Optical and electrical properties of nanolaminate dielectric structures

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Abstract. The aim of this study was formation of a multilayered transparent conductive nanolaminate structure with optimized conductivity vs. transparency parameters. The nanolayered structure comprised one or two thin layers of dielectric materials. The overall electrical conductivity was modified by tuning the size of the planar metal granules. Magnetron sputtering system with three different targets was used for layers deposition. The advantages are: the good reproducibility of a low-temperature process allows for effective process control and, optionally, selective formation of conductive areas in a dielectric structure. Our studies revealed that the relation between the sheet resistance and the maximum transparency in the visible spectral range depends on the size of the metal granules and the film thickness of the dielectric coating. The technology provides transparent conductive coatings with well-controlled optical and electrical properties.

1. Introduction

The wide application of transparent and conductive oxide (TCO) films for optoelectronics and photovoltaics has promoted the development of low-cost materials and technological processes. Most of the TCO films are binary or ternary compounds containing one or two metallic elements. The combination of conductivity and transparency is impossible to achieve in intrinsic stoichiometric oxides. The successful approach is to create electron degeneracy in wide band gap (greater than 3 eV) oxides by introducing in a controlled way non-stoichiometry and/or appropriate dopants \cite{1}. These conditions are conveniently achieved in oxides of tin, indium, zinc and their alloys in a thin-film form. There is an inherent limitation in the metal oxide conductivity that can be obtained by increasing the carrier concentration. When the densities become greater than $2\times10^{21}\text{cm}^{-3}$, the TCO exhibits plasma frequencies that shift from absorbing infrared wavelengths to visible light, reducing the transparency in the visible region \cite{2}. The requirement for transparency and the fundamental scattering mechanism establish an absolute limit to the TCO resistivity of about $4\times10^{-5}\Omega\text{cm}$, or, to obtain conductivity in such materials, they should be doped with an appropriate element. An alternative approach recently proposed consists of TCO/metal/TCO stacks. In order to improve the transparency and durability of a TCO film, a thin semitransparent metal layer is embedded between two TCO films. This multilayer structure has many advantages compared to a single-layer TCO coating. Good performance has been

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achieved with other TCO/metal/TCO structures, such as ZnO/Ag/ZnO [3,4], Al:ZnO/Ag/Al:ZnO [5, 6], InZnSnO₄/Ag/InZnSnO₄ [7], and InZnO₄/Ag/InZnO₄ [8], all with sheet resistance below 10 Ω/sq and maximum transmittance of about 85% with less than 100 nm total thickness. Thus, the substitution of ITO by alternative TCOs becomes easier with TCO/metal/TCO structures, because the metal interlayer allows one to decrease the overall resistivity even though the TCO electrical quality is not optimal [9].

The aim of this study is formation of an optically transparent and conductive nanolaminate dielectric structure. The idea is based on using the electronic conductivity in granular (discontinuous) types of materials [10]. The granules are metallic particles of sizes ranging usually from a few to hundreds of nanometers, embedded into an insulating matrix [10]. The nanolayer structure is formed using one or two different dielectric materials. The electrical conductivity can be modified by varying the size of the planar metal granules [11]. The advantages of this method are reproducibility of the deposition process, effective control of the layers and compatibility with methods for low-temperature selective formation of conductive areas into the dielectric structure. Our studies revealed that the relation between the sheet resistance and the maximum transparency in the visible spectral range depends on the dimensions of the metal granules and the film thickness of the dielectric layers. Another option for engineering the optical and electrical properties of nanolaminate structures is to use different metal and dielectric layers.

2. Experimental

Magnetron sputtering system with three different targets was used for the deposition of the layers. This system has been developed as low-temperature high-speed sputtering equipment to be used in experiments and is suitable for formation of thin-films of metals and insulating materials. The substrate holder has a size of 200 mm and three targets (75 mm) placed at eccentric positions. They are cooled by water (3 l/min). The targets and the substrate holder are vertically arranged at a distance of 8 cm. The substrate holder is spinning at a rate of 80 rpm/min. This configuration allows us to prepare thin films with a homogeneous thickness. The three targets give the possibility to deposit successively three different layers without opening the chamber.

The most important part of the deposition process of a nanolaminate structure with specified optical and electrical properties is the deposition of a discontinuous metal layer. The size and density of the metal granules depend on the duration of the sputtering, the RF power, the type of reactive gas (Ar or He) and the substrate holder rotation rate. Evaluation and optimization of the deposition process was performed by AFM observation of the structures deposited.

Figure 1 presents AFM images of nanogranular coatings produced by Ag sputtering on p-type Si wafers with thermally grown SiO₂ (40 nm) under the following deposition conditions: reactive gas Ar, RF power 200 W and two deposition times. The metal nanoparticles with a maximum height
approaching 20 nm (figure 1a) form a discontinuous layer and are randomly distributed. When the deposition time is raised, the granules become bigger and are located closer to one another. Indication for the density of the nanogranular layer may be obtained indirectly from the transmittance spectra. The optical properties of the nanolaminate structure dielectric/metal/dielectric (oxide/metal/oxide - OMO) were studied by means of a UV 3300 UV-VIS-NIR Shimadzu spectrophotometer.

TiO$_2$ films were deposited at an RF power of 300 W in Ar at a deposition rate of 10 nm/min. The film thickness was determined by a laser ellipsometer. Figure 2 shows the optical spectra of 40 nm and 100 nm thick layers.

The sheet resistance was measured using the four-point probe method, the van der Pauw method and I-V measurements of the resistors.

3. Results and discussions
The nanolaminate structures studied were TiO$_2$/metal (Ag)/TiO$_2$. The investigations revealed that the relation between the sheet resistance and the maximum transparency in the visible spectral range depends on the size of the metal granules, the film thickness of the dielectric coating, and the type of the metal used for the granular structure formation.

3.1. Dependence on the sputtering time of Ag granules
The nanolaminate structures TiO$_2$/metal (Ag)/TiO$_2$ were investigated by keeping the thickness of the TiO$_2$ layers at 50 nm, but varying the Ag sputtering time (4 s, 7 s and 25 s), which determines the dimensions and density of the metal granules. Table 1 presents the sheet resistance values for nanolaminate structures with different Ag layers.

For the structures investigated, the sheet resistance decreased as the optical transparency diminished [3, 6, 9]. The optical transmittance (see figure 3) and the sheet resistance are functions of the metal nanoparticles density in the middle layers. Similar results are reported for ZnO/Ag/ ZnO [12] and ZnO/Au/ ZnO [13] structures. The reflection of the multilayer system increased with the increase in the Ag layer thickness. The increase in the reflection in the near infrared region is due to the interaction of free electrons with the incident radiation.

3.2. Dependence on the metal granules type
In order to study the effect of the nanogranules of different metals, the dielectric layer used was TiO$_2$ deposited under the same conditions, but Ag was replaced by Ni or Cr. Table 2 presents the measured sheet resistance values of these new structures.

The optical spectra shown in figure 4 reveal a significant difference in the

Table 1. Sheet resistance measurements of nanolaminate structures with different Ag layers.

| Structure          | Sheet resistance [Ω/sq] |
|--------------------|------------------------|
| TiO$_2$/4'' Ag/TiO$_2$ | 75                     |
| TiO$_2$/7'' Ag/TiO$_2$ | 22                     |
| TiO$_2$/25'' Ag/TiO$_2$ | 6.5                    |

Figure 3. Optical spectra of TiO$_2$/Ag/TiO$_2$ with Ag layers of different thickness. The reflectance is shown as dotted lines.

Table 2. Sheet resistance measurements of nanolaminate structures with different metal layers.

| Structure          | Sheet resistance [Ω/sq] |
|--------------------|------------------------|
| TiO$_2$/5'' Cr/TiO$_2$ | 680                    |
| TiO$_2$/5'' Ni/TiO$_2$ | 680                    |
| TiO$_2$/10'' Ni/TiO$_2$ | 310                    |
transmittance of the two nanolaminate structures TiO$_2$/Cr/TiO$_2$ and TiO$_2$/Ni/ TiO$_2$ (Ni and Cr layers being deposited at a sputtering time of 5''), but it must emphasized that the sheet resistances of both structures are equal.

3.3. Engineering the optical properties of nanolaminate OMO structures

The studies, related to the research on the influence of the sputtering deposition process parameters on the optical and electrical properties of oxide/metal NPs/oxide (OMO), were aimed at finding the optimal conditions for the formation of transparent and conductive coatings. The TiO$_2$/Ag/TiO$_2$ nanolaminate structures produced possessed a very good reproducibility, high transparency and sheet resistance of 7 $\Omega$/sq. The sputtering time was 370 sec. The procedure included a variation of the film thickness of the top dielectric layer of TiO$_2$ that causes variation of the transmittance spectra. In figure 5, the optical spectra of three nanolaminate structures are presented; they have the same values of the sheet resistance, but the thickness of the second TiO$_2$ layer was varied. The structures were as follows:

- TiO$_2$ ($d$ = 28 nm)/Ag/TiO$_2$ ($d$ = 28 nm)
- TiO$_2$ ($d$ = 28 nm)/Ag/TiO$_2$ ($d$ = 56 nm)
- TiO$_2$ ($d$ = 28 nm)/Ag/TiO$_2$ ($d$ = 86 nm)

It can be seen that there is a shift of the transparency maximum from 480 nm to 640 nm and, respectively, the structures are slightly colored from bluish to yellow. This result can be used for spectral selectivity where it is needed.

The performance of a nanolaminate structure as a transparent conductive coating is described by the figure of merit ($F_{TC}$), as defined by Haacke [14] $F_{TC} = \frac{T^{10}}{R_s}$, where $T$ is the transmittance at 550 nm and $R_s$ is the sheet resistance. Table 3 summarizes the figure of merit values for similar dielectric structures prepared with different metals.

It can be concluded that the highest figure of merit, $F_{TC}$, achieved for a TiO$_2$/Ag/TiO$_2$ structure reached a value, which is competitive with the ones reported in literature [15].

3.4. Application of the electrical conductivity of OMO structures

Figure 6 presents the temperature dependence of the specific resistivity of the nanolaminate structures. The electrical resistivity of the conductive area at room temperature is $\rho = 9.9 \times 10^5 \Omega$ cm. Usually, the TCOs exhibit a semiconductor behaviour, namely, a negative temperature coefficient of resistivity (TCR) [15]. The nanolaminate structure with metal granulate demonstrates a metallic conductivity, because it has a positive TCR. Therefore, the carriers are delocalized due to thermal activation and the conductivity is dominated by phonon scattering. Similar observations of high conductivities, but with a positive TCR have been reported in the cases of TiO$_2$: Nb [16] and ZnO: Ga [17] layers. The
deposition method for obtaining OMO nanolaminate structures allows for a selective formation of conductive buses or areas without using an etching process. Figure 7 shows the structure of the conductive area on an oxidized silicon surface, which functions as a resistor.

| Nanolaminate structure | $T$ ($\lambda=550$ nm) | Sheet resistance [\(\Omega/\text{sq}\)] | $F_{\text{TC}}$ [$10^{-3} \Omega^{-1}$] |
|------------------------|------------------------|------------------------------------------|----------------------------------------|
| TiO$_2$/Ag/TiO$_2$     | 0,97                   | 7                                        | 105,3                                  |
| TiO$_2$/Cu/TiO$_2$     | 0,69                   | 16                                       | 1,5                                    |
| TiO$_2$/Al/TiO$_2$, annealed 400°C | 0,87                   | 40                                       | 6,3                                    |

4. Conclusions

The oxide/metal/oxide (OMO) structure is a good alternative to TCO films based on SnO$_2$:F, ZnO:Al, ZnO:Ga, Sn:In$_2$O$_3$, Zn$_2$SnO$_4$ etc. The technological process proposed is magnetron sputtering deposition, which is a new approach to the formation of a low-resistivity transparent electrode at room temperature without using high substrate temperature or a post-annealing process. Therefore, it is compatible with polycarbonate or flexible substrates as well. The advantages of the proposed technology are reproducibility of the parameters, effective methods for process control and a selective formation of conductive areas in a dielectric structure.

The nanolaminate structures TiO$_2$/Ag/TiO$_2$ were studied and optimized in terms of a high electrical conductivity and transparency.

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