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Study of the electrical and nanosecond third order nonlinear optical properties of ZnO films doped with Au and Pt nanoparticles

Martin Trejo-Valdez [a,*], Hugo Sobral [b], Hugo Martínez-Gutiérrez [c], Carlos Torres-Torres [d]

[a] ESIQIE, Instituto Politécnico Nacional, México, D.F. 07738, México
[b] Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Apartado Postal 70-186, México, D.F. 04510, México
[c] Centro de Nanociencias y Micro y Nanotecnologías del Instituto Politécnico Nacional, México, D.F. 07738, México
[d] Sección de Estudios de Posgrado e Investigación, ESIME ZAC, Instituto Politécnico Nacional, México, D.F. 07738, México

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ABSTRACT

Zinc oxide films doped with platinum and gold nanoparticles were deposited by the spray pyrolysis technique on glass substrates. A titanium dioxide sol–gel solution containing gold and platinum aqueous ions was employed for synthesizing the nanoparticles by ultraviolet-light irradiation. The conductive properties of the samples were characterized by the electrochemical impedance spectroscopy technique. Our results showed that the impedance of zinc oxide films doped with metallic nanoparticles was, by far, lower than typical measurements in zinc oxide films. A strong enhancement in the nanosecond nonlinear optical response was also obtained in the studied metallic doped films. A vectorial two-mixing experiment performed at 532 nm and 4 ns allowed us to evaluate the sample with a third order optical nonlinearity described by approximately $|\chi^{(3)}_{1111}| = 2.6 \times 10^{-8}$ esu.

1. Introduction

The localized surface plasmon resonance (LSPR) of noble metal nanoparticles is of particular interest due to its ability to modify light–matter interactions exhibited by bulk materials. When metallic nanoparticles are incorporated in a host media, it is possible to promote potential applications in sensing [1,2], enhanced spectroscopies [3–6], photocatalysis [7], and optical devices [8]. A notable characteristic of the LSPR absorption is the spectral position dependence of the corresponding absorption bands on the size and shape of the noble metal nanoparticles [9]. The existence of such dependences allows "tuning" the composition of the metal nanoparticles on the manifestation of resonance absorption by synthesis of metal nanoparticles with certain size and shape [10]. Besides, the use of metal nanoparticles (e.g., Au, Pt, Ag) deposited on metal oxide semiconductors (e.g., TiO_2, ZnO, SnO_2) produces an "antennae" effect which could activate electron states localized at the surface and subsurface of the photoactive metal oxide. Thus, the combination of metal nanoparticles and semiconductor metal oxides should improve their photoactive properties giving best materials for photo-processes applications [10]. In this way, it could be also expected that the nonlinear optical properties may take advantages of LSPR contributions together with the benefits of photoactive metal oxides. Different studies in metallic nanocomposites have pointed out that the optical Kerr effect, which is a third order optical nonlinearity, displays a dependence on the surrounding and temporal response of the nanoparticles [11]. Besides, changes in the nanostructured electrical attributes can notably influence the magnitude of absorptive nonlinearities related to the two-photon absorption or free carrier absorption [12]. Attractive applications to simultaneously manipulate electrical and optical characteristics for multi-functional systems can be contemplated [13]. Moreover, sensitive optical sensors can be obtained by engineering the extrinsic light absorption spectrum of metal oxides and the LSPR. As a result, a photoresponse material can be strongly dependent on its ability to interact with a specific optical wavelength.

The linear optical absorption of metallic nanoparticles is strongly dependent on LSPR. The LSPR phenomenon can be considered an interesting tool for tailoring optical properties of nanocomposites regarding that the LSPR excitations can be shifted for different wavelengths by changing the metal that conforms the nanoparticles. In a recent work, our group reported that the nonlinear optical properties of metallic nanoparticles can be mechanically engineered if they are encapsulated in a dielectric with high refractive index such as TiO_2 matrix [14]. It is well known that TiO_2 films present a refractive index that is higher than the correspondent magnitude for SiO_2; besides TiO_2 in amorphous or rutile morphology are very suitable for optical applications such as the design of waveguide devices. However, TiO_2 is also a dielectric material and in film form presents a high resistivity. In contrast, ZnO films exhibit good conductive properties, especially when it is doped with aluminum or fluoride ions. This is one our motivation to use ZnO as the host material to synthesize thin films with strong optical

* Corresponding author at: Instituto Politécnico Nacional, A. P. 07-300, C. P. 07738, México, D.F., México.
E-mail addresses: martin.trejo@laposte.net, mtrejov@ipn.mx (M. Trejo-Valdez).

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nonlinearity and good conductivity. In this direction, within this work the electrical properties of nanostructured ZnO thin solid films doped with TiO_2, Au and Pt nanoparticles were evaluated. In addition, a two-wave mixing (TWM) method at 532 nm and 4 ns was employed to explore the third order optical phenomena of the samples studied. Furthermore, regarding the remarkable nonlinear optical characteristics of the samples, potential applications to develop all-optical functions can be proposed.

2. Experimental details

All the thin films were synthesized by the spray pyrolysis deposition method. This technique is inexpensive and allowed us to obtain semi-conductor films with good optical quality. The precursor solutions for film deposition were obtained as follows:

The ZnO precursor solution was elaborated by mixing 50 mL of concentrated acetic acid with the same volume of a 0.4 M $Zn(CH_3COOH)_2$ aqueous solution. The last resulting solution was poured in a bottle containing 450 mL of absolute methanol.

The preparation of the TiO_2 doping solution containing gold and platinum was described elsewhere [15–17]. Initially, a TiO_2 solution was prepared from a Titanium i-propoxyde $[Ti(OC_3H_7)_4]$ solution with a C = 0.05 Mol/L, pH = 1.25, and a water/alkoxyde molar ratio of 0.8. This sol–gel solution, was stored in a dark bottle for at least one week, before it was used in the synthesis of films. The Au and Pt precursor solutions were Aldrich standard solutions, whose metal nominal concentration was 1000 mg/L. A volume of 0.75 mL of the Au standard and another one of 0.75 mL of the Platinum solution were mixed with 10 mL of the TiO_2 solution. The photo-catalytic reduction of the gold ions was carried out in a homemade ultraviolet-reactor with twelve ultraviolet-light sources. Each one was a black light blue UVA lamp (8 W, Hitachi). This light source provided a broad range of UVA light from 320 to 390 nm with λ max (emission) = 355 nm, and a light intensity of 732 mW/cm^2. The growing of nanoparticles was monitored by measuring the evolution of the plasmon band of the ultraviolet–visible (UV–vis) absorption spectra. After ultraviolet-light exposure, the source was turn off in order to start the recuperation of the irradiated TiO_2–AuPt solution that was used for doping a volume of 50 mL of the zinc acetate solution. For the doped ZnO solutions (ZnO–AuPt), the Au and Pt final concentrations were 5.78×10^{-5} M and 5.84×10^{-5} M, respectively. This solution was employed to prepare ZnO–AuPt films.

In a separate flask, another volume of 50 mL of the ZnO solution was mixed with 10 mL of a pure TiO_2 solution. With this last solution were synthesized the ZnO films containing only TiO_2. The ZnO/TiO_2 molar ratio was 10.

For the coating experiments, the precursor solution was poured into a dropping funnel which was connected to the spray system. The spray pyrolysis deposition setup consisted of a homemade sprinkler system that was built with two syringe needles which were arranged in a perpendicular way. Compressed air was used as the carrier gas that was controlled by a flow-meter. A 2 mL/min fixed flux was utilized. The employed substrates were commercial soda-lime glasses. The soda-lime glasses used as the substrates for the film deposition were firstly washed with a phosphate-free detergent solution, then rinsed several times with water and immersed in an acetone bath for 20 min. Then, these glasses were rinsed with absolute ethanol and dried with pure N_2.

For the film depositions, the substrates were placed on a fused tin bath, whose temperature was measured just below the substrate using a chromel–alumel thermocouple contained in a stainless steel metal jacket. The temperature of the tin bath was fixed at 420 °C and the deposition time was of 2.5 h. This time of deposition allowed us to obtain 50 nm thickness films with an error bar of about ±4%.

The structure of the samples was investigated by X-ray diffraction (XRD; Panalytical XPERT MRD). The XRD system was employed in a configuration for X-ray reflectivity in plane thin film phase by using ceramic X-ray tube Cu, Ni beta filter for Cu radiation, extended interface between tube tower & goniometer.

Additionally, field emission scanning electron microscopy (SEM; JEOL JSM-6701F). The voltages for SEM studies were operated between 4 kV and 15 kV. Scanning transmission electron microscopy (STEM, JEM-ARM200CF) was performed between 80 keV and 200 keV. A small drop of the ZnO–AuPt solution was placed on a copper grid for the STEM analysis. The elemental composition of these metallic particles was measured by energy dispersive X-ray spectroscopy (EDX) analysis. EDX evaluations were carried out in a JEOL JSC-6701F system with an accelerating voltage of 5 kV, takeoff angle of 35°, spatial resolution 129.127 μm, and live time of 50 s.

The electrochemical impedance spectra (EIS) of the samples were evaluated at 0.5 V by using an Autolab/PGSTAT302N high power potentiostat/galvanostat. A 10 mV amplitude modulated signal with an integration time of 1 s was employed. Two electrodes were coated on the film by the direct evaporation of carbon on the film surface which was previously protected with a grid. The pattern designed displayed the electrodes with a distance of 5 mm of separation. The experimental impedance curves were fitted by using Autolab Nova 1.7 software that also supplies a resistance–capacitor electric circuit. The repeatability for the electrical measurements was determined by performing ten measurements in two different days.

The linear absorption spectra of the samples were acquired with a Perkin Elmer XLS UV–vis spectrophotometer.

To explore the third order nonlinear optical response exhibited by the film, a TWM method was employed [16]. Pump and probe beams, with linear polarizations, were aligned to interact with the samples making a geometric angle between their propagation vectors of about 30°. The beams were provided by a Nd-YAG laser source (Continuum, Model SL II-10) emitting single pulses with maximum energy of 80 mJ. The beam waist diameter on the thin film samples was measured to be 6 mm and for the probe beam was 1 mm. The selected wavelength for the experiments was 532 nm with pulse duration of 4 ns.

The irradiances of the pump and probe beams at the sample were about 70 MW/cm^2 and 140 W/cm^2, respectively. The polarized irradiances of the transmitted beams in the two-wave interaction were measured in different cases of polarization of the incident waves making an angle, ϕ, between their planes of polarization.

The amplitudes of the transmitted fields were described by the mathematical expression [16]:

$$E_{1\pm}(z) = \left[E^0_{1\pm}J_0\left(\Psi^{(1)}_{\pm}\right) + \left(iE^0_{2\pm} - iE^0_{3\pm}\right)J_1\left(\Psi^{(1)}_{\pm}\right) - E^0_{4\pm}J_2\left(\Psi^{(1)}_{\pm}\right)\right] \exp\left(-i\Psi^{(0)}_{\pm} - \frac{\alpha(I)z}{2}\right), \tag{1}$$

$$E_{2\pm}(z) = \left[E^0_{2\pm}J_0\left(\Psi^{(1)}_{\pm}\right) + \left(iE^0_{4\pm} - iE^0_{1\pm}\right)J_1\left(\Psi^{(1)}_{\pm}\right) - E^0_{3\pm}J_2\left(\Psi^{(1)}_{\pm}\right)\right] \exp\left(-i\Psi^{(0)}_{\pm} - \frac{\alpha(I)z}{2}\right), \tag{2}$$

where $E_{1\pm}(z)$ and $E_{2\pm}(z)$ are the complex amplitudes of the circular components of the transmitted waves beams; $E_{3\pm}(z)$ and $E_{4\pm}(z)$ are the amplitudes of the self-diffracted waves, while $E^0_{1\pm}$, $E^0_{2\pm}$, $E^0_{3\pm}$ and $E^0_{4\pm}$ are the amplitudes of the incident and self-diffracted waves at the surface of the sample; $\alpha(I)$ is the irradiance dependent absorption coefficient; I is the total irradiance of the incident beams; $J_m(\Psi^{(1)}_{\pm})$ stands for the Bessel function of order m, z is the thickness of the nonlinear media, and

$$\Psi^{(0)}_{\pm} = \frac{4\pi^2 z}{n_0\lambda}\left[\left(A + \frac{n_0\beta}{2\pi}\right)\sum_{j=1}^{4}|E_{j\pm}|^2 + \left(A + B + \frac{n_0\beta}{2\pi}\right)\sum_{j=1}^{4}|E_{j\mp}|^2\right], \tag{3}$$