RHK Technology Brief

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# *In situ* Scanning Tunneling Microscopy of Individual Supported Metal Nanoclusters at Elevated Pressures and Temperatures

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Solid-state gas sensors and heterogeneous catalysts often consist of nanometer-sized metal particles on an oxide support, the former being the chemically active element. Because model catalyst studies often rely heavily on traditional surface science techniques, many important effects cannot be simulated comprehensively, due to the requirement of operating in UHV conditions. These limitations have stimulated efforts during the last decade to bridge the so called "pressure gap", and have resulted in the development of spectroscopic and imaging techniques for studying model catalysts in situ under elevated pressures and temperatures approaching realistic reaction conditions[1-5].

The goal for developing in situ scanning probe microscopy methods for studying the size-dependent chemical and physical properties of nanoparticles can be succinctly stated: to image with near atomic resolution a pre-selected area of the model catalyst during pressure and temperature excursions over a wide dynamic range. A major challenge for in situ STM studies is the inherent sensitivity of the tunneling process to minute disturbances at the tunnel junction due to tip and/or sample instabilities, or other ambient factors, e.g., noise transmittance, piezo creep etc. An additional complication is that often, the metal nanoparticles adhere only weakly to the oxide support leading to tip-induced particle mobility or bonding of the imaged particles to the tip. The presence of chemically active gases in the chamber may accelerate these processes.

In our lab, we have used RHK's UHV 300 STM system to develop a strategy for monitoring the evolution of individual oxide supported nanoparticles in situ during their growth, alloying, high temperature annealing and "real world" chemical treatment[6,7]. The RHK system has three important features that enabled

the successful realization of this project, namely: ultra-low current imaging (pA range), excellent mechanical and thermal stability, and most importantly, the Besocke-type design of the scanning stage, which enables in situ metal particle deposition.

## Reducing the Tip-Particle Interaction

Low current imaging conditions (and chemically inert tips) are crucial to minimize tip-particle interactions during pressure and temperature excursions. RHK's two stage preamplifier (IVP 200 or IVP 300 and IVP PGA) provides the capability to scan poorly conducting surfaces with large tunnel-junction impedances (50 - 100 G-0hm), ensuring a large tip-sample separation. In addition, the RHK SPM 100 control system provides the capability to perform in situ tip conditioning using well-defined voltage pulses, an important feature that enables the gentle removal of particles from the tip without straying from the area of interest.

## Indexing the Surface

Targeting individual particles during (or after) high-pressure or high-temperature treatments, can be carried out by nanoscale indexing of a region of the surface during deposition. This is achieved using a technique developed by our group that utilizes the STM tip, in tunneling range, as a mask during particle deposition (**Figure 1**). The wedge-shaped depleted zone created by the tip "shadow" is then a reference marker for returning to areas of interest after chemical (or any other) in situ treatments. The open design of the RHK UHV 300 facilitates easy access to the tunneling region, allowing 360 degrees (excluding piezos areas) for azimuthual access, and approximately 45-80 degree access with respect to the sample normal. Precisely positioned mini-dosers for metal deposition, mounted around the scan head on adjustable ports, were used to direct well-collimated atomic beams onto the tunnel junction region. Careful positioning and beam collimation are crucial to the delivery of metal atoms to the tunneling junction and for avoiding metal deposition onto the piezo scan head.

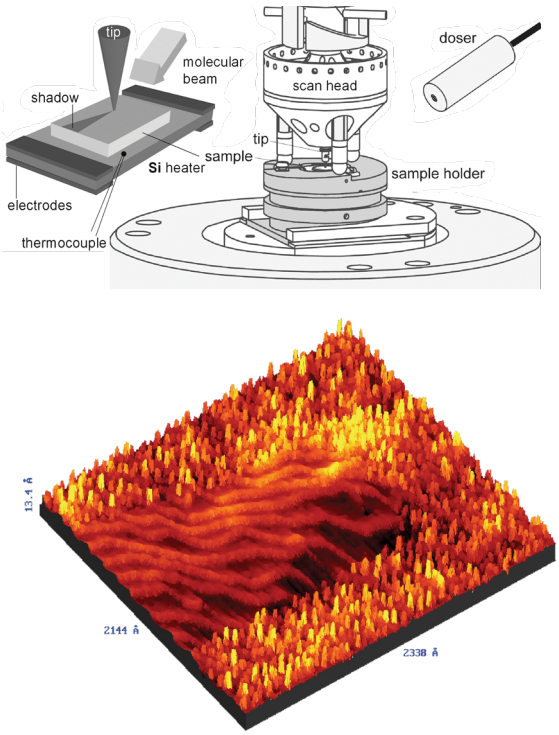


**Figure 1:** *Deposition scheme and sample assembly for surface nanostructuring using the "shadowing"technique. The STM tip is used as a mask for metal deposition at grazing angle and creates a "silhouette" nano-structure on the oxide surface. In the bottom image ca. 1.5 ML of Ag was deposited onto TiO2 (110).*

In addition to creating a fiducial mark for in situ studies of individual nanoparticles, the tip shadowing technique may also be used during deposition as a precisely controlled nano-mask (**Figure 1**) for the creation of more complex materials. This allows for the synthesis and direct comparison in situ of laterally separated, compositionally different nanostructures (see **Figure 2**) simply by tuning the geometry of the deposition setup and/or changing the deposited material. Unexposed (shadowed) areas containing exclusively Ag clusters, remain intact (top part of the **Figure 2B**) and distinctly separate from that part of the surface with pure Au and Ag-Au mixed clusters. By monitoring changes in the nucleation density and cluster size for the Ag-Au exposed area, the nucleation and growth kinetics as well as the morphology

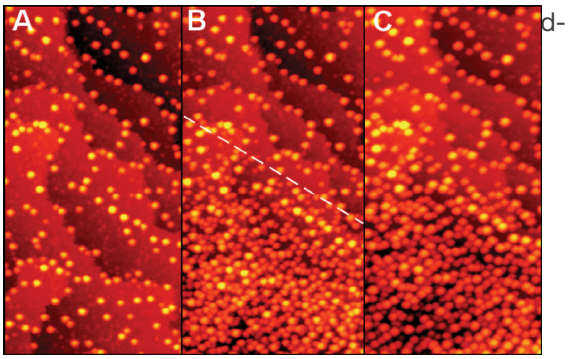


**Figure 2:** *A) TiO2 (110) surface covered with ca. 0.3 ML of Ag at room temperature in UHV. B) The same area where ca. 2 ML of Au was deposited onto Ag/TiO2 using the tip as the mask. The edge of the mask is marked with the dashed curve. Top area contains exclusively Ag nanoparticles, while the bottom contains newly formed Au clusters in between mixed Au-Ag clusters. C) The same area as in B imaged in situ at 7 Torr after 30 min of D2O exposure.*

## Imaging at Elevated Pressures

Using the approach described here, the complex problem of catalyst/sensor deactivation under environmental or reaction conditions can be addressed (see **Figure 3**). This is accomplished by slowly feeding a gas, or a mixture of gases (<0.05 Torr • l/s) into the imaging chamber with the STM tip partially retracted and parked at a pre-selected location. Alternatively, the tip can be left in tunneling range during the exposure. However, in the latter case, extra care is required with respect to the Z offset, to prevent a tip crash during the pressure excursions. There are several sources of tip/sample displacement due to changes in pressure. First, during the limited range ($10^{-10}$-5x10-5 Torr) of pressure excursion, there exists an onset (at approximately 10-6 Torr) where charged particles produced within poorly shielded regions of the chamber contribute to the tunneling current, and thus influence markedly the height of the STM tip operating in constant current mode. Secondly, although the elevated pressure scan is carried out at a constant sample temperature, modifying the thermal conductance of the sample environment changes the rate of heat dissipation at the sample stage and scan head. This, in turn, causes significant X, Y, and Z drift of the tip with respect to the pre-selected

location. For the UHV 300 sample stage used in our study, the lateral shift of the tip position was limited to ca. 2 microns for eleven decades of pressure change within the temperature range 300-450 K. Such an offset can easily be compensated for by indexing the surface using the "shadow" technique. Third, when gases (water vapor, for example) are used at pressures above their room temperature condensation point, microdroplets of the condensate can form between the X, Y, Z, and ground segments of the piezo elements. As a consequence, new conducting and/or capacitive coupling channels can be formed between the metalized segments of the piezo tubes. The latter causes crosstalk due to leakage currents between the different scanning/offset segments of the piezo tubes and in the signal circuit. Neither reliable tunneling nor meaningful scans can be performed under these conditions. In addition, electrical discharge can develop between neighboring metalized segments on the piezo tubes due to the inhomogeneity of the electrostatic field between them and the reduced dielectric strength of the condensate Electrical breakdown can occur within a certain range of gas pressures when sufficient voltages are present on the piezo tube and/or feedthroughs. The breakdown is, of course, dependent on the gas, potential difference between electrodes, the material, and the spacing. For the RHK SPM 100 control electronics used in this study, the potential difference between electrodes can be as much as 260 volts, a potential that exceeds the minimum breakdown voltage for a variety of gases. For most gases the "saddle" portion of the Paschen's curve corresponds to the product of pressure p and distance d at a value of ~.01–10 Torr•mm. Therefore, in situ imaging can be problematic for certain gases at pressures of 0.1-10 Torr due to the inter-electrode spacing for the piezos and feedthroughs of a typical microscope. In our experiments, the use of Ar, N2, CO, O2, and air, led to discharge phenomena within the pressure range 10-2-1 Torr. These discharges give rise to fluctuations in the offset potentials on the piezos. A practical solution to this problem is to interrupt imaging within the "dead" pressure region and reduce the voltage on the piezo elements well below that of the near Paschen's minimum.

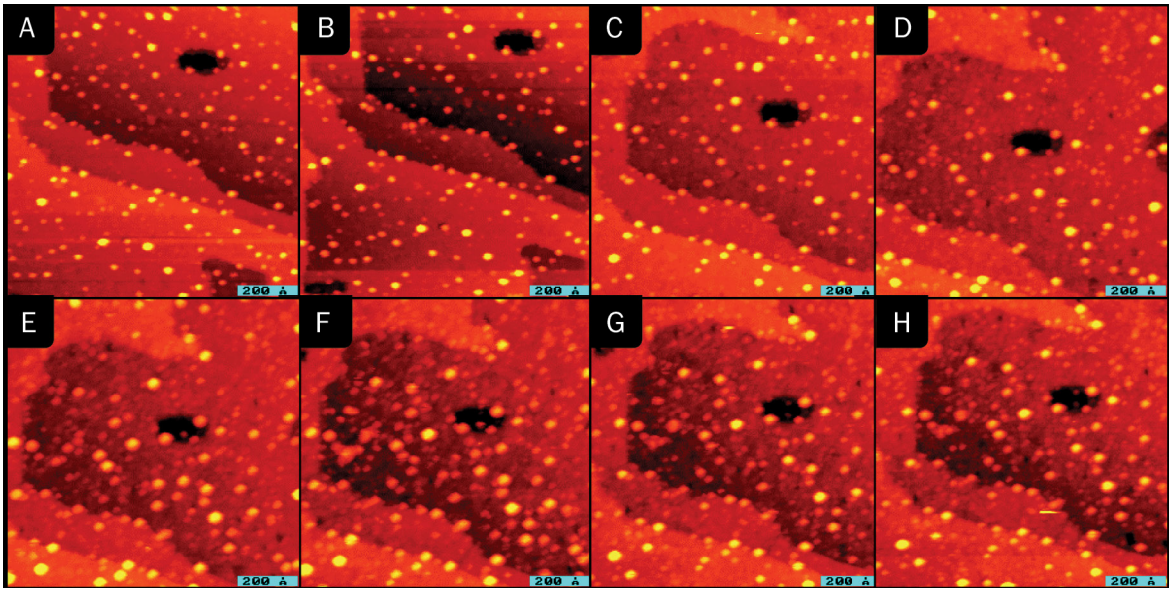


**Figure 3:** *The same area of a Au nanoparticle covered TiO2 sample is shown under UHV conditions and under CO oxidation (CO:O2 1:1) reaction conditions at 450 K. (a) 5x10-10 Torr, (b) 2x10-6 Torr, (c) 2.7 Torr, (d)-(h) 5.4 Torr. Although the particles on the surface in (a) are stable at UHV, elevated pressure CO:O2 treatment leads to changes in cluster size, density and substrate morphology.*

If atomic resolution is not required, an increase in the acoustic noise upon pressurizing the chamber is accommodated if the feedback-loop time constant is increased. Finally, in addition to any tip instabilities that may be caused by the gas, one must also consider restructuring of the imaged surface at elevated pressures, tip induced (electro) chemical reactions, and related imaging artifacts. Furthermore, for condensable gases, meniscus formation at the tip must be accounted for when imaging at elevated pressures. Using this method, a comparative study of the effect of elevated water and air exposures on Ag, Au, and Ag-Au nanoparticles was conducted.

In **Figure 4 (A,B)**, STM images of the mixed-metal Ag-Au/TiO2 system discussed in the previous section are shown: (B) as prepared in UHV, and (C) the same Ag, Au, and Ag-Au mixed clusters during exposure to 7 Torr of D2O vapor for 30 min. at room temperature. Comparing these two images, no remarkable changes can be seen for the Ag, Au, or Ag-Au mixed clusters, indicating the stability of the interface toward this particular elevated-pressure treatment. The morphology of this complex Au-Ag/TiO2 surface changes dramatically as the water vapor pressure reaches its saturation value at room temperature or as the sample is exposed to ambient conditions **(Figure 4**).

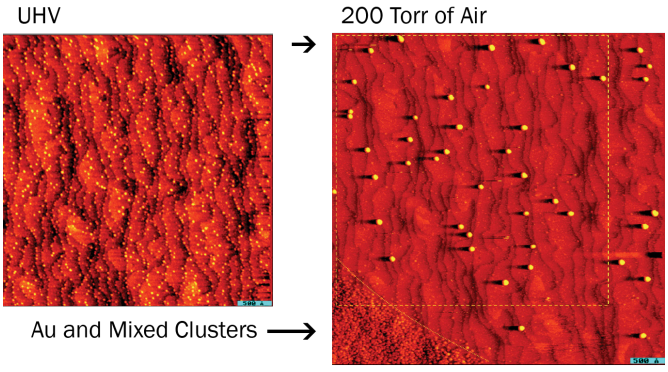


**Figure 4:** *Left: Ag precovered TiO2 (110) surface under UHV. On the right: the same surface with Au post deposition using tip as a mask exposed to 200 Torr of ambient air with approximately 70% humidity. As can be seen, Au and Ag-Au mixed nanoparticles (bottom left corner of the image) remain intact with gas treatment. On the other hand, Ag clusters exhibit remarkable sintering.*

## Thermal Excursions

The axial symmetry of RHK's UHV 300 scanning stage provides natural first order thermal drift compensation in the scanning plane. This design feature, combined with "tip shadow" indexing of the surface, facilitates the re-location of a pre-selected area, even after high temperature treatments. Although this temperature excursion method is an extension of the "snapshot" approach, **Figure 5** illustrates the power of this method and the advantages it has over in situ elevated temperature STM studies.

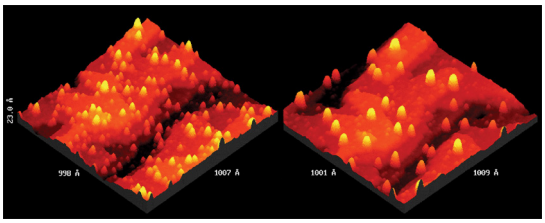

**Figure 5:** *(a) and (b), the same area of Au-covered TiO2 is shown before and after annealing to 950 K for 30 minutes. Dramatic morphology changes are observed upon heating, the major effect being cluster sintering.*

Specifically, (i) the same area can be probed over a wider temperature range where other commercial scanning tunneling microscopes cannot operate for extended periods; (ii) kinetic processes can be initiated and interrupted at any stage by changing the temperature (this latter advantage is not an option for isothermal high temperature studies which require an extended period in order to establish acceptably low thermal drift for STM imaging); and (iii) the lateral movement of clusters is not disturbed by tip proximity which is a significant problem for in situ high temperature STM studies on oxide-supported nanoparticles.

## Acknowledgements

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