Technical Physics Letters, 2024, Vol. 50, No. 3

07.2

Investigation of the influence of heat treatment and electrical power on the main characteristics of thin-film thermistors with a layer structure

© A.I. Belov, V.N. Novozhilov, K.V. Sidorenko

Lobachevsky State University, Nizhny Novgorod, Russia
E-mail: belov@nifti.unn.ru

Received September 21, 2023
Revised December 6, 2023
Accepted December 6, 2023

A layer version of the thermistor was created using the magnetron sputtering method, when the working layer of a spinel phase semiconductor film is applied to a metal film previously formed on a polycor substrate, forming an internal electrode. The influence of heat treatment and electrical power on the main characteristics of the obtained thermistors was studied. It has been established that the transition to a layer structure makes it possible to obtain chip thermistors with a resistance of less than 100 Ω while maintaining high temperature nonlinearity of the resistance. After temperature treatment at 400–500°C, thermistors acquire two to three orders of magnitude greater resistance and pronounced field nonlinearity, which determines the strong dependence of the resistance on the applied voltage. Samples of thermistors with an internal electrode made of Ni, and especially NiCr, after annealing at 500°C, exhibit high resistance to extreme electrical power of several watts.

Keywords: thermistor, magnetron sputtering, electrical properties, nonlinear properties, semiconductor oxides.

DOI: 10.21883/0000000000

Thermistors with a negative temperature coefficient of resistance (TCR) formed from transition metal oxides play a critical part in the fabrication of temperature and flow rate sensors, pressure gauges, etc. [1]. The operation of passive electronic devices in the form of thermistors relies on nonlinear thermal conductivity effects that are manifested in materials based on transition metal oxides. Materials of the Mn–Co–Ni–O system with a spinel structure (AB_2O_4) are among those most commonly used in the production of thermistors with a negative TCR. The structure, electrical characteristics, and thermal stability of Mn–Co–Ni–O spinel-type materials have been studied extensively [2–8].

The majority of thermistors are fabricated in a traditional ceramic process. At the same time, it is of great practical interest to fabricate thermistors with a two-dimensional configuration in a planar process. The appeal of film thermistors stems from their reduced size and the potential for their implementation in arrays, hybrid integrated circuits, and microassemblies. This is especially true for chip thermistors.

The highest TCR values are found in materials with a high resistivity; when the resistivity decreases, nonlinear characteristics become significantly less pronounced. In view of this, the production of thermistors with low (less than 100 Ω) nominal resistances and high temperature sensitivity presents severe difficulties. Estimates of the nominal resistance of thermistors of a single-layer design with a semiconductor film no thicker than $2\,\mu$m and oxide materials with a bulk resistivity of $2–2000\,\Omega \cdot$cm range from $\sim 10\,$kΩ to several tens of MΩ. These estimates were verified in a number of studies [4–6,9] focused on the thin-film semiconductor oxide technology.

Thermistors fabricated in the present study are specific in having an internal metallic layer that is coated completely by a film of a semiconductor material with a spinel-type crystal structure (Fig. 1, *a*). This approach appears to be promising in terms of reducing the nominal thermistor resistance values to several tens of Ω while maintaining fine nonlinear characteristics, which classical thermistor structures struggle to preserve.

The aim of the study is to examine the electrophysical characteristics of film thermistors with an internal NiCr-, Ni-, or Al-based electrode that were fabricated by radio-frequency magnetron sputtering of a semiconductor film of the $(Mn,Co,Cu)_3O_4$ spinel phase onto polycor substrates. The composition and structure of the sputtered film and the procedure of thermistor fabrication were detailed in [10]. Thermistors were produced in a chip form factor type 1206 ($3.2 \times 1.6\,$mm).

The thermistor design presented in Fig. 1, *a* provides an opportunity to shift considerably toward lower nominal resistances (compared to the resistances of similar thermistors without an internal metallic electrode) while preserving a pronounced temperature nonlinearity of resistance. Figure 1, *b* shows the typical current–voltage curve (CVC) of a thermistor with an internal metallic Ni layer and resistance dependences derived from this CVC. Having a relatively low resistance of $65 \pm 3\,\Omega$, the thermistor features a high temperature sensitivity coefficient [1] $B_{25-85} = 3500 \pm 200\,$K that was determined from the slope of the linearized dependence of resistance on reciprocal temperature ($\ln R$ on T^{-1}).

The key factor governing the resistance and other thermistor characteristics in the proposed design is the transition layer at the boundary between a semiconductor film and

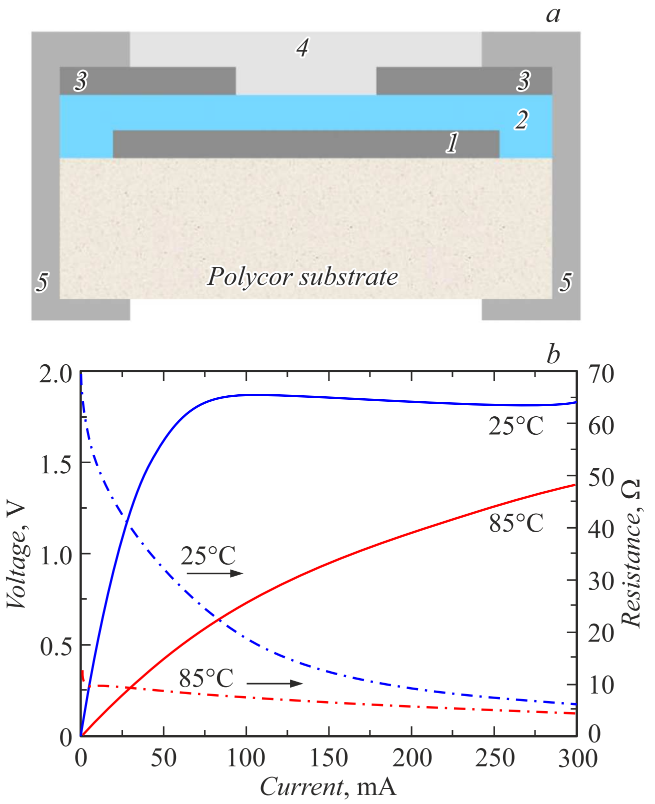

Figure 1. *a* — Schematic diagram of a film thermistor with an internal metallic layer. *1* — Internal metallic layer, *2* — semiconductor (Mn,Co,Cu)$_3$O$_4$ film, *3* — Ni contacts, *4* — protective layer, and *5* — enclosing electrodes. *b* — Typical CVC of the thermistor with a layer structure with $R_{25} = 65 \pm 3\,\Omega$, $B_{25-85} = 3500 \pm 200$ K and dependence of resistance on the passing current.

metallic electrodes. The parameters of this transition layer change significantly in the course of temperature processing of the semiconductor film at 400–500°C (needed for structural and phase stabilization of the film) due to the formation of a potential barrier, affecting the characteristics of a thermistor as a whole. The resistance of thermistors increases by two–three orders of magnitude, and non-ohmic properties (i.e., a strong dependence of resistance on the applied voltage) start manifesting themselves already at the initial CVC section (Fig. 2). A linear initial CVC section, which is a typical feature of classical thermistors and is characterized by a constant resistance and zero influence of thermal processes on the thermistor layer conductivity, is lacking in this case. At voltages above 0.01 V, a strong dependence of the layer structure conductivity on the field strength manifests itself.

The thermistor CVC assumes a „varistor“ shape with a stabilization voltage of 2–8 V in the thermal instability region. The voltage maximum ($U_{\max}$) in the CVC specifies the boundary beyond which a high-current process of thermistor self-heating develops. This process normally features a weakly pronounced section with a negative differential resistance. The most pronounced field dependence of the potential barrier height is observed for thermistors with an internal electrode made of Al. Thermistors with a resistance of 500–900 kΩ enter the self-heating regime at a voltage of 7–8 V, and the resistance of the structure within the 0.1–3 V voltage range varies from 636–1063 to 2.5–5.8 kΩ (Fig. 2, *b*). Potential barrier height $\varphi = \Delta \ln \sigma_{(T)} kT \approx 0.22$ eV may be estimated by the relative change in conductivity.

A strong dependence of the layer structure resistance on the applied voltage and the variation of barrier height with temperature suggest the presence of the Poole–Frenkel effect with the conductivity governed by equation $\sigma = \sigma_0 \exp(\chi E^{1/2}/kT)$, where χ is the Frenkel constant [9]. The initial CVC section is characterized by the dependence of resistance R on voltage U linearized in coordinates $\ln R^{-1}$–$U^{1/2}$ (inset in Fig. 2, *a*).

A similar transformation of the electrophysical parameters of a layer thermistor may be achieved through the use of load currents that induce significant levels of thermistor heating. An electrical load of 2–4 W applied for 30–60 s raises smoothly the nominal resistance of a layer thermistor (not subjected to thermal processing at 400–500°C). Repeating the load procedure multiple times, one may obtain resistance values ranging from the initial tens of Ω to tens of kΩ (or higher). Current heating is similar to volume thermal treatment in inducing a temperature-dependent nonlinearity with respect to voltage that triggers an increase in temperature sensitivity coefficient B_{25-85} within the initial CVC section, which goes from 3000–4000 to 5000–6500 K.

The voltage dependence of coefficient B_{25-85} is minimized in two limit thermistor states: the one with the lowest resistance $R < 100\,\Omega$ and, in contrast, the one with the highest resistance $R > 100$ kΩ (for an internal electrode made of nickel) or $R > 1$ MΩ (for an aluminum-based electrode). In the former case, a temperature-dependent potential barrier has not formed yet; in the latter case, it reaches a state during thermal processing when the internal electrode becomes tangibly insulated from the working semiconductor layer. For example, the thermistor with a Ni internal electrode has a resistance of $56 \pm 1\,\Omega$ and $B_{25-85} = 3440 \pm 70$ K at 0.1 V and $44 \pm 1\,\Omega$ and $B_{25-85} = 3270 \pm 60$ K at a voltage of 1 V. The samples with an aluminum internal electrode, which reached a resistance level of 3–8 MΩ in the course of thermal processing, have a nearly constant coefficient $B_{25-85} = 3437$–3371 K within the 0.01–10 V voltage range.

An electrical power load of several watts induces heating of a chip thermistor to a temperature of 400°C and above. The stability of thermistor characteristics under high currents becomes a crucial condition of their application as protection elements in electronic modules, transition process limiters, and voltage stabilizers. The resistance of a layer structure to high-intensity loads depends to a significant extent on the electrode material. The internal layer materials examined in the present study may be

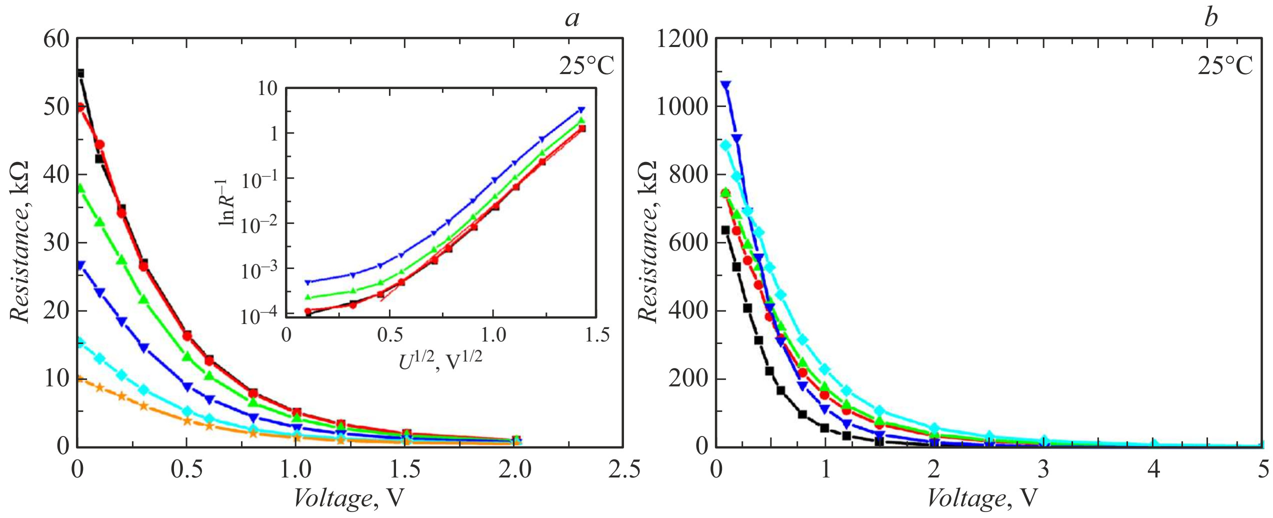

Figure 2. Voltage dependence of resistance for a set of thermistors with an internal electrode: *a* — based on nickel, annealing temperature $T_{ann} = 400^\circ$C (10–20 min); *b* — based on aluminum, $T_{ann} = 380^\circ$C (30–60 min). A CVC plotted in $\ln R^{-1}$–$U^{1/2}$ coordinates is shown in the inset.

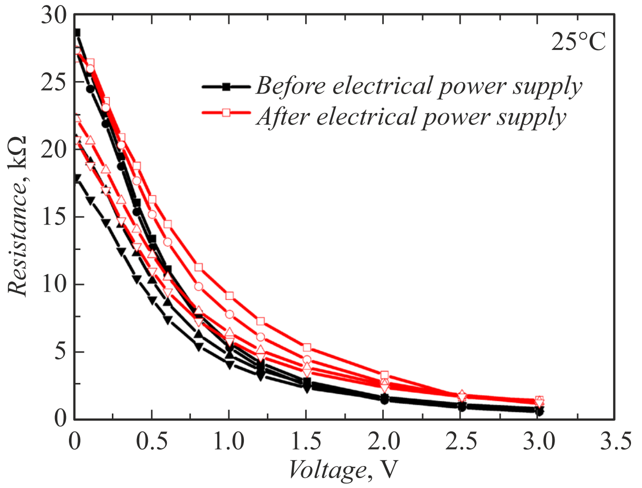

Figure 3. Dependence of the resistance of a set of thermistors with an internal NiCr layer annealed at 500°C before (filled symbols) and after (open symbols) the application of an electrical power load of 3 W.

arranged in the following order according to their capacity to withstand thermal and current overloads: Al, Cu, Ni, NiCr. Thermistors with a nichrome electrode annealed at 500°C retained their operating parameters after extreme power loads (3–4 W for 30 min; see Fig. 3).

The process of annealing of the layer structure, which enhances the thermistor resistance, shifts higher the voltage corresponding to the onset of self-heating and thermal instability. As the high-temperature treatment continues and the thermistor resistance grows further, the internal electrode becomes insulated from the semiconductor oxide layer. The layer structure degenerates to a classical planar one. As in the common planar thermistor structure, breakdowns are not observed under voltages of 100 V and higher.

The following experiment verifies that oxygen in the thermistor material exerts a significant influence on the barrier layer formation. Semiconductor oxide was formed on the internal electrode by depositing first a $\sim 0.1\,\mu$m layer in argon plasma (without oxygen) and then a layer with a thickness needed to reach the target semiconductor film parameters ($\sim 1.5\,\mu$m) in an argon–oxygen mixture. The resistance growth in such thermistors is much less pronounced (limited to several hundred Ω), while the resistance of samples without an additional layer increases to several tens or hundreds of kΩ under similar thermal processing regimes.

The presented data suggest that layer thermistor structures may be applied in the engineering of high-sensitivity fast-response thermal sensors and IR radiation detectors. The capacity of a layer structure to withstand high-intensity loads makes it promising for application in voltage stabilization and limiting elements and elements of protection of electronic modules from adverse transition processes and interference.

Funding

This study was supported by grant No. 22-29-20122 from the Russian Science Foundation (https://rscf.ru/project/22-29-20122/) and a grant from the Government of Nizhny Novgorod Oblast.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A. Feteira, J. Am. Ceram. Soc., **92**, 967 (2009). DOI: 10.1111/j.1551-2916.2009.02990.x

[2] L. He, Z.Y. Ling, Y.T. Huang, Y.S. Liu, Mater. Lett., **65**, 1632 (2011). DOI: 10.1063/1.3596454

[3] L. Chen, Q.N. Zhang, J.C. Yao, J.H. Wang, W.W. Kong, C.P. Jiang, A.M. Chang, Small, **12**, 5027 (2016). DOI: 10.1002/smll.201600470

[4] W. Di, F. Liu, T. Lin, H. Kong, C. Meng, W. Zhang, Y. Chen, Y. Hou, Appl. Surf. Sci., **447**, 287 (2018). DOI: 10.1016/j.apsusc.2018.03.200

[5] Q. Shi, W. Ren, W. Kong, B. Gao, L. Wang, C. Ma, A. Chang, L. Bian, J. Mater. Sci.: Mater. Electron., **28**, 9876 (2017). DOI: 10.1007/s10854-017-6742-8

[6] Y. Yin, J. Wu, W. Zhou, W. Ma, L. Jiang, Y. Gao, Z. Huang, J. Alloys Compd., **822**, 153705 (2020). DOI: 10.1016/j.jallcom.2020.153705

[7] I.T. Sheftel', *Termorezistory* (Nauka, M, 1973) (in Russian).

[8] F. Medvedev, P. Nikitin, G. Tekster-Proskuryakova, S. Teslenko, Elektronika: Nauka, Tekhnol., Biznes, No. 6 (42), 10 (2002) (in Russian).

[9] Kh.S. Valeev, V.B. Kvaskov, *Nelineinye metallooksidnye poluprovodniki* (Energoizdat, M., 1983) (in Russian).

[10] V. Novozhilov, A. Belov, Int. J. Mol. Sci., **24**, 742 (2023). DOI: 10.3390/ijms24010742

Translated by D.Safin