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.

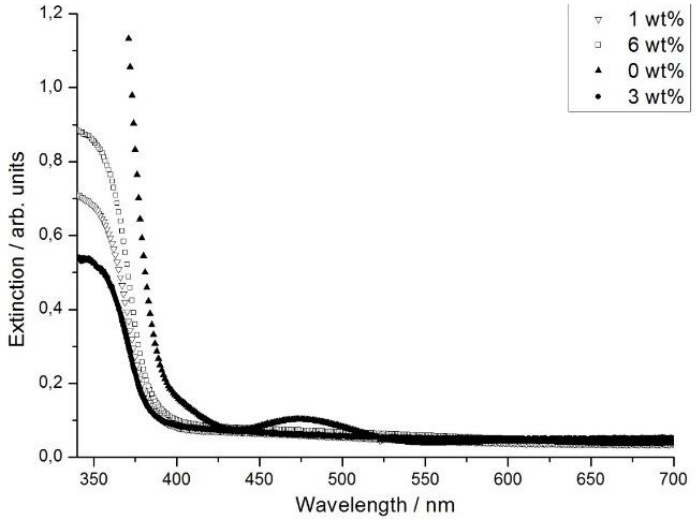

Fig. 2. Optical extinction spectra of ZnO, ZnO:Al (1 %), ZnO:Al (3 %) and ZnO:Al (6 %) films.

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 $|\varepsilon + 2\varepsilon_{\text{medium}}|$ is a minimum, which for the case of slowly varying $\text{Im}[\varepsilon]$ around the resonance simplifies to

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

This relationship expresses the strong dependence of the resonance frequency on the dielectric environment. The resonance redshifts as $\varepsilon_{\text{medium}}$ 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

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

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).

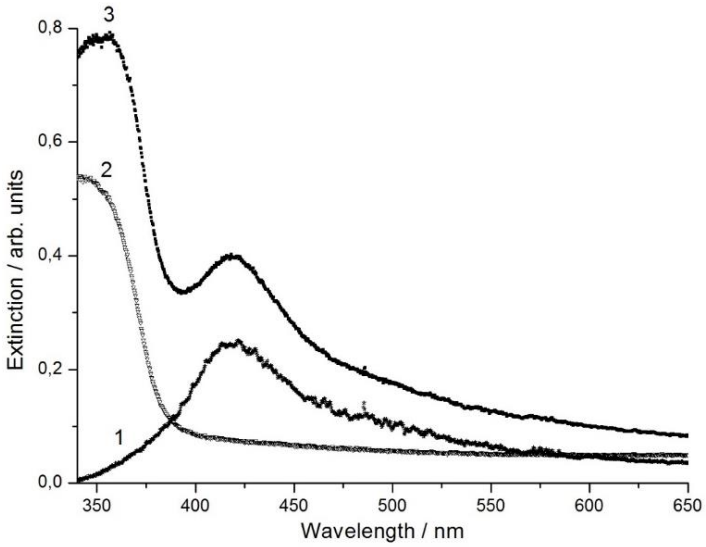

Fig. 3. Extinction spectra: 1- film of silver nanoparticles on fused quartz substrate; 2- ZnO:Al (3 %) film; 3- ZnO:Al (3 %) film with silver nanoparticles.

4.4. Photoconductivity of ZnO:Al/AgNP multilayer films. The dark current of ZnO:Al/ AgNP multilayer film was about $1.1 \cdot 10^{-4}$ 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.

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