Core- and valence-band energy-level shifts in small two-dimensional islands of gold deposited on Pt(100): The effect of step-edge, surface, and bulk atoms

M. Salmerón,* S. Ferrer,* M. Jazzar,† and G. A. Somorjai

*Molecular and Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
and Chemistry Department of The University of California, Berkeley, California 94720*

Photoemission techniques were used to study the electronic properties of two-dimensional islands of Au deposited on Pt(100) in the submonolayer range. Shifts of approximately 0.6 eV were observed in both valence-band and core-level binding energies from $\Theta = 1$ to 0.1. These shifts are interpreted in terms of the increasing proportion of island edges as the gold coverage approaches zero. Above $\Theta = 1$ the surface-bulk energy shift was found to agree with previously published data.

It is now well established, on the basis of photoemission experiments, that the electron binding energies of surface atoms in a solid material can be different from the ones corresponding to atoms located in the bulk.[1-3] In the case of gold, the surface-bulk energy shift has been observed for core- and valence-band levels[1,4] The basic idea for explaining these shifts is the following. As the coordination number z of a surface atom is intermediate between that of a bulk atom and a free atom ($z = 8-9$ vs 12 and 0, respectively), the electron binding energies are also intermediate between those of bulk and free atoms. The same argument also predicts a shift in the electron binding energies of atoms located at step edges and in other lower coordinations, relative to normal surface atoms. This effect has been observed recently in the case of Ir(332).[5] The production of well-controlled two-dimensional layers of Au on Pt(100) provides an excellent way of enhancing the contribution of atoms of low coordination. The two-dimensional character and low average coordination number of the Au islands have measurable consequences in their electronic properties. In this paper we show, for the first time, the changes occurring in three physical quantities: width and structure of the valence band, work function, and core-level binding energies as the size of the Au islands deposited on Pt(100) varies. This type of study has implications on heterogeneous catalysis research since, in principle, this can be useful in determining the degree of dispersion of a supported catalyst. We have chosen the Au-Pt(100) system since it displays a very peculiar activity for hydrocarbon reactions when the Au coverage is varied from zero to two monolayers.[6]

The experiments were performed in a standard ultrahigh vacuum chamber ($p = 10^{-10}$ torr), equipped with a Mg $K\alpha$ x-ray source, a He discharge lamp, a double pass cylindrical mirror analyzer for energy analysis of the emitted photoelectrons, as well as for the Auger spectroscopy, and also a low-energy-electron diffraction (LEED) system. Gold was evaporated from a W-wrapped gold wire that was heated resistively. The deposition of the noble metal was monitored by Auger spectroscopy and it was found that its growth follows a Frank–Van der Merve mechanism, i.e., layer by layer. This result is in agreement with previous findings in our laboratory.[7] The absolute value of the coverage Θ, measured in this way, is accurate to within 10%.

The LEED pattern, which initially showed the well-known "1×5" structure, changes in the course of the Au deposition in the manner described by Sachtler *et al.*[7] The patterns are indicated in Fig. 2 but will not be discussed here.

The work function of the Au-Pt(100) system was measured from the onset of the secondary electron cascade in the ultraviolet photoemission spectra (UPS). The absolute values reported are affected, then, by an error bar of ± 0.15 eV. The relative error bar is of ± 0.05 eV.

In Fig. 1, we show the evolution of the UPS spectrum of gold in difference form (Au-Pt, minus clean Pt), as a function of gold coverage. A continuous shift of the binding energy of the Au $5d_{3/2}$ derived band (d' to d peaks in Fig. 1) is observed when the coverage of gold increases. From $\Theta = 0.1$ to $\Theta = 1$, the shift is of 0.6 ± 0.1 eV and from $\Theta = 1$ to $\Theta = 6$, there is an additional shift of 0.5 ± 0.1 eV. There is also a shift of peak c' to c but its behavior is more complicated due to its overlap with a new peak that emerges above $\Theta = 1$ (peak b). The dashed curve is the result obtained by Citrin and Wertheim.[1] It corresponds to the UPS spectrum contributed by the first atomic layer of Au in a thick evaporated film. That curve was computed by subtracting two conveniently weighted curves for normal and grazing emergences. The agreement with our $\Theta = 1.1$ curve is good except for the peak around 2 eV, which is absent in our case. Perhaps this peak is a residue of the bulk derived emission labeled b in the figure.
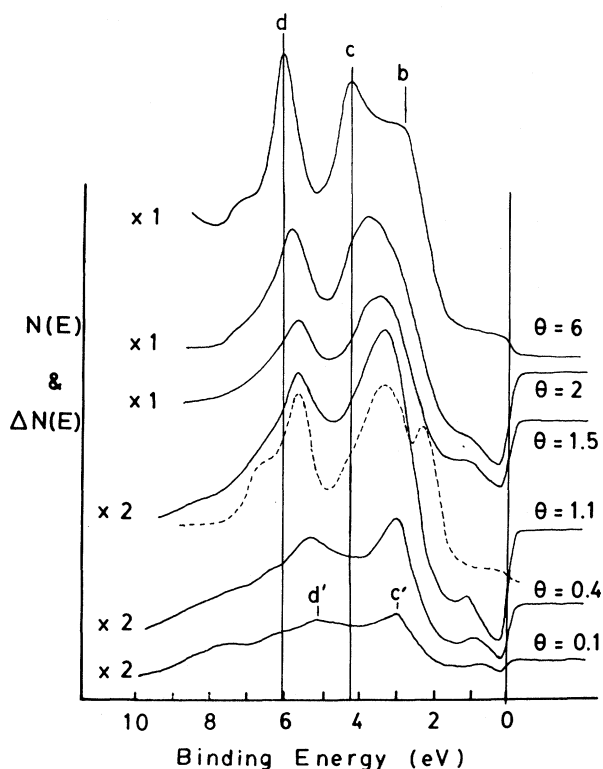
FIG. 1. He ɪ (21.2 eV) UPS spectra from Au deposited on Pt(100) for various coverages. Only the difference spectra are shown except for $\Theta \simeq 6$. Two peaks c' and d' are present for $\Theta < 1$ that shift to the multilayer positions c and d. Above $\Theta = 1$, a third peak appears that grows to the final peak labeled b.

FIG. 2. Variation of the work function ϕ, of the Au-Pt(100) system as a function of Au coverage. A very rapid decrease at low coverages is followed by a shallow minimum around $\Theta = 1$. The LEED patterns corresponding to the various stages are indicated.

As we can see then, apart from reproducing the shift in the valence-band spectrum from monolayer to multilayers observed by Citrin et al.,[1] we observe an additional 0.6-eV shift in going from $\Theta = 1$ to $\Theta = 0.1$ that reflects the decreasing average size (and average coordination number) of the two-dimensional gold islands.

Figure 2 shows the variation of the work function ϕ, as a function of Au coverage. From $\Theta = 0$ to $\Theta = 1$, there is a rapid decrease in ϕ. At $\Theta \simeq 1$, a shallow minimum is visible with a depth only slightly larger than the relative error bar in the experimental data. After this minimum, the work function saturates rapidly to its multilayer value of 5.42 eV, which is within the experimental error of the 5.47 eV found for Au(100).[8] We interpret the nonlinearity of ϕ from $\Theta = 0$ to 1, as a result of the contribution of the dipole moments associated with step sites at the edges of the gold islands. Besocke, Krahl-Urban, and Wagner and also Gardiner, Kramer, and Bauer[9,10] have shown that, for Au, Pt, and W stepped surfaces, the contribution of the dipole moment associated with the steps to the decrease in the work function is linear with increasing step denstiy on a fairly
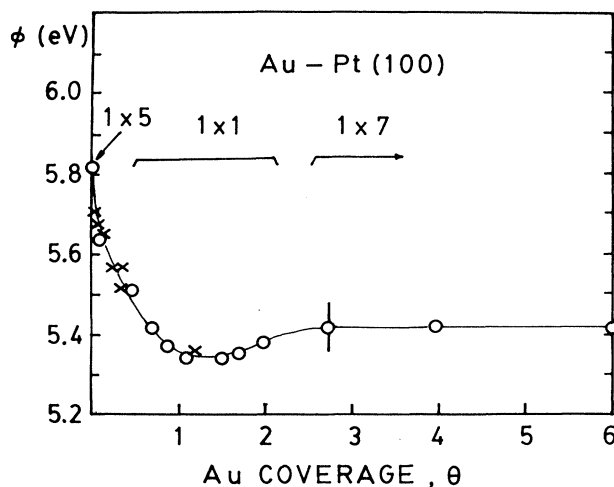
large range. If this is true also for the step sites of the borders of our gold islands, then, the deviation of ϕ from linearity between $\Theta = 0$ and 1 should be proportional to the total perimeter length of the Au islands. At low coverages the total perimeter increases with Θ until at a certain coverage the islands coalesce and the perimeter decreases afterwards. Although we do not know the dipole moment corresponding to the step edges of a gold island on Pt(100), in order to make an estimate we may take the value of 9.5×10^6 debye cm^{-1}, which corresponds to the dipole moment per unit step length of (100) steps of Au in a (111) Au surface.[9] By inserting this value into the Helmholtz equation we fitted our experimental data and obtained an order-of-magnitude estimate of the island perimeter or, equivalently, of the density of islands of 10^{12} to 10^{13} cm^{-2}.

The x-ray photoemission spectroscopy (XPS) $4f$ photoelectron peaks of Au show a continuous shift towards higher binding energies, measured relative to the substrate Pt $4f$ peaks, in going from $\Theta = 0.1$ to $\Theta \leq 4$ as shown in Fig. 3. We interpret this shift as the result of the changing intensities of three main components of the experimental peak: edge atoms, surface atoms, and bulk atoms that are not resolved in the experimental curve due to insufficient resolution (full width at half maximum $= 1.25$ eV). It is worth emphasizing that the sensitivity to the edge and surface components is provided by their overwhelming contribution at low coverages ($\Theta < 1$) and to the fact that their contribution changes noticeably when Θ increase above one monolayer. We thus calculated the expected shift in a very simple way, by counting the number of edge, surface, and bulk atoms of Au
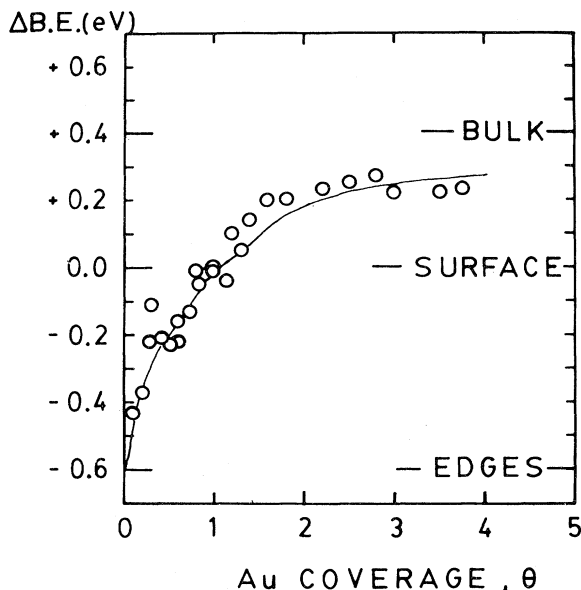
FIG. 3. Binding-energy shifts in the XPS $4f$ spectrum of Au as a function of Au coverage. The energies are referred to the monolayer position. The shift, which is due to the changing contributions of three unresolved components (step-edge, surface, and bulk atoms), has been computed in a very simple model. The resulting curve for expanding square islands is shown as the continuous curve in the figure.

as a function of Θ, for expanding square islands, and by using these values to generate a compound photoelectron peak. The best fit to the experimental data (continous curve in Fig. 3) was obtained for the following values of the parameters: island density $8 \pm 3 \times 10^{12}$ cm^{-2}, edge to surface $4f$ binding-energy shift 0.6 $\pm$ 0.2 eV, surface to bulk binding-energy shift 0.4 $\pm$ 0.1 eV. The bulk component appears only above $\Theta = 1$. Its increasing contribution is reduced,

though, by the finite escape depth of the emitted photoelectrons. In the computation we used the experimental attenuation of the nearby $4f$ peaks of Pt after depositing one gold monolayer. This gives an attenuation of 20%. The fit is very good considering the crudeness of the model. The density of islands is in agreement with our previous estimate based on work-function data. A few figures can be deduced from these data that illustrate the range of dimensions of the islands for $\Theta < 1$. For $\Theta = 0.1$, for example, 75% of the Au atoms are located on the edges of the islands. These islands have, then, an average size of 17 atoms. For $\Theta = 0.4$, these figures are 43% and 70 atoms, respectively.

The surface-bulk binding-energy shift of the $4f$ emission is in excellent agreement with the values of 0.40 $\pm$ 0.01 eV determined by Citrin et al.[1] and of 0.38 $\pm$ 0.01 eV as determined by Heiman, van der Veen, and Eastman.[4] The overall shift of 1.0 $\pm$ 0.2 eV is similar to that found by van der Veen et al. (0.75 eV) for step to bulk atoms in Ir(332).[5]

We have shown, then, that there is a measurable contribution of the edge atoms of two-dimensional overlayer islands to the electronic properties of these small metal clusters. To our knowledge this is the first time that the effect of the changing islands size is observed in the XPS, UPS, and work-function data. A more detailed paper is now in progress where these and other results will be extensively presented.

*Permanent address: Instituto de Física del Estado Solido del Consejo Superior de Investigaciones Científicas, and Department of Physics, Universidad Autónoma de Madrid, Madrid, Spain.

†Permanent address: University of Petroleum and Minerals, Dhahran, Saudi Arabia.

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