

Influence of the Annealing on the Structural, Optical and Electrical Properties of Transparent Conductive ZnO:Al/Ag/ZnO:Al Multilayer Stacks*

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Abstract. The multi-layer stacks ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) are prepared by r.f. magnetron sputtering on glass substrates with two different thicknesses of the middle Ag film, $x = 16$ and 20 nm. The ZnO:Al layers are deposited in Ar+H₂ atmosphere and the Ag layer in pure Ar. The substrates are not heated during the deposition of films. Two different stack structures are annealed in N₂+H₂ at 180°C for 50 min: the two-layer ZnO:Al/Ag(x) which is covered by the top ZnO:Al film after annealing and the three-layer ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm). Structural, optical and electrical properties of the as-deposited and annealed structures are studied. The TEM, SEM and AFM analysis confirm the semi-continuous structure of the middle Ag layer in the as-deposited stacks and formation of Ag grains after annealing. The grains size increases with the thickness of the Ag layer and after annealing. The transmittance and reflectance spectra of the as-deposited and annealed stacks demonstrate bands associated with Ag electrons plasma oscillations and d-shell electron inter-band transitions. The results are analyzed and explained by the changes in the grains size, interaction between them and overlapping between the quadrupolar and dipolar plasmon resonances. The as-deposited stacks ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) demonstrate low resistivity – 9.0×10^{-5} Ohm.cm ($x = 16$) and 4.0×10^{-5} Ohm.cm ($x = 20$ nm). The resistivity increases slightly after annealing. The study demonstrates potential for application of multilayer structures ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) for $x = 16$ nm and 20 nm at back side conductive electrode with plasmonic properties for improvement of the thin film solar cells with increased light harvesting

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1 Introduction

Development in the recent years of thin films Si solar cells requires an exploration of new materials as transparent conductive oxides (TCO) for improvement of the efficiency of photovoltaic conversion. ZnO is attractive material because of its physical and chemical characteristics: direct energy wide band gap (~ 3.2 eV at room temperature), high transmittance and refraction in visible and infrared region, texturing of the layer structure under the deposition or after etching, doping with different metals, low toxicity, etc. [1]. However, for application in thin films Si solar cells it is necessary to increase the conductivity of ZnO. Different methods are applied for doping of ZnO [2] or preparation of multilayer structures ZnO/noble metals (Cu, Au, Ag) [3,4]. The noble metals with their plasma resonance properties when they are surrounded by ZnO film with high refractive index modify the solar spectrum in the visible range that is appropriate for increasing the absorption of light in thin films Si solar cells [5]. Among the noble metals Ag is preferable because it has the lowest resistivity and plasma resonance in the visible range. The application of Ag is usually as nanoparticles (NPs) with sub wavelength size embedded in the ZnO film or deposited on the semiconductor. Profitable combination ZnO/noble metal is realized at the rear side of thin films Si solar cell in tandem with Ag or Al back reflector for backscattering of unabsorbed incident light passed through the cell [6]. In this case the system ZnO/noble metal is used as transparent conductive electrode and buffer which prevents the interaction between Si and the back reflector.

Different methods for deposition of the system ZnO/noble metal are used [7]. The r.f. magnetron sputtering gives the opportunity to deposit different materials on large areas for exploration and optimization of the properties of ZnO/noble metal multilayer structures [8].

In this work the structural, optical and electrical properties of as-deposited and annealed in atmosphere of N_2+H_2 at $180^\circ C$ for 50 min multilayer stack structures ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) prepared by r.f. magnetron sputtering on glass substrates in dependence on the Ag layer thickness for $x = 16$ nm and 20 nm are studied.

2 Experimental

ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) multilayer stack structures are prepared by r.f. magnetron sputtering on glass substrates with different thicknesses of the Ag layer, $x = 20$ nm. The substrates are not deliberately heated during the deposition. The sputtering atmosphere in case of the ZnO:Al layers is Ar+ H_2 (2 Pa+0.02 Pa) and in case of the Ag layer is pure Ar (0.2 Pa). The r.f. power for deposition of ZnO:Al is 50 W and in the case of the Ag layer it is 20 W. Two different multilayer structures are annealed in atmosphere of N_2+H_2 at $180^\circ C$ for

50 min – two-layer structures ZnO:Al(20)/Ag(x) and three-layer stack structures ZnO:Al(20nm)/Ag(20)/ZnO:Al(20nm). After annealing the two-layer structures are covered by the top ZnO:Al (20nm) layer.

Optical properties of the multilayer stacks are studied through transmittance and reflectance (direct and diffuse components) measurements by a spectrophotometer ShimadzuUV.3600 in the spectral range of 350–1200 nm. Structural properties are studied by TEM, SEM and AFM analysis. TEM images are obtained by JEOL JEM 2100 at accelerating voltage of 200 kV. SEM micrographs are obtained by an apparatus Philips 515. The AFM analysis is performed by apparatus NT-MDT Solver 47 Pro system in a “semi-contact” (taping) mode and the root mean square (rms) surface roughness is calculated by program Gwyddion. The electrical properties of the multilayer structures are measured by the four point probe method with VEECO instrument.

3 Results and Discussion

TEM and SEM micrographs of the as-deposited and annealed multilayer stacks are presented in Figure 1 and Figure 2, respectively. From the SAED patterns presented as insets in Figure 1 the phase composition of the samples is identified

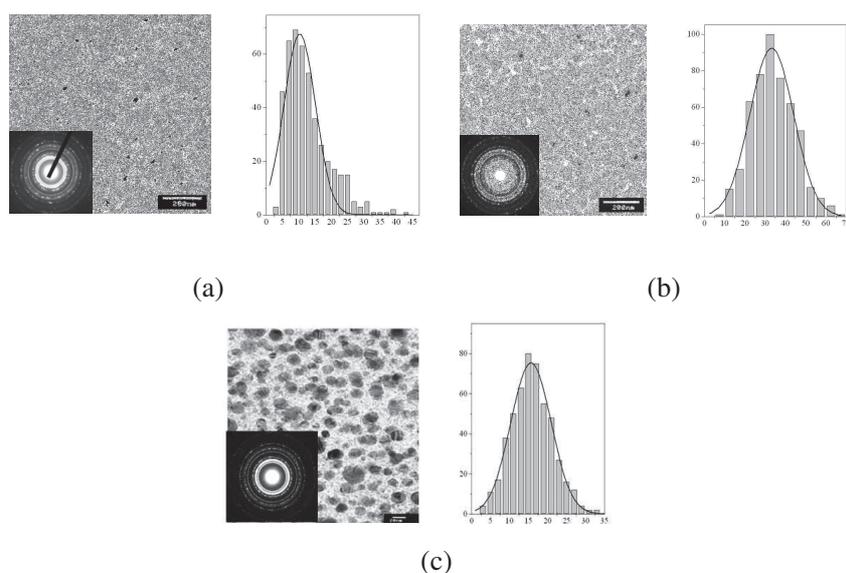


Figure 1: TEM micrographs, SAED and histograms of Ag particles size distribution of multilayer structures ZnO:Al(20nm)/Ag(20)/ZnO:Al(20nm): as-deposited, (a) annealed two-layers ZnO:Al/Ag(20), (b), and annealed three-layer ZnO:Al(20nm)/Ag(20)/ZnO:Al(20nm) (d) structures.

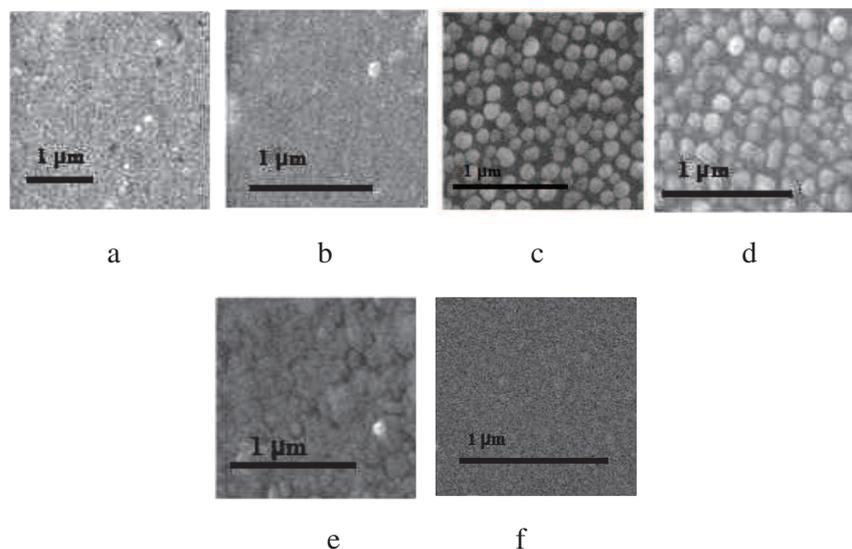


Figure 2: SEM micrographs of multilayer structures ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm): as-deposited (a and b), annealed ZnO:Al/Ag(x) structures (c and d) and annealed ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) structure (e and f) for $x = 16$ nm (a, c and e) and 20 nm (b, d and f), respectively.

as: hexagonal ZnO (PDF 89-1397), hexagonal Ag (PDF 87-0598), monoclinic Al_2O_3 (PDF 86-1410) and orthorhombic Al_2O_3 (PDF 88-0107) [9]. The NPs size distribution is calculated applying the program “Image J” [10].

TEM image of the as-deposited multilayer stacks ZnO:Al(20nm)/Ag(20)/ZnO:Al(20nm) (Figure 1a) reveals the presence of the Ag nano-grains with highly irregular shape which are connected in chains forming a semi-continuous structure of the Ag middle layer. The chains have high density and provide high surface covering. The mean size of the individual Ag NPs is about 10 nm. After annealing of the two-layer structure ZnO:Al/Ag (Figure 1b) the Ag islands are transformed into separated Ag grains with mean size of 33 nm. However, the semi-continuous structure of the Ag film in the three-layer stacks ZnO:Al/Ag/ZnO:Al is preserved after annealing (Figure 1c) and the mean size of the individual NPs decreases to 15 nm. This can be explained by the higher interaction between the Ag atoms and by the impeded diffusion of the Ag atoms from the two ZnO:Al surrounded films in the case of annealed three-layer structure.

SEM micrographs of the as-deposited multilayer stacks ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) (Figures 2a and 2b), confirm the presence of the Ag grains structure as it is seen in TEM micrographs. The annealing of the two-layer ZnO:Al(20nm)/Ag(x) structures leads to formation of larger Ag grains with

size of about 150–200 nm. The NPs has different size distribution and their shape is spheroidal or ellipsoidal. The annealing of the three-layer stack ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) (Figures 2e and 2f) results in preservation of the semi-continuous Ag film comprised of larger islands partially connected between them. It has to be noted that for determination of the Ag particles size distribution the shape of the NPs is accepted to be spherical, however in the case of elongated NPs formation (as is the case of annealed three-layer structure) they are regarded as aggregated of two or more individual particles with different diameters. This could be a reason for lower mean size of the NPs in the stacks with NPs connected in chains. The structural changes influence the mechanism of electron conductance of the multilayer structures [11].

The AFM pictures reveal the influence of the Ag layer with different thickness in the as-deposited and annealed ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) structures on their surface roughness. The as-deposited structure with $x = 20$ nm has higher rms roughness (9 nm, Figure 3b) than the structure with $x = 16$ nm (rms roughness of 4 nm, Figure 3a), due to the higher substrate covering and coalescence of Ag atoms in NPs and islands with higher sizes and different shapes during the deposition. The annealing of structure ZnO:Al(20nm)/Ag(x) leads to formation of rough morphology of the multilayer structure ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm), Figures 3c and 3d, due to the grain structure of the Ag layer. The rms roughness of the multilayer structure for $x = 16$ nm is 23 nm and for $x = 20$ nm is 10 nm. This can be explained with the process of coalescence of Ag atoms under heating (the interaction between the Ag atoms is higher than between the Ag atoms and the substrate) and higher substrate covering for the Ag layer thickness of 20 nm. Under annealing of three-layer structure ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) the process of coalescence of Ag atoms develops between ZnO:Al layers. The interaction between the Ag atoms in this case leads to coalescence into grains which form multilayer structures with higher rms roughness than in annealing of two-layer structures with $x = 16$ nm and 20 nm. Obviously, the grains grow more in height than laterally. Comparison between the rms roughnesses of the annealed three-layer structures indicates a higher roughness for the structure with Ag layer thickness of 20 nm (rms roughness of 25 nm, Figure 3f) than for Ag layer thickness of 16 nm (rms roughness of 16 nm, Figure 3e). This can be explained with the interaction between Ag atoms during the annealing based on the formed NPs in the as-deposited structure with higher Ag layer thickness.

The transmittance spectrum of the as-deposited ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) three-layer stack (Figure 4a) demonstrates a band with maximum at about 365 nm due to the quadrupolar electron plasma resonance of the Ag NPs and the near lying d-shell electrons interband transitions, more pronounced for the lower Ag thickness ($x = 16$ nm) due to the higher scattering from the grain structure of the film. Another band at about 460 nm is observed as well, due to the dipolar plasma resonance [11]. With Ag thickness increase

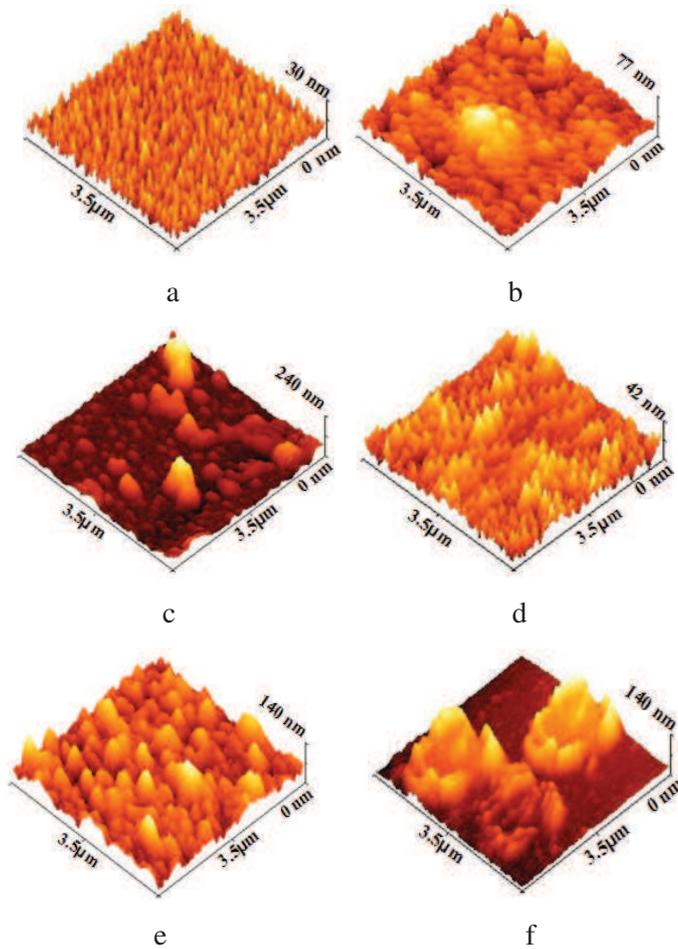


Figure 3: AFM pictures of multilayer stacks ZnO:Al/Ag/ZnO:Al: as-deposited (a), and (b), annealed two-layer ZnO:Al/Ag (c) and (d), annealed three-layer ZnO:Al/Ag/ZnO:Al (e) and (f) structures, for $x = 16$ nm (a, c, e) and $x = 20$ nm (b, d, f). The samples have rms roughness as follow: (a) 4 nm, (b) 9 nm, (c) 23 nm, (d) 10 nm, (e) 16 nm, (f) 25 nm.

this band associated with the overlapping of quadrupolar and dipolar resonances smears due to increasing in the size of NPs and interaction between them [11]. The transmittance decreases in the near IR spectral region due to the increased free carrier's plasma absorption. The spectrum of the multilayer stack with Ag layer thickness of 20 nm has higher transmittance value in all studied spectral region associated with lower scattering of the light due to the semi-continuous structure of the middle Ag layer. This is confirmed by the higher haze ratio in

Influence of the Annealing on the Structural, Optical and Electrical Properties of...

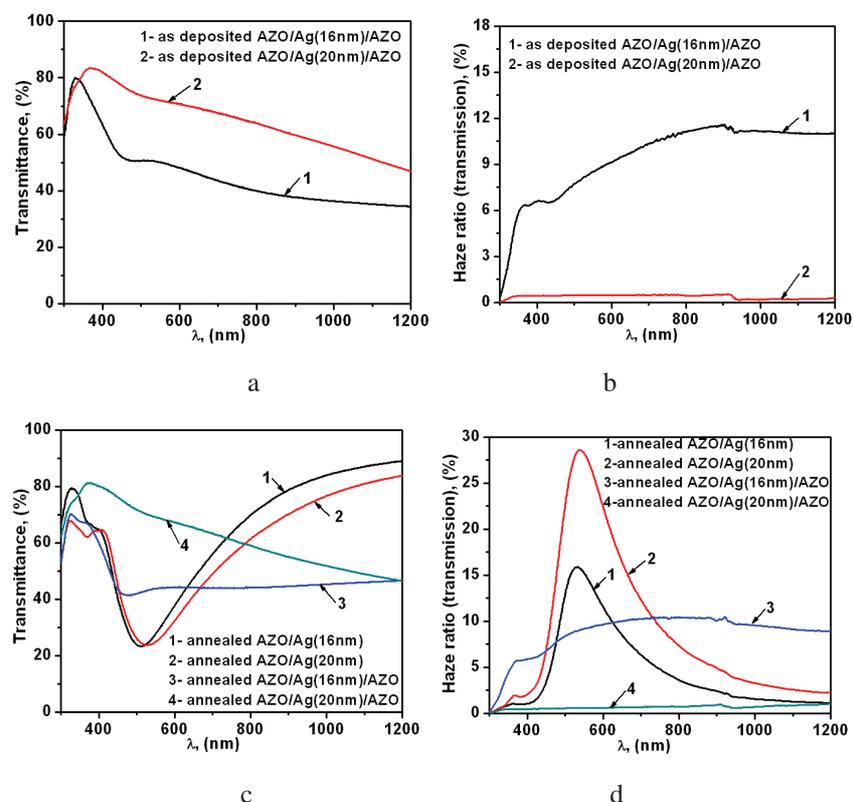


Figure 4: Transmittance spectra and the haze ratio in transmission of the as-deposited and annealed multilayer structures ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm): as-deposited, (a) and (b), annealed two-layer ZnO:Al(20nm)/Ag(x) and three-layer ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) structures, (c) and (d), for x = 16 nm and x = 20 nm.

transmission of the multilayer structure with Ag layer of 16 nm thickness (Figure 4b).

The transmittance spectra of the annealed structures ZnO:Al(20nm)/Ag(x) and ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm), Figure 4c, for x = 16 nm and 20 nm demonstrate the same bands, however they are red shifted in comparison with the spectra of as-deposited samples. The annealing of ZnO:Al(20nm)/Ag(x) structures for x = 16 nm and 20 nm leads to formation of deeper and wider bands at about 500 nm due to overlapping between dipolar and quadrupolar resonances and interaction between the Ag NPs [11] associated with the outlined grain structure of the Ag layer as it is seen from TEM and SEM pictures of annealed stacks. In the stacks with annealed three-layer structure the band associated with the

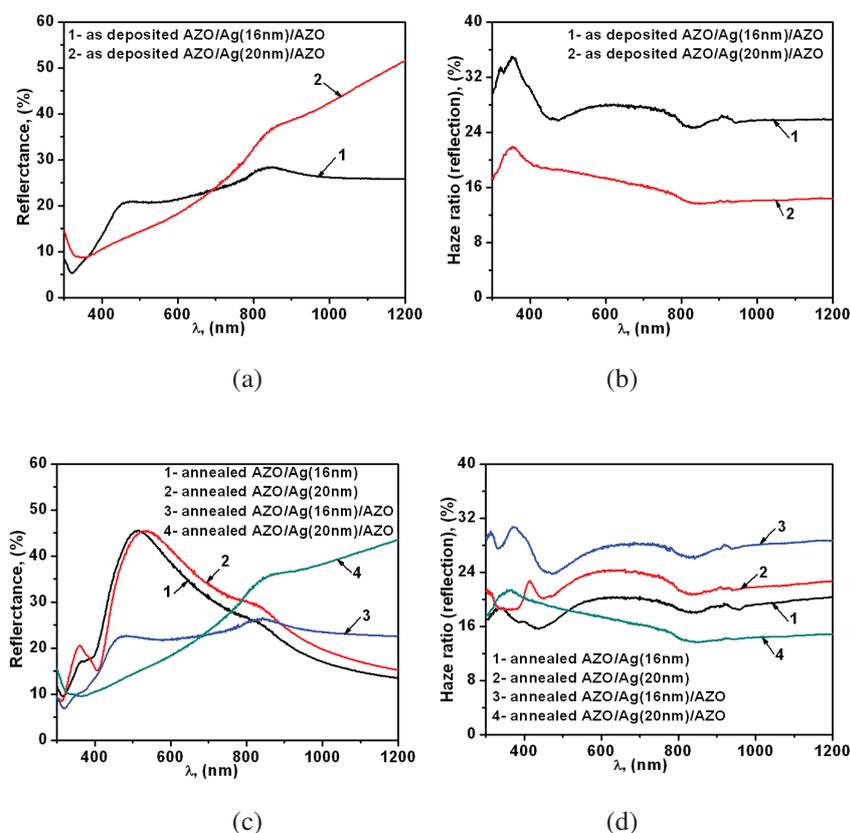


Figure 5: The spectra of reflectance (a and c) and the haze ratio in reflection (b and d) of the as-deposited and the both kinds of annealed two- and three-layer ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) stack structures with different thickness of the middle Ag film for $x = 16$ nm and $x = 20$ nm.

plasmon absorption is not so prominent due to the semi-continuous structure of the Ag film. In the IR range the stacks with annealed two-layer structures have higher value of transmittance due to the lower substrate covering with Ag NPs in comparison with the semi-continuous Ag film in the annealed three-layer stacks. The haze ratio in transmission demonstrates the same plasmon resonance band at about 500 nm which is more intensive in the spectra of the stacks with annealed two-layer structure (Figure 4d).

The reflectance spectra (Figure 5) of the as-deposited and annealed multilayer stacks ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) demonstrate the same bands as in the transmittance spectra. They are more prominent in the spectra of the stacks after annealing of the two-layer structures (Figure 5c). The haze ratio in reflec-

tion of the stacks with annealed three-layer structure with 20 nm thick Ag film practically does not change compared to the as-deposited (Figure 5b and d). The stack with annealed two-layer structure with 16 nm thick middle Ag film demonstrate lower haze ratio in comparison with the as-deposited which is due to the higher light absorption in the Ag grains with increased size after the annealing (Figure b and d). It should be noted that the feature in the optical spectra at about 800 nm is due to the change of the detectors for the different spectral regions.

The values of the resistivity of as-deposited and annealed only three-layer stacks ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) are presented in Table 1. The values of the resistivity of the stacks with annealed two-layer structures are not shown because their resistivities are out of range of the instrument for four point probe measurements. The resistivity of the as-deposited stacks ($4.0 \times 10^{-5} \Omega \cdot \text{cm}$, $x = 20 \text{ nm}$ and $9.0 \times 10^{-5} \Omega \cdot \text{cm}$, $x = 16 \text{ nm}$) is lower than the typical resistivity of the individual ZnO:Al film ($\sim 10^{-4} \Omega \cdot \text{cm}$ [8]). The resistivity of the annealed three-layer stacks increases slightly compared to the stacks with annealed two-layer structures which resistivity increases by several orders of magnitude.

The prepared multilayer stacks ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) demonstrate high conductivity and plasmonic properties in the visible range due to Ag nanoparticles. This suggests possibility for application in thin film solar cells to increase light trapping and their efficiency.

Table 1: Resistivity of as-deposited and annealed three-layer structures

ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm), x = 16 nm and x = 20 nm	ρ [Ohm.cm], as-deposited	ρ [Ohm.cm], annealed
ZnO:Al(20nm)/Ag(16nm)/ZnO:Al(20nm)	9.0×10^{-5}	3.0×10^{-4}
ZnO:Al(20nm)/Ag(20nm)/ZnO:Al(20nm)	4.0×10^{-5}	6.0×10^{-5}

4 Conclusion

Structural, optical and electrical properties of as-deposited and annealed multilayer structures ZnO:Al(20nm)/Ag(x) and ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) for $x = 16 \text{ nm}$ and 20 nm are studied. The transmittance and reflectance spectra of the as-deposited and annealed films demonstrate bands in the visible spectral region due to Ag electrons plasma oscillations and d-shell electrons inter-band transitions. The position of the bands, their intensity and width depend on the Ag layer thickness and annealing of the multilayer structure. The morphology and the structure of stacks depend on the thickness of the middle Ag film and annealing. The annealing leads to formation of grain structure of the Ag films in the annealed two-layer stacks. In the case of the annealed three-layer stacks the Ag film remains semi-continuous like the Ag film in the as-deposited structures. The as-deposited stacks ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) demonstrate low

resistivity 9.0×10^{-5} ($x = 16$ nm) and 4.0×10^{-5} Ω .cm ($x = 20$ nm). The resistivity of the multilayer structure ZnO:Al(20nm)/Ag(20nm)/ZnO:Al(20nm) changes lower after annealing in comparison with the same structure with Ag layer thickness of 16 nm and with ZnO:Al(20nm)/Ag(x) structures, for $x = 16$ nm and 20 nm, respectively. The results of the study of structural, optical and electrical properties are analyzed and explained by the changes in the grains size, interaction between them and overlapping between the quadrupolar and dipolar plasmon resonances. The study demonstrates potential for application of multilayer structures ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) for $x = 16$ nm and 20 nm at back side conductive electrode with plasmonic properties for improvement of the thin film solar cells with increased light harvesting.

Acknowledgements

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