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# Laser stimulated light reflection reduction for silver nanoparticle-attached aluminum-doped zinc oxide substrate

I.V. Kityk<sup>a,\*</sup>, X. Chen<sup>b</sup>, M. Oyama<sup>b</sup>, E. Gondek<sup>c</sup>, P. Armatys<sup>d</sup>, P. Karasinski<sup>e</sup><sup>a</sup> Electrical Engineering Department, Czestochowa University of Technology, Aleja, Armii Krajowej 17/19, PL-42-201 Czestochowa, Poland<sup>b</sup> Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan<sup>c</sup> Institute of Physics, Cracow University of Technology, Podchorążych 1, 30-084 Krakow, Poland<sup>d</sup> AGH – University of Science and Technology, Faculty of Physics and Applied Computer Science, al. A. Mickiewicza 30, 30-059 Krakow, Poland<sup>e</sup> Department of Optoelectronics, Silesian University of Technology, B. Krzywoustego 2, 44-100 Gliwice, Poland

## HIGHLIGHTS

- Principal role of Ag NP sizes on the output reflectivity decree is observed in AZO films.
- The optimal nanoparticle sizes are 40 nm.
- The process is slowly relaxed.

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## ABSTRACT

A principal possibility to operate the light reflection within the 350 nm–680 nm spectra wavelength range and related extinction efficiency of silver nanoparticle-attached aluminum-doped zinc oxide substrate using an external laser light was shown. The treatment was performed by a nanosecond Nd:YAG (1064 nm) and Er:glass (1540 nm) lasers and by the corresponding bicolor regime. The principal role of the interfaces separating the ZnO:Al substrate and topology of Ag NP is established using AFM analysis of the Ag NP possessing 20 nm, 40 nm and 60 nm average sizes. Different possible physical mechanisms are discussed including quadrupolar interaction of the electromagnetic wave and nano-composites following the overlap between the surface plasmon resonance and the nano-trapping levels. The high selectivity to the photoexcited wavelength is explored. The sensitivity to the observed photoinducing laser wavelengths is discussed.

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## 1. Introduction

The problem of enhanced light absorption for particular photovoltaic devices, such as active layers and electrodes is very actual [1,2] now due to the search of a way to increase their photovoltaic efficiency. The problem is actual for all types of photovoltaic cells: from organic ones to inorganic silicon. One of the approach is based on the incorporation of the Ag NP into the active layer, such as Si nanoparticles [3] which leads to a decrease of reflectance in the effective spectral range of the sun rays, i.e. 320 nm–650 nm [4,5]. Usually it was used for the silicon photovoltaics due to the poor absorption of silicon, because of excitation of quadrupolar resonances, and their high radiative scattering efficiency, which can predominantly scatter in the forward direction. It is interesting

that the minimal reflectance decrease was observed for the Ag NP with an average diameter from several to 10 nm and the origin of the effect is observed within a framework of quadrupolar resonances. The first results are very promising, for instance in Ref. [6] a seven-fold photocurrent increase of the photocurrent in the photocells on dielectric cells at wavelength 1050 nm was achieved. The effect is prevalingly caused by the photon trapping of the Ag NP. Similar effects were achieved in Refs. [7,8]. Additionally the occurred wave guide modes, occurring at the interface between the semiconductor and the Ag NP, also effectively interact with the excited surface plasmon resonances (SPR), favoring coupling for the desired spectral range. By appropriately varying NP sizes, their topology and inter-particle distances one can suppress the total reflectance from the corresponding substrate in the wide spectra range [9]. More theoretical details may be found in the review [10]. However, all the considered approach were mainly devoted to silicon medium and its derivatives, however the same approach may be extended for electrodes like the transparent ITO electrodes

\* Corresponding author.

E-mail address: [iwank74@gmail.com](mailto:iwank74@gmail.com) (I.V. Kityk).

[11] or ZnO electrodes. The latter have an advantage due to their higher spectral angle and because all the interaction will take place between the doped trapping levels and the surface plasmons excitations. Additionally in the recent work [12] it was shown that the metallic nanoparticles deposited onto the ITO using a seeded method, which allowed us to avoid the direct contact between the metallic NP and the substrate, may be used as promising materials for the photoinduced changes. Because the ZnO is more polarizable than ITO one can guess that the use of the Al-doped ZnO (AZO) substrate may be very promising here. As a consequence in the present work we study the photoinduced reflection and related extinction for the silver nanoparticles of sizes 20 nm, 40 nm, 60 nm deposited on AZO substrates. The origin of the phenomenon was based on the excitation of quadrupolar resonance, and their high radiative scattering efficiency

The principal experimental methods given in Section 2. Section 3 will be devoted to the AFM analysis of the samples as well as to interaction of the laser light with the titled nanocomposites and corresponding discussion. Photoinduced treatment and their relation with the morphology of the samples.

## 2. Experimental methods

### 2.1. Preparation of AgNP-attached AZO

Commercially available silver colloid solutions (the diameters; 20, 40 and 60 nm) were purchased from Sigma-Aldrich. 3-aminopropyltrimethoxysilane (APTMS) was also from Sigma-Aldrich. Aluminum-doped zinc oxide (AZO) coated glass plates were the products of Geomatec Co. Ltd., Japan.

To prepare AgNP-attached AZO, initially, a piece of an AZO plate (1.0 cm × 1.0 cm) was pre-washed with sonication, first in acetone, then in ethanol, and finally in pure water, followed by drying with N<sub>2</sub> gas. Next, the AZO was immersed in the mixture of ethanol and APTMS (100:2, v/v) at 28 °C overnight to prepare APTMS-modified AZO. It was washed with ethanol to remove residual APTMS and dried with N<sub>2</sub> gas. As the final step, the APTMS-modified AZO was immersed in a colloidal solution of 20 (or 40, 60) nm AgNPs for 2 h at 28 °C. After washing with pure water and drying with N<sub>2</sub> gas, the AgNP-attached AZO could be prepared.

### 2.2. AFM technique

Topography and phase contrast images for the 20, 40 and 50 nm AgNPs were studied at ambient conditions using the atomic force microscope, Agilent 5500AFM working in noncontact mode. AFM micrographs were monitored by the Gwyddion software. For each sample, several places were examined in the scale of 5 × 5 mm<sup>2</sup>. Generally there were regions possessing grains covering the substrate. The regions with grains were well defined. Additional analysis was performed for the places situated outside the places without grains. Phase imaging was concerned to the monitoring of the phase between the signal that drives the cantilever oscillation and the cantilever oscillation output signal. Variation of the phase reflects changes in the mechanical parameters such as elasticity, adhesion or friction of the sample surface. The system's feedback loop operates in the usual manner, using variations in the cantilever's deflection or vibration amplitude to measure the sample morphology. The phase lag is detected while the topographic image is being taken so that images of the topography and material features can be collected simultaneously.

By analyzing the data concerning the morphology of the AgNP, one can conclude that they are highly mono-dispersed by sizes and the inter-particle distances are well defined, however one can clearly see the places where some aggregations occur. The latter

are dependent on the sizes of the average the AgNP and the inter-particle distances. Such well defined structure of grains together with their separation from the AZO substrate is a principal requirement for their application as materials for effective interactions between external electromagnetic light and the surface plasmon modes of the Ag NP.

### 2.3. Photoinduced treatment and optical measurements

We have used two 10 ns lasers as the photoinduced sources. The first one was a Nd:YAG lasers with wavelength 1064 nm, and the second one was an Er:glass one possessing a fundamental laser wavelength 1540 nm. The pulse frequency repetition of the laser beam was equal to about 15 Hz. Additional treatment was performed simultaneously for the fundamental and the second harmonic generation where the pulses were spacially separated as described in Ref. [13]. The power density was successively varied by the changes of the pulse energy. Diameter of the beam was about 5 mm. Additionally the illuminated part was monitored by the thermocouple which controls the photo heating. The optical fiber spectrophotometer was used for controlling the photoinduced reflection as well as the extinction for the spectral range 380 nm–680 nm. The duration of the photo treatment was controlled by saturating the total optical spectral signal. The same conditions were put for the geometry of the fundamental and doubled frequency beam. The latter was achieved by the BiB<sub>3</sub>O<sub>6</sub> crystals following the phase matching conditions for the particular wavelength [14].

## 3. Results and discussion

In Fig. 1 typical space distribution of the nanograins with average size 60 nm is presented. One can clearly see their substantially non-homogenous surface distribution.

It is important that for the laser beam with diameter of about 3 mm such surface distribution is effectively averaged and the output reflected/transmitted signals are obtained independent of the distribution. It is a very crucial factor which shows that the role of even non-uniformly distributed nanoparticles is averaged.

For the Ag NP less 40 nm in size there occurs some additional aggregations (see Figs. 2–4). The latter decreases from one side of the effective nano-surfaces. At the same time such aggregates interacting with the AZO substrates may be more polarizable towards light. However it may be spectral dependent because

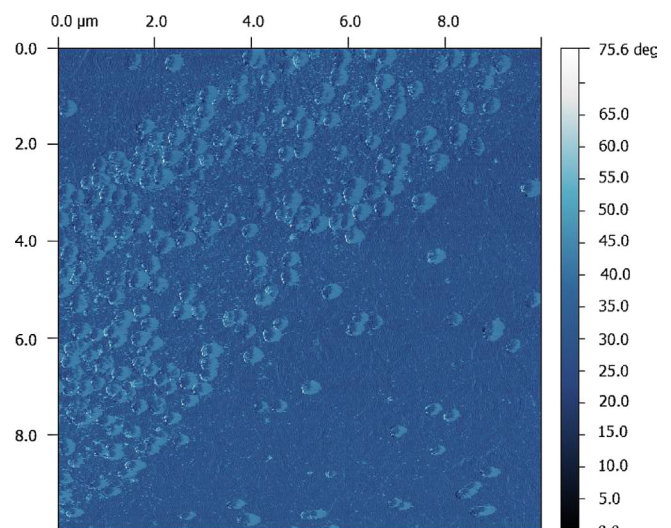


Fig. 1. AFM picture of the 60 nm Ag NP/AZO. Top view in the scale 10 μm.

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