Photoactive n-type oxide AZO-AgNP-AZO multilayer films for photovoltaic application

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Abstract. We report on the simulation of the absorption cross-section of an aluminum-doped zinc oxide (AZO) - silver nanoparticles (AgNP)-AZO multilayer structure by the finite element method in Comsol Multiphysics. A key feature of our approach is consideration of two plasmon materials such as AgNP and highly doped AZO. The simulation is based on the Drude-Lorentz-Sommerfeld model. The absorption cross section spectra were obtained for structures with different thicknesses of AZO layers and different amounts of silver nanoparticles, and at a different incidence of illumination. As a result, several resonance peaks were detected in the absorption cross-section spectra. The enhancement of absorption in the visible and near-infrared regions of the spectrum is associated with plasmon oscillations of interacting silver nanoparticles and a plasmon resonance in an AZO nanolayer, respectively. The presence of several resonances in the visible region, as well as the resonance in the near-IR region, makes this material promising for photovoltaics.

1. Introduction

Worldwide trends show new developments in the search for alternative energy sources. Current efforts are focused on increasing the efficiency of photovoltaic devices while reducing their cost. Multilayered oxide films with metal nanoparticles are promising functional components for photovoltaic devices. In the last decade, the metal nanoparticles have come to be viewed as "activators" in photovoltaics, owing to their plasmon properties [1]. The excitation of nanoparticles at the plasmon frequency leads to an increase in their absorption and scattering cross sections. The frequency of the plasmon resonance is determined by the material of particles, their shape and the material of environment [2, 3]. At least three possibilities exist for the realization of metal nanoparticles in photovoltaic systems. First, the local near-field amplification caused by the excitation of plasmon oscillations results in the increasing generation of charge carriers [1]. Near-field effects were identified by an increase in the photocurrent in solar cells sensitized by the dye and in organic polymer-based solar cells [4-6]. The second approach is based on a possibility to redirect the radiation to an active layer of a solar cell by increasing the scattering cross section of metal nanoparticles at the plasmon resonance wavelength [7, 8]. The third approach suggests that the plasmon particles embedded in an environment of a semiconductor act as elements that accumulate light energy and trigger the mechanism of photoinduced charge separation. The first research in this direction was published in 1996 and pointed to the generation of electron-hole pairs in a TiO₂ semiconductor in
contact with a plasmon metal nanoparticle [9]. Zhao and co-authors were the first to register a photocurrent generated by a TiO$_2$ electrode coated with gold and silver nanoparticles under the action of visible radiation. Later, a number of papers have confirmed the phenomenon of photoconductivity in such structures by detecting the generation, injection, and regeneration of "hot" electrons [10, 11].

In this work, we consider optical properties of a multilayer structure consisting of silver nanoparticles (AgNP) and AZO. AZO is of interest as a host material due to the fact that it is a transparent semiconductor that exhibits plasmon properties in the near–IR region [12].

2. The model

In this work, we use the experimentally measured parameters of the composite AZO-AgNP-AZO structures [13] as the initial data for the absorption cross-section simulation. The composite structure fabricated by the sol-gel technique consists of ZnO:Al (AZO) layers deposited by centrifugation on a quartz substrate with an intermediate layer of silver nanoparticles. AgNP were deposited from a silver colloidal solution.

The structure parameters for the simulation were determined based on the scanning electron microscopy data and the data on the thickness of the AZO layers checked by the interference method. The shape of all nanoparticles was assumed to be spherical with an average nanoparticle diameter of 40 nm and a distance between them of 10 nm. This approximation was sufficient to simulate the position of plasmon resonances in the structure. The dispersion in shape and size of nanoparticles in the real structure leads to broadening of the peaks in the absorption spectra.

Simulating optical properties of metal nanoparticles was based on the solution of the Maxwell equations by approximate methods. The spectral dependences of the dielectric permittivities of the material were analyzed in the framework of the Drude-Lorentz-Sommerfeld model. For noble metals (silver and gold), the real parts of the permittivity become negative in the visible range of the spectrum, which determines their optical properties. The quasistatic approximation of the Mie scattering theory allows considering a metal nanoparticle as an oscillating dipole.

The absorption cross section is determined by the following expression [14]:

$$\sigma_{abs} = k \text{Im}\{\alpha(\lambda)\},$$

where $\alpha = 4\pi^{3} \frac{\varepsilon(\lambda) - \varepsilon_{m}(\lambda)}{\varepsilon(\lambda) + 2\varepsilon_{m}(\lambda)}$ is the polaribility in the case of spherical metal nanoparticles with a radius $r$, $k$ is the wave vector, $\varepsilon(\lambda)$ is the dielectric permittivity of metal nanoparticles, and $\varepsilon_{m}(\lambda)$ is the permittivity of the surrounding medium.

The simulation was carried out by the finite element method (FEM) for the periodic structure shown in figure 1 in the RF module of Comsol Multiphysics software. A key feature of the model is the consideration of metal nanoparticles embedded in a medium of a heavily doped semiconductor that exhibits metal properties and demonstrates a plasmon resonance in the near-IR region (a low-loss material). Optical characteristics were calculated using Comsol Multiphysics and accounting for the spectral dependences of AZO permittivity [12].

![Figure 1. Schematic representation of the AZO-AgNP-AZO structure: $\varphi$ is the azimuth angle and $\theta$ is the colatitude angle of incident light.](image-url)
3. Results
In this work, the absorption cross section spectra (figure 2, 3), the electromagnetic field distribution (figure 4(a)), and the field amplification at resonant wavelengths (figure 4(b)) for various thicknesses of AZO layers and for various incident illumination of the AZO-AgNP-AZO structure in the wavelength range of 340-1600 nm were simulated. The simulation of the absorption cross section spectrum of a silver nanoparticle enclosed in a spherical shell of AZO was carried out (figure 5).

The optical properties of an assembly of metal nanoparticles are determined both by the properties of individual particles and by the electrodynamic interaction between them [15]. Multiple peaks appearing in the optical absorption cross section spectrum are related to the splitting of the resonance due to the interaction of nanoparticles with each other. Silver nanoparticles located in the AZO layer can be characterized by a distribution function of the eigenfrequency of collective excitations. This distribution is broader in comparison to the homogeneous width of the resonances, so that the width of the extinction spectrum of the entire ensemble of particles is precisely determined by the inhomogeneous distribution of the resonance frequencies [16]. Owing to the broadening of the spectra for the real structure, the peaks corresponding to the interaction of non-neighboring particles are absent in the absorption cross section spectra.

![Absorption cross section spectra](image)

**Figure 2.** Absorption cross section spectra of the AZO-AgNP-AZO structure on a quartz substrate under normal illumination (1 - the structure consisting of one silver nanoparticle in AZO layers on a quartz substrate; 2 - the AZO-AgNP-AZO structure with an AZO layer thickness of 45 nm on a quartz substrate; 3 - the AZO-AgNP-AZO structure with an AZO layer thickness of 90 nm on a quartz substrate). The insert shows the absorption cross section for the AZO layer on a quartz substrate.

The number of silver nanoparticles interacting with each other in the layer and the thickness of the surrounding AZO layer vary depending on the angle of light incidence at the AZO-AgNP-AZO structure. Thus, the plasmon peak located in the near-IR region at the azimuthal angle ($2\pi/3$) is the consequence of the increasing the fraction of AZO in the environment.
Figure 3. Absorption cross section spectra of the AZO-AgNP-AZO structure on a quartz substrate at different angles of light incidence (1 – $\varphi = 0, 2\pi/3$, $\theta = 0$; 2 – $\varphi = 0, \theta = \pi/3, 2\pi/3$). The insert shows the absorption cross section spectrum for the angle of incidence: $\varphi = 0, \pi/4$.

Figure 4. FEM simulation results for the AZO-AgNP-AZO structure under illumination of a 980 nm wavelength normal to the surface of the structure (a) – the electromagnetic field ($E_y$) in the AZO-AgNP-AZO structure; (b) – the field enhancement in the AZO-AgNP-AZO structure. The field near the nanoparticles is enhanced by up to 100 times.
4. Conclusions

The absorption cross section spectra of AZO-AgNP-AZO structures were simulated at various angles of incidence light and at different thicknesses of AZO layers. The presence of peaks in the spectra indicates the excitation of resonances at the corresponding wavelengths. The analysis of the obtained spectra indicates that the optical properties of the structure correspond to the core-shell model (silver nanoparticle – AZO). The resonance in the near-IR region depends on the plasmon properties of AZO. The presence of plasmon resonances in the visible and near IR ranges indicates the possibility of formation of hot electrons in the structure and an increase in the photosensitivity of the material, which makes it promising for photovoltaics.

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Figure 5. The absorption cross section spectrum of a silver nanoparticle (with a diameter of 40 nm) in an AZO shell (10 nm thick).
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