Three-dimensional localization of electrons on Ag islands

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Image states on Pd(111) with various coverages of Ag were investigated by two-photon photo-emission spectroscopy for temperatures between 90 and 1300 K. The formation of three-dimensional islands, smooth layers, and surface alloys is identified. The transition from one-dimensional localization in front of the surface to three-dimensional localization on top of Ag islands with diameters between 10 and 100 Å is observed. The high-resolution spectroscopy of image states provides a new tool to study the growth mode, morphology, and island size distribution of ultrathin metal films.

An electron in front of a metal surface is subject to an attractive potential through the induced image charge. If the electron can neither penetrate into the metal due to a gap of the projected bulk band structure, nor leave the surface because its energy is below the vacuum energy E_{vac}, it is localized perpendicularly to the surface. Due to the long-range image potential a series of bound states converging towards E_{vac} is formed.[1] These have been observed on many metal surfaces, and their binding energies and lifetimes are well understood.[2] In an earlier paper[3] we have reported results for image states on Pd(111) with various coverages of Ag deposited at room temperature. The image-state series for the bare Pd substrate and Ag layers of different height can be easily distinguished due to their different energies. At intermediate coverages the states corresponding to the two nearest full-monolayer coverages can be observed simultaneously. These results prove that the vacuum energy of the patch at which the electron is trapped is the reference level for the image-state series. This is the concept of the local work function.[3,4] Since the electrons can be unambiguously assigned to patches of different Ag coverage, they are localized laterally on the surface in addition to the perpendicular direction. The question arises whether effects of the localization of the electrons parallel to the surface can be observed. Alternatively speaking, one can ask what the minimum size of an island which can support image states is. The ultimate lower limit would be a single atom on the surface. For this extreme case the distinction between image states and atomic levels or localized surface states would break down. The screening of the external charge is the origin of the image potential; this screening affects also the energy levels of an adsorbed atom on a metal surface. Consequently, the existence of image states requires homogeneous areas of a certain minimum size which should be of the order of the perpendicular extension (≈ 4 Å) of the image state.[3,4] It is instructive to note that the case of single atoms on a substrate can lead to a homogeneous surface if the separation between the atoms is smaller than the minimum size needed to support an image state. This situation occurs for an alloy surface which is inhomogeneous on the atomic scale, but appears homogeneous to the image states, as we will show below.

Two-photon photoemission[2] is the technique for the high-resolution spectroscopy of image states. The excitation scheme is illustrated in the left half of Fig. 1 for the case of the clean Pd(111) surface. The lowest ($n = 1$) image state is populated with an electron from the continuum of bulk states below the Fermi level E_F after absorption of a photon of energy $2h\nu$. A second photon of energy $h\nu$ lifts the electron above the vacuum level. The emitted electrons are analyzed with respect to their kinetic energy and detected using an electron spectrometer. The photons are the ground and frequency-doubled wave of a dye-laser system. Experimental equipment, sample preparation, and coverage calibration are identical to our previous work.[3]

In this study we took advantage of the possibility to cool the sample with liquid nitrogen. At room temperature Ag grows on Pd(111) in a layer-by-layer mode.[3,5] At lower temperature the mobility of the Ag atoms should be reduced, and a change of the growth morphology is expected. The lowest spectrum in Fig. 2 is for 1 monolayer (ML) of Ag deposited at 90 K. We observe two series of image states and the spectrum looks similar to the one for 1.35 ML of Ag adsorbed on Pd(111) at room temperature.[3] The series at lower energy comes from two-layer-thick Ag areas, and the other from one-layer-thick
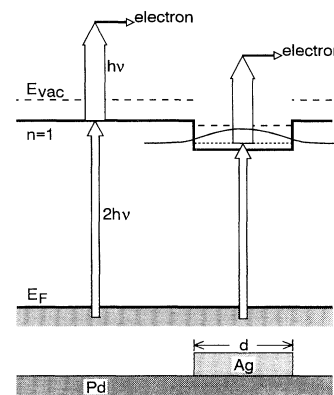

FIG. 1. Schematic of the two-photon photoemission process on Pd(111). For a small Ag island of diameter d the energy shift (dotted line) and the wave function for a laterally localized image-state electron is shown.
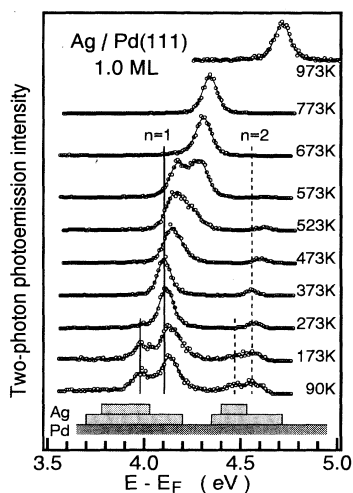
<u>48</u>   15 496

FIG. 2. Two-photon photoemission spectra for 1-ML Ag on Pd(111) deposited at 90 K and after heating to the indicated temperatures for 60 s. The energy scale is relative to E_F.

FIG. 3. Energy of image states [$n = 1$ (2) filled (open) symbols] and vacuum energy E_{vac} as a function of temperature for 1.8 ML of Ag on Pd(111). The inset shows the variation with coverage for a heating temperature of 673 K. The short horizontal lines and the dashed curve give the corresponding quantities for Ag films deposited at 300 K (Ref. 3.)

areas. Since the coverage is 1 ML we must have patches which are not covered by Ag.[6] Hence, we have three-dimensional islands as indicated in the bottom of Fig. 2. The intensity ratio of the peaks corresponding to different layer heights is roughly 1:2 as expected for diffusion-limited growth.[7]

The spectra show pronounced changes after heating the sample for 60 s to the temperatures given in Fig. 2. The measurements were always done at 90 K. Longer heating periods did not produce changes in the spectra, so 60 s is sufficient to reach an equilibrium configuration of the surface. After heating just above room temperature, the series at lower energies has disappeared and only electrons from one-layer-thick Ag areas are observed. The spectrum for 373 K is identical to the one where 1 ML of Ag is deposited at room temperature.[3] The Ag atoms from the second layer have filled the holes in the first layer and the Ag film forms a smooth layer.

For heating temperatures above 500 K the image state gets broader and shifts to higher energy. At about 600 K we observe one narrow peak, which does not shift in energy up to about 750 K. Due to the narrow symmetric line shape, it must be an image state on a homogeneous surface. Since its energy is between the values for 1 ML of Ag and clean Pd, we assign it to a surface alloy. Support for an incorporation of Ag atoms into the Pd surface comes from the observation that the temperature is well below the desorption temperature of 1100 K for Ag from Pd(111), and that Ag atoms two and three layers deep in the fcc Pd(111) structure were identified by photoelectron forward-scattering experiments for samples heated to 700 K.[5] Above 750 K the image state shifts further in the direction of the clean Pd(111) surface. The Ag evaporates or gets incorporated deeper into the bulk. At about 1200 K we observe the image states and the work function for the clean Pd(111) surface.

The same qualitative behavior is seen at other coverages. In Fig. 3 the energies of the first (closed symbols)
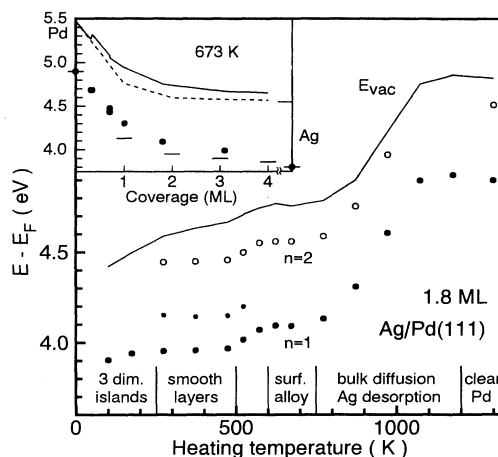
and second (open symbols) image state versus the annealing temperature for 1.8 ML Ag/Pd(111) are shown. The larger symbols denote the image states on the mainly existing two-layer-thick Ag areas, and the smaller ones on the less frequent one-layer-thick areas. The solid line connects the measured values for E_{vac}. At 90 K the energies of the image states and the work function ($E_{vac} - E_F$) are lower than at room temperature. At this coverage we have three-dimensional islands with heights above three layers, where the image states from individual layers cannot be resolved.[3] The reduction of the work function is much larger than expected from the contribution of higher islands. This is often observed for rough surfaces.[4] Between room temperature and 500 K we observe constant energies for the image states. The work function shows a small variation since it averages over the whole surface, whereas the image states exist only on the homogeneous patches of the surface.

Between 600 K and 750 K a stable surface alloy is observed for all coverages. The inset in Fig. 3 shows the $n = 1$ image-state energy and the vacuum energy after heating different Ag coverages to 673 K. These energies are always higher than the corresponding values for the image states on completed layers (short horizontal lines) or the work function measured after deposition at room temperature (dashed line).[3] The increased energies cannot be explained by a reduced coverage due to evaporation of Ag, since for smooth layers only the image-state energies indicated by the short horizontal lines are observed. The continuous shift reflects the change of the concentration of the surface alloy with coverage.

The image states give us a tool with which we can clearly distinguish between three-dimensional islands, layer-by-layer growth, and surface-alloy formation. Changes in the morphology of the surface are directly reflected by the electronic states. One important result is that we can associate the image states with the partic-
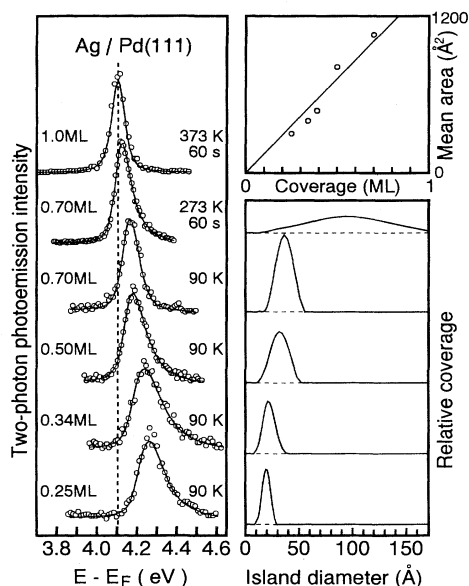
FIG. 4. Two-photon photoemission spectra for various amounts of Ag on Pd(111) deposited at 90 K (left panel). The energy shift relative to a smooth film (dashed line) is due to the lateral localization of the image state. From the experimental data distributions of the coverage by islands of various diameters are derived (right panel). The integral over the curves corresponds to the coverage given in the left panel. The mean area of the islands is proportional to the coverage (top right).

ular island where they are located. In the following we will study the localization effects for small islands.

In the left panel of Fig. 4 we show the spectra for small coverages of Ag adsorbed at 90 K. A shift of up to 200 meV to higher energy compared to the case of a smooth 1-ML Ag film (top spectrum and dashed line in Fig. 4) is observed. The shift decreases with increasing coverage and can be further reduced by heating (see the spectrum for 273 K in Fig. 4). The linewidth is larger than for image states on homogeneous surfaces and the line shape is asymmetric with a tail at the high-energy side. At these low coverages no significant occupation of two-layer-high islands is expected[7] and there is no intensity to the left of the peaks (compare to Fig. 2).

We assign the shifts to the lateral confinement of the image-state electrons on the Ag islands. This situation is illustrated in the right half of Fig. 1. The solid line shows the energy of the $n = 1$ image state for one layer of Ag on Pd(111). The dashed line indicates the corresponding vacuum energy, which happens to lie below the $n = 1$ state for Pd(111) in this case. If the island diameter d becomes smaller the electron becomes localized in the lateral dimension. The lateral part of the wave function is shown in Fig. 1 for an energy shift of 170 meV (dotted line). The energy of a particle in a box of extension d is proportional to $1/d^2$. This dependency is found approximately also for the finite potential well in the diameter range relevant to this work. The decreasing energies of the states with increasing coverage (or temperature) are then easily explained by the growth of the island size.

The broad asymmetric line shape reflects the island-size distribution through the $1/d^2$ dependence of the energy shift.

For a quantitative interpretation of the spectra we assumed a separation of the wave function into a perpendicular and a lateral part. Perpendicular to the surface the image states for the homogeneous surfaces are retained and the energy shift due to the lateral localization is described by a simple particle-in-a-box model. The (finite) potential depth is the difference of the energies of the first image state between the clean Pd(111) surface and the 1-ML Ag film (see Fig. 1). For islands on close-packed substrates, triangular or hexagonal islands are commonly observed[8,9] which we approximate by a two-dimensional round box. Different shapes would mainly alter the factor relating the energy shift to $1/d^2$, but would not change our conclusions in a qualitative way, as long as all islands have similar shapes. We simulated our spectra in the following way: The spectrum for an image state on an island of finite diameter is the spectrum of the homogeneous 1-ML Ag film shifted according to the energy obtained for the particle-in-a-box model. For a distribution of island sizes we have to perform a weighted average of such shifted spectra. Using a least-square-fit procedure we obtained the distributions of the coverages by islands of various diameters shown in the right panel of Fig. 4. The solid lines in the left panel show the fits of our model to the experimental data. The distributions are normalized, so the area under the curve is proportional to the coverage. For 0.25-ML Ag adsorbed at 90 K the mean island size is about 7 Ag atoms in diameter and at 0.70 ML it is about 14 Ag atoms. After heating of the Ag film the islands become larger. This is illustrated in Fig. 4 for the 0.70-ML Ag film which after heating to 273 K shows a broad distribution with a mean value of ≈ 100 Å. The distributions start at ≈ 10 Å diameter which is determined by the energy range of the experimental data. This cutoff does not lead to any unphysical shape of the curves. The smallest islands observed by scanning tunneling microscopy studies for metal-on-metal systems are of similar diameter[8] which corresponds roughly to islands consisting of seven close-packed atoms. Such heptamers have been possibly identified as the equilibrium configuration for Ag on Pt(111).[10]

For the data at 90 K the height of the distributions is almost independent of coverage and the mean area of the islands grows proportionally to the coverage (Fig. 4, top right). This behavior can be explained if the density of nucleation centers is constant (in the coverage range studied here) and fixed by the experimental conditions such as evaporation rate and temperature. From the slope of the solid line we obtain the density of nucleation centers at 90 K to 7×10^{12} cm^{-2}. This corresponds to a diffusion length of ≈ 20 Å. For 0.7 ML the onset of coalescence of islands cannot be excluded.

In retrospect, we can now understand the spectra in the 500-K range of Fig. 2. The $n = 1$ state shifts to higher energy and a second somewhat broader peak appears close to the position for the surface alloy. The obvious interpretation is that the island size is reduced by the loss of Ag atoms which are incorporated into the

surface to form the alloy. This demonstrates again the power of high-resolution spectroscopy of image states for the study of the morphology of ultrathin metal films.

There is a close correspondence of the electrons localized on Ag islands to electrons confined in artificially produced structures known as quantum dots.[11] For quantum dots the currently achievable dimensions are considerably larger and one deals normally with many electrons per dot. In our case the Coulomb repulsion between two electrons would be equal to the depth of the potential for distances around 20 Å. In order to populate a larger island with more than one electron, femtosecond laser pulses would be needed.[12] Such experiments would open the possibility to study the electron-electron interaction and exchange directly. We have yet to discuss the higher excited states due to the lateral confinement: The first excited states have a node perpendicular to the surface and are, therefore, not observable in our experiments at normal emission. In our simple model with the decoupled perpendicular and lateral wave functions, symmetry would forbid a coupling between the excited states due to the lateral and perpendicular localization. Obviously, there is also the need to go beyond the abrupt box potential. The self-consistent calculation of the image potential is still a challenge even for homogeneous surfaces[13] and up to now, image states on a corrugated surface have been treated only in a crude hard-wall approximation.[14] One basic limitation for all experiments is the experimental resolution and the intrinsic linewidth of the image states. In addition to experimental improvements,[15] the limitations due to the intrinsic linewidth can be overcome by using other substrates [e.g., Cu(111)] or higher members of the image series.[16]

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