Laser grown gold nanoparticles on zinc oxide thin films for gas sensor applications

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Nanostructures formed by gold clusters and zinc oxide thin films have been synthesized by means of two step pulsed laser deposition. Zinc and gold targets were subsequently submitted to pulses generated by an UV KrF* (λ=248 nm, $\tau_{FWHM} \cong$ 20 ns, ν=2 Hz) excimer, as well as a frequency tripled Nd:YAG (λ=355 nm, τ~10 ns) laser sources. The optical properties of the obtained nanostructures have been correlated with their surface morphology determined in turn by the growth parameters. The obtained results proved the possibility to tailor the gold / zinc oxide nanostructures optical properties by the proper choice of the number of laser pulses used for the ablation of the gold targets. The tunable optical features in the visible- near infrared spectral region allow for the design of nanostructures with pre-defined optical characteristics for advanced gas sensor applications.

1. Introduction

Preparation and characterization of noble metal nanoparticles/oxide matrix composites attracted increasing interest in recent years due to the large number of potential applications, from nanoscale electronics and optics to nanobiology systems and nanomedicine [1-4]. All these technological fields valorize the drastically different physical and chemical properties of noble metal nanoparticles as compared to those of the corresponding bulk materials. The identification of direct correspondence between synthesis parameters of nanoparticles on the surface or embedded into oxide matrices as well as their functional properties concentrates therefore significant attention [5-8].

As known, ZnO is an appropriate candidate for optical applications due to its high transparency and low reflection within the visible - IR spectral range [9, 10]. Due to the absence of any contribution in the absorption / reflection spectra in the visible-IR spectral range, it represents also an ideal raw material for the growth of the Au nanoparticles with the purpose to investigate their optical characteristics.

This work is a development of our studies on ZnO thin films and Au/ZnO nanostructures deposition on (001) Si and (001) SiO$_2$ substrates [11-13]. Investigations of the local electric properties of the Au covered ZnO surfaces revealed the metallic character of the Au nanoparticles [13]. This feature justifies the use of the obtained nanostructures in advanced technological applications. Moreover, these previous studies permitted us to identify

the optimum experimental conditions that allow for the growth of ZnO films with c-axis oriented crystal structure.

In this article special attention is paid to the correlation for the first time between the optical properties and surface morphology of the laser grown Au / ZnO nanostructures as well as the synthesis process parameters. We mention that we could not identify in the literature similar studies on laser deposited Au nanoparticles. The main purpose of this paper is to investigate whether the optical properties of the laser grown Au / ZnO nanostructures can be controlled and therefore pre-defined through their surface morphology, determined in turn by the experimental synthesis conditions.

2. Materials and methods

Both the ZnO thin films and Au nanoparticles were grown by pulsed laser deposition. A pulsed Quantel Mo. YG851 Nd:YAG (λ=355 nm, τ_{FWHM}~10 ns, ν=10 Hz) laser source was used for the multipulse irradiation of the Zn and Au targets. The laser fluence incident on the targets' surface was set at 6.6 J/cm^2. Prior to each experiment the irradiation chamber was pumped down to a residual pressure of 6x10^{-4} Pa residual pressure. For the synthesis of each ZnO thin film 70000 subsequent laser pulses were applied to the Zn targets in 20 Pa oxygen pressure. The Au nanoparticles were grown in a second step in vacuum by the irradiation of the Au targets with up to 9000 laser pulses.

Both targets were mounted on a vacuum-compatible computer controlled XY table which allows for the

uniform irradiation of a 10x10 mm^2 surface area. This large scanned area avoids the significant changes in the targets' surface morphologies caused by the action onto the same irradiation site of a large number of laser pulses. (001) Si and (001) SiO$_2$ were chosen as substrate materials. The substrates were positioned parallel to the targets at a distance of 40 mm and were maintained during the deposition process at a temperature of 300 °C.

The targets and substrates were carefully cleaned with acetone in ultrasonic bath before introducing them into the irradiation chamber. Additional target cleaning was performed by a preliminary ablation step which proved to be essential for removing the last contaminants and impurities. During this process a shutter was interposed between the targets and the substrate, parallel to them.

The surface morphology of the deposited ZnO thin films and Au / ZnO nanostructures was studied by atomic force microscopy (AFM) in acoustic (dynamic) mode, with a PicoSPM apparatus from Molecular Imaging. The optical absorbance and reflectivity measurements were carried out with a double beam spectrophotometer (ThermoSpectronic) within the (200-1000) nm wavelength range.

3. Results and discussion

Under visual inspection the reference ZnO films were completely transparent. Their thickness, measured by wavelength dispersive X-ray spectroscopy, was about 80 nm. The films' average transmittance in the visible-IR spectral range when grown on quartz substrate exceeded 90%. On the other hand, the cyan blue-like color of the ZnO thin films covered with Au was a first indication for the formation of Au clusters [14]. The Au / ZnO nanostructures color further changed to golden with the gradual increase of the Au coverage.

Fig. 1 shows typical AFM images and the corresponding surface local height histograms of reference ZnO films grown on (001) Si (Fig. 1 a,c) and (001) SiO$_2$ quartz (Fig. 1 b,d) substrates. As can be observed, both the diameters and heights of the ZnO grains grown on quartz substrate are larger as compared to those on Si. Previous results showed that the crystallization of ZnO films is enhanced and the average size of ZnO particles is superior on quartz as compared to Si, independent on the deposition technique [15, 16]. Indeed, the mean grains diameter and surface local height are estimated to be about 20 nm and 7 nm for the laser deposited ZnO films on Si, but about 60 nm and 30 nm for those deposited on quartz substrate (Fig. 1).

The further evolution of the surface morphology during the second irradiation step conducted for the growth of Au nanoparticles on the ZnO films deposited on Si substrate is presented in Fig. 2. The observed 3D growth of Au on the ZnO thin films surfaces could be associated with the reduced reactivity of Au to oxygen as well as metal adatom migration and island nucleation [17, 18]. With the increase of the number of applied laser pulses incident on the Au targets, i.e. with the increase of the Au coverage, the nanoparticles (grains) in plane diameter increases, accompanied by the decrease of their local heights. The average particles diameter and height reach around 60 nm and 2.5 nm in case of the largest Au coverage (Fig. 2 b,d). Moreover, the grains density decreases with the increase of the Au coverage proving, together with the decrease of their relative height, the partial coalescence of the Au nanoparticles during their growth. Indeed, as reported in Ref. 19 the increase of the coupling between the nanoparticles leads to a gradual change of the reflected color from green to a metallic gold, as occurred in our experiments.
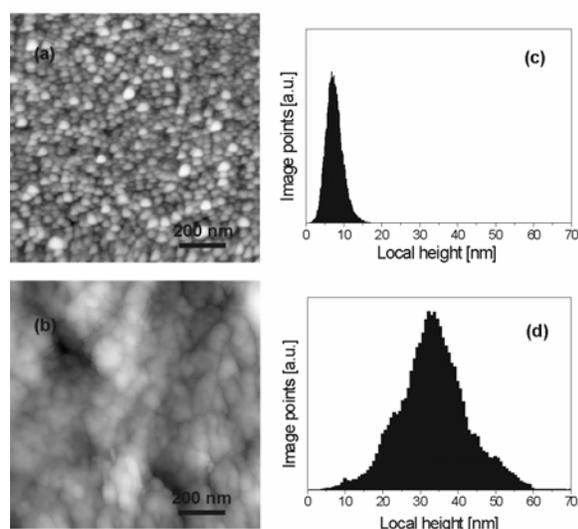

Fig. 1. AFM images and the corresponding surface local height histograms of reference ZnO thin films deposited on (a, c) (001) Si and (b, d) quartz substrates.
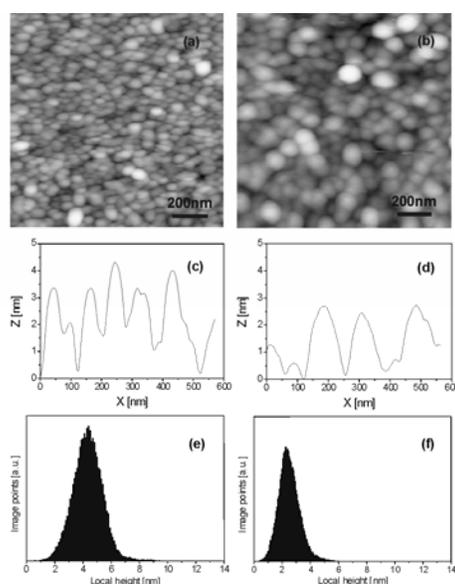

Fig. 2. AFM images and the corresponding surface profiles as well as local height histograms of ZnO thin films on (001) Si substrates with Au coverage obtained with (a, c, e) 4200 or (b, d, f) 9000 laser pulses incident on the Au targets.

The typical optical reflection spectra of the uncovered ZnO thin film and the Au / ZnO nanostructures are given in Fig. 3. The first minimum at around 370 nm of the reflection spectra correspond to the energy band gap of ZnO at 3.3 eV, followed by a sharp maxima peaking at around 380 nm. As well known from the theory of optical transitions in semiconductors, a peak in the reflectance spectra is appearing in the vicinity of a band edge [20]. With the increase of the Au coverage the optical characteristics of the Au / ZnO nanostructures gradually change in the visible-IR spectral range from transparent (Fig. 3 a) to a highly reflecting metallic like behavior (Fig. 3 c). In addition, a reflection minimum centered at around 520 nm appears in the Au / ZnO nanostructures spectra. The intensity of this band increases with the increase of the number of laser pulses incident on the Au target, i.e. the increase of the Au coverage.
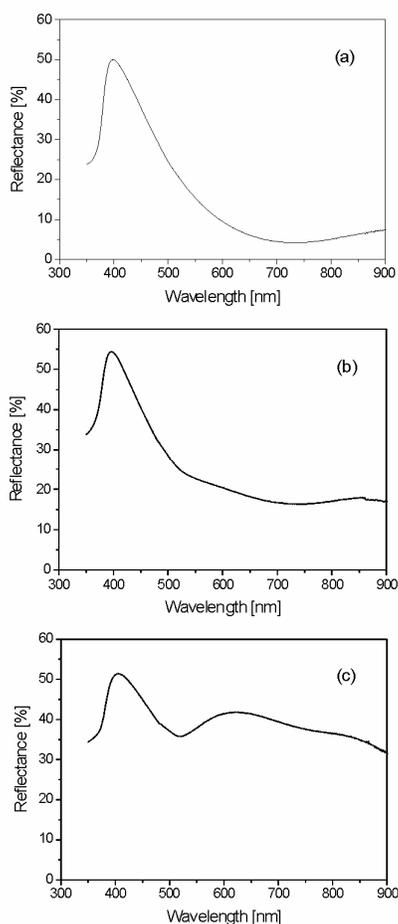

Fig. 3. Reflection spectra of thin films deposited on (001) Si substrates: (a) reference ZnO film, and ZnO films with Au coverage obtained with (b) 4200, or (c) 9000 laser pulses incident on the Au targets.

The main reflection minimum around 520 nm is associated with the surface plasmon resonance (SPR)

absorption band of Au nanoparticles [21, 22]. As known, the incident photons of this wavelength are converted to surface plasmons as a result of interaction with the free electron distribution of gold nanoparticles surface, leaving a gap in the reflected light intensity [22]. The much weaker band at longer, around 800 nm wavelength (Fig. 3c) could be assigned to the contribution of larger aggregates, composed by Au nanoparticles [5].

As reported, the size dependent feature of SPR absorption can allow for the production of noble metal nanoparticles containing composite systems with tunable optical properties [8, 16, 22-26]. The main geometrical parameters that induce changes in the surface plasmon resonance band are the Au nanoparticles i) in-plane diameters [23, 24], ii) aspect ratio [25], iii) height [26], iv) shape [16], or v) volume fraction in case of nanocermet (nanoparticles embedded in ceramic matrix) thin films [8].

As a general rule it was found that both the increase of nanoparticles diameter and / or the decrease of their height, i.e. the rise of aspect ratio, cause the same changes in the reflection / absorption spectra of the composite systems. This is the shift of the surface plasmon resonance absorption band towards higher wavelengths. However, the aspect ratio of the Au clusters grown on the surface of ZnO films deposited on quartz substrates are similar to the structures deposited on Si (Fig. 4). The average particles diameter and height for the highest Au coverage reach around 160 nm and 7 nm, respectively.
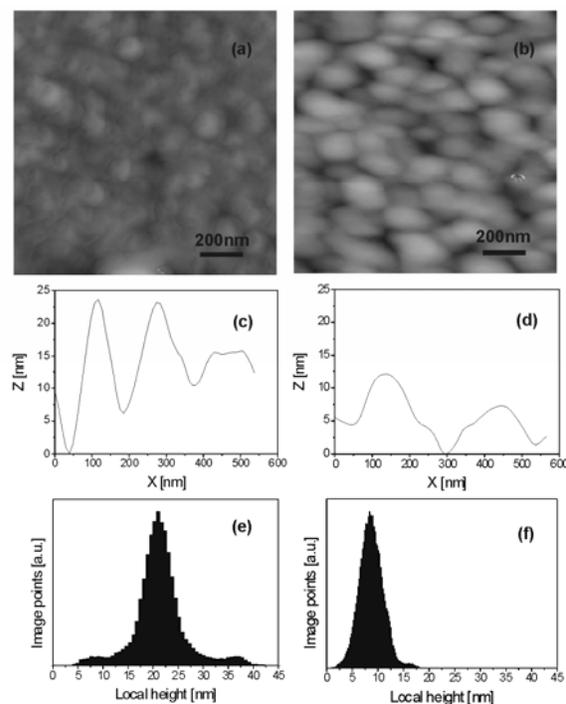

Fig. 4. AFM images and the corresponding surface profiles as well as local heights histograms of ZnO thin films deposited on quartz substrates with Au coverage obtained with (a, c, e) 4200, or (b, d, f) 9000 laser pulses incident on the Au targets.

Nevertheless, the absorption band of the Au / ZnO structures deposited on quartz substrates are red-shifted to around 650 nm, as compared to the structures deposited on Si (Fig. 5). It was reported that the most relevant geometrical parameter on the SPR wavelength in case of Au particles is their in-plane diameter [6]. This could explain the observed red-shift of the SPR absorption band of Au clusters grown on the surface of ZnO films deposited on quartz, as compared to those deposited on Si.

The absorption spectrum of the structure deposited at the highest Au coverage (Fig. 5 c) contains a broad band in the visible-IR spectral region. The broadening of the absorption band could be due to the increase of particles diameter with the increase of the Au coverage until their partial coalescence. As a result, the optical properties converge towards those characteristic to bulk material [19, 27].
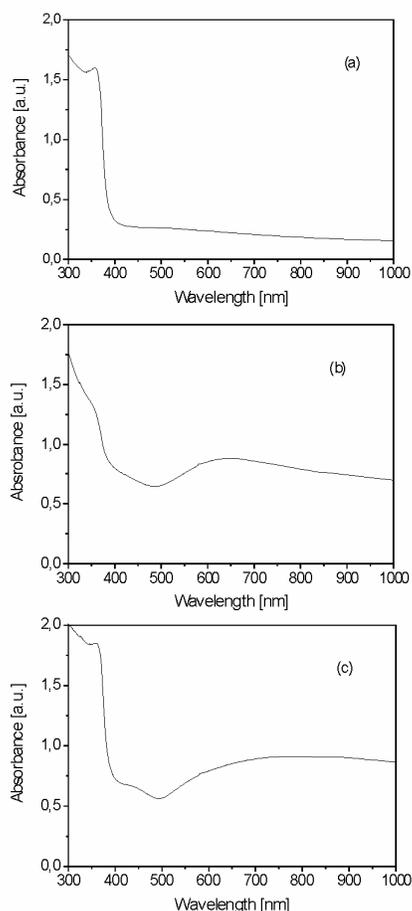
surface topography as well as the degree of the Au corevage, i.e. number of laser pulses applied for the ablation of the Au targets (see Figs. 2 and 4). The Au deposition rate was estimated by wavelength dispersive X-ray spectroscopy (WDX) and was found to be around 0.02 Å / laser pulse. This low value allows for the accurate control of the amount of Au deposited on the ZnO films surface and thus, of the nanoparticles morphology. The established dependence between the Au nanoparticles morphology and SPR absorption permits the continuous tuning of the optical properties of the Au / ZnO nanostructures in the visible spectral range.

4. Conclusions

We investigated the interrelations between the optical properties and surface morphology of Au nanoparticles / ZnO thin films nanostructures deposited on Si and quartz substrates. Both the ZnO films and Au nanoparticles were grown by pulsed laser deposition. A frequency tripled Nd:YAG laser (λ=355 nm, τ_{FWHM}~10 ns, ν=10 Hz) was used for the two steps irradiation of the Zn and Au targets. The deposition of the ZnO films was performed in a low pressure oxygen atmosphere, while the Au nanoparticles were grown in vacuum. We have demonstrated for the first time the possibility of the size controlled growth by pulsed laser deposition of Au / ZnO nanostructure systems with predetermined optical properties. Our results demonstrated that through the control of growth parameters (e.g. number of laser pulses used for the irradiation of the Au targets, which determine the amount of the Au coverage and the morphology of the Au nanoparticles) we can achieve the continuous tuning of the SPR peak. The ability to predict and modify in a controlled manner the optical properties of a nanocomposite system is useful in many key technological applications from biology to engineering of photonic and opto-electronic devices, as well as in chemo- and biosensing.

Fig. 5. Absorbtion spectra of thin films deposited on (001) SiO$_2$ substrates: (a) reference ZnO film, and ZnO films with Au coverage obtained with (b) 4200, or (c) 9000 laser pulses incident on the Au targets.

Our results indicate that the Au nanoparticles morphology is determined by the base ZnO thin films

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