Scanning Tunneling Microscopy / Spectroscopy of supported Pd and PdO nanoparticles deposited by Pulsed Laser Deposition

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Recent years have seen a rising interest in the study of surface properties of metal and metal-oxide nanoparticles according to their use in a wide range of applications as heterogeneous catalysis, magnetic nanostructures and gas sensing devices.

In particular atomic clusters supported on different substrates represent an interesting system for the study of cluster structural and electronic properties by means of scanning probe microscopies or advanced spectroscopic techniques.

A fact which is very attractive in this field is certainly the transition of these properties when going from bulk to small clusters. Since these differences are expected to affect the catalytic behaviour of a given material, the investigation of the basic mechanisms of catalysis and their dependence on the structure and size of the clusters are of great interest to those who investigate catalytic processes.

We here report on the pulsed laser deposition, in situ Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS) investigation of supported Pd and PdO clusters produced by means of nanosecond Pulsed Laser Deposition (PLD), on different surfaces. The main peculiarity of in situ measurements is that the coupled system PLD-STM allows the transfer of the samples from the preparation chamber to the analysis chamber without exposing them to the atmosphere pressure and the contaminations of the air.

Among other deposition techniques, nanosecond PLD can be successfully employed for the synthesis of clusters and nanostructured films with a great versatility in terms of structure, chemistry and morphology of the deposits. In fact, depending on the substrate and the deposition parameters (background gas pressure, target-substrate distance) it is possible to obtain different growth regimes, as surface modification, random paving or self-organization of clusters on the surface.

The PLD flexibility in the production of clusters with different size and the possibility to realize nano-patterns constituted by self-organized clusters on a surface may be of interest e.g. in view of nanoelectronic applications.

Different depositions were performed on Au(111) and Al$_2$O$_3$/NiAl(100) substrates. Deposition in the presence of an inert background atmosphere (Ar in the 1-100 Pa range) results in the soft landing of the ablated species. In such conditions Pd clusters self-organize on the Au(111)-22x$\sqrt{3}$ herringbone structure in aligned parallel nanostripes (Fig. 1). The morphology of the observed patterns (cluster density, size and alignment) has been investigated as a function of deposition parameters. When increasing the deposited material, Pd clusters tend to self-organize in zig-zag structures which reproduce the underlying Au(111) herringbone structure.

On the other hand, when deposition is performed in an oxygen containing atmosphere, palladium oxide clusters are obtained, as revealed by Scanning Tunneling Spectroscopy (STS) and confirmed by Raman spectroscopy measurements on thin films. In this case no self alignment is observed (Fig. 2).
STS is used also to investigate modifications of the substrate surface states consequent to cluster deposition. This technique, by virtue of the very high lateral resolution, is proposed as a complementary source of valuable information with respect to conventional electron spectroscopy.

Depositions of Pd/PdO on Au(111) represent a simplified, preliminary study to a more complex model catalysis experiment: in a real catalyst the support material is usually not catalytically active by itself but is rather chosen for its thermal stability at high temperatures under reaction condition. Frequently used support materials are Al₂O₃, SiO₂ and TiO₂.

In the present work the initial stage of oxidation of ultra-thin films of Al₂O₃ grown on NiAl(100) surface have been investigated on the basis of STM and STS measurements. The main result is the identification of two different growth regimes: microscopically rough areas of amorphous Al₂O₃, alternating with a network of elongated oxide stripes along well defined directions with respect to the NiAl(100) surface. Such epitaxial oxide film can be used in the future as a “more real-like” support for Pd and PdO clusters deposited with PLD system.

**Fig.1.** STM image of Pd clusters self organized on Au(111) herringbone structure, forming parallel nanostripes.

**Fig.2.** STM image of PdO clusters on Au(111).

**Fig.3.** STM image of NiAl(100) surface after exposure to 10L oxygen at room temperature.