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Influence of interfactants on thin metal film growth

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Abstract

The growth of Pb on Si(1 1 1) with and without Ag as an interfactant is studied in the temperature range from 270 to 375 K by microscopy and spectroscopy. Whereas Pb grows on the Si(1 1 1)-7 × 7 surface in the Stranski–Krastanov (SK) mode, the growth mode on the Si(1 1 1)-$\sqrt{3} \times \sqrt{3}$-$R30°$-Ag surface changes from layer-by-layer below 300 K to SK mode above 300 K. Spectroscopy shows that Ag remains at the interface between the substrate and the growing Pb film. The influence of the interfactant on the growth is attributed to the increase of the island density by an order of magnitude and to the changes of the growth kinetics resulting from this increase. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Growth; Metallic films; Silver; Lead; Silicon

1. Introduction

The controlled growth of thin metal films is important both in science and technology. The sometimes extreme requirements – only a few atomic layers thick and atomic flat films – can only be fulfilled under special conditions. In general the growth in heteroepitaxy can be classified in three modes [1]: Frank–van der Merwe (FM) (layer-by-layer), Stranski–Krastanov (SK) (layer plus three-dimensional (3D) islands) and Volmer–Weber (VW) (3D islands). Because SK and VW growth is unfavorable for thin film growth one of the major goals in the last decade has been to overcome the thermodynamical driving forces – namely the energy balance of the free surface energies of the substrate, the adsorbate and the interface. Besides the possibility of decreasing the deposition temperature so much that the growth kinetics causes a quasi-layer-by-layer growth, methods involving a second adsorbate have been developed. This predeposited adsorbate can either act as a surfactant [2] or as an interfactant [3]. In the first case the surfactant swims up on the growing film, in the second case the interfactant remains at the interface between substrate and growing film. The second method is the subject of this work, as illustrated by the growth of Pb on Si(1 1 1) with Ag as an interfactant.

2. Experimental

The experiments were carried out in the SPELEEM instrument in part at the Technical

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University Clausthal, Germany, in part at the synchrotron ELETTRA, Italy. The instrument, the method and the beamline are described elsewhere [4–7]. The sample could be cooled to 260 K. Pb was deposited at a rate of 0.5 ML/min. 1 monolayer (ML) is defined as the atomic density of the Pb(1 1 1) plane (1 ML $= 9.43 \times 10^{14}$ atoms/cm^2). All experiments were video recorded and subsequently frame grabbed or measured with a slow scan CCD camera. The electron energy in the images shown is 8 eV, which gives good step contrast and high intensity.

3. Results and discussion

The growth of Pb on the Si(1 1 1)-7 × 7 surface has already been described elsewhere [8] and will be reviewed only briefly here for comparison with the growth on the interfactant covered surface. In the temperature range studied the first layer in the SK-growth of Pb on the Si(1 1 1)-7 × 7 surface is completed between 0.77 ML at 273 K and 0.65 ML at 351 K as judged by the appearance of the second layer islands. At a total coverage of 0.9 ML, i.e. 0.13 ML after the first layer closed, the nucleation process itself is completed, because no new island appears at higher coverage. The density of islands remains constant upon deposition of about one additional ML and decreases thereafter only due to the agglomeration of islands. The islands grow mainly in height but laterally only slowly. Even at a total coverage of 5.9 ML the Pb film is not closed but has elongated holes.

The growth mode is drastically influenced if one monolayer of Ag is deposited at 800 K onto the Si(1 1 1)-7 × 7 surface, forming a Si(1 1 1)-$\sqrt{3} \times \sqrt{3}$-$R30°$-Ag surface (in the following Ag-$\sqrt{3}$). The growth of Pb on this surface proceeds as follows. The saturation coverage of the first Pb layer depends linearly on the deposition temperature, ranging from 0.5 ML at 360 K to 0.9 ML at 270 K. At 288 K Pb grows on the Ag-$\sqrt{3}$ surface in a layer-by-layer mode as shown in Fig. 1. After completion of the first layer at 0.7 ML Pb forms islands with a much higher nucleation rate than in the case of Pb on top of the first Pb layer on the 7 × 7 surface. The image quality is restricted by the high nucleation rate and the limited resolution (70 nm) of these images. In the lower part of Fig. 1 the growth in the region of the square in the upper center image is shown with higher magnification and better resolution. The nucleation of the sixth Pb layer starts at 4.77 ML on a closed flat film. The newly formed islands appear as bright small circles whereas the larger step structures are due to the morphology of the Ag-$\sqrt{3}$ surface. Upon further deposition new islands are still formed (5.0 ML) followed by lateral growth and coalescence (5.23 ML). Finally the layer starts to close and the growth process repeats itself: the image at 5.92 ML is very similar to that at 4.77 ML (the asterisk marks the same surface spot). This image sequence shows a quasi perfect layer-by-layer growth which is mediated by the Ag pre-deposited onto the Si(1 1 1).

In the following we compare the temperature dependence of the growth on the Si(1 1 1)-7 × 7 and on the Ag-$\sqrt{3}$ surface. In Fig. 2 a total of 2 ML Pb was deposited at different temperatures on the Si(1 1 1)-7 × 7 surface (top) and on the Ag-$\sqrt{3}$ surface (bottom). On the Si(1 1 1)-7 × 7 surface Pb grows in the investigated temperature range above 273 K in the SK mode. A decrease of the deposition temperature from 351 to 273 K causes only a drastic increase of the island density by about two orders of magnitude. In the same temperature range the fraction of the surface area covered by the SK-islands increases from 31% at 351 K to 60% at 273 K. On the Ag-$\sqrt{3}$ surface Pb grows above 300 K in the SK mode, too, but below 300 K in the FM mode. The nucleation rate of Pb on top of the first Pb layer on the Ag-$\sqrt{3}$ surface is about a magnitude higher than on top of the first layer on the 7 × 7 surface. The maximum island density of these islands is shown in an Arrhenius plot (Fig. 6) together with the island density on a closed 3 ML thick Pb layer which is practically a Pb(1 1 1) surface. The temperature dependence of the island density is discussed and explained in Ref. [8].

As described before the growth of the Pb film was studied at various temperatures. Fig. 3 shows the fraction p_i of the surface covered by islands as a function of the total coverage θ for the Si(1 1 1)-7 × 7 (Fig. 3a and b) and the Ag-$\sqrt{3}$ system

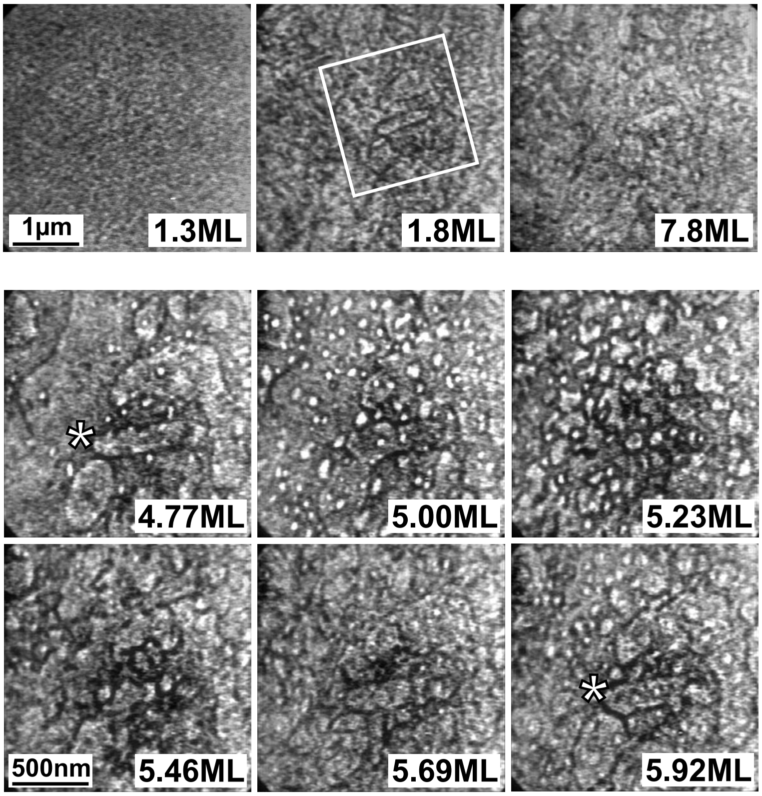

Fig. 1. Growth of Pb on the Ag-$\sqrt{3}$-surface at 288 K.

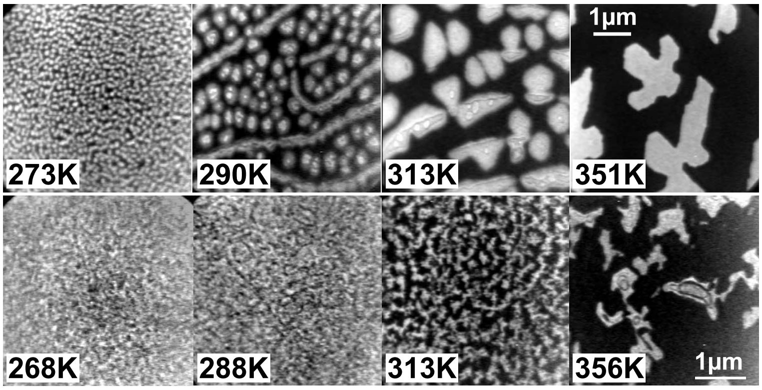

Fig. 2. Temperature dependence of the film structure at a total coverage of 2 ML Pb, grown on the Si(1 1 1)-7 × 7 surface (top) and Ag-$\sqrt{3}$-surface (bottom).

(Fig. 3c and d). The right side shows the left side with a scaled-up coverage axis, where θ^* is the coverage in excess of the first closed layer. The slope at the beginning of the growth of Pb on the 7 × 7 surface (see Fig. 3b) is not one at all temperatures studied indicating that Pb is already incorporated

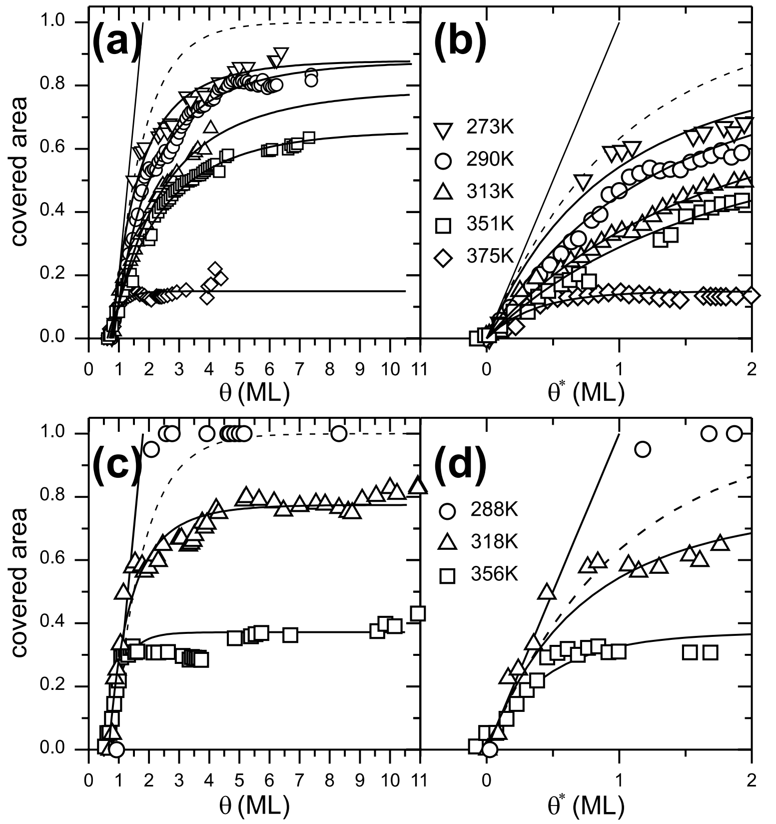

Fig. 3. Surface area covered by islands during the SK growth of Pb on (a) and (b) the Si(1 1 1)-7 × 7 surface and (c) and (d) on the Ag-$\sqrt{3}$ surface. θ^* is the coverage in excess of the first layer.

on top of the monolayer islands long before they completely cover the surface. If one assumes that all the Pb atoms condensed on the lowest layer (dark in the images) are incorporated at the edges of the monolayer islands (i.e. no upward diffusion from the lowest layer) but not those condensed on top of them (i.e. no downward diffusion onto the lowest layer) then the monolayer island coverage should increase with total coverage as indicated by the dashed lines in Fig. 3. The difference between these and the measured curves indicates that not only atoms adsorbing on top of the monolayer islands do not diffuse across the island edge but also atoms from the lower level climb on top of the island. This is not necessarily a consequence of kinetic limitations by Ehrlich–Schwoebel barriers but probably simply due to the attempt to achieve the 3D equilibrium shape in the SK mode after the completion of the initial two-dimensional (2D) layer. The slope increases with decreasing temperature, indicating that fewer of the adatoms which are adsorbed between the islands are diffusing to the top of the islands.

Compared to the Si(1 1 1)-7 × 7 system the slope of the data of the Pb growth on the Ag-$\sqrt{3}$ surface is at the beginning much higher, up to 0.5 ML. After the first islands are formed the fraction of the covered surface increases about linearly with slope 1 (Fig. 3d).

The strong influence of the Ag-$\sqrt{3}$ layer on the growth mode can also be seen in Fig. 4 which shows the temperature dependence of the fraction of covered surface at 1 ML after the first islands nucleate (full symbols). On both surfaces the fractions increase linearly with inverse temperature, but on the Ag-$\sqrt{3}$ surface much stronger:

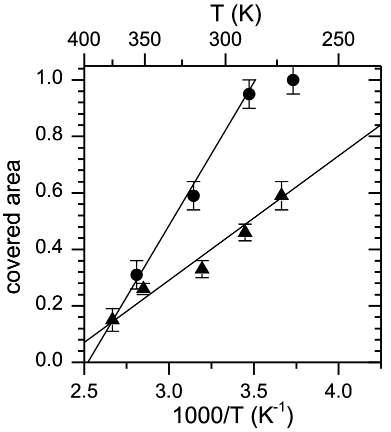

Fig. 4. Temperature dependence of the fraction of the surface area covered by islands in the Si(1 1 1)-7 × 7 (▲) and the Ag-$\sqrt{3}$-surface system (●) at a coverage of 1 ML after the first islands nucleate.

from 30% at 360 K to 100% at about 290 K. Below 290 K Pb grows in the FM mode whereas the growth of Pb on the 7 × 7 surface shows a much weaker change of the fraction of the surface covered by 3D islands (from 15% at 380 K to 60% at 275 K). The straight line of the 7 × 7 surface extrapolates to 1 at about 220 K for the 7 × 7 system which agrees with results reported earlier [9] that FM growth occurs below 200 K.

The coverage dependence seen in Fig. 3 may be described by the following rate equation:

$$dp_l/d\theta^* = -\alpha p_l - \beta(1 - p_l) \tag{1}$$

p_l is the fraction of the surface, covered by only the first ML, θ^* the total coverage in excess of the first layer (e.g. $\theta^* = \theta - \theta_0$ with θ being the total coverage and $\theta_0 = 0.77$ ML that of the first layer at 290 K), α is the fraction of the adatoms adsorbed on the first layer which is incorporated at the edge of the 3D islands, or in other words: $1 - \alpha$ is the fraction of the adatoms which climb from the first layer onto the islands. β is the fraction of the adatoms adsorbed on the islands – they cover the fraction $p_i = 1 - p_l$ of the surface – which diffuse downward to the first layer. In case of $\alpha = \beta = 1$ we have the ideal situation of FM growth: $p_l = 1 - \theta^*$ (corresponds to the straight lines in Fig. 3). For $\beta = 0$ (no downward diffusion from the island to the lowest layer) and $\alpha = 1$ (no upward diffusion) $p_l = \exp(-\theta^*)$ (dashed lines in Fig. 3). Assuming no downward diffusion ($\beta = 0$) but allowing coverage dependent upward diffusion ($\alpha \leqslant 1$) gives:

$$p_l = \exp(-A(\theta^*)) \quad \text{with } \alpha(\theta^*) = dA(\theta^*)/d\theta^*. \tag{2}$$

We can fit (full curves in Fig. 3) our experimental data with an exponential decrease: $\alpha(\theta^*) = \alpha_0 \exp(-\theta^*/\gamma)$. $\alpha(\theta^*)$ is plotted in Fig. 5 for the Si(1 1 1)-7 × 7 (a) and the Ag-$\sqrt{3}$ surface (b) for different temperatures. As α is the fraction of the adatom adsorbing between the islands which do not diffuse upward on top of the island, the larger α the more lateral growth. Fig. 5a shows that the best lateral growth, that is at least upward diffusion, occurs always at the very beginning and decreases with increasing coverage (e.g. α decreases to the half of its initial value at 2.2 ML at 290 K). A clear tendency is visible: the lower the temperature the larger $\alpha(\theta^*)$. Whereas at 350 K only 40% of the adatoms stay already at the beginning in the lowest layer, that is 60% diffuse upwards on the islands, no adatoms diffuse initially upward at 273 K. The reason for this temperature dependence is the limitation of the upward diffusion across the island edges at lower temperatures.

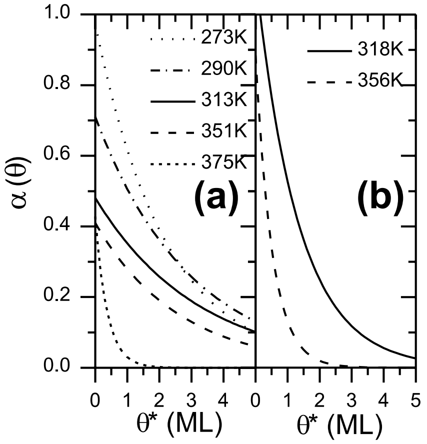

Fig. 5. Parameter $\alpha(\theta^*)$ from the fitting the curves in Fig. 3 for the SK-growth of Pb on (a) the Si(1 1 1)-7 × 7 surface and (b) on the Ag-$\sqrt{3}$-surface.

The coverage dependence of $\alpha(\theta^*)$ on the Ag-$\sqrt{3}$ surface is similar to that on the 7×7 surface with two important differences: (i) the starting values on the Ag-$\sqrt{3}$ surface are much higher than on the 7×7 surface (e.g. 100% for 318 K on Ag-$\sqrt{3}$ and 48% at 313 K on 7×7) and (ii) α decreases much faster on the Ag-$\sqrt{3}$ surface, for example to the half of its initial value at 1 ML at 318 K. This means that in the initial stage of growth nearly all adatoms adsorbed on the first layer contribute to the lateral growth of the island. A look at the original data in Fig. 3d shows that this model does not fit the data points below 1 ML very well: instead of a nonlinear increase as seen in Fig. 3b the fraction of the covered area increases linearly with slope 1 and changes the slope abruptly to a lower temperature-dependent value. The reason for the bad fit is the assumption of the model, that no downward diffusion occurs ($\beta = 0$). However, a slope = 1 means that not only all adatoms adsorbed between the islands have to contribute to the lateral growth ($\alpha = 1$) but also all adatoms adsorbed on the islands have to diffuse downward ($\beta = 1$). After the sudden slope change at about $\theta^* = 0.5$ ML, the data are fitted quite well by the exponential fit – so that now downward diffusion is likely to be negligible ($\beta = 0$).

The data may be interpreted as follows: the average size of the islands is $A_i = p_i/n_i$, where $p_i = 1 - p_l$ is the fraction of the covered surface (Fig. 3) and n_i the island density. During the initial lateral growth (0.1 ML $< \theta^* <$ 1 ML) n_i can be set constant at the maximum island density (circles and triangles in Fig. 6 for Ag-$\sqrt{3}$ and 7×7, respectively). After the formation of a nucleus on the Pb-covered substrate, this nucleus grows laterally to a 2D island. At that stage $p_i = \theta^*$ and consequently the average island size grows linearly with coverage. Adatoms adsorbing on this 2D island have two possibilities: (i) they can create a stable nucleus on it, starting 3D growth or (ii) they can diffuse downward and be incorporated into the 2D island. The probability with which these two processes occur depends on the size A_i of the island and the adatom diffusivity on top of the island. The average size of the area S within which an adatom can diffuse on top of an island before it is incorporated into a stable nucleus is $S = 1/n_x^{\mathrm{top}}$ where n_x^{top} is the maximum density of the nuclei. Two cases may be distinguished:

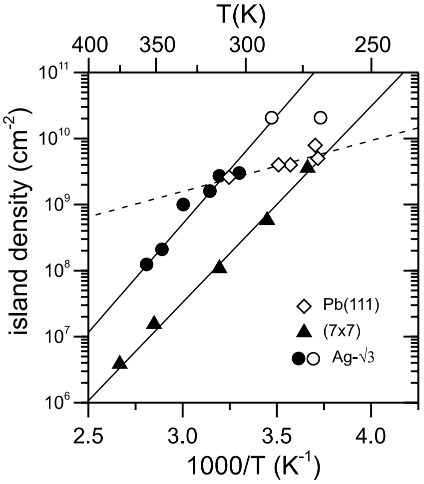

Fig. 6. Arrhenius plot of the maximum island density on the first Pb monolayer on the Si(1 1 1)-7×7 surface, on the Ag-$\sqrt{3}$ surface and on the Pb(1 1 1) surface (closed 3 ML thick Pb layer). Open symbols for FM growth, full symbols for SK growth. The FM values for the Ag-$\sqrt{3}$ system (open circles) are a lower limit.

1. if $A_i \gg S$ then the 2D island is so large, that only one or more nuclei are formed on top of the island. Only at the edge of the island a denuded zone with width $\sqrt{S}$ without nuclei exists.
2. if $A_i < S$ then the 2D island is so small, that the adatom diffusing on the island will reach the island edge long before they can form a stable nucleus. Because there is no Ehrlich–Schwoebel barrier – layer by layer growth of Pb/Pb(1 1 1) was found down to 20 K [10] – the adatoms will diffuse across the island edge and are incorporated into the 2D island.

This means once an island has nucleated it grows laterally as a 2D island. The average island size A_i increases linearly with the coverage θ^* until it has about the mean diffusion area S of an adatom on top of the island ($A_i \approx S$). Then nucleation on top is possible and the island starts to grow three-dimensionally (SK-growth). But if the size A_i of the island is so large, that neighboring islands can merge ($A_i \approx 1/n_i$), the layer closes before nucleation on top can set in (FM-growth).

Thus we have a condition for the growth kinetics driven growth mode: if $n_\mathrm{i} \ll 1/S = n_x^\mathrm{top}$ then SK growth occurs, if $n_\mathrm{i} \gg n_x^\mathrm{top}$ FM growth.

What does this mean for the growth of Pb on Si? Assuming that the diffusion and the nucleation process on top of the 2D island, that is in the third Pb layer, is the same as on a three ML thick Pb film one can use for n_x^top the maximum island density on Pb(1 1 1) (diamonds in Fig. 6). The average island size A_i on the Ag-$\sqrt{3}$ surface at $\theta^* = 0.5$ ML is 4.9×10^{-3}, 36×10^{-3} and 234×10^{-3} μm at 288, 318 and 356 K, respectively, whereas the average diffusion area $S = 1/n_x^\mathrm{top}$ – with n_x^top set to the value of the dashed curve in Fig. 6 – on top of the islands is 28×10^{-3}, 49×10^{-3} and 88×10^{-3} μm^2. For 288 K the condition $A_\mathrm{i} < S$ is fulfilled, which explains the FM growth at that temperature. At 313 K $A_\mathrm{i} \approx S$, so that during further deposition the growth will switch from 2D to 3D. At 356 K the islands are already large enough that nucleation on top can occur.

On the 7×7 surface the average island size A_i at $\theta^* = 0.5$ ML is 43×10^{-3}, 193×10^{-3} and 1.04 μm^2 at 290, 313, and 351 K, respectively, whereas the average diffusion area S is 29×10^{-3}, 45×10^{-3} and 83×10^{-3} μm^2 (from Fig. 6, dashed line: $S = 1/n_x^\mathrm{top}$ of Pb(1 1 1)). Because of the larger A_i value the growth sooner becomes 3D with increasing temperature on the base Si surface than on the Ag-$\sqrt{3}$ surface.

After having shown that one layer of Ag can influence the growth of Pb on Si(1 1 1) drastically from SK to FM growth (below 300 K), the question has to be addressed where the Ag is located. Two extremes are thinkable: (i) Ag swims up onto the growing Pb film and (ii) Ag remains at the interface between the Si substrate and the Pb film. In the first case Ag would act as an surfactant as found for numerous systems, for example, Sb in the growth of Ge on Si(1 1 1) and Si(1 0 0) [11–13], Pb in the growth of Co on Cu(1 1 1) [14]. If Ag would act as a surfactant it would have to be displaced by Pb from the Si surface and stay on top of the growing Pb film. Such an exchange process between Pb and Ag on the Si(1 1 1) surface is very unlikely from the energetic point of view: the Ag–Si bond (2.82 eV/atom) [15,16] is stronger than the Pb–Si bond (2.65 eV/atom) [17]. In addition, Pb has a lower surface energy than Ag and will always stay on top of Ag. The SPELEEM instrument allows to demonstrate this immediately by switching from the microscopic to the spectroscopic mode. Fig. 7 shows Ag 4d valence band spectra at Pb coverages of 0, 1 and 8 ML on Si(1 1 1)-7×7, taken at a deposition temperature of 260 K. After the deposition of only 1 ML of Pb the Ag intensity decreased by a factor of about 3.5; finally, after 8 ML Pb only the weak Pb valence band is visible. Because the mean escape depth of the emitted electrons is only about 0.5 nm at a kinetic energy of about 40 eV, this spectroscopic measurement is very surface sensitive. The decrease of the Ag intensity can only be explained by an exponential attenuation by the overgrowing Pb film. Ag does not swim up onto the top of the Pb film, but remains at the interface and is therefore an interfactant in the growth of Pb on Si(1 1 1).

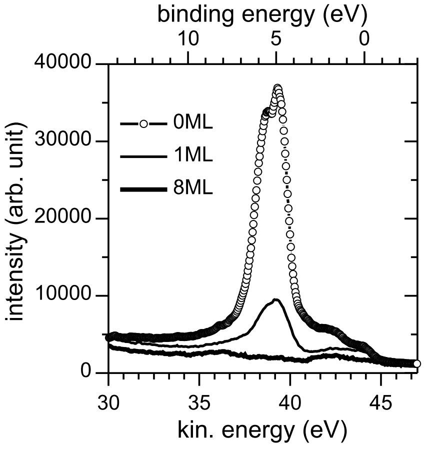

Fig. 7. Valence band spectrum of a Ag-$\sqrt{3}$-surface covered with 0, 1 and 8 monolayers of Pb.

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