Oxide/ metal/oxide nanolaminate structures for application of transparent electrodes

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Abstract. Transparent and conductive oxide/ metal/ oxide nanolaminate structures were deposited on glass and polymer substrate by RF magnetron sputtering without substrate heating. The Ag nanoparticles with different size and distance between neighboring particles were located on the interface of two thin oxide layers. This sputtering configuration allows obtaining thin films with homogeneous thickness. The three targets give the opportunity to deposit successively three different layers without opening the chamber. The developed process for transparent conducting coating is a low temperature and it is suitable for application on organic materials as substrate and foils. The experiment with different substrates manifest that the optical transparency of the conducting coating depends on substrate material. The obtained results have demonstrated that the nanolaminate structures oxide/metal/oxide (OMO) as TCO coating are especially suitable for applications in flexible electronics and optoelectronics

1. Introduction

In general, TCOs are degenerated n-type semiconductors with intrinsic doping by native donors such as oxygen vacancies and/or interstitial metal atoms and additional extrinsic doping by donor impurities. There is an inherent limitation in the metal oxide conductivity that can be obtained by increasing the carrier concentration, because the Coulomb interaction between the free electrons and the ionized donor centers from which they are generated provides a source of scattering that is inherent to the doped material. In addition, for metal oxides with a high number of free carriers, some absorption of the incident radiation by interaction with the electron gas takes place around the characteristic electron plasma frequency which increases with increasing carrier concentration. When the densities become greater than $2 \times 10^{21}$ cm$^{-3}$, the TCO exhibits plasma frequencies that shift from absorbing infrared wavelengths to visible light, reducing the transparency in the visible region [1]. The requirement of transparency and the fundamental scattering mechanism establish an absolute limit to the TCO resistivity of about $4 \times 10^{-5}$ $\Omega$.cm or obtaining conductivity in such materials, they should be doped with an appropriate element. Recently, it was reported for the preparation of an optically transparent and conductive nanolaminated dielectric structure [2]. The idea is based on usage of electronic conductivity in granular (discontinuous) type materials [3]. The granules are metallic particles of sizes ranging usually from a few to hundreds of nanometers, embedded into an insulating matrix. The nanolaminate structure is formed using one or two different dielectric materials.

In present study, transparent and conductive oxide/ metal/ oxide nanolaminate structures were deposited on glass and polymer substrate by RF magnetron sputtering without intentional substrate heating.
heating. The Ag nanoparticles were located on the interface of two thin oxide layers. The observed optical and electrical properties were dependent on the substrates. The nanolaminate structures showed high optical transmittance and good electrical conductivity.

2. Experimental
RF magnetron sputtering system with three different targets has been used for the deposition of the layers. The sputter gas is argon. This system has been developed as low-temperature high-speed sputtering equipment for use in experiments and is suitable for thin film deposition of metals and insulating materials. The substrate holder has a size of 200 mm in diameter. The three targets (75 mm in diameter) are at the eccentric position. They are cooled with water (3 l/min), so little radiation heat is generated. The targets and the substrate holder are vertically arranged at a distance of 8 cm. The substrate holder is spinning with a rate of 10 - 80 rpm. This configuration allows obtaining thin films with a homogeneous thickness. The three targets give the opportunity to deposit successively three different layers without opening the chamber. The most important part of the deposition process of nanolaminate structure with specified optical and electrical properties is the deposition of discontinuous metal layer. The sizes and density of the metal granules depend on the duration of the sputtering, RF power, type of reactive gas (Ar or He) and the rotation rate of substrate holder.

The optical properties of the nanolaminated structure dielectric/metal/dielectric (oxide/metal/oxide-OMO) are studied by means of UV-VIS-NIR Shimadzu spectrophotometer UV 3300. The sheet resistance has been measured using the four-point probe method.

3. Results and discussions
The studied nanolaminate structures are Oxide/metal (Ag)/Oxide layers (OMO). The investigations reveal that the relation between the sheet resistance and the maximum transparency in the visible spectral range is depending on the size of the metal granules, the film thickness of the dielectric layer, the type of the oxide, which is used for the formation of the OMO structure.

3.1. Influence of the thickness of the oxide layers
The nanolaminate structures TiO$_2$/metal (Ag)/TiO$_2$ have been investigated by keeping the 10 s sputtering time of Ag (10 s), but varying the sputtering time of TiO$_2$ layers. The glass substrate is 1.4 mm thick. Table 1 represents the sheet resistance values for nanolaminate structures with different thickness of oxide layer.

| Structure                                  | Sheet resistance [Ω/□] |
|--------------------------------------------|------------------------|
| Sample 1- TiO$_2$ (1 min)/10s Ag/TiO$_2$ (3 min) | 12                     |
| Sample 2- TiO$_2$ (1 min)/10s Ag/TiO$_2$ (2 min) | 11                     |
| Sample 3- TiO$_2$ (3 min)/10s Ag/TiO$_2$ (3 min) | 10                     |

The sheet resistance has not considerable changed with varying the thickness of the consisting metal oxides. On the other hand, the transmittance is changed with changing the film thickness of TiO$_2$ layer. Interestingly, the best transparency is manifested by the nanolaminate structure with thickest bottom and top TiO$_2$ layer and the transmittance is 90 % at wavelength 550 nm, the sample 1 and 2 possess values of 78 and 82 % at 550 nm, respectively. The highest reflectance is observed for sample 2- TiO$_2$ (1 min)/10s Ag/TiO$_2$ (2 min) (see figure 1).
Figure 1. Transmittance and reflectance spectra of samples 1, 2 and 3, described in table 1. Transmittance is measured using bare glass substrate as background.

The effect of the layer of Ag nanoparticles is found to be similar for other nanolaminate structure, using different metal oxide. The studied structures are MoO\textsubscript{x}/Ag/MoO\textsubscript{x}, where molybdenum oxide films are deposited by magnetron sputtering, using MoO\textsubscript{2} target in Ar atmosphere. The RF power is 150 W for deposition of MoO\textsubscript{x} and 200 W for deposition of Ag nanoparticles. There are studied two structures and pure MoO\textsubscript{x} layer.

Table 2. Sheet resistance of nanolaminate structures varying MoO\textsubscript{3} thickness

| Structure                                       | Sheet resistance [Ω/□] |
|-------------------------------------------------|------------------------|
| Sample 1 - MoO\textsubscript{x} (90 s)/10s Ag/MoO\textsubscript{x} (90s) | 7                      |
| Sample 2 - MoO\textsubscript{x} (90 s)          | 280                    |
| Sample 3 - MoO\textsubscript{3} (45 s)/10s Ag/MoO\textsubscript{x} (45s) | 10                     |

* The labels 90s and 45s mean the deposition time

Figure 2. Transmittance and reflectance spectra of samples 1, 2 and 3, described in table 2 of MoO\textsubscript{x} and MoO\textsubscript{x} (90s)/Ag (10s)/MoO\textsubscript{3} (90s). Transmittance is measured using bare glass substrate as background.
The nanolaminate structure of sample 3 has the same film thickness of MoO\textsubscript{x} as the sample 2, but the difference is the presence of intermediate layer with Ag nanoparticles. The pure MoO\textsubscript{x} film is very transparent in the visible spectral range above 90%. As it can be seen from figure 2, the reflection of the multilayer system increased with Ag layer. The increase in the reflection in the near infrared region is due to the interaction of free electrons with the incident radiation.

3.2. Influence of the substrate used
Studies on structures of the type ITO/Ag/ITO on organic substrates were reported in several papers [4-6]. The results are related to transparent conducting oxide (TCO) materials containing indium as dopant.

3.2.1. Optical and electrical properties of the nanolaminate structures on Plexiglass
Poly(methyl methacrylate) (PMMA), also known as acrylic glass as well as by the trade name Plexiglas, is a transparent thermoplastic often used in sheet form as a lightweight or shatter-resistant alternative to glass substrate. The used PMMA substrate is 1.5 mm thick, the deposited nanolaminate structure is TiO\textsubscript{2} (6 nm)/Ag NPs/TiO\textsubscript{2} (12 nm). The measured sheet resistance of this structure is 9 Ω/□.

![Figure 3](image)

**Figure 3.** Transmittance and reflectance spectra of TiO\textsubscript{2} (6 nm)/Ag NPs/TiO\textsubscript{2} (12 nm). The transmittance is measured against air (solid lines) and the reflectance is dotted line. The spectrum of bare PMMA substrate is given only for comparison.

The transmittance of the nanolaminate structure is near 80% in the visible spectral range and drops significantly for wavelength above 800 nm, meanwhile the reflectance below 10% up to 700 nm and then increased in the near IR spectral region.

3.2.2. Optical and electrical properties of the TiO\textsubscript{2}/Ag/TiO\textsubscript{2} structure on flexible substrates
Nanolaminate structure of type TiO\textsubscript{2} (20 nm)/Ag (NPs)/TiO\textsubscript{2} (20 nm) is sputtered simultaneously on four types substrates including glass substrate, two substrates of PVC foil with thickness 0.3 µm, and 0.15 µm and Hostaphan foil with thickness 0.1 µm. Hostaphan® is a family of PET (polyester) foils. The measured sheet resistance is presented in table 3.

The structures on PVC substrates have a greater sheet resistance in comparison with the glass substrate due to the rough surface of the material. Perhaps in this case the uniform distribution of the silver nano-granules is disrupted by increasing the distance between them. Structures deposited on
PVC substrates have higher sheet resistance in comparison with the same structures on glass substrates. (see Table 3). This may be due to rough surface of the PVC material. Probably, in this case the uniform distribution of the silver nano-granules is disrupted with increasing the distances among Ag granules.

Table 3. Sheet resistance of nanolaminate structure TiO$_2$ / Ag/TiO$_2$ on different types of substrates

| Structure                          | Sheet resistance [Ω/□] |
|-----------------------------------|----------------------|
| Sample 1 - on glass substrate    | 8                    |
| Sample 2 - structure on PVC foil  | 285                  |
| Sample 3 - PVC foil, 0.15 µm      | 375                  |
| Sample 4 - Hostaphan foil, 0.1 µm | 8                    |

Figure 4 shows that the layers on the PVC substrate have smaller transparency compared to those on glass. The transmittance spectra is measured using the relevant substrate as background. Optical and electrical properties of the nanolaminate structure on Hostaphan foil do not differ substantially from the sample on glass.

Figure 4. Transmittance spectra of TiO$_2$/ Ag NPs/TiO$_2$ on four types of substrates.

Table 4. Sheet resistance of nanolaminate structures on Hostaphan foil 0.1 µm thick substrate.

| Structure                                      | Sheet resistance [Ω/□] |
|-----------------------------------------------|----------------------|
| Sample 1-TiO$_2$(20nm)/Ag(NPs)/TiO$_2$(15nm) | 7.5                  |
| Sample 2- TiO$_2$ (10 nm)/Ag(NPs)/ TiO$_2$ (20nm) | 8.0                  |
| Sample 3 - TiO$_2$ (20nm)/Ag(NPs)/ TiO$_2$ (20 nm) | 8.0                  |
To demonstrate the possibilities for optimization of the properties of nanolaminates as the TCO layer, samples with different thicknesses of TiO$_2$ were tested. The electrical conductivity did not change significantly (see Table 4), but the effect on the transmittance spectra was observed. Figure 5 shows the transmittance spectra of three different nanolaminate structures deposited on Hostaphan foil with thickness 0.1 μm. It can be seen that they possess almost the same transparency.

4. Conclusions
The developed method for transparent conducting coating is a low temperature process and it is suitable for application on organic materials as substrate and foils. The experiment with different substrates manifest that the optical transparency of the conducting coating depends on substrate material. One suitable material is proved to be Hostaphan. The obtained results have demonstrated that the nanolaminate structures oxide/metal/oxide (OMO) as TCO coating are especially suitable for applications in flexible electronics and optoelectronics.

5. References
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