Morphology and local electronic structure of metal particles on metal oxide surfaces: a scanning tunneling microscopic and scanning tunneling spectroscopic study

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Abstract

Metal particles (Au, Pd and Ni) with an average diameter between 7 to 100 Å have been prepared on thin metal oxide films (TiO₂, MgO and Al₂O₃), epitaxially grown on refractory metal substrates (Mo(100) or Re(0001)), and imaged using scanning tunneling microscopy (STM). Information regarding the local electronic structure has been obtained using scanning tunneling spectroscopy (STS). Controlled manipulation of the metal particles with the STM tip is also demonstrated.

1. Introduction

Since its invention by Binnig and Rohrer in 1982 [1,2], scanning tunneling microscopy has been widely used to study the geometric structure of various metal and semiconductor surfaces with Å resolution ([3] and references therein). These studies have provided considerable new insights into the chemistry and physics of solid surfaces. The ability to access the local electronic structure makes STM a unique and powerful method in comparison to other scanning microscopies such as scanning electron or atomic force microscopies.

Metal particles containing from several to a few hundred atoms supported on metal oxide surfaces are of both fundamental and practical interest because of their wide use in catalysis, electronic devices and sensor applications [4,5]. However, the large bandgap of most metal oxide supports (7.8 eV for MgO and 8.7 eV for Al₂O₃) prevent the use of STM to study metal particles supported on these surfaces. In order to circumvent the problems associated with the poor conductivity of metal oxides, thin metal oxide films, grown epitaxially on refractory metal substrates, have been utilized in our laboratories to support metal particles for a variety of surface science investigations [6,7] including STM and STS studies. In this report, we present STM and STS results for Au, Pd and Ni particles supported on TiO₂(001), MgO(100) and Al₂O₃(0001) films.

2. Experimental

The experiments were carried out in an ultrahigh vacuum (UHV) chamber (base pressure ~ 1 × 10⁻¹⁰ Torr) equipped with a UHV-STM (Omicron) and
capabilities for Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and temperature programmed desorption (TPD). The metal oxide films were prepared by vapor depositing the metal precursor onto refractory metal single crystal surfaces (Mo(100) for TiO$_2$ and MgO, Re(0001) for Al$_2$O$_3$) in a controlled oxygen background. The films were subsequently annealed to 1000–1200 K in an O$_2$ background to improve their crystallinity. These metal oxide films have been extensively characterized in our laboratories [6,7] with respect to their stoichiometry, oxidation states and long-range order using the full complement of surface science techniques. Metal particles were then vapor deposited onto the oxide film surfaces at 300 to 350 K.

3. Results and discussion

Fig. 1 shows three STM images of 1.8 monolayers (ML) of Au on a 2.0 ML TiO$_2$ film (top, 2 V, 0.5 nA), 1.2 ML Pd on a 8.0 ML MgO film (middle, 4 V, 0.5 nA) and 0.04 ML Ni on a 3.6 ML Al$_2$O$_3$ film (bottom, 5 V, 0.2 nA). In each of these three cases, hemispherical metal particles with a narrow size distribution are apparent. On the Au/TiO$_2$/Mo(100) surface, a corrugation of significantly larger scale (alternating bright and dark areas) is also observed in addition to the corrugation due to the Au particles. The average height difference between the bright and dark areas is ca. 8 Å and can be attributed to the corrugation of the TiO$_2$/Mo(100) support. While the dark areas correspond to Au supported on MoO$_x$, the bright areas are due to Au clusters supported on TiO$_2$. It is noteworthy that the Au particle density on TiO$_2$ is higher than that on MoO$_x$, consistent with a stronger interaction between Au and TiO$_2$ than between Au and MoO$_x$. The average Au particle diameter is ca. 25 Å, with an average height of 12 Å. For Pd on MgO, the particles have an average diameter of 30 Å and a height of 9 Å, indicating a much flatter profile for the Pd particles than the Au particles. This result is consistent with the anticipated stronger interaction between Pd and MgO compared to that between Au and TiO$_2$. For 0.04 ML Ni on Al$_2$O$_3$, the particle diameters range from 7 to 16 Å. Most of the Ni particles have a height of only 3 Å, corresponding to one atom layer height, while a small fraction has a height of 6 Å. It should be noted that the Ni particles are relatively stable under our scanning conditions (5 V, 0.2 nA); no apparent changes were observed even after several consecutive STM scans.
Because of the inherent relatively weak interaction between the metal particles and the oxide supports of this study, one might anticipate that the metal particles could be easily manipulated with the STM tip. Also the use of a metallic STM tip, e.g. W, might lead to spillover of the metal cluster onto the STM tip upon close approach. Both phenomena were indeed experimentally realized and are demonstrated in Fig. 2, which provides two sets of STM images before (left) and after (right) the tip has approached the Ni clusters marked with an arrow. The close approach in each case was executed by applying a bias voltage of 2 V and a feedback current of 3 nA within a $30 \times 30 \, \text{Å}$ topographic scan directly above the particles noted by the arrows. It can be seen clearly that the Ni clusters marked with the arrows have been removed or moved by the STM tip. It is also apparent that double or ghost images are observed subsequent to the Ni particle manipulation. For example, every particle in the upper-left image has a twin particle in the upper-right image, while the particles in the bottom-left image have twin particles in the lower-right image. A ghost-free image can be achieved subsequently by an in-situ re-sharpening of the STM tip by applying a pulse bias voltage of up to 8 V. It is also clear in Fig. 2 that the metal particles located above, below, and to the left of the removed particles show no change in the

![STM images](image_url)
apparent size and shape before and after removal of the designated particle. However, the images of the particles located to the right of the removed particles are significant altered. For example, particles 3 and 4 are closest to the removed particle compared to any other particles in the bottom two images, however, these particles are not modified upon removal of the designated particle. In contrast, particles to the right, although located further away from the removed particle, are strongly modified upon removal of the designated particle. Fig. 3 shows line-profiles of the particles labelled as 1 and 2 in the top images. While particle 1 shows a clear increase in the apparent particle height and diameter subsequent to removal of the indicated particle to its left, particle 2 shows no significant change in the particle size and shape (which is also true for all other particles in these images). Assuming a hemispherical shape for the particles, the calculated volume increase of particle 2 after removal of the indicated particle can account for all the volume loss associated with the removed particle. Since the STM images are taken with the STM tip scanning from left to right in our experiments, these results imply that the STM tip transferred some of its mechanical energy to the particles causing them to move. The STM tip simply acts as a 'broom' to sweep the particles from left to right, pushing the particles onto the adjacent particle which serves as a trap or nucleation center. Apparently during the particle manipulation, either some of the

Fig. 3. Line-profiles of the two Ni-particles in the top STM images of Fig. 2.

Fig. 4. STS spectra (right) and the corresponding topographic scan (300 × 300 Å).
atoms of the particle are transferred to the tip or mechanical deformation of the tip occurs resulting in the subsequently observed ghost images.

STS measurements were also carried out on the Ni particles at 0.1 ML coverage supported on 3.6 ML Al2O3. These results are displayed in Fig. 4 with the corresponding topographic scan (300 × 300 Å, 5 V bias, 1.5 nA). The STS data were acquired during the topographic scan by stopping the scan at selected pixels, interrupting the STM feedback loop, then sweeping the bias voltage through the region of interest. The topographic scan can be used to correlate the STS curve with a particular geometric feature and, as well, provides a check for tip stability during the measurements. Four I–V curves are shown in the right panel of Fig. 4; these were averaged over 8 (area 1), 156 (area 2), 140 (area 3) and 8 (area 4) points within the square areas indicated in the topographic scan.

Curves 2 and 3, acquired for the Al2O3 substrate, show a bandgap of ca. 6 eV, consistent with the insulating nature of the Al2O3 film. However, the bandgap indicated by STS is significantly smaller than the Al2O3 bulk bandgap of 8.7 eV, but consistent with previous ELS measurements which show a surface bandgap of 6 to 7 eV for Al2O3 [8]. This reduction in the surface bandgap from that of the bulk has been attributed to the lower coordination of the surface atoms compared to the bulk atoms [8] and reduced Madelung potential on the surface.

Area 3 in Fig. 4 is ca. 3 Å recessed compared to area 2, and corresponds to a single step in the Al2O3 film. A much deeper step (ca. 9 Å) around area 1 is also seen in Fig. 4. STS (I–V curve 1) of area 1 shows a non-zero current at 0+ and 0− bias voltage, indicating metallic character within this area. Area 1 thus likely corresponds to the Re substrate, which is either covered with chemisorbed oxygen or is in the form of ReO3, a metallic oxide.

An I–V curve acquired for a Ni cluster with a diameter of 15 Å and a height of 6 Å is also shown in Fig. 4 (curve 4). Very similar I–V curves were obtained for other Ni-clusters of comparable sizes, all indicating a bandgap of ca. 0.6 eV near the Fermi-level. Several mechanisms can give rise to an apparent band gap in the I–V curve. For metal particles supported on an ideal insulating oxide support, no tunnel current should be observed for a bias voltage smaller than the bandgap of the oxide substrate. In very thin oxide films, however, charge on the metal particles can be dissipated into the metal substrate via tunneling through the thin oxide film. Depending upon the magnitude of the tunneling through the oxide film compared to the tunnel current used in the STM measurements, an apparent bandgap could be observed for metal particles with diameters comparable to the oxide thickness. In order to rule out this possibility, I–V curves were measured for identical Ni clusters at various tunneling currents (0.1–1 nA). No change was observed for the measured band gap with variation in the feedback current. These results indicate that electronic charge dissipation is a relatively fast process under our experimental conditions and that the observed band gap cannot be due to the oxide substrate.

A second possible explanation is that the apparent bandgap is due to a coulomb blockade [3]. However, a coulomb blockade should either give rise to a staircase behavior in the I–V curve for single electron charging, $e^2/2C$, that exceeds $kT$ or the I–V curve will be smeared out when $kT$ is greater than $e^2/2C$ [9,10]. In the present experiments, only a single step near the Fermi level is observed at either negative or positive bias voltage up to 4 eV under various conditions. Therefore, in the present studies the observed band gap is dominated by an intrinsic depletion of the density of states near the Fermi level within the small Ni particles. Such band gaps have been observed previously by First, et al. [11], for Fe particles on the GaAs(110) surface and by Suzuki and Fukuda [12], for Al particles on the GaAs(110) surface. The cause of this depletion of the density of states can either be due to quantum size effects [11,12] or to spillover of the oxide (or oxygen) from the support to the metal particles. However, the magnitude of the bandgap measured here is much smaller than the bandgap of NiO (4.3 V) and most consistent with that expected for quantum size effects [11,12].

In summary, the feasibility of using thin metal oxide films to support metal particles for STM imaging has been demonstrated. Metal particles containing from < 10 atoms to several hundred (see Fig. 1c) have been successfully imaged and shown to be stable under our imaging conditions. This work also has shown that STS measurements can provide infor-
mation regarding the electronic structure of isolated features in the STM image. Furthermore the controlled manipulation of metal particles on oxide surfaces using an STM tip has also been demonstrated.

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References