

## Palladium Nanocrystals on Al<sub>2</sub>O<sub>3</sub>: Structure and Adhesion Energy

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We have investigated the structure and morphology of nanosized palladium clusters supported by a thin Al<sub>2</sub>O<sub>3</sub> film on NiAl(110) using scanning tunneling microscopy. Well-ordered clusters with a diameter above  $\approx 40$  Å were imaged with atomic resolution, allowing a crystallographic identification of the cluster facets. A new method to obtain quantitative information on the work of adhesion (adhesion energy) of metal clusters deposited on oxides is introduced. For Pd on Al<sub>2</sub>O<sub>3</sub> we obtain a value of  $W_{\text{adh}} = 2.8 \pm 0.2$  J/m<sup>2</sup>. This result is at variance with values recently derived on the basis of *ab initio* density-functional theory.

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The metal-oxide interface is of extreme importance in many technological applications including microelectronic devices, oxide-supported transition-metal catalysts, and metal-ceramic-based sensors. Extensive investigations have been undertaken to improve the understanding of the physics and chemistry of the metal-oxide interface. In particular, several studies have addressed the growth of thin metal layers and metal clusters on well-characterized oxide surfaces [1–5]. In spite of the efforts, quantitative information on the metal-oxide interface such as adhesion and interface energies are, in general, unknown, and attempts to characterize metal clusters deposited on oxides at the atomic level have so far not been successful.

In this Letter, we report a scanning tunneling microscopy (STM) study of Pd nanoclusters deposited on an Al<sub>2</sub>O<sub>3</sub> film grown on NiAl(110), and show that atomic resolution on crystalline Pd clusters can indeed be obtained. We show how a detailed characterization of the cluster morphology can be used to derive important parameters such as the adhesion energy of the clusters. The new experimental procedure is not limited to Pd on Al<sub>2</sub>O<sub>3</sub>, but may be applied to other systems as well. We discuss the results in relation to recent theoretical efforts and point out that quantitative experimental data of this type can form a much-needed basis for comparison between experimental results and theory. Transition-metal nanocrystals deposited on an oxide may form an ideal playground for atom-resolved studies of chemical reactions on realistic model catalysts.

Experiments were carried out in an ultrahigh vacuum chamber equipped with standard facilities for sample preparation and characterization, as well as a fully automated, high-resolution STM. The Al<sub>2</sub>O<sub>3</sub> film was prepared by the well-established technique of oxidation of a NiAl(110) crystal [6] and has a thickness of only 5 Å. Palladium was evaporated at a constant rate from a thin Pd wire wound around a W filament, which could be heated

resistively. The Pd deposition rate was  $\sim 0.16$  monolayer per minute (ML/min). The STM was operated in the constant-current mode at room temperature, and the data are displayed in a gray-scale representation with darker levels corresponding to lower-lying areas. Since Al<sub>2</sub>O<sub>3</sub> is an insulator with a band gap of  $\sim 8$  eV, tunneling at bias voltages less than  $\sim 4$  eV will take place to/from states in the underlying NiAl(110) surface. Hence the apparent heights of Pd clusters recorded at low bias voltage have been reduced by the thickness of the oxide (5 Å) in order to get the correct height [7].

The Al<sub>2</sub>O<sub>3</sub> film formed by oxidation of NiAl(110) has been characterized previously [6,8]. As the defect structure is important for the growth of the Pd clusters, we briefly mention the aspects with special relevance to this study. The oxide film grows in two reflection domains, shown in Fig. 1(a). Three types of major defects

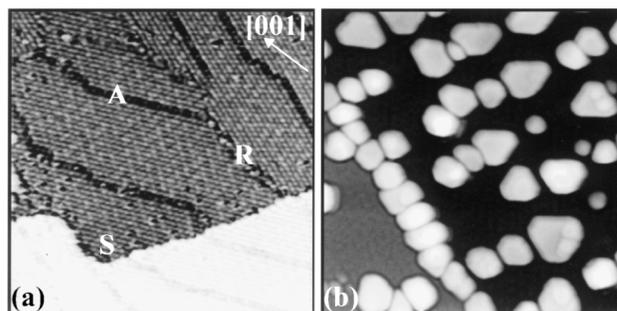


FIG. 1. (a) A STM image ( $500 \times 500$  Å<sup>2</sup>) of the aluminum oxide film formed on NiAl(110) by oxidation. A step edge (S), a reflection domain boundary (R), as well as an antiphase domain boundary (A) are indicated. Tunnel current  $I_t = -0.4$  nA, sample bias  $V_s = -1.3$  V. (b) A  $650 \times 650$  Å<sup>2</sup> image recorded after deposition of  $\approx 2$  ML of Pd at room temperature. Palladium clusters have nucleated preferentially at a step and at domain boundaries. Both crystalline and less ordered clusters are seen.  $I_t = -1.0$  nA,  $V_s = -0.9$  V.

are present on the surface: oxide step edges resulting from atomic steps in the underlying NiAl(110) substrate, domain boundaries between the two reflection domains, and antiphase domain boundaries that are spaced on the average by  $\approx 100 \text{ \AA}$ , and separate oxide areas inside a reflection domain (relieving strain due to mismatch between the film and the substrate). All of these defect sites are preferential nucleation sites resulting in line structures of Pd clusters along the step edges and domain boundaries, as illustrated in Fig. 1(b) and shown previously by Bäumer *et al.* for low Pd coverage [9]. Since low coverage images show Pd nucleation almost exclusively along step edges and domain boundaries, the role of point defects on nucleation is only minor.

The step edges are the most prominent nucleation sites, but well-ordered clusters are rarely found here. On high quality films, i.e., films with large domains, up to  $\approx 50\%$  of the clusters, which have nucleated away from the step edges, appear crystalline in shape as shown in Fig. 1(b). On films of lower quality, a prominent line structure is observed only at low coverage, whereas at higher coverage, the clusters are nearly uniformly distributed. The fraction of well-ordered clusters is much lower, but importantly, the morphology of these clusters is equivalent to that observed for high quality films. It thus appears that the quality of the film is not of crucial importance in the present work.

We first address the atomic-level structure of the nanocrystals. As observed in Figs. 2(a) and 2(b), it is indeed possible to zoom in and obtain atomic resolution on the top layer of the ordered clusters. The atomic arrangement of the top layer facet is seen to be that of a (111) layer, with a nearest neighbor distance (measured as an average over several clusters) of  $d = 2.76 \pm 0.07 \text{ \AA}$ , equivalent to that of the (111) plane of Pd ( $d = 2.75 \text{ \AA}$ ). Thus, there is no evidence of any significant strain in these clusters. This was not to be expected either. Recent measurements based on transmission electron microscopy have shown that, for both Pt and Pd clusters residing on an  $\text{Al}_2\text{O}_3$  film, the lattice constant decreases with decreasing cluster size. For Pd, a lattice constant reduction of 5% was observed for  $12 \text{ \AA}$  clusters [10,11]. The smallest Pd clusters, which we have been able to image with atomic resolution, have a width of  $\approx 40 \text{ \AA}$ , and most of the crystalline clusters are higher than four layers.

It is possible to obtain atomic resolution across the entire cluster surface as shown in Fig. 2(a). At the edge of the top facet, the tunneling current from the tip will change from being drawn from the outermost tip-apex atom to being drawn from somewhere on the side of the tip, frequently resulting in loss of resolution. In a few cases it has, however, been possible to maintain the atomic resolution a few layers down on the larger facets. This is the case for the cluster in Fig. 2(b), where the atomic positions of the uppermost few layers are marked in the lower left corner, clearly demonstrating that the

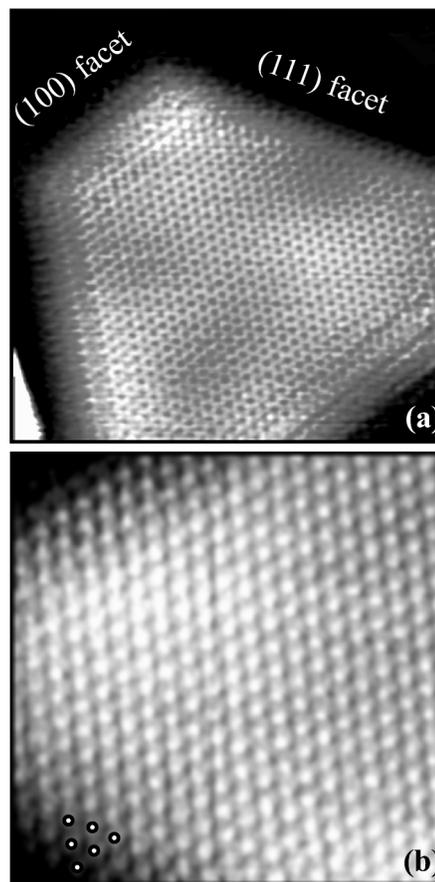


FIG. 2. Atomic-resolution images of crystalline nanosize Pd clusters. (a)  $95 \times 95 \text{ \AA}^2$ ,  $I_t = -0.8 \text{ nA}$ ,  $V_s = -5.0 \text{ mV}$ . (b)  $45 \times 45 \text{ \AA}^2$ . The resolution is kept a few layers down the sides, allowing identification of the side facets. The dots indicate atomic positions consistent with a (111) facet.  $I_t = -1.8 \text{ nA}$ ,  $V_s = -1.5 \text{ mV}$ .

larger side facets are (111) facets. According to the Wulff construction (see below), the smaller facets are (100) facets. The Wulff construction predicts different slopes of the two facets, and the identification of the facets has been confirmed by comparing the apparent steepness of the side facets.

Having identified the crystallographic planes of the nanocrystals, we next address the cluster morphology. Since the apparent shape results from a convolution between the actual cluster and tip shapes, care should clearly be taken when analyzing the detailed three-dimensional shape of the clusters based on STM measurements. Three parameters that characterize the clusters can, however, be measured convincingly from STM line scans: the height, as long as the cluster lies isolated from other clusters, the width of the top facet, and the ratio between the side lengths of the top facet. These parameters have been measured on 45 well-ordered clusters formed by Pd evaporation at room temperature, for coverages from about 0.25 to 2.5 ML, where 0.25 ML was the lowest coverage

at which hexagonal-shaped clusters were observed, and 2.5 ML was the coverage at which a maximum number of hexagonal clusters appeared. The smallest clusters, which we have observed to appear crystalline, have a top facet 20–30 Å across and are 5–10 Å high, corresponding to 2–4 layers. Such small clusters were observed only at low Pd coverage. There was a clear tendency for smaller clusters to have the largest height-to-width ratios (aspect ratios). We interpret this as an indication that initially the clusters grow quite high compared to the width, but when the clusters reach a height about 15 Å, they grow preferentially in width, relaxing towards the equilibrium shape. The height-to-width ratio,  $h/w$ , varied between  $\sim 0.35$  for the smallest clusters and  $\sim 0.15$  for the largest clusters analyzed. However, for the clusters with a top-facet width larger than  $\sim 55$  Å, the height-to-width ratio stabilized at  $0.18 \pm 0.03$ . For these clusters, the ratio of the top-facet side lengths,  $s = s_{100}/s_{111}$ , was  $0.4 \pm 0.1$ .

The equilibrium shape of a *free* Pd cluster can be found from the Wulff construction if the surface energies of the close-packed surfaces are known [12]. For a supported cluster, a similar scheme can be used by replacing the free energy of the surface in contact with the substrate with an effective surface energy,  $\gamma^*$ , which is the difference between the interface energy and the surface energy of the substrate [13]:

$$\gamma^* = \gamma_{\text{interface}} - \gamma_{\text{substrate}}. \quad (1)$$

Thus, for negative values of  $\gamma^*$ , the height of the supported cluster becomes less than half the height of the free cluster. As inferred from the atom-resolved STM images (Fig. 2), the Pd clusters reside on (111) facets. Figure 3 shows how a free cluster of that orientation gets truncated when supported on the oxide with a negative effective surface energy,  $\gamma^*$ . The main facets are (111) and (100), while the (110) facet develops only for larger clusters.

Since the detailed geometry of the supported cluster is determined by the (effective) surface energies, an experimental value of  $\gamma^*$  can be derived from the observed morphology of the clusters. A straightforward analysis leads to the following expression for small clusters, where the (110) facet can be neglected:

$$\gamma^* = \sqrt{\frac{3}{2}} \frac{h}{w} \gamma_{100} - \gamma_{111}, \quad (2)$$

where  $\gamma_{100}$  and  $\gamma_{111}$  are the (100) and (111) surface energies, respectively.

The bonding properties of the cluster to the oxide film can be characterized by the work of adhesion,  $W_{\text{adh}}$ , which is the energy per unit area needed to pull the system apart to its constituents, assuming no plastic or diffusional modifications. The work of adhesion is defined by the Dupré equation:

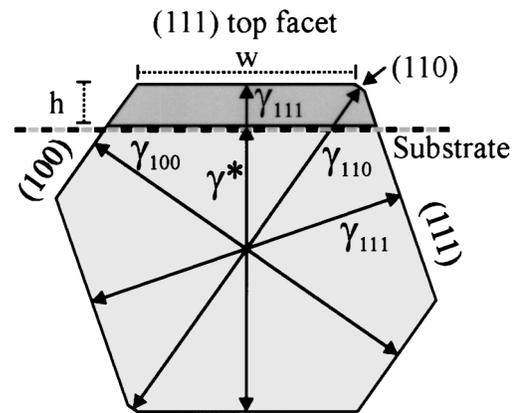


FIG. 3. Cross section of a Pd cluster based on the Wulff construction using theoretical surface energies [14],  $\gamma$ , for the three low-index Pd surfaces. The figure shows the shape of both a free cluster and a cluster supported on a (111) plane, obtained from the modified Wulff construction for a negative value of the effective surface energy  $\gamma^*$ . The (110) facet develops only for clusters with  $w \geq 80$  Å.

$$W_{\text{adh}} = \gamma_{\text{oxide}} + \gamma_{\text{metal}} - \gamma_{\text{interface}} = \gamma_{\text{metal}} - \gamma^*. \quad (3)$$

Introducing a relative work of adhesion,  $\tilde{W} = W_{\text{adh}}/\gamma_{111}$ , we can express  $\tilde{W}$  in terms of the height-to-width ratio  $h/w$  and the ratio  $g = \gamma_{100}/\gamma_{111}$  between the surface energies:

$$\tilde{W} = 2 - \sqrt{\frac{3}{2}} \frac{h}{w} g. \quad (4)$$

Furthermore, if we express the ratio of the surface energies  $g$  in terms of the side-length ratio  $s$ , we obtain the following expression for the relative work of adhesion:

$$\tilde{W} = 2 - \frac{3}{\sqrt{2}} \frac{h}{w} \frac{s+1}{2s+1}. \quad (5)$$

In this way, the relative work of adhesion has been expressed purely in terms of parameters which are experimentally observable. To convert to absolute numbers, the Pd(111) surface energy  $\gamma_{111}$  is needed. Theoretical surface energies derived from density-functional-theory calculations have been published by Methfessel *et al.* [14] and by Vitos *et al.* [15]. For Pd(111) the results were 1.64 and 1.92 J/m<sup>2</sup>, respectively, in fair agreement with values (not orientation specific) derived from experiments [16,17]. Using the theoretical values (which include relaxation) of Methfessel *et al.*, we obtain from the STM data an effective surface energy,  $\gamma^* = -1.2 \pm 0.2$  J/m<sup>2</sup>, and the work of adhesion for Pd on the aluminum oxide film,  $W_{\text{adh}} = 2.8 \pm 0.2$  J/m<sup>2</sup>. Inspection of Eq. (5) reveals that the derived value of  $W_{\text{adh}}$  is robust to minor errors in  $h/w$ . The error bar on  $W_{\text{adh}}$  comprises both statistical errors and a possible systematic error in cluster

height of  $\sim 1\text{--}2$  Å, originating from the compensation for the oxide film thickness.

For most metal-on-oxide systems, the work of adhesion is either unknown or badly determined, and the theoretical understanding of the metal-oxide interface is still quite limited due to the complexity of the system. Studies of trends have been undertaken based on semiempirical cluster and slab calculations (for a review, see Ref. [18]). Only recently have *ab initio* density-functional calculations been carried out by Bogicevic and Jennison [19] on metal adsorption atop a 5 Å oxide film on Al(111). For a full monolayer of Pd on the thin aluminum oxide, a work of adhesion of  $1.7\text{ J/m}^2$  was derived, using the local-density approximation (LDA). For a 4 ML Pd film, this figure changed to  $1.95\text{ J/m}^2$ , while a calculation using the general gradient approximation (GGA) for the exchange-correlation term resulted in a value of only  $1.05\text{ J/m}^2$ .

The values obtained by Bogicevic and Jennison deviate substantially from our experimental value of  $2.8 \pm 0.2\text{ J/m}^2$ . We discuss three possible explanations for this discrepancy: (a) The structure of the ultrathin  $\text{Al}_2\text{O}_3$  film on Al(111) [19] probably deviates from the  $\text{Al}_2\text{O}_3$  film grown on NiAl(110). It is, however, unlikely that a difference in oxide-film structure would influence the morphology of the well-ordered clusters sufficiently to reconcile the large difference between experimentally and theoretically derived energies. (b) Our analysis is based on the assumption that the Pd clusters have their equilibrium shape. In order to stimulate the formation of equilibrium-shaped clusters, deposition of Pd above room temperature was investigated. However, even a moderate increase in temperature by 100 K led to enhanced nucleation at domain boundaries, and to the loss of Pd due to penetration of the oxide film [20] (which in turn may change the interface energy). The experimental results given above refer to crystalline clusters formed by deposition of Pd at or slightly above room temperature. We consider the fact that the Pd spontaneously forms crystalline clusters with well-defined height-to-width ratios and side-length ratios as strong evidence that the clusters are in equilibrium. (c) While the experimentally derived adhesion energy appears well defined, the large dependency of the calculated adhesion energy on details of the computational approach (LDA vs GGA) seems very surprising. A work of adhesion of  $1.05\text{ J/m}^2$  would correspond to a  $h/w$  ratio of  $\sim 0.6$ , 3–4 times higher than the measured values. There is clearly a need for reliable data on other metal-oxide systems to allow for further comparison between experimental and theoretical results.

In summary, we have presented a new method to obtain quantitative values for the work of adhesion of metal clusters on oxides. For Pd clusters deposited on a thin  $\text{Al}_2\text{O}_3$  film created by oxidation of NiAl(110), atomic resolution has been demonstrated on clusters with a diameter above  $\approx 40$  Å, allowing a crystallographic identi-

fication of the cluster facets. Quantitative information on the work of adhesion has been derived from a detailed comparison between the observed shape of the clusters and that resulting from a Wulff construction based on calculated surface energies. For Pd on  $\text{Al}_2\text{O}_3$  we have obtained a value of  $W_{\text{adh}} = 2.8 \pm 0.2\text{ J/m}^2$ . This result is at variance with values recently calculated on the basis of density-functional theory.

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