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Self-Assembled Nanostructures as Templates for the Integration of Nanoparticles in Oxide Surfaces

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Abstract

Under properly selected growth conditions, complex oxide thin films might exhibit a tendency towards self-organization allowing obtaining regular arrays of three-dimensional nanostructures. This behavior, together with their rich physics, offers enormous potential for the implementation of new nanodevices. Among complex oxides, manganese perovskites exhibiting colossal magnetoresistance and half-metallic character have emerged as promising candidates for the implementation of new spintronic devices.

Manganite thin films are often elastically strained, due to film-substrate lattice mismatch, and this lattice strain can, in some cases, select preferential growth modes leading to the appearance of different self-organized nanostructured morphologies. It is shown that under properly chosen growth conditions long range ordered arrays of nanoobjects, running along the steps direction defined by the miscut angle of the underlying substrate, can be obtained in highly epitaxial $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) thin films. These results suggest that self-organization process is directly guided by the topological features of the underlying substrate and highlight the relevance of growth kinetic effects. The use of those nanoobjects arrays as nanostencils for fabricating arrays of nanoparticles is also explored.

Keywords: Self-assembled nanostructures; Magnetoresistance; Oxide surfaces; Spintronics

Introduction

The recent idea of using biomolecules with magnetic particles as magnetic markers in living organisms opens the door to a new generation of magnetoresistive detectors with sensitivity over the standard detection by fluorescence [1,2]. This technology is based on the detection of nanometric magnetic labels biologically functionalized by ultra-sensitive magnetic field microsensors due to the change in the resistance. Resistive devices, based on the giant magnetoresistive (GMR) or tunnel magnetoresistive (TMR) effects, have been intensively studied in the emerging field of spintronics [3,4]. Nowadays, magnetic junctions are key components in several commercial products in different areas and recently have been used in new types of test of biomolecular systems with integrated recognition [5-7]. Moreover, a huge increase of tunnelling magnetoresistance has been observed in TMR nanometric junctions based on metallic nanoparticles. Well-defined structures at nanometric scale present an increasing interest due to their unique physical properties allowing envisaging new technological applications. In particular, the large surface to volume ration in nanoparticulate systems holds very promising expectatives in catalysis.

A major challenge in nanotechnology is to find a way of positioning nanoelements on surfaces in regular patterns, with nanometric precision yet over large surface areas either by deposition techniques (bottom-up approach) or by lithography plus nanofabrication techniques (top-down approach). Fabrication of artificial nanostructures of oxide materials by top-down approach requires sophisticated technology and has been recognized as a hard-attainable issue. For these reasons, the fabrication of ordered nanostructures, via spontaneous self-organization, is a topic of major relevance. An attractive route is based on using self-assembly properties of basic building blocks to create the patterned nanostructure. In this sense, directed self-organization based on template-assisted processes is a very promising and fast developing research topic in different fields.

The tendency of some oxides towards self-organized growth, forming regular arrays of 3D uniform structures, offers enormous potential for the preparation of nanotemplates that can be used for the fabrication of long range ordered nanostructured systems [8].

In this article, we explore the possibility of using long range ordered arrays of nanoobjects, obtained by spontaneous self-assembly in epitaxial $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films, as nanostencils for fabricating arrays of metallic nanoparticles (sub-50 nm range) prepared by physical and chemical methods. The preparation of Au nanoparticles arrays by a self- organization process guided by the nanostructured surface morphology of the underlying LSMO is demonstrated to illustrate the suitability of the method.

Materials and Methods

LSMO thin films were grown on (001)-oriented $SrTiO_3$ substrates by rf magnetron sputtering from a stoichiometric ceramic target [9]. The crystal structure was characterized by X-ray diffraction (XRD) with Cu Kα radiation. Pole figure has been recorded using a Bruker AXS GADDS system equipped with a 2D X-ray detector. The surface morphology was analyzed by atomic force microscopy (AFM) working

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in tapping mode (Molecular Imaging PicoSPM and Cervantes from Nanotec Electronica) and by Scanning Electron Microscopy (SEM) using a QUANTA FEI 200 FEG-ESEM microscope. Image processing was done using the software Mountains (Digital Surface).

Gold nanoparticles were prepared in two different ways, by physical methods and by chemical routes. In the first way, gold nanoparticles were obtained by rf magnetron sputtering from gold target in Ar atmosphere at high temperature (from 700°C to 800°C) [10], after depositing LSMO films with different surface morphologies. In the second way, the gold nanoparticles were synthesized according to modified procedure reported by K. C. Grabar et al. [11]. A 200 mL of 1 mM $HAuCl_4$ water solution was placed into round-bottom flask fitted with reflux condenser and heated under vigorous stirring until boiling. And then a 10 ml of 38.8 mM sodium citrate solution was quickly added. The color was changed from pale yellow to wine red. After 15 min the colloidal solution was removed from the heating plate and allowed to cool with continued stirring. Typical absorption spectrum of Au nanoparticles in water is shown in Figure 1. According to TEM image of Au nanoparticles, inset Figure 1, the size was around 40 nm (reasonably well size distribution was observed) [12]. A 20 µl of Au nanoparticles stock solution was placed onto substrate and spin coated at 4000 rpm for 5 s (Static mode). The same procedure was repeated once more with additional drop of 20 µl of gold solution.

Results and Discussion

A careful selection of the growth conditions of LSMO films on top of STO substrates with well defined terrace-step morphology allows obtaining variety of long-range ordered nanostructured LSMO thin films [8,9]. The substrates are typically cut at a vicinal angle and their surface present atomic-height steps, which can induce inherent growth instability at the step edges during film growth playing a crucial role in the final morphology of the films. The appearance of self-organized nanostructures (regular arrays of nanoholes or mounds) can be achieved by properly choosing the deposition rate conditions and surface mobility in a narrow window of the morphological phase diagram, delimiting step-flow and step-bunching regime. The long-range order of nanostructured arrays is directly promoted by the underlying stepped substrate.

Atomically flat LSMO films grow on top of STO substrates in the step flow regime preserving the terrace-step morphology of the underlying substrates, thus make them perfect templates for nanoparticle aligning (Figure 2). Figure 2a shows a wide area SEM image with nanodots concentration in the range of ~400-500 nanodot/µm². LSMO atomic steps promote preferential nucleation of Au nanoparticles at the step edges leading to the spontaneous formation of long-range ordered arrays (see corresponding height-height correlation function showing the regular lines). From wide area SEM images, we have analyzed nanoparticle size distribution. A narrow size distribution is found, fitted by log-normal distribution (see insert (down) in Figure 2b). The most probable nanoparticle diameter is around 10 nm, nevertheless some nanoparticles up to 40 nm in diameter are found.

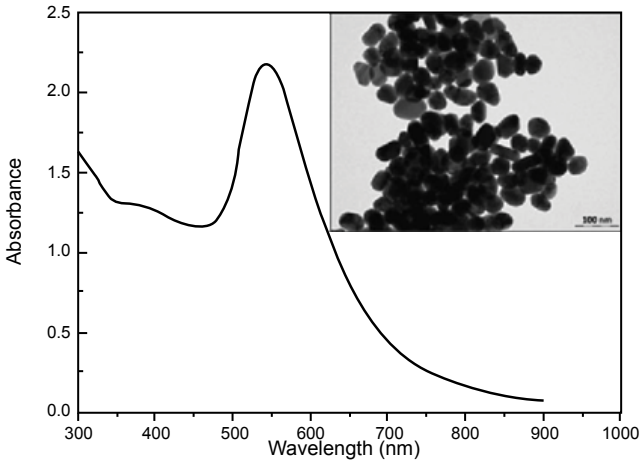

Figure 1: Absorption spectrum of Au nanoparticles in water. Inset: TEM image of Au Nanoparticles.

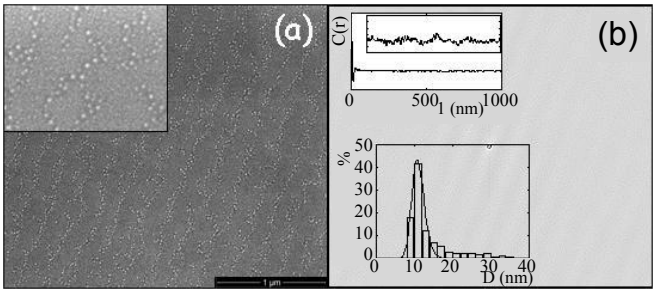

Figure 2: (a) SEM image of regular lines of gold nanoparticles organized on top of LSMO thin films. Inset: small area SEM image (500×300 nm²) (b) Corresponding autocorrelation functions. Upper inset shows profile normal to gold nanoparticles lines and the down inset shows the nanoparticle histogram fitted by log-normal distribution.

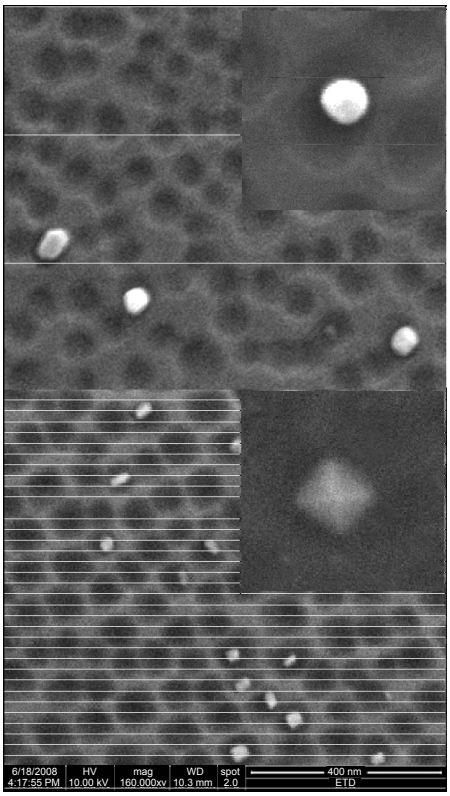

Figure 3: SEM images of LSMO films grown with Au nanoparticles obtained by (a) chemical route and (b) physical methods.

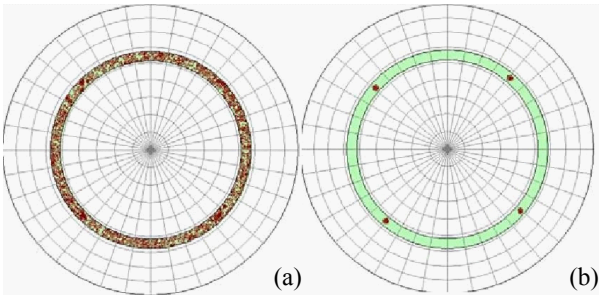

Figure 4: X-ray diffraction pole figure taken by using (111) diffraction peak of gold nanoparticles grown by rf sputtering on top of LSMO (a) smooth films with terrace-step morphology and (b) presenting self-organized holes.

Besides atomically flat films with step-terrace morphology, nanostructured LSMO films are also very promising templates for guided self-assembly of nanoparticles (sub-50 nm range). Figure 3 shows the SEM images of LSMO thin films with the gold nanoparticles prepared via (a) chemical routes and (b) physical methods. It is found that independently of the fabrication method gold nanoparticles are preferentially allocated inside the holes. The preliminary results with the other type of metallic particles (Ag, Pt, Fe etc.) indicate that the proposed methodology is not restricted only to gold nanocrystals.

It is also observed that depending on the form of the holes and the deposition method used nanoparticles might eventually be faceted nanocrystals. In the case of regular square shape holes the preferential formation of gold nanocrystal with octahedral shape is found, although the total potential energies for large gold clusters indicate that the decahedral structure is more stable than the observed one [13].

Finally, Au nanoparticles grown by rf sputtering on top of flat films with regular step-terrace morphology exhibit preferentially spherical shapes with no traces of faceting. Moreover, no epitaxial relation is found between gold nanoparticles and LSMO films (Figure 4a), as observed before in Ref [14]. In contrast, when Au is sputtered on nanostructured LSMO films with regular holes gold nanoparticles grow epitaxially on top of manganite films (Figure 4b) exhibiting octahedral shape with faceting. This is a very interesting result because the catalytic activity of these faceted nanocrystals is known to be strongly enhanced compared with that of rounded shaped nanoparticles [15].

In summary, we have shown that self-organized periodic nanopatterned LSMO surfaces can be used as nanotemplates for the fabrication of long range ordered networks of metallic nanoparticles, envisaging a new promising route for the implementation of magnetic and magnetoelectronic devices. In particular, when grown on very flat thin film with step-terrace morphology, the gold nanoparticles align in ordered regular lines. In the presence of self-organized holes, gold particles are preferentially allocated inside of the holes irrespective to the nanoparticle's preparation method. Moreover, in the case of regular holes gold particles prepared by rf magnetron sputtering are epitaxially grown on top of LSMO thin film.

Acknowledgments

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