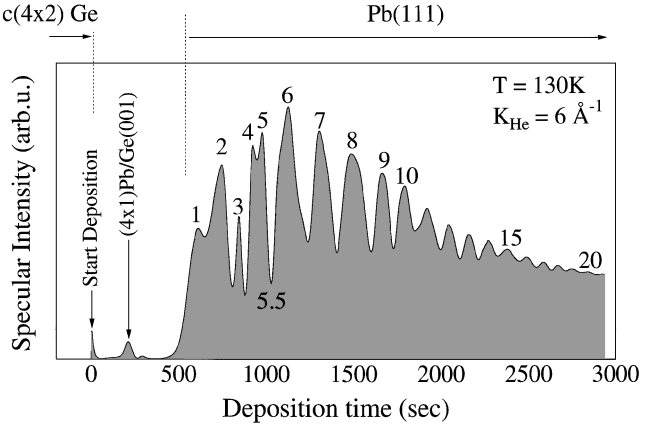


FIG. 1. He specular reflectivity during Pb/Ge(001) deposition at 130 K. The absolute diffraction intensity is to scale. The deposition flux was kept constant ($\sim 140^{-1}$ ML/sec). A progressive number labels the deposition stages which have been analyzed in detail. The diffraction symmetries characteristic of different deposition stages are also given.

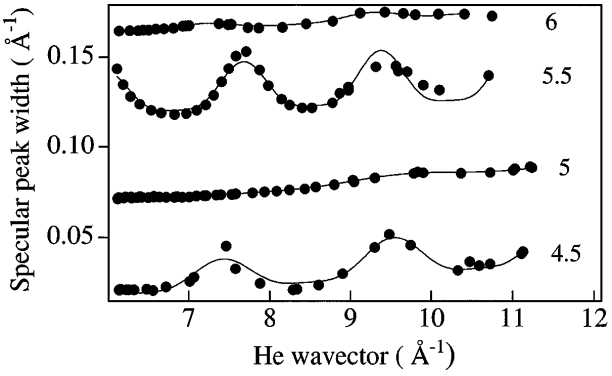


FIG. 2. Specular peak width (FWHM of the Lorentzian contribution, filled circles) as a function of the He wave vector $k_{\mathrm{He}}$ taken at four different stages of Pb deposition. The stage number corresponds to the labeling of Fig. 1. For the sake of clarity, the stages *5*, *5.5*, and *6* have been shifted upward of 0.05, 0.1, and 0.15 Å$^{-1}$, respectively. Full lines are the best fits to the function given in Ref. [26].

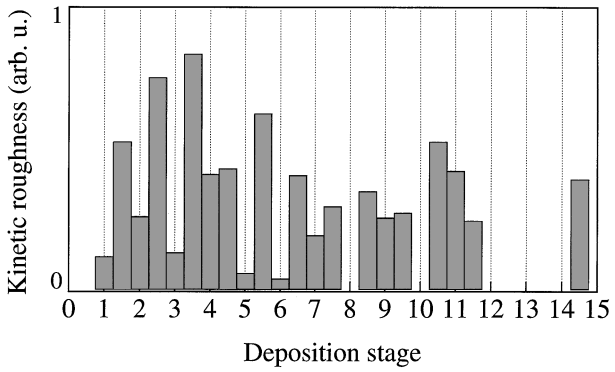


FIG. 3. The amplitude of the specular peak width oscillations with $k_{\mathrm{He}}$ for different deposition stages. Low values correspond to flat surfaces (i.e., low step densities), whereas the high ones reflect a higher surface roughness. Alternating flat and rough stages are seen up to the stage *6* and reflect the oscillating roughness during the layer-by-layer growth.

monolayer, whereas for half integer coverage the surface is locally rough. Up to the growth stage *6*, alternating flat and rough surface morphologies are met, indicating that the Pb(111) growth is two-dimensional. This result is best visualized in Fig. 3, where the amplitude of the width oscillations is reported for different deposition stages. Later on, the distinction between the rough and flat surface morphology becomes less well pronounced, probably due to an overall increase of the interface width.

Figure 4 shows the Pb(111) monatomic step height for increasing deposition stages as obtained from the FWHM vs $k_{\mathrm{He}}$ analysis [26]. The value of $h$ oscillates as much as $\pm 15\%$ around the value of the Pb(111) bulk interlayer separation ($d_{\mathrm{bulk}} = 2.86$ Å), but, with increasing Pb film width, it dampens out and the monatomic step height eventually stabilizes at the bulk value. At the same time no detectable displacements of the (0, 1) Bragg peak were observed, thus indicating that the variation of the step height is not accompanied by any lateral displacement of the Pb(111) unit cell [27]. The observed structural oscillations are thus attributed to the quantum size effects of the growing film. In this case the overall film thickness $D$ is expected to be some multiple of the Fermi electron half-wavelength $\lambda_F/2 = 1.83$ Å [28]. The total film thickness $D$ can be calculated from the measured $h$ values if we assume that the step height does not depend on the lateral environment, but only on the local film thickness, i.e., on the number of layers below the considered terraces. Then the film thickness $D_n$ after the formation of the $n$th layer is larger than $D_{n-1}$ by the step height $h_{n-1/2}$ (where $n$, $n - 1$, and $n - 1/2$ correspond to the deposition stages as labeled in Fig. 1). Thus we can write

$$D_n = \sum_{2}^{n} h_{i-1/2} + d_0 \,, \tag{1}$$

where it is assumed that the interface with the substrate introduces an arbitrary value $d_0$ for the first interlayer separation. The value of $d_0$ is determined by requiring it to minimize the mismatch between the growing film thickness and the corresponding multiple of $\lambda_F/2$. The mismatch has been evaluated for the first few Pb(111) layer growth, where only the two outermost layers are effectively exposed; i.e., layer-by-layer growth occurs. The minimum mismatch occurs for $d_0 = 1.64$ Å, and the corresponding results are reported in Table I, where it is seen that a major deviation from the multiple of $\lambda_F/2$ only occurs for the four-layer thick film.

It is interesting to note that irregularities in the growth reflectivity, such as detected on our system, have been observed also for other systems affected by QSE [3,11], possibly indicating that the step height variations are a characteristic manifestation of the structural QSE.

In conclusion, we have found that Pb/Ge(001) growth at low temperatures proceeds layer-by-layer, with a (111) orientation, rotated by 45° with respect to the Ge(001) substrate. The monatomic step height between terraces was found to depend on the number of grown layers and to

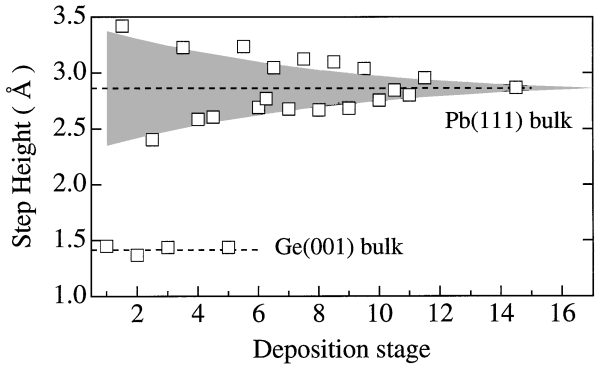


FIG. 4. The best fit values for the Pb(111) monatomic step height $h$ for different stages of Pb/Ge(001) growth (open squares), as obtained from the width (FWHM) analysis. All values oscillate around the Pb(111)-bulk step value (dashed line at 2.86 Å). The shaded region is the best fit to an exponential damping of the $h - d_{\mathrm{bulk}}$ value, as obtained from the peak width measurements. The value of the underlying Ge(001) monatomic step is also indicated.

TABLE I. Mismatch $2D_n/\lambda_F$ between the overall *Pb* film thickness and the Fermi half-wavelength (third column), as determined by Eq. (1). The $h_{n-1/2}$ values (second column) are the experimental measurements from Fig. 4 and give the height of the $n$-layer thick film with respect to the $n - 1$ one. The deposition stages correspond to the labeling of Fig. 1.

| Layer ($n$) | $h_{n-1/2}$ (Å) | $\frac{D_n}{\lambda_F/2}$ |
|---|---|---|
| 2 | 3.42 | 2.2 |
| 3 | 2.41 | 2.97 |
| 4 | 3.23 | 5.63 |
| 5 | 2.61 | 6.04 |
| 6 | 3.23 | 9.16 |

display an oscillating behavior. At the same time no lateral variations of the surface unit cell size has been detected. The step height oscillations are then attributed to the quantum size effects. We have shown that these structural relaxations effectively reduce the mismatch between some multiple of $\lambda_F/2$ and the overall Pb film thickness.

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[20] The Pb bulk lattice parameter is 4.95 Å, and the distance between equivalent rows on the (111) surface is 3.50 Å.

[21] As long as Pb film grows pseudomorphic with the substrate the overall diffracted intensity by far exceeds that of the specular, whereas for thicker Pb films most of the He scattering intensity is detected in the specular direction. This indicates that the surface valence charge explored by HAS is substantially more corrugated in the initial substrate-pseudomorphic stages, which agrees nicely with the surface resistivity measurements on Pb/Si(111) and Pb/Au/Si(111) by Jalochowski *et al.* [3] who observed a rather low surface conductivity for Pb film thicknesses up to ca. 4–5 ML, whereupon it suddenly recovers its Pb bulk value.

[22] For our scattering geometry the specular phase relation reads $\Phi = \Delta k_\perp h = 2k_{\mathrm{He}} \cos 55° h$.

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[25] The surface is not exactly stepless; what one observes for these flat stages is that there is a very weak variation corresponding to a step height of ~1.4 Å [that is, the Ge(001) step height], which reflects the underlying Ge morphology.

[26] The specular intensity $I(k_{\mathrm{He}})$ and width FWHM$(k_{\mathrm{He}})$ have been fitted at different deposition stages to the function $[A\cos(\Delta k_\perp d + \delta)]^{2n} e^{B\Delta k_\perp}$, where $d$ is the step height. $\delta = 0, \pi$, and $n = 1, 2$, respectively, for the peak intensity and width. The exponential damping $\exp[B\Delta k_\perp]$ phenomenologically describes the variable intensity due to Debye Waller effects and flux variations as the He beam temperature is increased. Because of the relatively high interference order (~7, 8) the step height $d$ variations are detected with a ~0.01 Å resolution.

[27] The resolution for the parallel momentum measurement is better than 0.3% of the surface unit vector.

[28] The value $\lambda_F = 3.66$ Å was evaluated from the Fermi energy of the bulk Pb, $E_F = 9.8$ eV and effective mass in the [111] direction of $m^* = 1.14 m_0$, after Ref. [9].