



## Photoinduced absorption of Ag nanoparticles deposited on ITO substrate

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### ARTICLE INFO

#### Article history:

Received 7 July 2010

Received in revised form

14 December 2010

Accepted 15 December 2010

Available online 23 December 2010

#### Keywords:

Nanoparticles

Surface plasmon resonance

Photoinduced absorption

### ABSTRACT

Substantial changes of absorption after illumination by 300 mW continuous wave green laser at 532 nm were observed. The effect of indium tin oxide (ITO) substrate was explored versus Ag nanoparticles (AgNPs) size, their regularity and surface plasmon resonance. The ITO substrate features play a crucial role for the formation of homogenous AgNPs. The attachments of AgNPs on ITO surface as well as their homogeneity are significantly changed under the influence of the laser treatment. We study the Ag NP deposited on the two different substrates which play a crucial role in the photoinduced absorption. The dependence of the photoinduced absorption versus the time of optical treatment is explained within a framework of the photopolarization of the particular trapping levels on the borders between the ITO substrate and the Ag NP.

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### 1. Introduction

Incorporation of Ag nanocrystal (NC) into indium tin oxide films (Ag-ITO) could enhance the conductivity of transparent oxide which is very crucial for the optoelectronic applications [1]. It is important that the incorporation of silver NC decreases the crystallization temperature and inhibits the growth of indium oxide. Ag-ITO films possess a hierarchical structure. In Ref. [2], it was established that the spectra of transmittance and sheet resistance are sensitive to the Ag film thickness. Whereas the spectral range, at which the maximum transmittance is achieved, can be changed by adjusting the ITO films thickness. Such features open a possibility of operation by their properties by additional laser induced treatment [3]. Ag-ITO films were fabricated by a modified sol-gel method. In Ref. [4] it was established an efficient photoinduced method to operate by average sizes and heights of silver nanoparticles deposited on transparent and conductive substrates by seed-mediated growth method. The studies were done with indium tin oxide (ITO) and fluorine tin oxide (FTO) substrates having 4 and 14  $\Omega$ /square sheet resistance, respectively. These two substrates are responsible for different photoinduced aggregation

of silver NC. The substrate resistance determines the observed photoinduced aggregation features. In the observed phenomena principal role play electron-phonon interactions which cause the occurrence of the periodical structure of the  $\mu\text{m}$  sizes [5].

However, all the previous studies were done for the pulsed laser treatment. For the further studies it would be interesting to perform the studies using continuum wavelength (cw) laser beams. Using of the cw laser treatment will favor additional changes of the local thermoheating and accordingly the contribution of the electron-phonon interactions including the anharmonic ones. Such interactions are principal for the formation of the localized polarized states determining additional light absorption in the vicinity of the photoabsorption. The use of the 532 nm cw laser is of especial interest due to the close spectral position of the probing laser wavelength to the surface plasmon resonance wavelength. Additional changes were observed during the bicolor coherent laser treatment both in the spectral positions as well as in the corresponding kinetics [6]. Following all the previous works we have established that the ITO substrate resistance plays a crucial role here and may be responsible for the observed photoinduced absorption. As a consequence in the present paper we present the principal results for the studies of the photoinduced absorption during the different times of the treatment by the 300 mW cw 532 nm laser.

In Section 2, we will present the technology of the sample's synthesis together with the FE-SEM pictures giving the parameters of the Ag NC surfaces (shape, inter-particle distance, sizes, etc.).

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Here also will be presented a brief description of the measurement set-up, particularly, for the photoinduced optical treatment. The obtained optical results and their correlation with the Ag NC parameters will be given in Section 3 together with appropriate discussion.

## 2. Experimental

The attachment method of Ag NCs on ITO has been described previously [7]. Briefly, as the actual procedures, an ITO substrate was first immersed for 2 h in a seed solution containing 4 nm Ag nanoparticles, which was produced by the  $\text{NaBH}_4$  reduction of  $\text{AgNO}_3$  in the presence of trisodium citrate. Then, after washing of the ITO surface by pure water and drying by nitrogen gas, the ITO was immersed in a growth solution, which contained  $\text{AgNO}_3$ , ascorbic acid, NaOH and cetyltrimethylammonium bromide. Through this two-step treatment, Ag NC could be attached on ITO substrates [7].

Two types of ITO substrates were used in this work. ITO-4  $\Omega$  is the product of Kuramoto Seisakusho Co., Ltd. Japan, whose resistance was ca. 4  $\Omega$ /square sputtered on glass substrate. ITO-50  $\Omega$  is produced by CBC Optics Co., Ltd., Japan, whose surface resistance was ca. 50  $\Omega$ /square. The JEOL JSM-7400F field emission scanning electron microscopy (FE-SEM) instrument was used to characterize the growth of Ag NC on the ITO surfaces.

The photoinduced treatment was performed by 300 mW green laser. The spectral changes were measured by the spectrophotometer Ocean Optics with spectral resolution 0.1 nm. The illumination was performed at angles varying from 25° up to 30°. The photoinduced beam was equal to about 3 mm in diameter. The stability of the laser beam was equal to about 5%.

## 3. Results and discussion

Fig. 1 presents the typical FE-SEM images of Ag NC attached ITO substrates. Using the seed-mediated growth method, the surfaces of the ITO were modified by the growth of Ag nanoparticles as shown in the FE-SEM images. The background image was different depending on the resistance of ITO. It was recognized that small Ag NC could be attached on the ITO substrates without using peculiar bridging reagents.

The optical studies of the photoinduced absorption spectra were limited to the spectral range 300–650 nm. In Fig. 2 are presented the photoinduced absorption changes of silver coating on the Ag-ITO (4  $\Omega$ ) film for the sample I. The measurements were done for different times of treatment by the green cw laser with wavelength 532 nm possessing power about 300 mW. One can see that the photo stimulated absorption spectra obtained for the higher times of optical treatment (15 min and 25 min.) are substantially higher than for the samples irradiated during the 5 min. Following the presented dependences one can conclude that for treatment time 25 min there occur spectral maxima situated at 449 nm and 600 nm. Following Fig. 2, one can see that maximal photoinduced absorption was observed for the laser time treatment 25 min. After the switching off of the cw laser treatment we have established a slow decrease of the occurred photoinduced maxima. It is interesting that for the cw treatment time 15 min there occur additional clear maxima at wavelength equal to about 509 nm. The observed maxima are caused by photoinduced polarization of the trapping levels.

Fig. 3 presents the absorption changes spectra of silver coating on the Ag-ITO (50  $\Omega$ ) film (sample II). In this case, the measurements were done also at three different times of treatment by the same laser. Following Fig. 3, one can see that the maximal changes (0.33 and 0.58) of the absorption spectra were achieved for time of treatment equal to about 25 min.

This spectral maxima of the photoinduced absorption were observed at wavelengths equal to about 450 and 600 nm. Further decrease of the laser treatment time leads to faster decrease of the corresponding absorption. For less time of treatment (about 15 min) the maxima were observed at almost the same wavelengths and the maximally achieved photoinduced absorption was equal to about 0.54. Substantially less effect was observed for times of treatment equal to about 5 min with the maximum equal to about 0.43. It is crucial that even after the 5 min of the treatment the

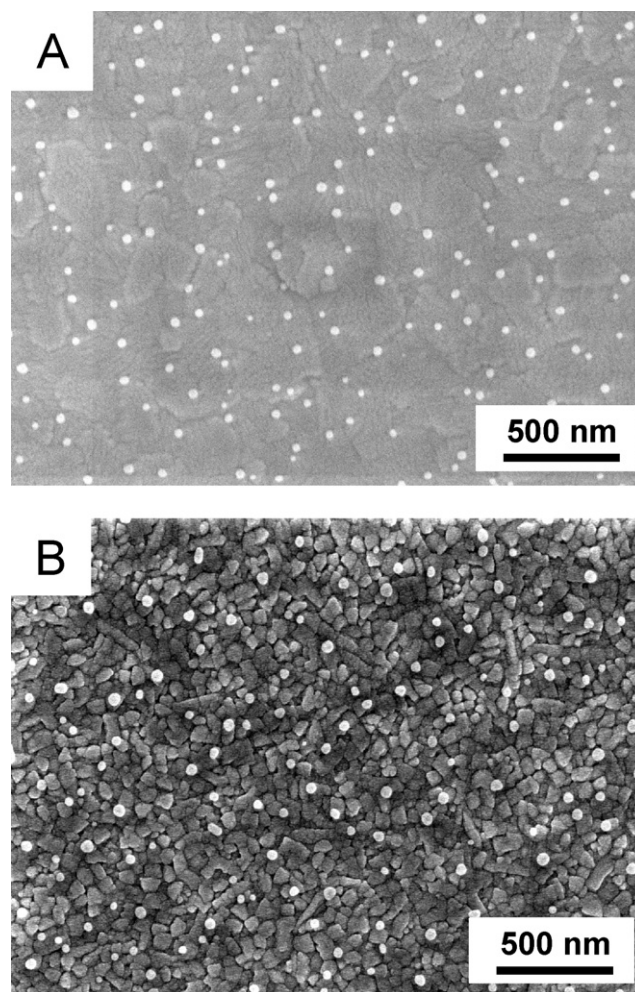


Fig. 1. Typical FE-SEM images of silver NC-attached ITO surfaces. (A) ITO-4  $\Omega$  and (B) ITO-50  $\Omega$ .

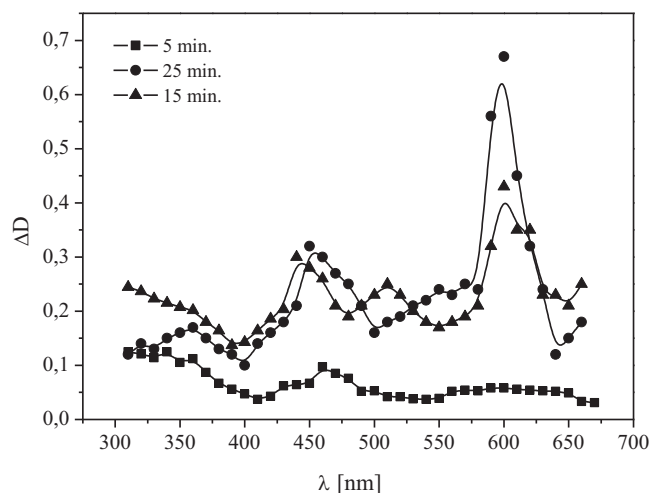


Fig. 2. The changes of the absorption during illumination by the 532 nm cw laser for the sample I.

photoinduced absorption in ITO with resistance 50  $\Omega$  for the spectral maxima at 600 nm occurs substantially earlier than for the first samples possessing 4  $\Omega$  sheet resistance. This is a consequence of the different localization of the photoinduced carriers on the borders separating the ITO substrate and the Ag NC. For all the samples

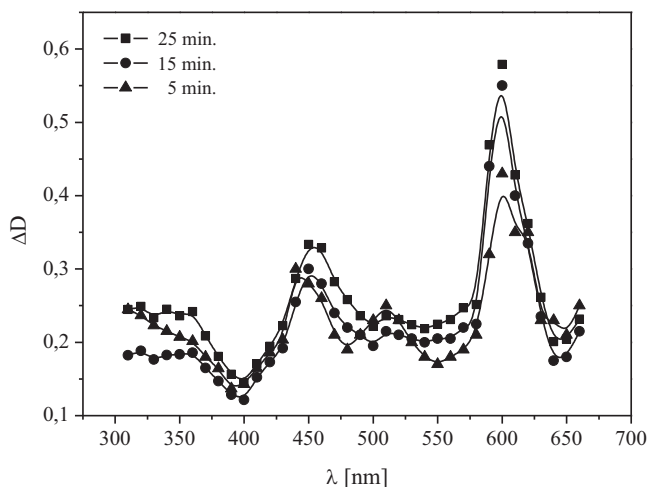


Fig. 3. The changes of the absorption during illumination by the 532 nm cw laser for the sample II.

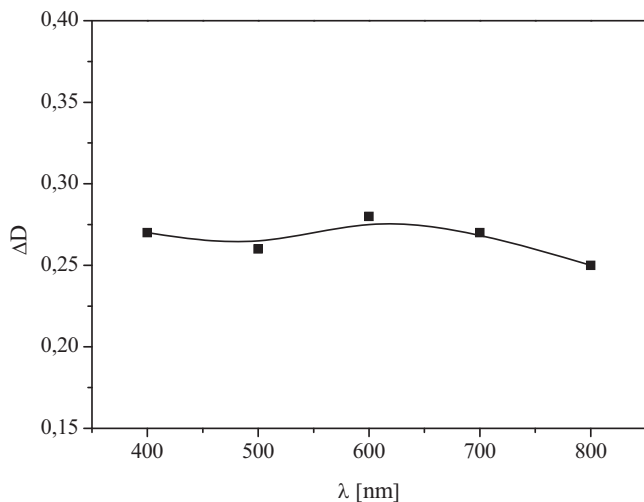


Fig. 4. The changes of the absorption for the pure ITO substrate during 25 min of illumination by the 532 nm cw laser.

the photoinduced absorption exists only during cw laser treatment and substantially decrease after the switching off of the optical treatment. In turn, without the laser treatment, no photoinduced absorption is observed.

For comparison in Fig. 4 are presented the changes of absorption for the pure ITO substrates. One can see that the changes are spectrally independent contrary to the ITO/Ag NP substrates. Additionally they are not dependent on the ITO resistivity. Such differences may confirm the principal role of the ITO/Ag NP interfaces.

So one can conclude that the sheet resistance of the ITO plays a principal role both for the morphology for the silver NC as well as for the polarizability of the main trapping levels. This may be used for operation by their phototransparency features.

The principal mechanisms of the observed effect is caused by the photoinduced local thermoheating. It is known that such effects may be caused by activation of the electron–phonon anharmonic subsystem. These effects usually form some local non-centrosymmetry which is described by the third rank polar tensors and which is responsible for the observed effects. The existence of the effect is caused by two contributions: the first one—originated from the electron polarization and another—due to the thermoheating. More general theory is described in Ref. [8].

#### 4. Conclusions

Following the performed studies of the photoinduced absorption using the photo inducing cw 532 nm green laser with power about 300 mW we have established that there occurs the drastic changes of the absorption within the spectral range 400–800 nm. The changes are crucially dependent on the sheet resistivity of the ITO substrates and on the time of the cw-treatment. The principal influence of the photoinduced carriers on the particular trapping levels was found. One can see that the induced absorption spectra obtained for the larger times of optical treatment (15 min, and 25 min) are substantially higher than for the samples irradiated during the 5 min.

Following the dependencies presented one can conclude that: for time of treatment 25 min there occurs spectral maxima situated at 449 nm and 600 nm. It is crucial that even after 5 min of the treatment the changes of the absorption for the spectral maxima at 600 nm for the samples with 50  $\Omega$  sheet resistance occur substantially earlier than for the first samples possessing 4  $\Omega$  sheet resistance. This is a consequence of the different localization of the photoinduced carriers on the borders separating the ITO substrates and the Ag NC.

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