Materials Physics and Mechanics 29 (2016) 145-149 Received: November 28, 2016

ELECTRICAL AND OPTICAL PROPERTIES OF TRANSPARENT CONDUCTING ZnO:Al/AgNP MULTILAYER FILMS

E.V. Shirshneva-Vaschenko[1*], I.M. Sosnin[2], R.K. Nuryev[1], I.A. Gladskikh[1], T.G. Liashenko[1], V.E. Bougrov[1], A.E. Romanov[1,3]

[1]ITMO University, Kronverkskiy 49, Saint Petersburg, 197101, Russia

[2]Togliatti State University, Belorusskaya str. 14, Togliatti, 445667, Russia

[3]Ioffe Physical Technical Institute, Polytechnicheskaya 26, Saint Petersburg, 194021, Russia

*e-mail: ev.vaschenko@gmail.com

Abstract. In this work, zinc oxide thin films doped with Al were prepared using sol-gel deposition technique. Fabricated films were up 1 μm thick and contain several layers of ZnO:Al deposited on quartz substrate. The films had prevalent (001) growth orientation. The resistivity of the films was reduced significantly after annealing in vacuum (10^{-5} Pa) at 650 ºC and achieved 0.3 Ω·cm. The optical properties of ZnO:Al/AgNP films were tested. The extinction spectra of the films showed the shift of AgNP plasmon resonance with respect to the position being characteristic to silver nanoparticles on fused quartz substrate. The optical radiation action increased the conductivity of ZnO:Al/AgNP films 5 times. An observation of photocurrent was associated with the excitation of plasmon resonance in nanoparticles and was described by the mechanism of "hot" electrons injection in the conduction band of ZnO: Al.

1. Introduction

Transparent conducting oxides (TCO) have received great attention owing their electrical and optical properties and widely used as transparent electrodes in flat panel displays, solar cells, touch panels [1-5]. Most known are indium tin oxide (ITO), fluorine doped tin oxide (FTO), or doped zinc oxide. All of them are belong to the class of wide band gap semiconductors.

Nowadays worldwide development is in progress ofthe search of alternative energy sources. The efforts are directed on increase of the efficiency of photoelectric devices with reduction of their cost. Multilayered oxide film with metal nanoparticles as an effective element of photoelectric conversation is the promising functionality component for photoelectric devices.

In the last decade, the metal nanoparticles owing to plasmon properties are considered as "activators" in photovoltaics [6]. The plasmon particles embedded in an environment of a semiconductor act as an accumulating light energy element that starts the mechanism of photo-induced charge separation. First, the effect of plasmon induced charge separation was published in 1996 and pointed to the generation of electron-hole pairs in the semiconductor of TiO_2, which are located in contact with the metal resonance particle [7]. Up to date there are studies related to plasmon generation of «hot» electrons applied to photovoltaic and photocatalysis devices. Most of these studies devoted to the investigation of gold and silver nanoparticles in contact with TiO_2 [8-14].

In this study, electrical and optical properties of transparent conducting ZnO:Al/AgNP multilayer films were investigated. ZnO:Al multilayers were deposited onto substrate by sol-gel technique. Silver nanoparticles were deposited from silver colloidal solution. As a result our technology allowed to fabricate conducting layers with plasmon nanoparticles.

2. Preparation and characterization of samples

ZnO:Al films were prepared by sol-gel method using spin coating technique. The sol solution consisted of zinc acetate dehydrate [$Zn(O_2CCH_3)_2$, ZnAc] and aluminum nitrate [$Al(NO_3)_3$] was dissolved in ethanol with concentration of 0.7 mol/l. Monoethanolamine (MEA) was used as a stabilizer. The molar ratio of MEA/ZnAc was 1:1. The investigations were carried out up to 6 % Al/Zn volume fraction. To yield a homogeneous solution the prepared sol was stirred at room temperature. The fused quartz plates with 15 mm in diameter were used as substrate. The film was deposited layer by layer on the substrate. The total thickness of ZnO:Al films was 0.4-0.5 μm.

The phase crystallinity and structural properties of the films were analyzed by X-ray diffractometer Rigaku Ultima IV with CuKα radiation (λ = 0.1542 nm). Figure 1 shows diffraction patterns of undoped ZnO film and ZnO films with Al content of 1 % and 3 %. All films are polycrystalline with hexagonal wurtzite type structure and prevalent (0001) growth orientation; c-axis is perpendicular to the substrate. As shown in Fig.1 there are no significant differences in diffraction patterns for doped and undoped ZnO films except slightly shift of (001) peak.

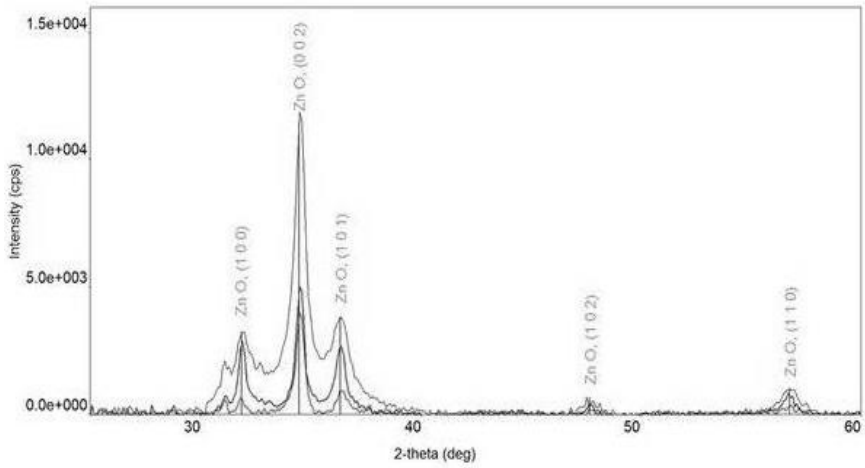

Fig. 1. XRD patterns of ZnO, ZnO:Al (1 %), ZnO:Al (3 %) films (up to down).

Impurity phases such as Al, Al_2O_3 have not been detected which indicates that ions Al^{3+} replace ions Zn^{2+} without lattice disturbance of hexagonal wurtzite ZnO structure. The substitution of zinc by aluminum leads to shortening of c-axis since the aluminum ionic radius less than the ionic radius of zinc. Therefore, according to Bragg relation this displacement leads to the increase of diffraction angle as observed in diffraction patterns for (001) peak.

The surface morphology of the films was studied by scanning electron microscope JEOL JCM 6000. ZnO:Al films had a grain structure with grains size of 15-30 nm.

3. Electrical properties of ZnO:Al films

In this work the effect of heat treatment conditions at drying and annealing regimes of ZnO:Al films with different content of Al (1-6 %) on their electrical properties was studied. The electrical resistivity of films was measured by 4-probe method with used source meter Keithley 2450.

The electrical resistivity decreased with increasing of Al content and reached minimum at Al/Zn ratio of 3 %. An inverse dependence of films resistivity on aluminum concentration in ZnO:Al occured due to higher electron mobility of donor ions Al^{3+} replaced cation positions Zn^{2+}. The further increase of aluminum concentration led to increasing of resistivity due to limited number of vacancies for substitution. Extra atoms of aluminum worked as additional scattering centers decreasing therefore the conductivity.

As a part of investigation the dependence of electrical resistivity of ZnO: Al (3 %) film on annealing conditions was studied. The lowest resistivity of the film was about 0,3 Ω·cm on condition of annealing of each deposited layer at 650 °C. Moreover, the last annealing was occurred in vacuum (10^{-5} Pa). The electrical resistivity of ZnO: Al films owing to absence of chemisorbed oxygen on oxide films surface decreased by annealing in vacuum.

4. Optical and photovoltaic properties of ZnO:Al/AgNP multilayer films

Optical absorption measurements of films were performed with fiber spectrometer AvaSpec-2048.

4.1. Optical properties of ZnO:Al films. Figure 2 shows the extinction spectra of ZnO, ZnO:Al (1 %), ZnO:Al (3 %) and ZnO:Al (6 %) films. All films are transparent with sharp absorption edge in near UV. The films transmittance is about 90% in the visible region at wavelength above 500 nm.

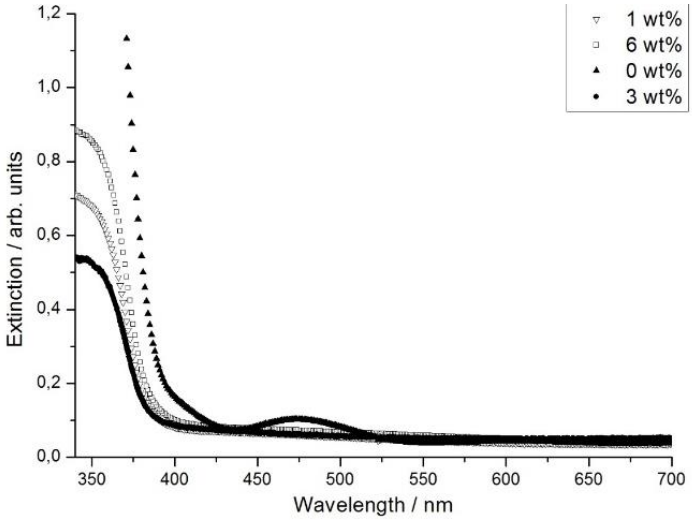

Fig. 2. Optical extinction spectra of ZnO, ZnO:Al (1 %), ZnO:Al (3 %) and ZnO:Al (6 %) films.

By increasing of the percent ratio Al/Zn the absorption edge is shifted to shorter wavelength (a blue-shift). The maximum shift is observed at 3% aluminum content.

4.2. Localized surface plasmons: theory. Plasmonic excitations or collective oscillations of the conducting electrons caused by the oscillating electromagnetic field of the light being incident on metal nanoparticle. The subsequent polarization effects and restoring forces allow for the occurrence of resonance behavior [15]. The interaction of a particle size *r* with the electromagnetic field can be analyzed using the simple quazi-static approximation provided that $r \ll \lambda$. In this case, we can consider spheroid nanoparticle as a homogeneous, isotropic sphere of radius r located in a uniform, static electric field $\overrightarrow{E_0}$. In [16] it was shown that applied field induces a dipole moment inside the sphere of magnitude

$$\vec{p} = 4\pi\varepsilon_0\varepsilon r^3 \frac{\varepsilon-\varepsilon_{medium}}{\varepsilon+2\varepsilon_{medium}}\overrightarrow{E_0}. \quad (1)$$

Here ε is the wavelength dependent complex dielectric function of the metal of the nanoparticle and ε_{medium} is that of surrounding dielectric.

To describe the surface plasmon resonance the polarizability α is introduced, defined via

$$\vec{p} = \varepsilon_0\varepsilon\alpha r^3\overrightarrow{E_0}. \quad (2)$$

In the case of spherical metal nanoparticle with radius r the complex function α is given as

$$\alpha = 4\pi r^3 \frac{\varepsilon-\varepsilon_{medium}}{\varepsilon+2\varepsilon_{medium}}. \quad (3)$$

The polarizability experiences a resonant enhancement under the condition that $|\varepsilon + 2\varepsilon_{\mathrm{medium}}|$ is a minimum, which for the case of slowly varying $\mathrm{Im}[\varepsilon]$ around the resonance simplifies to

$$\mathrm{Re}[\varepsilon] = -2\varepsilon_{\mathrm{medium}}. \quad (4)$$

This relationship expresses the strong dependence of the resonance frequency on the dielectric environment. The resonance redshifts as $\varepsilon_{\mathrm{medium}}$ is increased. For silver spherical nanoparticles in air a resonance position is around 350 nm.

Plasmon resonance of spheroid nanoparticle is observed as a peak in the optical extinction spectrum. For a sphere of volume V and dielectric function ε, the expression for the extinction cross section is

$$C_{\mathrm{ext}} = 9\frac{\omega}{c}\varepsilon_{\mathrm{medium}}{}^{3/2}V\frac{\mathrm{Im}[\varepsilon]}{(\mathrm{Re}[\varepsilon]+2\varepsilon_{\mathrm{medium}})^2+\mathrm{Im}[\varepsilon]^2}\ [17]. \quad (5)$$

Here ω is the frequency of an incident light.

4.3. Optical properties of ZnO:Al/AgNP multilayer films. To prepare multilayers ZnO:Al/AgNP films a thin layer of silver nanoparticles in aqueous solution was deposited on a fused quartz substrate dried and annealed. Over the prepared film of silver nanoparticles layers of ZnO: Al (3 %) were deposited and annealed at 650 °C in air.

The extinction spectrum of the film ZnO: Al (3 %) with silver nanoparticles demonstrates plasmon resonance (Fig. 3). The peak in the extinction spectrum of the film ZnO: Al (3 %)/AgNP is shifted relative to the peak position for silver nanoparticles on quartz to longer wavelengths (a redshift). It should be noted that the display of the plasmon peak in the extinction spectrum of the film ZnO: Al/AgNP shows on the fact that silver atoms do not react with atoms of ZnO:Al. The shift of the peak position in extinction spectrum of the film ZnO: Al/AgNP causes by covering silver nanoparticles by ZnO:Al layers with refraction index higher 1 (for air).

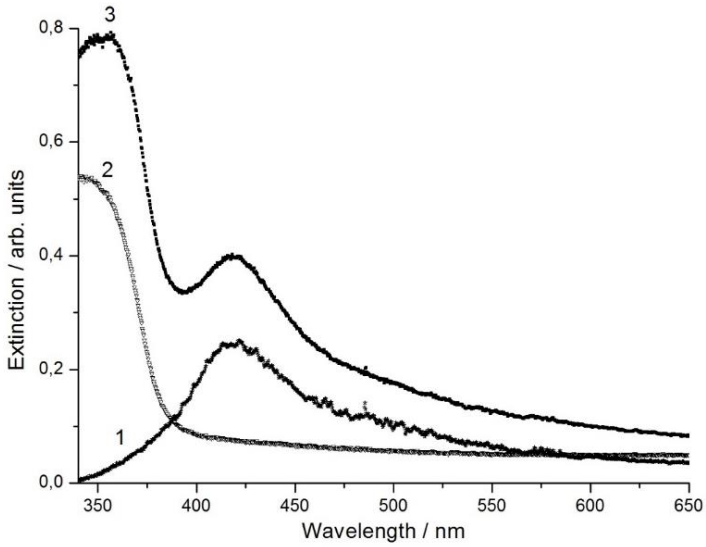

Fig. 3. Extinction spectra: 1- film of silver nanoparticles on fused quartz substrate; 2- ZnO:Al (3 %) film; 3- ZnO:Al (3 %) film with silver nanoparticles.

4.4. Photoconductivity of ZnO:Al/AgNP multilayer films. The dark current of ZnO:Al/ AgNP multilayer film was about $1.1\cdot10^{-4}$ A. For reference ZnO:Al film without silver nanoparticles prepared from the same sol and in the same temperature conditions had the same value of dark current.

The conductivity of ZnO:Al/AgNP films was increased 5 times up to 5.0 10^{-4} A by the optical radiation action (daylight). This photoeffect caused by the excitation of plasmon

resonance in silver nanoparticles and could be described by the following mechanism. Non-radiative damping of the plasmon resonance in silver nanoparticles led to the formation of "hot" electrons with sufficient energy to overcome the energy threshold at nanoparticle/metal-oxide interface and to inject them in the conducting band of semiconductor. Plasmon silver nanoparticles can generate "hot" electrons with energies from the Fermi level up to 4 eV. The concentration of "hot" electrons and their energy distribution depended on the size and shape of the nanoparticles, the maximum concentration was observed in the plasmon resonance frequency [18].

5. Conclusions

In this work, the dependences of electrical properties of ZnO:Al films with different percent content of Al prepared at different temperature conditions were studied. The lowest resistivity of the ZnO:Al film with Al/Zn fraction 3 % was about 0.3 Ω·cm on condition of annealing of each deposited layer at 650 °C and the last annealing was occurred in vacuum (10^{-5} Pa). ZnO:Al films had sharp absorption edge in near UV. The films transmittance was about 90 % in the visible region at wavelength above 500 nm. The extinction spectra of the ZnO:Al/ AgNP multilayer films demonstrated the shift of AgNP plasmon resonance with respect to the position being characteristic to silver nanoparticles on fused quartz substrate. The optical radiation action increased the conductivity of ZnO:Al/AgNP films 5 times. An observation of photocurrent was associated with the excitation of plasmon resonance in nanoparticles and was described by the mechanism of "hot" electrons injection in the conduction band of ZnO: Al. The photoeffect allowed to consider ZnO:Al/ AgNP multilayer films as functional element of photovoltaic devices.

This work was supported by Russian Science Foundation (grant RSF No.14-29-00086).

References

[1] X. Wang, L. Zhi, K. Müllen // *Nano Letters* **8** (2008) 323.
[2] J. Wu, H.A. Becerril, Zh. Bao, Z. Liu, Y. Chen, P. Peumans // *Applied Physics Letters* **92** (2008) 263302.
[3] T. Kawashima, T. Ezure, K. Okada, H. Matsui, K. Goto, N. Tanabe // *Journal of Photochemistry and Photobiology A: Chemistry* **164** (2004) 199.
[4] J. Lee // *Nanoscale* **4** (2012) 6408.
[5] A.R. Madaria, A. Kumar, C. Zhou // *Nanotechnology* **22 (**2011) 245201.
[6] H.A. Atwater, A. Polman // *Nature Materials* **9** (2010) 205.
[7] G. Zhao, H. Kozuka, T.Yoko // *Thin Solid Films* **277** (1996) 147.
[8] Y. Tian, T. Tatsuma // *Journal of the American Chemical Society* **127** (2005) 7632.
[9] K. Yu, Y. Tian, T. Tatsuma, // *Physical Chemistry Chemical Physics* **8** (2006) 5417.
[10] T. Toyoda, S. Tsugawa, Q. Shen // *Journal of Applied Physics* **105 (**2009) 034314.
[11] D. Gong // *Journal of Solid State Chemistry* **189** (2012) 117.
[12] M.W. Knight, H. Sobhani, P. Nordlander, N.J. Halas // *Science* **332 (**2011) 702.
[13] Y.K. Lee, C.H. Jung, J. Park // *Nano Letters* **11** (2011) 4251.
[14] Y. Nishijima, K. Ueno, Y. Yokota // *The Journal of Physical Chemistry Letters* **1** (2010) 2031.
[15] M. Schmid, R. Klenk, M.Ch. Lux-Steiner, M. Topič, J. Krč //*Nanotechnology* **22** (2011) 1.
[16] Stefan A. Maier, *Plasmonics: fundamentals and applications* (Springer Science & Business Media, 2007).
[17] Craig F. Bohren, Donald R. Huffman, *Plasmon-Induced Hot Carriers in Metallic Nanoparticles* (John Wiley & Sons, 2008).
[18] A. Manjavacas, J.G. Liu, V. Kulkarni, P. Nordlander // *ACS Nano* **8** (2014) 7630.