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Electrical and holographic characterization of gold catalyzed titania-based layers

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Abstract

The sensing properties of titanium oxide have been tailored through doping with niobium and dispersion of nanosized Au particles. The microstructural features of the gold-titania composite system were investigated by transmission electron microscopy and the electronic properties of Au nanoparticles were specifically investigated by electron holography. Holography provides quantitative determination of the mean inner potential with the high spatial resolution attained by transmission electron microscopy. Large increase of the mean inner potential has been measured for ultra small Au particles arising from the nano-scale assembling. Electrical tests were performed at low operating temperatures and demonstrated the considerable enhancement of CO sensitivity owing to the extremely high catalytic activity of gold particles.

Keywords: Electron microscopy; TiO_2; Sensors

1. Introduction

The fascinating and unusual properties of nanostructured materials stimulated the development and the technological exploitation of materials with characteristics that cannot be obtained in homogeneous bulk systems. In particular, the development of chemical sensors based on nanostructured semiconducting metal-oxides offers the opportunity for investigation of fundamental phenomena and fabrication of devices.

The nano-scale assembling of the material and the subsequent modification of the physical properties should be thoroughly investigated by highly spatially resolved techniques. For a proper structural characterization, transmission electron microscopy (TEM) offers the capability to investigate the local atomic arrangement of atoms with unrivalled spatial resolution. As a technique complementary to TEM, electron holography has been recently pursued to the study of nanostructured materials and to the measurement of local modification of physical properties. Indeed, holography allows measurement of local variations in the electronic configuration of the material, surface charging effects, presence of electric or magnetic fields.[1] Electron holography allows for the measure of the mean inner potential (MIP), i.e. the electrostatic potential averaged on the unit cell of the crystal lattice.

In this work, Au-TiO_2 layers were prepared by chemical vapor deposition with the purpose of tailoring the electrical and gas-sensing properties. Among the noble metals used for heterogeneous catalysis, bulk particles of gold do not favor surface adsorption of reactants. However, gold was recently demonstrated to be very efficient for oxidation or hydrogenation processes, the catalytic properties being activated by a nanometric particle size[2] between 2 and 10 nm. In particular, extremely high activity for CO oxidation was recorded at low temperature. TiO_2 was demonstrated to be more active than other supporting materials, such as alumina or zirconia. The established catalytic activity in CO oxidation processes envisages interesting gas-sensing behavior.[3–7]

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Introduction of Nb dopant in TiO_2 will also be discussed. An increased electrical conductance is expected for the Nb-doped films, with the expectation to overcome the low number of free charge carriers typical of pure titania. This characteristic limited the low-temperature operation of TiO_2 up to now.[8,9]

We have therefore undertaken a research plan to investigate Au-titania thin-films for low-temperature sensing of CO. The microstructural features of the composite system was investigated by electron microscopy, while the electronic structure of single Au clusters was characterized by electron holography.

2. Film preparation

Preparation of the layers was carried out by a two-step procedure: titania-based thin films were deposited and stabilized by thermal treatment. Then, dispersion of gold nanoparticles was performed. For a comparative investigation of the effects of Nb-addition and gold-catalysis, pure films of TiO_2 were also prepared maintaining the deposition parameters.

Either pure or Nb-doped titania was prepared by reactive magnetron sputtering starting from metallic target of Ti or Ti-Nb. Deposition was carried out in reactive Ar/O_2 atmosphere with a substrate temperature of 300 °C. The titania layers were stabilized through annealing at 600 °C in air before dispersion of the Au catalyst.

Gold was deposited out by RF sputtering in inert Ar atmosphere. The operating parameters, i.e. substrate temperature, operating pressure and dc sputtering power, have been carefully adapted in order to achieve the highest surface coverage with fine Au particles. A uniform dispersion of grains, averaging 4 nm in radius and even as small as 1 nm, has been obtained. Longer deposition times do not improve the dispersion of gold over titania but promote the formation of large polycrystalline gold agglomerates.

Fig. 1 summarizes the microstructural features of the titania-based nanocomposites, as determined by TEM analysis. Formation of nanosized TiO_2 anatase films was achieved, irrespectively of the presence of Nb. Rutherford Backscattering spectroscopy measured a Nb/Ti atomic ratio of 0.24 ± 0.02. Measurement of the oxygen content (2.7 ± 0.3 with respect to Ti) indicated that the layers are stoichiometric, assuming a +5 valence state for Nb. The amount of Nb is below the solubility limit (about 5%) in titania, and the thermal treatment did not result in surface segregation of Nb and nucleation of mixed Nb-Ti-O oxides. Nb ions, substitutionally soluted to Ti, are therefore expected to increase the electrical conductivity, acting as donor-dopant.[8]

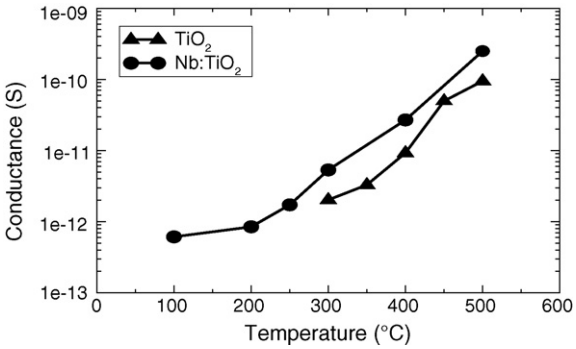

Fig. 2. Comparison between the conductance in air for the film of pure TiO_2 and Nb-doped TiO_2.

3. Sensing of CO at low temperature

The gas-sensing properties of the layers were tested using the conventional flow-through technique. All measurements were executed in a temperature-stabilized chamber at 20 °C under controlled humidity.

Preliminary measurement of the electrical conductance in air showed the effect of Nb doping, as illustrated in Fig. 2. The electrical conductivity is significantly increased, allowing exploitation of the sensing behavior at a low-temperature regime.

Fig. 3 reports the response of the Nb-doped TiO_2 and the Au-catalyzed Nb-doped TiO_2 layers to different CO concentrations. The response R has been defined as the relative variation of the

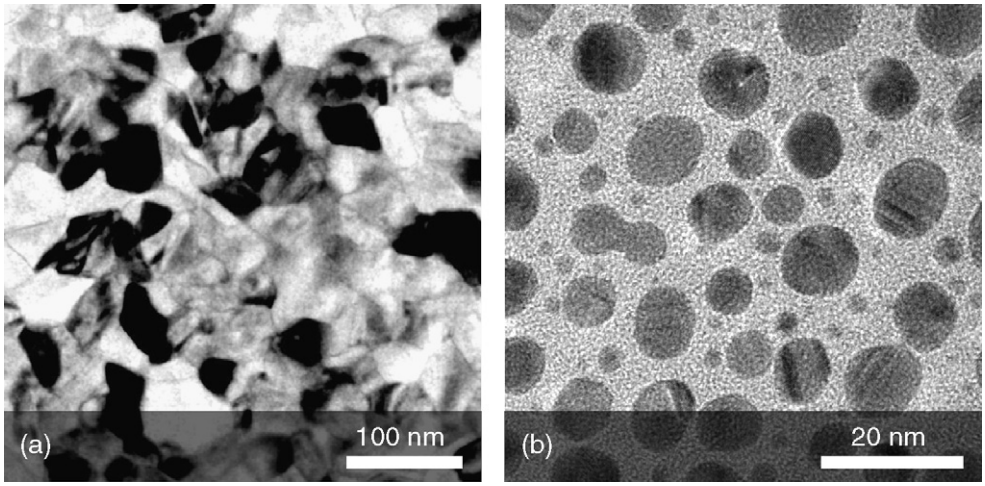

Fig. 1. TEM images of the TiO_2-based composite film: (a) the polycrystalline TiO_2 anatase layer stabilized by Nb; (b) planar view of the dispersion of nanostructured Au particles.

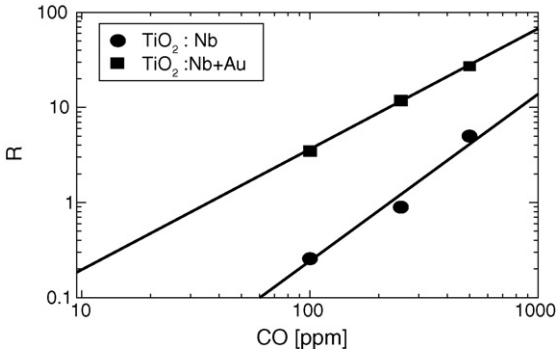

Fig. 3. Response of Au-doped Nb:TiO_2 and Nb:TiO_2 films to several CO concentrations at 300 °C operating temperature.

film conductance:

$$R = \frac{G_{\text{gas}} - G_0}{G_0} \tag{1}$$

Nb doping shifts the figure of merit down to lower temperatures, but does not promote significantly the sensitivity to CO. Fig. 3 shows that the enhancement of CO sensitivity arises from the catalytic effect of gold.

The highest sensitivity is achieved at 200–250 °C, a temperature not usually employed for CO sensing, as the typical detection range is 300–400 °C. A very low detection limit may also be envisaged for this film.

The catalytic properties of Au particles greatly enhance the response towards CO irrespective of the presence of Nb. Au-doped Nb:TiO_2, featuring fast response and recovery (about 1–2 min), appears to be promising for low-temperature application.

In summary, electrical tests highlighted a considerable improvement of titania-based layers due to Nb doping and the catalytic effect of Au. The Au-Nb:TiO_2 sample with the highest sensing performances also also exhibits the finest dispersion of Au. By increasing the Au coverage, the response to CO resulted lower. These evidences suggest that the effect of gold is mainly related to the size of the nanoparticles rather than to the overall content.

4. Electron holography of gold particles

TEM is an excellent tool to investigate structural properties of nanoparticles, but does not provide directly information on the electronic properties. Since it has been proposed that the interesting properties of gold may arise from a confinement of the electronic charge in small clusters, we implemented the advanced technique of electron holography to investigate this feature.

When the electronic beam interacts with the specimen, the phase of the wave associated to the electron beam is shifted. The phase shift $\Delta\varphi$, in absence of free charges and magnetic fields, is proportional to the product of the MIP, V_0, and the projected specimen thickness, t:

$$\Delta\varphi = C_{\text{E}} V_0 t \tag{2}$$

where C_{E} is an interaction constant, which depends only on the energy of the incident electrons.[1]

The MIP is a volume average of the electrostatic potential over the unit cell of the infinite crystal lattice and, assuming spherically symmetric atoms, can be written as the second moment of the electric charge over the atomic volume:

$$V_0 = \frac{1}{\Omega}\int_{\text{cell}} V(r)\,\mathrm{d}^3 r = -\frac{2\pi}{3\Omega}\int_{\text{atom}} r^2 \rho_{\text{a}}(r)\,\mathrm{d}^3 r \tag{3}$$

This expression clearly shows how the MIP is dependent on the outer electron shells distribution, which is responsible for the chemical bonds in the material.[10,11]

MIP was theoretically calculated for almost every element of the periodic table by modeling the charge distribution of crystal lattice. For a bulk gold crystal, MIP ranges between 25.02 and 31.05 V, according to calculations by Radi[12] and Sànchez and Ochando.[13]

The holographic experiments have been carried out in a FEG TEM Tecnai F20 operating at 200 keV and equipped with an electron biprism. In conventional TEM, the phase change of the electron beam is not directly accessible from the recorded image. A holographic image is the interference pattern produced by the superposition of an unperturbed reference electron beam and the one transmitted through the specimen. From Fourier analysis of the hologram, the two-dimensional map of the phase shift is

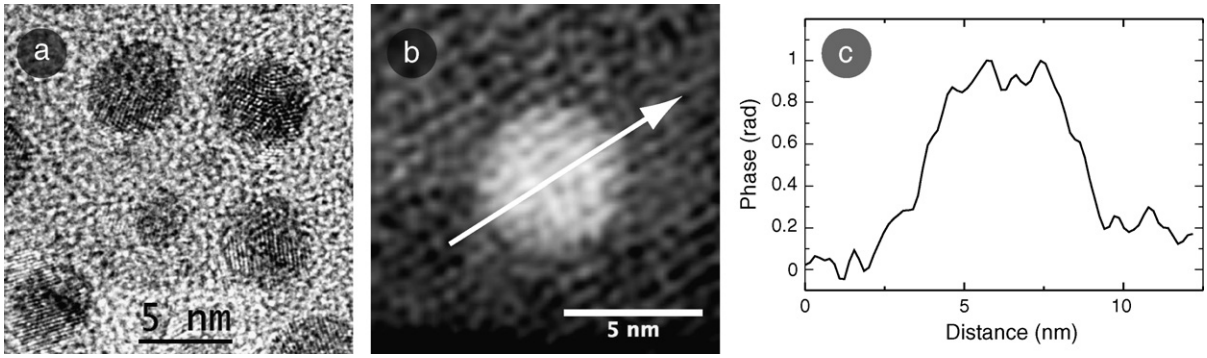

Fig. 4. (a) High-resolution TEM image of small Au particles. (b) Reconstructed phase-shift map for gold particles as measured by electron holography. (c) Experimental phase shift profile along the direction indicated by the arrow.

retrieved. Holograms are reconstructed with a spatial resolution of 0.2 nm and a phase precision of 0.1 rad.

For holographic experiments, Au particles were deposited on a thin carbon film by sputtering at the same conditions previously described for dispersion over the TiO_2 layers.

The high resolution TEM image in Fig. 4a shows the regular shape of the gold nanoparticles. Fig. 4b shows the reconstructed phase map for a gold particle with a circular shape. The corresponding line scan is reported in Fig. 4c.

Formula (2) indicates that the knowledge of the projected thickness is needed to obtain the value of MIP from the phase profile. According to specific literature, Au particles have a large contact surface with the supporting material.[14] This hypothesis is reinforced by different experimental observations performed in the TEM at different tilt angles. Based on the simplified assumption of hemispherical shape, the MIP value is then obtained from phase profile by numerical fitting. The MIP for a particle having a radius of 3 nm resulted to be 38 ± 4 V. Moreover, a value of 55 ± 10 V was measured for as small a particle as 1.5 nm. These experimental evidences can be associated to a modification of the electronic configuration of Au particles, owing to their reduced size.

The measured increase of MIP agrees with the data reported by Okazaki et al.[15]; in addition, the achieved spatial resolution and accuracy in phase retrieval will allow to investigate surface interaction[6] at the phase boundary between metallic-Au and semiconducting-TiO_2.

5. Conclusions

Composite films of Au-catalyzed Nb-doped TiO_2 were prepared for enhanced gas-sensing and for operation in the low-temperature regime. Indeed, gas detection at temperature between room temperature and few hundreds of degrees Celsius is highly interesting as novel applications may be envisaged in the field of remote sensing, miniaturized devices, and biosensing.

Electrical characterizations highlighted a considerable improvement as the samples were one order of magnitude more conductive and achieved the highest gas sensitivity at an operating temperature about 100 °C lower than pure TiO_2 films. Owing to the catalytic effect of Au, the films resulted highly sensitive to CO.

The role of Au is fundamental and electron holography investigated modification in the mean inner potential, a physical quantity well defined for bulk crystals and strongly related to the distribution of outer valence electrons. Holographic experiments allowed accurate measurement of MIP for single gold particles down to 1.5 nm in size.

The significant increase of MIP value recorded for the smallest particles indicates electronic reconfiguration and the enhancement of the CO sensitivity of the layers can be attributed to the presence of these catalytically active particles.

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