Optical and electrical properties of TiO$_2$/Pt/TiO$_2$ nanolaminate structures

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Abstract. We report the results of a study on the optical and electrical properties of nanolaminate TiO$_2$/Pt/TiO$_2$ structures fabricated using RF magnetron sputtering. The effect was investigated of the discontinuous Pt layer on the optical transmittance, electrical conductivity and morphology of the TiO$_2$/Pt/TiO$_2$ structure. On the basis of the theory of electronic tunneling transport between metal granulates in a dielectric matrix, a new technological approach is proposed of preparing high-sensitivity strain sensors based on resistors with a nanolaminate structure containing Pt granulates.

1. Introduction
Recently, we reported the development of an optically transparent and conductive nanolaminated dielectric/metal/dielectric (DMD) structure [1]. The concept is based on the usage of electronic conductivity in materials of granular (discontinuous) type [2]. The granulates are metallic particles of sizes ranging usually from a few to hundreds of nanometers embedded into an insulating matrix. The nanolaminate DMD structure is formed using one or two different dielectrics. The electrical conductivity is modified by plane-located metal granulates. The advantages of this approach include high reproducibility of the technological parameters, easy process control, and selective formation of conductive areas in the dielectric structure. It should be noted also that the conductive nanolaminate structures are transparent in the visible spectral range. The optical transmittance and the sheet resistance are functions of the metal nanoparticles density in the intermediate layer.

Usually, the transparent and conductive oxide (TCO) films exhibit semiconductor behavior, namely, a negative temperature coefficient of resistivity (TCR). In contrast, the nanolaminate structure with metal granulates demonstrates a metallic conductivity, i.e., a positive TCR. Therefore, the charge carriers are delocalized due to thermal activation and the conductivity is dominated by phonon scattering. The strain effects in such nanolaminate structures with Ag granulates have already been reported [3]. The disadvantage of such a structure is that its properties degrade during most of the

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common wet chemical and plasma treatments used in the MEMS technologies. Thus, the necessity arises of finding chemically-stable materials for metallic nano-granulates.

In this work, TiO$_2$/Pt/TiO$_2$ sandwich films were fabricated using RF magnetron sputtering. This technique has many advantages, including large area deposition, high deposition rate, simple equipment and easy operation. The electrical and optical properties of the nanolamine structures with Pt nanoparticles were studied as depending on the sputtering deposition time of the Pt target. It was found that their electrical and optical properties do not change after thermal annealing at 400 °C for 60 min, as well as during the usual wet chemical and plasma treatments. A new technological approach was developed for preparing high-sensitivity strain sensors based on resistors with a nanolamine structure containing Pt granulates.

2. Experimental – deposition procedure

The layers were deposited on an RF magnetron sputtering system with three targets. This system was developed to be used for low-temperature high-speed sputtering deposition and is suitable for thin-film deposition of metals and insulating materials. The substrate holder has a size of 200 mm, with three targets (75 mm) located at eccentric positions. The water-cooled (3 l/min) targets and the substrate holder are vertically arranged at a distance of 80 mm. The holder is rotating at a rate of 80 rpm. This configuration allows one to prepare thin films with homogeneous thickness. The three targets provide options to deposit successively three different layers without opening the chamber. In this work, the TiO$_2$ films were deposited at an RF power of 300 W in Ar$_2$ ambient at a deposition rate of 10 nm/min. The film thickness was determined by an LEF 3M laser ellipsometer equipped with a He-Ne laser operating at the wavelength of 638.2 nm.

The surface morphology was investigated by AFM measurements carried out using a Multimode V device (Bruker, ex. Veeco, Santa Barbara, CA). The imaging was performed in tapping mode, with a scan rate of 2 Hz and image resolution of 512 lines using silicon cantilevers with a length of 125 µm and Al reflective coating on the backside (MPP-11120-10, Bruker). These probes have a nominal resonance frequency of 300 kHz and a typical force constant of 40 N/m, with the nominal tip radius being less than 10 nm. At least three different areas on the sample surface were studied. The image analysis was performed by means of the SPIP$^\text{.tm}$ 6.1.0 software.

Figure 1 presents AFM images of a nanogranulate coating prepared by sputtering Pt on polished Si wafers with thermally-grown SiO$_2$ (400 nm) under the following deposition conditions: Ar$_2$ reactive gas, RF power of 200 W and deposition time of 10 s. The metal nanoparticles with a maximum height approaching 0.9 nm form a discontinuous layer and are randomly distributed.

![AFM images of a Pt nanogranular coating](image_url)

**Figure 1.** AFM images of a Pt nanogranular coating, a) top view; b) 3D view.
Figure 2 presents AFM images of the surface of the TiO$_2$/Pt/TiO$_2$ nanolaminate structure. Its morphology (rough surface) is formed by platinum granulates with a maximal height of 2.63 nm and a grain diameter of about 14 nm.

![AFM image](image)

**Figure 2.** AFM image of a sputtered nanolaminate TiO$_2$/Pt/TiO$_2$ structure: a) top view; b) 3D view.

3. Results and discussions

3.1. Optical and electrical properties

The two TiO$_2$ layers in the nanolaminate TiO$_2$/Pt/TiO$_2$ structures examined had an equal thickness of 20 nm, but we varied the sputtering time Pt (7 s, 10 s and 15 s). The latter determines the size and density of the metal granulates. The two parameters, namely, the optical transmittance and the sheet resistance, depend on the metal nanoparticles density in the intermediate layer. One expects that the optical transmittance will decrease as the sputtering time, i.e., the thickness of the Pt layer, increases.

As demonstrated in figure 3, the optical transmittance does decreases as the Pt layer thickness increases.

The values of sheet resistance for nanolaminated structures with different Pt layers are presented in table 1.

![Transmittance spectra](image)

**Figure 3.** Transmittance spectra of nanolaminate structures, sample 1 refers to TiO$_2$/Pt(7s)/TiO$_2$, sample 2 to TiO$_2$/Pt(10s)/TiO$_2$ and sample 3, to TiO$_2$/Pt(15s)/TiO$_2$. The spectra are measured using a bare glass substrate as a reference.

The electrical conductivity values can be explained by the average tunneling conductance $G$ between metal granulates. It is convenient to introduce the dimensionless conductance $g$, measured in units of the quantum conductance $e^2/h$, then $g = G/(2e^2/h)$ [2]. The samples with $g > 1$ exhibit metallic transport properties, while those with $g < 1$ show insulating behavior. The dependence of the tunneling...
probability on the inter-granular distance suggests the suitability of the material as a high-sensitivity strain sensor [4, 5]. The resistivity of a dielectric(TiO$_2$)/metal(Pt)/dielectric(TiO$_2$) (DMD) resistor increases if the material is tension-strained, as the average distance between the particles increases and the tunneling probability decreases. If the electron transport in the nanogranular metal is of tunneling nature, then the nanolaminate structures can be used as strain resistors.

3.2. Four-cantilever self-sensing test device
Figure 4 displays a top-view of the four-cantilever test device. A single DMD resistor 1 is positioned on each cantilever $C_1$ and all four resistors are connected with patterned metal tracks 2 in a full-bridge configuration [3]. Since all resistors have the same value, the output bridge signal is compensated when the cantilevers do not move, or move synchronously. Because asynchronous oscillations occur at resonance, a bridge misbalance might be observed at the particular resonance frequencies of the cantilevers, if the resistors are strain-sensitive. The frequency response of the device was detected by means of the set-up presented schematically in figure 5. A sweeping signal in the frequency range of 10 kHz to 100 kHz from a signal generator was used to drive a piezo actuator that caused the cantilevers to vibrate.

Figure 6 shows a plot of the output characteristic of the four-cantilever device. The figure displays also the correlation between the detected frequencies of the bridge misbalance and resonance frequencies of the cantilevers $C_1 – C_4$. The coincidence of the said frequencies proves the sensitivity to strain of the TiO$_2$/Pt/TiO$_2$ DMD resistors.

4. Conclusions
We explored the electrical conductivity and optical transparency of TiO$_2$/Pt/TiO$_2$ nanolaminate structures. Since the structures possessed high chemical robustness and good compatibility with surface micromachining technologies, we successfully integrated them in a four cantilever test devices. Based on the theory of tunneling electronic transport in nanogranular metals in a dielectric matrix, we were able to verify experimentally that the nanolaminate TiO$_2$/Pt/TiO$_2$ resistors are sensitive to strain.
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