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Thin-film TiPbO$_3$ varistors obtained by two-source magnetron sputtering

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Abstract. The paper presents the method of obtaining thin films of TiPbO$_3$ by two-source magnetron sputtering DC-M. The films were obtained in a reactive process of sputtering metallic targets of titanium (Ti) and lead (Pb). The research involved the impact of the time of sputtering of the respective targets on voltage-dependent resistance of the obtained films for different power conditions, pressures of process gases and the powers provided on the targets. The obtained nonlinearity coefficients and the current-voltage $I(U)$ characteristics were within the following range.

1. Introduction
These Varistors are electrical elements characterised by extreme nonlinearity of the current-voltage ($I$-$U$) dependency. As such, they are widely used as protection devices against surges in electrical and power equipment. The varistors that are manufactured on an industrial scale include a film of sintered zinc and other metal oxides with a thickness between several millimetres to several centimetres. The power energy industry uses varistors with a wide range of actuation voltage – from several volts into thousands. The manufacture of varistors with increasing reliability and uniform microstructure and resistivity distribution is still a challenge for researchers. A number of sophisticated methods have been employed to obtain such varistors: advancing technological processes, applying chemical methods of powder uniformisation, or introducing optimisation formulas based on network modelling techniques. The available varistors can protect systems and circuits in a wide range of voltages – from several volts in case of low-voltage varistors present in electronic circuits, to several thousand volts in power networks. The manufacture of varistors with increasing reliability and uniform microstructure and resistivity distribution is still a challenge for researchers. Non-linear electric conductance in ceramic varistors is made possible by the barriers to electric potential at the perimeters of the granules, the presence of which is related to the energetic and spatial distribution of trapping states on interfacial surfaces [1, 2]. The form of the current-voltage characteristics $I(U)$ points to the existence of a several underlying mechanisms related to electrical conductivity, and is a function of both the chemical composition and the heat treatment conditions [3]. A number of sophisticated methods have been employed so as to obtain such varistors: by advancing technological processes, by applying chemical methods of powder uniformisation, or by introducing optimisation formulas via network modelling techniques [4]. The available varistors can protect systems and circuits in a wide range of voltages – from several volts in case of low-voltage varistors present in electronic circuits, to several thousand volts in power networks. Today, research efforts focus on developing new materials and methods of manufacture of voltage-dependent resistance.
Lead titanate (TiPbO$_3$) is one of such promising materials. It shows ferroelectric and piezoelectric properties, and voltage-dependent resistance. Magnetron sputtering is the most beneficial method of obtaining thin-film structures. Magnetron systems make it possible to clean and harden the substrate, activate the surface, and to apply films within a single process. The films obtained in this manner are characterised by decent hardness and adhesion to the substrate in relation to the original material.

2. Experiment

Thin films of TiPbO$_3$ were obtained in the process of reactive sputtering of metallic targets of lead and titanium with a purity of 99.99%. Two WMK-50 magnetron launchers were used (Fig. 1). The partial pressure of oxygen and argon were identical and amounted to $p_{O_2}$ = $p_{Ar}$ = 1.33 Pa, thus the final pressure of the process mixture amounted to $p$ = 2.66 Pa. The magnetron launchers are powered with a DPS (DORA POWER SYSTEM) pulsed current source with a maximum output of 16 kW and a maximum voltage of 1.2 kV. The group frequency of the source was adjustable in the range from 5 Hz to 5 kHz. The use of a pulsed current source (Fig. 2) makes it possible to vary the load concentration in the area between the target and the substrate, since cyclical changes in the electric force rearranges ions/electrons in the area of the influence of the force. During the current pulse time $t_1$, process gas ions actively sputter the target, whereas the electric and magnetic field holds it within the plasma area. The disappearance of the electric field (between the pulses $t_2$-$t_1$) releases ions/atoms that condense on the substrate thus forming the film.

Due to the different points of melting (lead: 327 °C, titanium: 1688 °C), boiling (lead: 1749 °C, titanium: 3287 °C) and different heat conductivity (Ti-22.4 W m$^{-1}$ K$^{-1}$, Pb-35.3 W m$^{-1}$ K$^{-1}$) it is difficult to sputter these elements using the same power densities and over the same periods of time. To overcome this difficulty a multiplexer was designed that powers both magnetron launchers in an alternating manner. The multiplexer makes it possible to vary the switching frequency and sputtering time depending on the target (Fig. 3). This solution makes it possible to obtain single layers of TiPbO$_3$ , as well as structures made of alternating layers of TiO$_2$ and PbO. This, in turn, makes it possible to influence the size of connections and interfaces between the granules. The switching frequency of the targets was set at 5 Hz for the purposes of the research presented in this paper. The total time of applying layers amounted to 30 min. Maximum power provided on the targets amounted to 300 W. The distribution of sputtering time between the respective targets ranged varied from 100% to 25%. The distance between the target and the substrate amounted to 10 cm.

**Figure 1.** The arrangement of two magnetrons in a vacuum chamber.
3. Results

The current-voltage characteristics were measured with a Keithley 617 electrometer with a voltage increase of 100 mV/min. Fig. 4 presents a comparison of the measured current-voltage characteristics of the obtained voltage-dependent resistance films. It can be observed that the TiO$_2$ layer is characterised by strong nonlinearity of $I(U)$. The calculated nonlinearity coefficient amounted to $\alpha=24$. On the other hand, in case of PbO layers this relation is nearly linear. Nonlinearity occurs for polarisation voltage above 1 V. Figure 5 shows the $I(U)$ characteristics of TiO$_2$ layers doped with PbO. The doping was effected by changing the distribution of the sputtering time of titanium and lead metallic targets. Lead and titanium targets were sputtered with a power of 300 W and with a switching frequency of 5 Hz. It can be noted that doping substantially lowers the nonlinearity coefficient - down to the 4 to 10 range.

Figure 4. Current as a function of voltage for PbO and TiO$_2$ layers.

Figure 2. Drawings of rectangular modulated discharge current pulse d.c. mode bias DC-M.

Figure 3. Time of sputtering the respective targets: $t_1$ – Ti target sputtering time, $t_2$ – Pb target sputtering time.
4. Summary
The TiO$_2$ layers obtained by magnetron sputtering show voltage-dependent resistance with high nonlinearity coefficient $\alpha=24$. The layers of PbO do not show voltage-dependent resistance. By adjusting the time and power of sputtering the targets, and the switching frequency it is possible to increase the nonlinearity coefficient. The actuation voltage of the voltage-dependent resistance layers can be adjusted by varying their thickness (by regulating the total sputtering time).

References