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Au cluster growth on ZnO thin films by pulsed laser deposition

E. György [a,*], J. Santiso [a], A. Figueras [a], A. Giannoudakos [b], M. Kompitsas [b], I.N. Mihailescu [c], C. Ducu [d]

[a] *Consejo Superior de Investigaciones Cientificas, Instituto de Ciencia de Materiales de Barcelona, Campus UAB, 08193 Bellaterra, Spain*
[b] *National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute, Vasileos Konstantinou Avenue 48, 11635 Athens, Greece*
[c] *Institute of Atomic Physics, P.O. Box MG 36, 77125 Bucharest, Romania*
[d] *University of Pitesti, Targul din Vale 1, 110040 Pitesti, Romania*

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Abstract

Nanostructures formed by Au nanoparticles on ZnO thin film surface are of interest for applications which include medical implants, gas-sensors, and catalytic systems. A frequency tripled Nd:YAG laser (λ = 355 nm, $\tau_{FWHM} \sim 10$ ns) was used for the successive irradiation of the Zn and Au targets. The ZnO films were synthesized in 20 Pa oxygen pressure while the subsequent Au coverage was grown in vacuum. The obtained structures surface morphology, crystalline quality, and chemical composition depth profile were investigated by acoustic (dynamic) mode atomic force microscopy, X-ray diffraction, and wavelength dispersive X-ray spectroscopy. The surface is characterized by a granular morphology, with average grain diameters of a few tens of nanometers. The surface roughness decreases with the increase of the number of laser pulses applied for the irradiation of the Au target. The Au coverage reveals a predominant (1 1 1) texture, whereas the underlying ZnO films are *c*-axis oriented. A linear dependence was established between the thickness of the Au coverage and the number of laser pulses applied for the irradiation of the Au target.

Keywords: Au/ZnO nanostructures; Pulsed laser irradiation

1. Introduction

Noble metal/oxide systems became an interesting field of investigation during the last few years [1–4]. It is well known that the presence of metal nanoparticles on the surface of oxide thin films enhances sensitivity and selectivity in gas sensor applications, creating preferential adsorption sites [5,6]. Moreover, the metal nanoparticles/oxide thin film systems find useful applications in catalysis, photocatalysis, novel optoelectronic devices, or biosensors [7,8]. In particular, Au/ZnO catalysts are active for oxidation of carbon monoxide to carbon dioxide and methanol synthesis [9,10]. The methanol yields are comparable to those obtained with commercial Cu/ZnO-based catalysts [11,12]. Moreover, the rate of methanol formation per surface area of gold particles was reported to depend on the size of Au nanoparticles, increases with the decrease of the average nanoparticles diameter, suggesting that the reaction zones are the periphery around the Au particle.

Zinc oxide (ZnO) has a hexagonal wurtzite structure. It is a wide band gap (E_g = 3.2 eV) II–VI n-type semiconductor with high thermal and chemical stability, and good transparency in the infrared-visible spectral region [13]. We established the experimental parameters which led to the growth of crystalline ZnO films on (0 0 1) Si and (0 0 1) SiO_2 substrates by pulsed laser deposition (PLD) [14,15].

PLD permits the growth of thin films with required thickness, from a few nanometers to the order of a few micrometers [16,17]. In addition, the incorporation of contaminants in the films during their synthesis is reduced as compared to classical techniques [18,19]. The possibility to grow multistructures consisting of subsequent deposition of different materials by the simple change of the targets submitted to the laser radiation stands also among the advantages of PLD [16].

* Corresponding author. Tel.: +34 935801853; fax: +34 935805729.
E-mail address: egyorgy@icmab.es (E. György).

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In this article we report the growth of Au nanoparticles on ZnO thin films surfaces by PLD. Au nanoparticles on ZnO thin films surfaces were previously deposited by only a few groups [20–22]. The Au/ZnO nanostructures were grown by RF sputtering [20,21] and evaporation techniques [22].

The aim of this work is to establish a precise control of Au coverage thickness by the determination of the growth rate at the incident laser fluence value used for the ablation of the Au targets, as well as the investigation of the crystalline quality of the Au/ZnO nanostructures. We mention that no similar studies of pulsed laser deposited Au on ZnO could be identified in the literature.

2. Experimental

The growth of the Au/ZnO nanostuctures was conducted inside a stainless steel vacuum chamber. Before each deposition experiment the chamber was evacuated down to a residual pressure of 6×10^{-4} Pa. For the irradiation of the Zn and Au targets we used the third harmonic of a Quantel Mo. YG851 Nd:YAG laser ($\lambda = 355$ nm, $\tau_{FWHM} \sim 10$ ns) source, at a repetition rate of 10 Hz. The laser fluence incident on the target surface was fixed at 2 J/cm^2.

The ZnO films were deposited in identical experimental conditions. We applied 70,000 subsequent laser pulses on the Zn targets for the growth of each film. The depositions were performed in 20 Pa oxygen pressure. The thickness of the subsequent Au coverage was varied by increasing the number of laser pulses incident on the Au targets from 300 to 9000. The deposition of the Au coverage was conducted in 6×10^{-4} Pa vacuum.

Both the Zn and Au targets were placed on a vacuum-compatible computer controlled XY table, to avoid drilling or significant changes in surface morphologies under the action of multi-pulse laser irradiation. The Si (0 0 1) substrates were positioned at 40 mm from the targets parallel to them. The substrates were heated during the growth of both the ZnO thin film and the subsequent Au coverage at a temperature of 200 °C.

The surface morphology of the Au/ZnO nanostructures was studied by scanning electron microscopy (SEM) using a Philips 515 electron microscope, and atomic force microscopy (AFM) in acoustic (dynamic) mode using a PicoSPM apparatus from Molecular Imaging. The crystalline status was investigated by X-ray diffraction (XRD) in θ - 2θ configuration with a DRON UM1 diffractometer (Cu Kα, $\lambda = 1.5418$ Å radiation). The wavelength dispersive X-ray spectroscopy (WDX) studies were performed with a Cameca Camebax SX-50 equipment (15 kV, 100 nA, 1 μm diameter spot area, 2 s integrating time per point).

3. Results and discussion

In Fig. 1 we present a typical SEM micrograph of the Au/ZnO nanostructure. The Au coverage was obtained with 9000 laser pulses. As can be observed, the surface of the deposited structures is smooth. Nevertheless, spherical particulates with diameters from a few hundreds up to a few micrometers can be evidenced, with a density of about 5×10^5 cm^{-2}. Their shape, dimensions and density suggest that they were expulsed from the surface of the irradiated targets. This phenomenon is characteristic for structures obtained by PLD. We note that these features are common for all studied structures and do not depend on the number of pulses used for the deposition of the Au coverage.

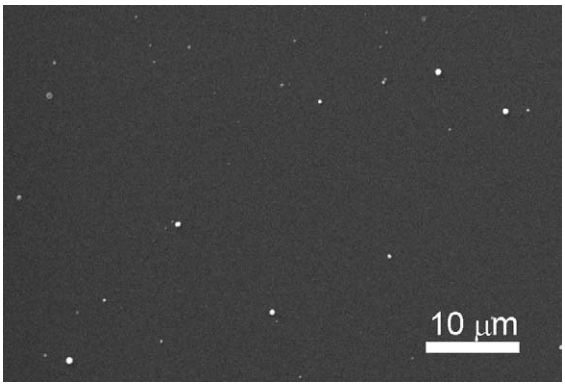

Fig. 1. SEM image of ZnO film with Au coverage obtained with 9000 laser pulses used for the irradiation of the Au target.

On the other hand, the AFM images (Fig. 2a and b) reveal a granular surface morphology, with average grain diameters of a few tens of nanometers, increasing with the increase of the laser pulses applied for the irradiation of the Au target. In Fig. 2c and d, we show the corresponding surface profiles.

From the WDX data we calculated, with the aid of a computer simulation program, the average thickness values of the Au coverage as well as the underlying ZnO films. From the observed linear dependence between the Au coverage thickness and the laser pulses used for the ablation of the Au targets we can deduce a constant deposition rate of about 0.02 Å/laser pulse.

On the other hand, the surface profiles obtained by AFM showed that the root mean square (r.m.s.) surface roughness decrease with the increase of the laser pulses used for the irradiation of the Au target (Fig. 2c and d). Corroborating these results, one can conclude that coalescence must take place filling in the gaps between the grains. Indeed, initial 3D islands growth followed by cluster coalescence was observed also in case of Au/ZnO nanostructures obtained by RF sputtering [20]. This process led to the diminishment of the r.m.s. surface roughness. At laser pulses higher than about 8000 the average thickness of the Au coverage calculated by WDX becomes larger than the surface local heights of uncovered ZnO films. The thickness of the underlying ZnO films was estimated from the WDX data at about 80 nm.

In Fig. 3, we show the diffractograms of Au/ZnO nanostructures obtained with 300 (curve a) and 600 (curve b) laser pulses incident on the Au targets. We also indicated the diffraction lines corresponding to the hexagonal phase ZnO and cubic phase Au patterns [23]. As can be observed, with 300 incident laser pulses the diffractogram of the Au/ZnO structure contains only the lines of hexagonal phase ZnO at 34.4° and 36.2° corresponding to the (0 0 2) and (1 0 1) lattice plane

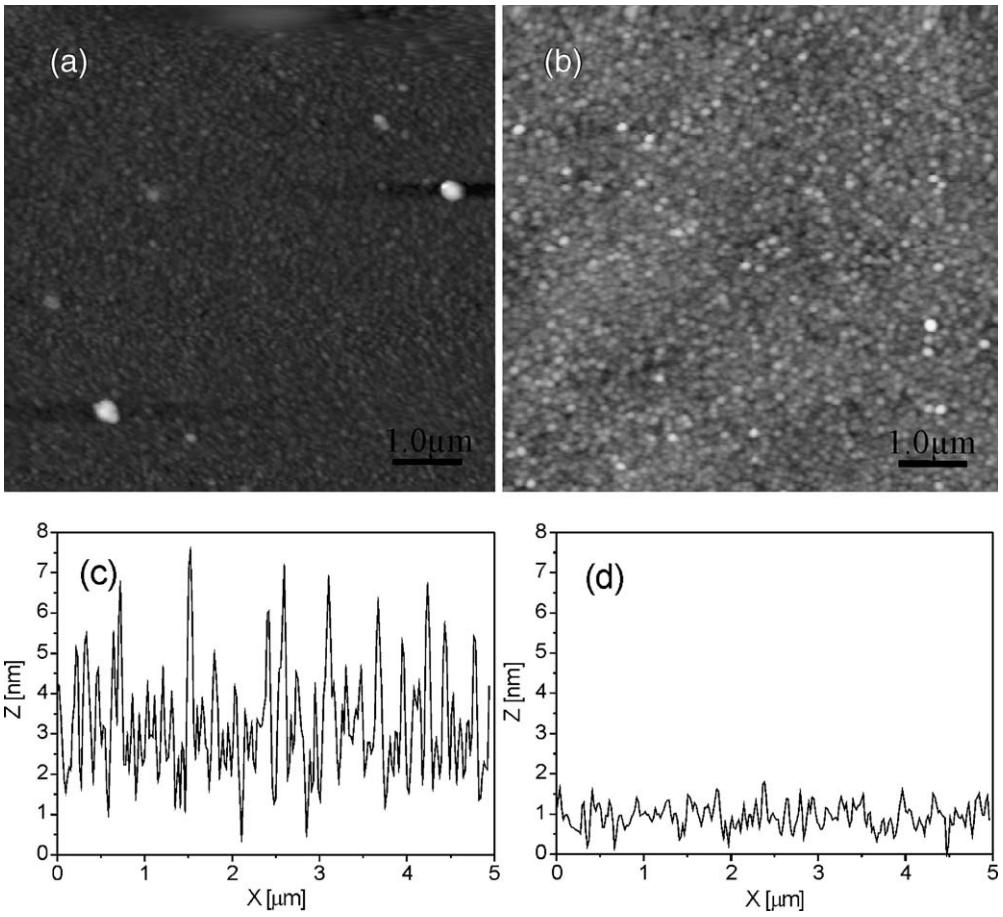

Fig. 2. AFM images and surface profiles of ZnO films with Au coverage obtained with (a and c) 300 and (b and d) 9000 laser pulses used for the irradiation of the Au target.

reflections (curve a). The intense line at 34.4° indicates that the films are composed by crystallites with the *c*-axis grown preferentially perpendicular to the plane of the substrate surface. Nevertheless, with additional 300 laser pulses besides those already mentioned an additional line appears at 38.2° attributed to the (1 1 1) lattice plane reflection of cubic phase Au (curve b). Diffractograms composed by lines corresponding to the same lattice planes were observed also for Au/ZnO nanostructures obtained with higher number of laser pulses applied for the ablation of the Au targets. Moreover, the intensity of the Au (1 1 1) line increases with the increase of the number of pulses (see curve c corresponding to the Au/ZnO structure obtained with 9000 laser pulses incident on the Au target), proving the growth of Au crystallites along the (1 1 1) preferred orientation.

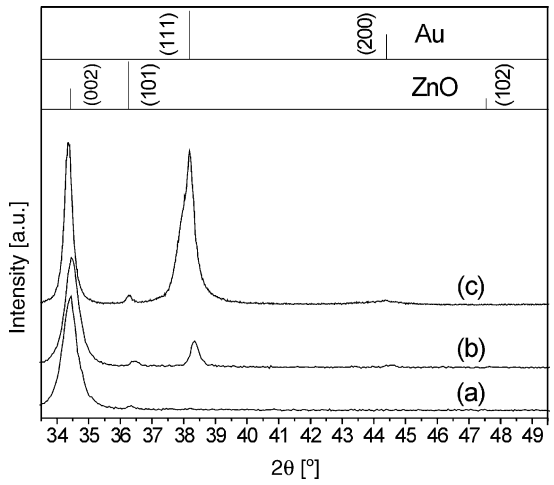

Fig. 3. X-ray diffractograms of ZnO films with Au coverage deposited with (a) 300, (b) 600, and (c) 9000 laser pulses used for the irradiation of the Au target, as well as diffraction patterns of hexagonal ZnO and cubic Au as referred in the JCPDS 36-1451 and 04-0784 files, respectively.

We note that these features are in some aspects similar to the results presented in Ref. [20] concerning Au clusters deposited on ZnO thin films by RF sputtering. However, in the mentioned study the ZnO films deposited by RF sputtering were submitted to post-deposition annealing in oxygen atmosphere to improve their structural quality, and then were used as substrates for the Au deposition. Similar to our results, the subsequently deposited Au clusters grew with a predominant (1 1 1) texture.

Our investigations are also congruent with time resolved emission spectroscopy investigations of laser generated plasmas in front of Au targets presented in Refs. [24,25]. In the mentioned studies the growth mechanisms of the Au thin films were correlated with the kinetic energy values of the ablated Au species impinging on the substrate surface, determined by the experimental parameters. The formation of highly oriented Au (1 1 1) structures was achieved at large

kinetic energy values of the ablated Au species impinging on the substrate surface. In our case the low ambient gas pressures and short target-substrate distances creates the favorable conditions for the highly (1 1 1) oriented Au structures growth.

4. Conclusion

Au nanoparticles were grown on the surface of ZnO thin films by pulsed laser deposition. A frequency tripled Nd:YAG laser (λ = 355 nm, $\tau_{FWHM} \sim 10$ ns) was used for the successive irradiation of the Zn and Au targets, respectively. The deposition of the ZnO films was performed in a low-pressure oxygen atmosphere, whereas the Au coverage was deposited in vacuum. The surfaces have a granular morphology with average grains diameters of a few tens of nanometers. With the increase of the number of laser pulses applied for the irradiation of the Au target the r.m.s. surface roughness decreases by filling in the gaps between the Au nanoparticles. The XRD results indicate that the ZnO films deposited on the (0 0 1) Si substrates are *c*-axis oriented. The subsequently deposited Au clusters on the ZnO films grow under (1 1 1) preferred orientation.

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