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Nanostructuring thin Au films on transparent conductive oxide substrates

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ABSTRACT

Fabrication processes of Au nanostructures on indium-tin-oxide (ITO) surface by simple, versatile, and low-cost bottom-up methodologies are investigated in this work. A first methodology exploits the patterning effects induced by nanosecond laser irradiations on thin Au films deposited on ITO surface. We show that after the laser irradiations, the Au film break-up into nanoclusters whose mean size and surface density are tunable by the laser fluence. A second methodology exploits, instead, the patterning effects of standard furnace thermal processes on the Au film deposited on the ITO. We observe, in this case, a peculiar shape evolution from pre-formed nanoclusters during the Au deposition stage on the ITO, to holed nanostructures (i.e. nanorings), during the furnace annealing processes. The nanorings depth, height, width, and surface density are shown to be tunable by annealing temperature and time.

1. Introduction

The generation of nanostructured materials on surfaces is a new thrust in materials science both from basic scientific understanding viewpoint and technological applications. Nanostructured materials have attracted much recent attention due to their important roles in many technological areas such as heterogeneous catalysis, photonics, single electron and quantum devices, solar cells, etc. In recent years, in particular, nanostructured materials fabricated by metal nanoclusters (NCs) and thin metal nano-grained films deposited on insulator and semiconductor substrates have emerged in the developing of several devices exploiting the peculiar metal/substrate interaction at the nanoscale [1–3]. The study of the morphology of such films with the variation of thickness and processing gives an idea about the growth mechanism of these films. Study of morphology and understanding of growth mechanism are, also, essential to fabricate nanostructured materials in a controlled way for desired properties. In fact, such systems are functional materials since their chemical and physical properties (catalytic, electronic, optical, mechanical, etc.) are strongly correlated to the structural ones (size, shape, crystallinity, etc.). As a consequence, the necessity to develop bottom-up procedures (in contrast to the traditional top-down scaling scheme) allowing the manipulation of the structural properties of these systems raised.

In this framework, the interest in assembling Au nanostructures onto conductive transparent substrates, as indium-tin-oxide (In_2O_3:SnO_2, ITO), has increased [4–7] as the resulting interfaces show interesting optical properties exhibiting structure-dependent transmission/absorption spectra due to the occurrence of localized surface plasmon resonance effects (LSPR). Such effects could be successfully used in plasmonic solar cells to increase the energy conversion efficiency [8–12] (it is a well-known fact that metal nanoparticles can be used to scatter light by exciting them at their SPR). ITO films are widely used in optical devices due to the high electrical conductivity and high transparency at visible light wavelengths [13–15]. ITO thin film is a highly degenerate n-type semiconductor which has a low electrical resistivity (usually $\sim 2–4 \times 10^{-4}\ \Omega$ cm). The low resistivity of ITO films is due to a high carriers concentration because the Fermi level is located above the conduction level. The degeneracy is caused by both oxygen vacancies and substitutional tin dopants created during film deposition. The carriers concentration of high conductivity ITO films is in the range of 10^{20}–10^{21} cm^{-3}. Furthermore, ITO is a wide band-gap semiconductor (3.5–4.3 eV), which shows high transmission in the visible and near-IR regions of the electromagnetic spectrum. So, ITO films are, today, routinely used for applications in transparent electrodes for display devices, transparent coating for solar energy heat mirrors and window films in p–n heterojunction solar cells.

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So, a strong demand for simple, versatile, and low-cost bottom-up fabrication and manipulation procedures of Au nanostructures on the ITO surface exists.

In this sense, in this work we investigate standard (furnace annealings) and non-standard (laser annealings) methodologies to nano-structure and pattern thin Au films on ITO.

2. Materials and methods

Samples were prepared starting from 150 nm thick ITO film sputter-deposited on soda lime glass (Donnelly Corporation). Resistivity, carriers mobility and concentration were determined by Hall-effect measurements. The values are $1.55 \times 10^{-4}\ \Omega$ cm, 9.98 cm^2/Vs, and $4 \times 10^{21}\ cm^{-3}$ respectively. Transmittance of 86% within the visible light region was measured by a double beam type spectrometer.

Au depositions were carried out, at room temperature, by a RF Emitech K550X sputter coater onto the glass/ITO slides which were clamped on the cathode located straight opposite of the Au source (99.999% purity target). The electrodes (cathode and Au source) were laid at a distance of 40 mm under Ar flow keeping a pressure of 0.02 mbar in the chamber. The thickness of the deposited Au film can be controlled by tuning the electron emission current I (from 10 to 50 mA by 5 mA step) and the deposition time (from 5 to 2400 s by 1 s step). The average effective thickness d_F of the resulting Au film was checked by Rutherford backscattering spectrometry using 2 MeV $^4He^+$ backscattered ions at 165°. The physical unit of the thickness measured by RBS is atoms/cm^2 and, in the case of a uniform film coverage, it can be converted to nanometers using the Au bulk atomic density (5.9×10^{22} atoms/cm^3). However, most of the metallic films are discontinuous, mainly the thinnest films, when deposited on insulator or semiconductor substrates. In this case we intend the film thickness d_F as an "effective thickness" corresponding to the thickness of the corresponding continuous film. In particular, in this work we deal with two samples containing, respectively, 2.95×10^{16} Au/cm^2 and 1.5×10^{17} Au/cm^2. The correspondent effective thickness d_F are, respectively, 5 and 25 nm.

Laser irradiations were performed by a pulsed (12 ns) Nd:Yttrium Aluminium Garnet YAG laser emitting at 532 nm (Quanta-ray PRO-Series pulsed Nd:YAG laser). The laser spot has a circular shape with a diameter of 4 mm. The laser intensity profile is Gaussian characterized by a full width at half maximum of 1 mm. The maximum of the laser intensity decreases of 3% within a circular area of 600 μm in diameter centred at the maximum of the laser intensity (so, the analyses presented in this work were performed within 300 μm from the centre of the laser spot). The error in the fluence measurement is 25 mJ/cm^2. In the following, we will analyse the Au films evolution as a function of the laser fluence E (mJ/cm^2). E is the product of the pulse intensity I (W/cm^2) by the irradiation time Δt = 12 ns. So, in the following, the laser fluence of 500, 750, and 1000 mJ/cm^2 correspond to laser intensities of 5×10^7, 7.5×10^7, and 1×10^8 W/cm^2, respectively. Furthermore, for the present experiments, 1 pulse per sample was performed.

Standard annealing processes were performed using a Carbolite horizontal furnace in dry N_2 at the two temperatures 573 and 673 K and in the 1200–6000 s time range.

The atomic force microscopy (AFM) analyses were performed using a Veeco-Innova microscope operating in high amplitude mode. Ultra-sharpened Si tips were used (MSNL-10 from Veeco Instruments, with anisotropic geometry, radius of curvature ~2 nm, tip height ~2.5 μm, front angle ~15°, back angle ~25°, side angle ~22.5°), and substituted as soon as a resolution loose was observed during the acquisition. The AFM images were analysed by the SPMLabAnalyses V7.00 software. In particular, we quantified the NCs radius R surface-to-surface spacing l by the AFM analyses using the SPMLabAnalyses V7.00 software that defines each grain area by the surface image sectioning of a plane that was positioned at half grain height. In this way we can obtain the distributions of R and l as a function of E. Each distribution was calculated on a statistical population of 200 NCs. From these distributions we can determine the radius and surface-to-surface distance mean values (<R>, and <l>) and the deviation on such values (ΔR and Δl). In addition, we can evaluate the NCs surface density N (NCs per unit area) by direct inspection of the AFM images and counting; N was evaluated as the average value obtained by counting on three different 1 μm × 1 μm AFM images and the relative error was obtained by the averaging procedure.

Scanning electron microscopy (SEM) analyses were performed using a Zeiss FEG-SEM Supra 25 Microscope using 5 kV of accelerating voltage.

3. Results and discussions

3.1. Depositions

Fig. 1(a) shows a 10 μm × 10 μm AFM image of the starting ITO surface: the typical whiskers structure of DC sputter- and evaporated-grown ITO films is observable [16–18]. Fig. 1(b) reports a 10 μm × 10 μm AFM image of a 5 nm thick Au film deposited on the previous ITO surface. The image shows the formation of Au NCs with mean diameter of 11.6 ± 3.3 nm and surface density (NCs per unit area) $N_T \approx 6.2 \times 10^8\ cm^{-2}$, onto a Au quasi-continuous film (the inset shows a 2 μm × 2 μm AFM image for a clearer vision). Finally, Fig. 1(c) reports a 10 μm × 10 μm AFM image of a 25 nm thick Au film deposited on the ITO surface. It shows the formation of Au NCs with mean diameter of 34.2 ± 3.7 nm and surface density (NCs per unit area) $N_T \approx 6.4 \times 10^8\ cm^{-2}$, onto the Au quasi-continuous film. The presence of the underlaying quasi-continuous Au film can be inferred from Fig. 2, where the morphology of the starting ITO surface and of the starting 5 and 25 nm thick Au films can be observed on the nanoscale (Fig. 2(a–c), respectively). In particular, from Fig. 2(b), we can observe that the 5 nm thick Au film is formed by very small nanoparticles (diameters <3 nm) touching between them and forming the quasi-continuous underlaying film. In the 25 nm thick film, these nanoparticles have laterally grown to form percolating islands resulting in a typical quasi-continuous percolating morphology (eventually, continuing the deposition from these percolating film a continuous Au film can be formed by a hole filling process) [19]. These morphology sequence is typical for metal films on insulator substrates due to weak interaction between the metal and the oxide [3,19]. In general [1,2], at the early stages of growth metal particles may grow on the surface through homogeneous nucleation, i.e., island formation due to nucleation on defect-free terraces, and heterogeneous nucleation, i.e., islands formation at steps and other defects. In order for islands to form on the substrate, atoms deposited from the vapour phase undergo a series of kinetic processes, including thermal accommodation onto the substrate, surface diffusion of the adatoms on the surface, dimer formation to initiate nucleation, then island formation and growth. To minimize the surface area, the clusters adopt a hemispherical shape (as in Fig. 2(b)). Nucleation continues until a maximum number of densities of nuclei are reached, where the probability for a diffusing adatom to be captured by an existing cluster is much higher than that for it to join with a second adatom to a new nucleus. As more and more atoms are deposited, small islands may grow, contact each other, and then fully coalesce, i.e., two islands merge into larger, but still compact islands. The formation of a larger compact island by coalescence of two smaller islands may be accompanied by a wiping action in which part of the substrate which was covered initially is wiped clean, i.e., it covers less surface [19]. This results