Influence of annealing on the optical, structural and electrical properties of ZnO:Al/Ag/ZnO:Al multilayer stack structures

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Abstract. Multilayer stack structures ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm) with different thickness of the middle Ag(x) layer – x = 6 nm, 10 nm, 12 nm, 16 nm and 20 nm, were prepared by r.f. magnetron sputtering. The ZnO:Al and Ag layers were deposited by magnetron sputtering on glass substrates without heating. The two-layer structures ZnO:Al(20)/Ag(x) were annealed in N₂ + H₂ at 180 °C, 50 min., and then capped by the top ZnO:Al(20 nm) layer. The optical, structural and electrical properties were studied of the as-deposited and of the annealed three-layer stacks. The TEM, SEM and AFM analyses demonstrated changes of the stack structure with the Ag film thickness and after annealing. The transmittance and reflectance spectra revealed bands of Ag electrons plasma oscillations and inter-band d-shell Ag electrons which were red-shifted after annealing. The as-deposited structures had low resistivity (1×10⁻³ to 4×10⁻⁵ Ω cm), which decreased with the thickness of the Ag film due to the change in the carrier transport mechanisms. The value of the resistivity increased after annealing.

1. Introduction

Systems consisting of layered structures, namely, transparent conductive oxide (TCO)/noble metal (Cu, Au, Ag) have been recently studied intensively because of the possibility for application in thin film solar cells [1]. The difference in the work functions of the TCO and the noble metals offers an opportunity to increase the conductivity of the TCO as a rear electrode [2]. The main tasks in the development and fabrication of thin-film solar cells are increasing the light absorption, minimizing the reflection losses and increasing the reflection of the light transmitted through the solar cell.

This work addresses the optical, structural and electrical properties of three-layer stack ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm) structures with different thicknesses of the middle Ag(x) layer, x = 6 nm, 10 nm, 12 nm, 16 nm and 20 nm. The influence of the annealing in N₂ + H₂ at 180 °C, 50 min., is studied in the case of annealing the first two-layers ZnO:Al(20 nm)/Ag(x) structures before depositing the top ZnO:Al film.

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2. Experimental
ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm) multilayer structures were deposited on glass substrates by successive r.f. magnetron sputtering of ZnO:Al and Ag targets without intentional heating. The Ag layers had thicknesses of 6 nm, 10 nm, 12 nm, 16 nm and 20 nm. The ZnO:Al layers were deposited in an atmosphere of Ar (2 Pa) + H2 (0.02 Pa), and the Ag layers, in Ar (0.2 Pa) at a r.f. power of 50 W and 20 W, respectively. The two-layer structures ZnO:Al(20)/Ag(x) were annealed in N2 + H2 at 180 °C, 50 min., and then capped with the top ZnO:Al(20 nm) layer. The TEM images were obtained by a JEOL JEM 2100 microscope, and the SEM micrographs, on a Philips 515 apparatus. The optical properties of the stacks were measured by a Shimadsu UV.3600 spectrophotometer in the wavelength range 350 – 1200 nm. The feature at about 800 nm in the optical spectra is an artifact due to the change of the detectors for the different spectral ranges. The electrical properties were measured by the four-point probe method using a VEECO instrument.

3. Results and discussion
TEM and SEM micrographs of the multilayer stack structures ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm), as-deposited and after annealing of the two-layer structures, are shown in figure 1 and figure 2. The phase composition of the samples was identified from the SAED patterns presented as insets in figure 1, as follows: hexagonal ZnO (PDF 89-1397), hexagonal Ag (PDF 87-0598), monoclinic Al2O3 (PDF 86-1410) and orthorhombic Al2O3 (PDF 88-0107) [3]. The TEM and SEM micrographs of the as-deposited structures reveal an increase in the Ag grains size as the thickness of the middle Ag layer is increased from 6 nm to 12 nm. The Ag grains aggregate into chains in the stacks with x = 16 nm (figure 1c), while the Ag film’s structure is transformed from a discontinuous one to a semi-continuous one (x = 20 nm, figure 1d). Annealing the two-layer ZnO:Al(20 nm)/Ag(x) structure results in an increase of the Ag grain size due to coalescence (figure 1e, f, g, h and figure 2e, f, g, h). In the stacks with x = 16 nm and x = 20 nm, the structure of the Ag films is transformed from a semi-continuous island-like one into a structure with separate grains of spheroidal and ellipsoidal shape (figure 1g and h and figure 2g and h). Similar results have been reported by other authors [4].

Figure 1. TEM micrographs of as-deposited (a, b, c and d) and annealed (e, f, g and h) multilayer stacks ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm) with different thickness of the Ag film for x = 6 nm (a and e), 12 nm (b and f), 16 nm (c and g) and 20 nm (d and h). The markers correspond to 200 nm.
Figure 2. SEM micrographs of as-deposited (a, b, c and d), and annealed (e, f, g and h), multilayer stacks ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm) for x = 6 nm (a and e), 12 nm (b and f), 16 nm (c and g) and 20 nm (d and h). The markers correspond to 1 µm.

Figure 3. AFM pictures of multilayer structures ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm): as deposited, (a) x = 6 nm, (b) x = 16 nm, (c) x = 20 nm; and after annealing of the two-layer structure ZnO:Al(20 nm)/Ag(x), (d) x = 16 nm and (e) x = 20 nm.

leads to an increase in the rms roughness to 9 nm due to the formation of NPs of different size and shape partially connected in chains (figure 3c). The annealing results in increasing the surface roughness due to a coalescence of the Ag atoms. After annealing, the rms roughness of the stacks with x = 16 nm is 23 nm; the roughness of the stack with x = 20 nm is 10 nm. The lower value of the rms roughness after annealing of the stack with x = 20 nm can be explained with the denser covering of the surface by Ag grains.

The transmittance spectra of as-deposited stacks ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm) (figure 4a) show a band with a maximum near 365 nm due to the quadrupolar resonance and the near-lying interband electron transitions of the electrons of the entirely filled Ag atoms’ d-shell [5]. These inter-band transitions were observed in the spectra of all samples. Increasing the Ag layer thickness at x > 10 nm leads to this band being red-shifted due to the influence of the quadrupolar resonance as a result of the increased size of the NPs in the middle Ag film. The transmittance has a minimum at about 460 nm due to the dipolar electrons plasma oscillations, deeper and red-shifted as the size of the Ag NPs increases in the samples with Ag layer thickness of 6 nm and 10 nm. A further increase in the Ag layer thickness from 12 nm to 20 nm increases the degree of substrate covering by Ag NPs so that the interaction between them becomes stronger. As a result, an overlapping between the quadrupolar and dipolar resonances occurs [5] and this band is smeared. Above 600 nm in the case of stacks with Ag layer thickness of 6 nm and 10 nm, the transmittance increases as the wavelength is increased; after 700 nm it changes weakly due to the lower degree of substrate covering by Ag NPs. The structures with a Ag layer thickness between 12 nm and 20 nm show a monotonic decrease in the transmittance above 550 nm. This can be explained by the plasmonic absorption of the free electrons in the Ag films, which
exhibit a higher degree of substrate covering and conductivity [5]. The same bands of typical inter-band d-shell electrons transitions and electron plasma oscillations are observed in the spectra of the stacks with an annealed ZnO:Al(20 nm)/Ag(20 nm)/ZnO:Al(20 nm) structure. They are red-shifted compared to the spectra of the as-deposited samples. The changes observed in the transmittance spectra after annealing can be explained by the changes in the size and shape distributions of the Ag NPs during the annealing.

The haze ratio in transmission is higher in the as-deposited stacks with lower Ag layer thicknesses (6 nm and 10 nm), and in the annealed stacks with higher Ag layer thickness (x > 10 nm). It has to be noted that the haze ratio is higher in the whole spectral range in the stacks after annealing. This can be explained by the evolution of the structure of the middle Ag layer and the stronger interaction between the Ag NPs as the thickness is increased during annealing. The transition from a discontinuous to a continuous Ag layer structure in the as-deposited multilayer stacks ZnO:Al(20 nm)/Ag(20 nm)/ZnO:Al(20 nm) when the Ag layer thickness is increased leads to a decrease in the diffuse transmittance, and, thus, to a lower haze ratio in comparison with the annealed samples.

The reflectance and the haze ratio in the reflection spectra of the as-deposited (figures 5a and b) and annealed (figures 5c and d) multilayer structures demonstrate typical plasma electron oscillations and inter-band d-electrons transition bands due to the presence of Ag NPs in the film. These bands are more prominent in the spectra of the annealed stacks. The higher reflectance observed in the spectra of the as-deposited stacks with x > 10 nm is due to the higher free carriers density in these stacks with a higher degree of substrate covering by the Ag film and a higher conductivity (figure 6). The haze ratio in reflection is about 15–25% in as-deposited and annealed stacks in the visible region. In the as-deposited stacks with a lower thickness of the middle Ag films (x = 6 and 10 nm), the value of the haze ratio at about 365 nm is higher than in the samples with a higher size of the Ag NPs due to the stronger plasmon resonance. In these stacks, the presence of Ag NPs of a smaller size and the higher surface roughness result in a higher diffuse reflectance and a higher haze ratio. After annealing, the haze ratio

Figure 4. Spectra of transmittance and haze ratio in transmission of multilayer stack structures ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm): as-deposited (a and b) and annealed (c and d), for x = 6 nm (curves 1), 10 nm (curves 2), 12 nm curves (3), 16 nm (curves 4) and 20 nm (curves 5).

Figure 5. Spectra of reflectance and haze ratio in reflection of multilayer stack structures ZnO:Al(20 nm)/Ag(x)/ZnO:Al(20 nm): as-deposited (a and b) and annealed (c and d), for x = 6 nm (curves 1), 10 nm (curves 2), 12 nm (curves 3), 16 nm (curves 4) and 20 nm (curves 5).
of the stacks with thickness of the middle Ag film ($x = 6, 10, 12$ and $16$ nm) does not depend significantly on the thickness. The same spectral bands are seen as in the reflectance spectra. The multilayer structure with $x = 20$ nm has a higher haze than the haze of the other annealed structures due to the formation of a grain structure in the Ag (20 nm) film and the higher degree of substrate covering leading to higher light scattering.

The resistivity of the as-deposited stacks decreases with the thickness of the Ag film from $1 \times 10^{-3}$ to $4 \times 10^{-5}$ $\Omega \cdot$cm due to the larger size of the Ag NPs and the higher degree of substrate covering (figure 5). The barrier height between the grains decreases and the conductivity of the layer undergoes a transforms from a thermally activated hopping mechanism to a metallic type one [5]. A similar behavior of the resistivity of multilayer ZnO:Al/Ag/ZnO:Al structures has been reported by other authors [6]. After annealing of the ZnO:Al(20 nm)/Ag($x$) stacks, the values of the resistivity increase and exceed $10^5$ $\Omega \cdot$cm, related to the outlined grain structure of the Ag films.

4. Conclusions

The optical, electrical and structural properties were studied of as-deposited and annealed at 180 $^\circ$C multilayer stack structures ZnO:Al(20 nm)/Ag($x$)/ZnO:Al(20 nm) for $x = 6$ nm, 10 nm, 12 nm, 16 nm and 20 nm. The TEM and SEM analyses demonstrated an increase of the size of the NPs in the middle Ag film with its thickness and after annealing. The structure of the Ag film is transformed from a semi-continuous to a discontinuous islands-like one in the Ag films with a higher thickness after annealing.

The transmittance and reflectance spectra of the as-deposited and annealed films demonstrated bands in the visible spectral region due to Ag electrons plasma oscillations and d-shell electrons interband transitions. The position and width of the bands depended on the Ag NPs size and shape distributions in the middle Ag films, which were determined by the thickness of the Ag film and the process of annealing. The same bands associated with the plasmonic effect and d-shell electrons interband transitions were observed in the haze ratio spectra in transmission and reflection. The as-deposited stacks with the thickness of the middle Ag films of 20 nm exhibited a high conductivity and high values of the reflectance and plasmonic light scattering, which makes them suitable for application as rear contacts in thin film solar cells thus increasing the light trapping.

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