INFLUENCE OF RESIDUAL THERMAL STRESSES ON THE STRAIN SENSITIVITY OF THICK $Sn_{0.9}Sb_{0.1}O_2$-BASED FILMS

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The influence of residual thermal stresses resulting from the mismatch between the thermal expansion coefficients of the film and the substrate on the strain sensitivity of thick resistive $Sn_{0.9}Sb_{0.1}O_2$-based films has been studied. It has been found that the value of the gauge factor measured by the three-point bending method depends on the sign of residual stresses at the film—substrate interface. This phenomenon can be explained by a significant influence exerted by the processes of charge path reorganization on the variation of electrical resistance during deformation.

1. Introduction

A thick film resistor (TFR) is a composite made up of conductive particles which are distributed in a dielectric matrix that provides the film consolidation and its adhesion to a substrate. Ceramics, crystalline glass, and enameled steel are used as substrates. Nowadays, TFRs find the extensive application in sensor electronics as the detecting elements of various transducers. Films on the basis of ruthenium compounds are widely used for fabricating the sensing devices for strain sensors based on the piezoresistive effect — the variation of the electrical resistance of a material under the influence of an elastic deformation [1–3]. The gauge factor $\gamma = \Delta R/R\varepsilon$, where R is the electrical resistance of the resistor and ε is the relative deformation, falls within the limits of 3—20 for the majority of films [1]. Although, by the absolute value of the strain sensitivity, TFRs are at a disadvantage in relation to semiconductors and discontinuous thin films, they exceed, nevertheless, them in a number of parameters, which determines the successful application of the former. Challenging remain the search for thick-film materials possessing a high strain sensitivity and the study of factors that affect its magnitude.

This work is aimed at studying the influence of residual stresses induced by a mismatch between the thermal expansion coefficients (TECs) of the film and the substrate on the strain sensitivity of $Sn_{0.9}Sb_{0.1}O_2$-based TFRs.

2. Experimental Technique

TFR specimens were fabricated by the screen printing method from pastes that contained the powders of the stannic oxide solid solution doped with antimony (3.3 at.%), the powders of lead-boron-silicate glasses, and an organic binder that burnt out altogether in the course of heat treatment. The content of glass in the pastes was 50 wt.%. Enameled steel, alumina and nitride-alumina ceramics, and crystalline glass were applied as substrates. The properties of substrates that were used in the work are quoted in the Table. The electrical resistance, the temperature coefficient of resistance (TCR), and the current-voltage characteristics (CVCs) of the films were measured following standard techniques [4, 5]. The gauge factors of the specimens were measured using the three-point bending method [6]. Residual stresses were studied by means of the polarization-modulation method of investigating stresses in composites [7]. The film microstructure was studied making use of a Stereoskan S4-10 device and JXA-733 and CAMEBAX SX-50 microanalyzers. The X-ray phase analysis was carried on a DRON-2.0 installation with filtered Cu K_α-radiation. The strength of the film—substrate adhesion was determined by the pull-off method. The substrate roughness was measured with the help of a G-174 profilometer.

3. Experimental Results and Their Discussion

Depending on the direction of deformation — along or across the direction of electric current flow — the

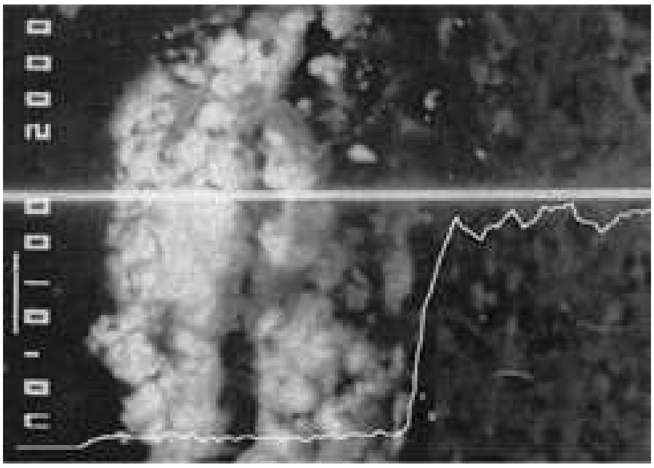


Fig. 1. Image of the transverse section of a TFR on a substrate that contains 94.4% of Al_2O_3, obtained in the mode of reflected electrons, and the signal proportional to the aluminum concentration along the scanning path. The substrate is on the right side. Light regions correspond to high concentrations of tin and antimony

longitudinal (γ_l) and transverse (γ_t) gauge factors are distinguished. In this work, measurement were carried out in the tension (γ_l and γ_t) or the compression (γ_t) mode. For all the films, the value of γ_t at compression was equal by modulus to its value at tension and had an opposite sign. The absolute value of the longitudinal gauge factor was about 30% larger than that of the transverse one for all the films.

For films on steel and alumina substrates, tensile strains led to the reduction of the resistance, while compressive strains, on the contrary, to its increase, so that the gauge factor of the films was negative. After unloading, the resistance of the specimens studied returned to its initial value. The absence of the irreversible changes of the film resistance testifies that the film deformation did not go beyond the limits of the film elasticity range. The character of the film resistance behavior was not changed after the following deformation cycles as well.

Films on crystalline-glass and nitride-alumina ceramic substrates were characterized by positive gauge factors, i.e. tensile strains led to the resistance growth, and compressive ones to its reduction. Loading the films on crystalline-glass substrates in tension, the range of elasticity was confined to deformations of about 1.5×10^{-4}. The lowest loadings resulted in irreversible changes of resistance for the films on aluminum nitride substrates; therefore, the gauge factor of those films was not calculated. The Table exhibits the values of the resistance, the TCR, and the gauge factors for films on various substrates.

Among the factors by which the substrate influences the film properties, in addition to the mismatch between their TECs, one points out the chemical interaction between a substrate material and the film, and the roughness of the substrate surface [2, 8, 9]. The X-ray phase analysis showed that the chemical interaction between films and substrates used in the work was absent. The difference between the substrate surface roughness values was insignificant (see the Table). We had not found any substantial differences between the resistances and the TCRs of the $Sn_{0.9}Sb_{0.1}O_2$-based films that had been printed onto the surfaces characterized by various roughness degrees [9]; hence, this factor can be neglected. A number of authors [2, 6] considered that the influence of alumina substrates on the TFR properties can be caused by the penetration of Al_2O_3 molecules from the substrate into the glass matrix. Experimental results evidence for the absence of such a process in the $Sn_{0.9}Sb_{0.1}O_2$-based TFRs. In Fig. 1, the image of a transverse section of a TFR on

Properties of the substrates and the thick resistive films

Property	Substrate material (the content of the main component in wt.%)				
	Enameled steel	Ceramics (99.8% Al_2O_3)	Ceramics (94.4% Al_2O_3)	Crystalline glass	Ceramics (98% AlN)
	Substrates				
TEC $\alpha_s \cdot 10^7$, K^{-1}	110	80	60	52	46
Elastic modulus, E_s, GPa	200	395	302	130	340
Roughness, R_a, μm	0.65	0.6	0.75	0.65	0.7
	Thick resistive films				
γ_l	−13.8	−13.2	−12.8	+45.1	—
γ_t	−10.2	−9.8	−9.6	+33.7	—
R, k$\Omega/\Box$	149.8	161.5	259.7	290.5	316.5
TCR 10^3, K^{-1}	−0.75	−0.98	−1.25	−1.42	−1.51
σ_f, MPa	−511.1	−212.3	−12.2	67.6	122.7

the alumina substrate, obtained in the reflected electron mode, is shown, as well as the signal proportional to the aluminum concentration along the scanning path.

The influence of the mismatch between the TECs of the film and the substrate on the TCR of the films based on ruthenium compounds has been studied rather completely [2, 8]. Different values of the TCR for films on different substrates are explained by the fact that the substrate, which has a TEC distinct from the TEC of the film, tenses or compresses the latter if the temperature of the substrate changes, which makes an additional contribution to the resistance variation. In work [9], we demonstrated that, in the case of $Sn_{0.9}Sb_{0.1}O_2$-based films, the influence of the substrate on the film properties is also assosiated with the emergence of residual thermal stresses at the film—substrate interface. The strength of film–substrate adhesion exceeded 50 kg/cm^2 for all combinations considered in the work, which evidenced for strong bonding. The mismatch between the film and the substrate TEC brings about stresses in the TFR if the latter, in the course of heat treatment, is cooled below the glass solidification temperature. As a result, the film is in a two-axis strained state at room temperature with the following stresses along the axes [10]:

$$\sigma_{\rm f} = \frac{(\alpha_{\rm s} - \alpha_{\rm f})\Delta T}{(1-\nu_{\rm f})(1/E_{\rm f} - 1/k \cdot E_{\rm s})}, \qquad (1)$$

where α_s and α_f are the TECs of the substrate and the film, respectively; E_s and E_f are the moduli of elasticity of the substrate and the film, respectively; ν_f is the Poisson's ratio of the film; k is the ratio of the thicknesses of the substrate and the film; and ΔT is the temperature interval. The modulus of elasticity and the TEC of the film were calculated following the rule of mixtures for matrix structures [10]. The results of calculations of the residual thermal stress magnitude by formula (1) are given in the Table; here, the negative values correspond to compressive stresses.

Stresses induced by the mismatch between the TECs of the film and the substrate were estimated experimentally making use of the polarization-modulation method. The operation of the experimental installation is based on the registration of phase variations of the orthogonal components of a linearly polarized light wave; those variations arise when light is reflected from a specimen. The refractive indices for light waves propagating along the direction of distortion (stress) and perpendicular to it are different, and their difference Δn is proportional to the amplitude of elastic strains. The phase change of the radiation reflected from the specimen is caused by the anisotropy of the refractive index and leads to the elliptic polarization of light. Experimentally measured is the intensity of the circular component of elliptically polarized light. Since not only stresses in the layers contribute to the intensity of reflected light but surface defects as well, additional measurements were carried out in order to exclude the influence of the latter. In Fig. 2, the distributions of the refractive index anisotropy across the interfaces between the film and various substrates, taking into account the surface-induced contribution to the intensity of the light wave reflected from the specimen, are shown. The curves Δn, which correspond to the stress distributions, are in a qualitative agreement with the physical picture of the stress difference across the film—substrate interface [7]. From the data presented in Fig. 2, it follows that the sign of residual stresses and the relation between their magnitudes for films on various substrates agree with the results of calculations quoted in the Table.

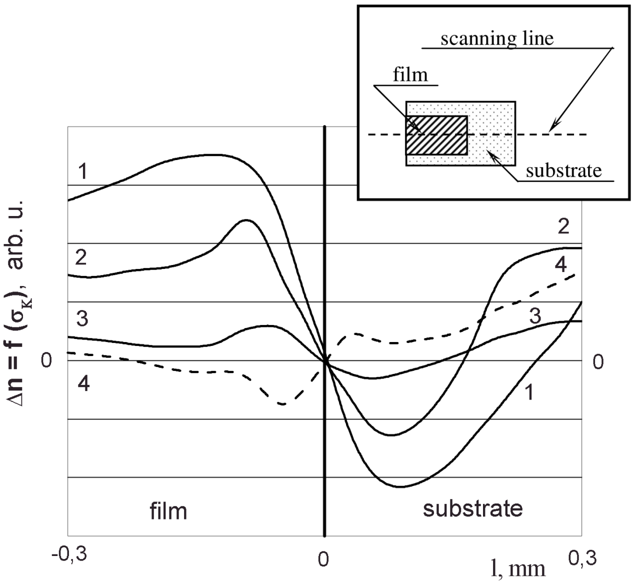
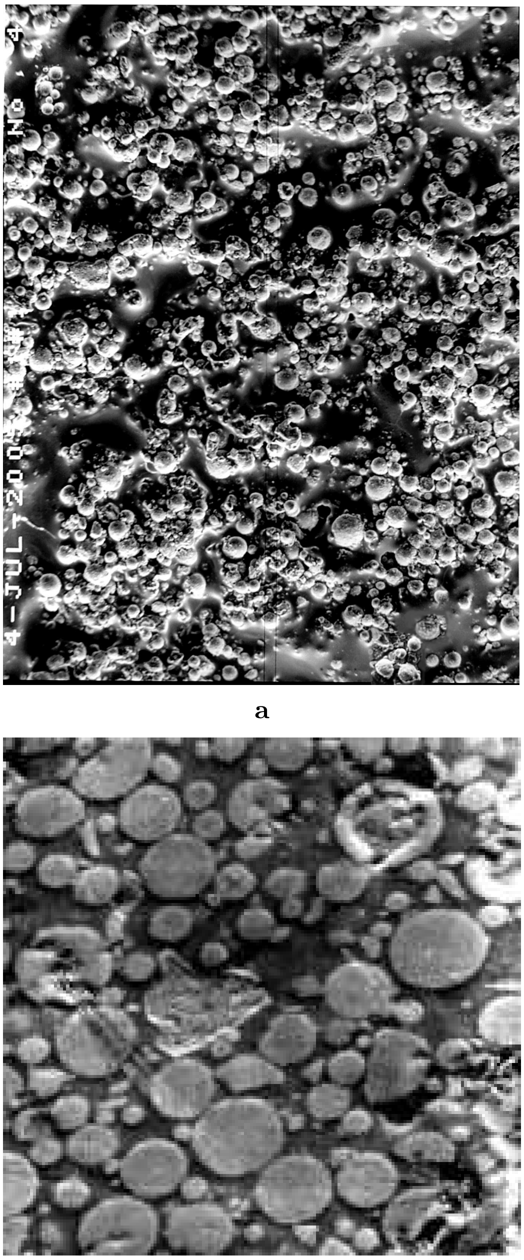


Fig. 2. Distributions of the refractive index anisotropy Δn across the interface between the film and various substrates: *1* — enameled steel, *2* — alumina ceramics (99.8% of Al_2O_3), *3* — alumina ceramics (94.4% of Al_2O_3), and *4* — crystalline glass

Thus, films on substrates fabricated from crystalline glass or AlN-based ceramics ($\alpha_s < \alpha_f$) remain tensed after heat treatment. The reduction of the substrate TEC and, hence, the increase of the residual tensile stresses lead to the growth of the resistance and the TCR by absolute value (see the Table). The gauge factor of



a

b

Fig. 3. Photos of the surface (magnification 250, *a*) and the section (magnification 700, *b*) of a film on the substrate that contains 94.4 % Al_2O_3. Light regions correspond to conductive particles, dark ones to glass

films on the crystalline-glass substrate is positive. Films on substrates fabricated from steel and alumina ceramics ($\alpha_s > \alpha_f$) are compressed. The gauge factor of those films is negative. The increase of the residual compressive stresses leads to the increase of the absolute value of the gauge factor and the reduction of the absolute value of the TCR of the TFR and its resistance.

The substantial influence of residual stresses on the electrical resistance and the TCR is caused by the piezoresistive effect [8] and results from high and positive values of the gauge factor of films under consideration. It is important to note that the residual compressive stresses can lead to negative γ values if the measurements are carried on by the three-point bending method. The longitudinal gauge factor of the films on enameled steel substrates, which was measured by us earlier using the method of uniaxial tension [9], was positive and amounted to 60.1. The comparison between the TCRs of films on different substrates results in approximately the same γ values. The difference between the TCRs of films on two different substrates, which is caused by the piezoresistive effect, is equal to [8]

$$\mathrm{TCR}_1 - \mathrm{TCR}_2 = \frac{2(\alpha_{s1} - \alpha_{s2})(\gamma - 1 - \nu_f)}{1 - \nu_f}, \qquad (2)$$

where subscripts 1 and 2 correspond to different substrates. In work [9], putting the gauge factor in Eq. (2) equal to 60, we obtained a satisfactory agreement between the measured and the calculated TCR value for $Sn_{0.9}Sb_{0.1}O_2$-based films.

Consider the structure of thick $Sn_{0.9}Sb_{0.1}O_2$-based TFRs. In Fig. 3, the photos of the surface and the section of a film on a substrate that contains 94.4 % of Al_2O_3 are exhibited (the variation of the substrate material does not change the film microstructure type, so that the photos of the films on different substrates used in the work do not differ visually from those presented in this figure). The figure demonstrates that spherical or nearly spherical $Sn_{0.9}Sb_{0.1}O_2$ particles are separated from one another by the interlayers of a glass phase from several Angströms to several microns in width and form branched chains in the film bulk. Charge carriers transportation through the potential barriers created by the dielectric interlayers between neighbor particles occurs by means of the activation tunneling [4, 5]. For the films where the tunnel mechanism of conductivity prevails, the piezoresistive effect is associated with the deformation-induced change of conditions, i.e. the parameters of the potential barrier, for the charge carrier tunneling [2, 11, 12]. In this case, the gauge factor correlates with the tunnel transmittance D of the barrier between particles,

$$\gamma \approx D = 4\pi(2m^*\varphi)^{1/2}\Delta/h, \qquad (3)$$

which has been confirmed experimentally for discontinuous thin films [11, 12]. In formula (3), m^* is the effective electron mass, φ the average height of the potential barrier, Δ the width of the barrier between conductive islands, and h the Planck's constant. The estimation by formula (3) shows that the value of γ for $Sn_{0.9}Sb_{0.1}O_2$-based TFRs cannot exceed 15—20, which is substantially smaller than the values obtained by the uniaxial tension method or by three-point bending method for the films on crystalline-glass substrates (see the Table).

The authors of works [3, 13] consider the high strain sensitivity of TFRs to be related with the critical behavior of conductivity, which is inherent to inhomogeneous material in the vicinity of the percolation threshold, i.e. at those concentrations of the conductive phase, when an infinite conductive cluster is formed and the insulator—conductor transition occurs. Near the percolation threshold, the dependence of the resistance of percolation materials on the conductive phase concentration is described by the expression [13]

$$R \sim (x - x_c)^{-t}, \quad (4)$$

where x is the concentration of the conductive phase, x_c the threshold concentration, and $t \approx 2$ is the critical index of conductivity. Researches that were carried out by us earlier [4] showed that the electrical resistance of studied films obeyed dependence (4) in a wide range of concentrations with the critical index value $t = 2.8$. The enlargement of the critical index value and the extension of the concentration interval, where dependence (4) holds true, are associated with the fact that percolation is put into effect mainly by the tunneling through interparticle interlayers [13]. Another feature of the films under investigation is a high value of the percolation threshold $x_c = 0.23$, which evidences for the matrix structure of the films. It is related with the fact that, unlike the films on the basis of ruthenium compounds which have the chain structure and a low percolation threshold, the $Sn_{0.9}Sb_{0.1}O_2$-based films were fabricated using the powder of the conductive phase with a rather big diameter of particles (of about 1 μm), i.e. close to the diameter of the glass powder particles.

The tunnel-percolation character of film conductivity means that the external influence on the electrophysical properties of TFRs is not reduced to the variation of the tunnel barrier parameters only, but also includes the processes of formation (destruction) of conductive links between particles, i.e. the processes that bring about the modification of the conductive cluster configuration. In this connection, it is of interest to study the corresponding current-voltage dependences. According to the model of a dynamic random resistor network [14], if the electric field strength grows, the processes of formation of new conductive links through interlayers that were earlier inaccessible for tunneling make the conductivity higher. The field strength threshold, at which the deviation from the Ohmic behavior starts, and the rate of electroconductivity growth depend on the effective structural characteristics of the composite. The study of the field dependences of the resistance of the films on various substrates showed that the film deformation that is caused by the mismatch between the TECs of the film and the substrate affects the CVC shape: the reduction of the substrate TEC leads to the increase of the field strength threshold and to the more intensive growth of the film conductivity in the nonlinear region. Figure 4 depicts the dependences of the logarithm of the film resistance on the electric field strength for the films on steel and crystalline-glass substrates. For the films on alumina substrates, the corresponding dependences are similar. The presented data serve thus as a confirmation of the fact that the deformation of $Sn_{0.9}Sb_{0.1}O_2$-based films is accompanied by the reconstruction of current paths and modifies the effective structural characteristics. Therefore, proceeding from the results of measurements of the strain sensitivity, making allowance for the estimations by formula (3), and taking the structural features of the films concerned into account, one can draw the conclusions that the contribution of such processes to the deformation-induced variation of resistance is comparable with the contribution from the variation of the interlayer

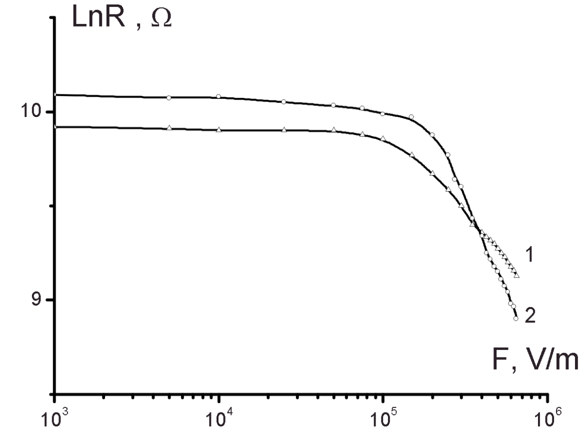


Fig. 4. Dependence of the logarithm of the film resistance on the electric field strength for TFRs on steel (*1*) and crystalline-glass (*2*) substrates

thickness, and that both the method of measurements and the sign of residual stresses govern the progress of those processes.

The influence of the method of measurements is connected with the fact that, in contrast to uniaxial tension, measurements that are carried on in the framework of the three-point bending method produce a rather complicated strain-stress state in the specimen from the very beginning. Reports about the researches concerning the influence of the nonuniformity of a strained state on the conductivity of strain-sensitive materials are practically absent. Among the information available, one may point out work [15], where the influence of bending on the resistance of threadlike silicon crystals with a positive gauge factor was studied. It is of interest that the specimen bending, i.e. such deformation at which the average strain value over the cross-section of a strain gage is equal to zero, gave rise to a reduction of the resistance. For $Sn_{0.9}Sb_{0.1}O_2$-based TFRs, the estimation of the influence of the nonuniform character of deformation on the processes of current path reconstruction becomes even more difficult owing to the availability, in the film bulk, of considerable stresses induced by the mismatch between the TECs of the conductive and insulating phases [16].

On the basis of the results obtained, the following conclusions can be made concerning the influence of residual stresses on the resistance change of the films under investigation if measurements are carried on by the three-point bending method. Negative values of γ, which mean the growth of the conductivity of the films at their tensing in the course of the three-point bending procedure, testify that, for films with residual compressive stresses, the reconstruction of the conductive cluster configuration gives rise to the increase of the effective conductive volume. The deformation-induced contribution of such processes to the variation of electroconductivity exceeds the similar contribution of the potential barrier parameter variation. During loading the films on crystalline-glass substrates which have already been tensed owing to their heat treatment in tension, the processes of link destruction prevail, and the reconstruction of the conductive cluster configuration results in the reduction of the effective conductive volume. The latter phenomenon, together with the contribution made by the increase of the width of tunnel interlayers, leads to a considerable growth of the electrical resistance. The gauge factor of the films on crystalline-glass substrates is positive and, by absolute value, several times larger than γ for the films on steel and alumina substrates. At the same time, the growth of the residual tensile stresses leads to a sharp reduction of the region, where films demonstrate elastic behavior, so that, in the films on nitride-alumina ceramic substrates, the resistance changes irreversibly at tension, which evidences for the emergence of microcracks.

4. Conclusions

The influence of the substrate on the electrophysical properties of $Sn_{0.9}Sb_{0.1}O_2$-based films is caused by the emergence of thermal stresses at the film—substrate interface. A high strain sensitivity, which this influence evidences for, is related to a change of the parameters of tunnel barriers between conductive particles and the reconstruction of current paths, with both phenomena occurring simultaneously in the course of deformation. The important role of the processes of current path reconstruction reveals itself in the dependence of the gauge factor on the method of measurements and the sign of residual stresses emerged owing to the mismatch between the TECs of the film and the substrate.

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ВПЛИВ ЗАЛИШКОВИХ ТЕРМІЧНИХ НАПРУЖЕНЬ НА ТЕНЗОЧУТЛИВІСТЬ ТОВСТИХ ПЛІВОК НА ОСНОВІ $Sn_{0,9}Sb_{0,1}O_2$

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Р е з ю м е

Досліджено вплив залишкових термічних напружень, що виникають як наслідок неузгодження коефіцієнтів термічного розширення плівки й підкладки, на тензочутливість резистивних товстих плівок (РТП) на основі $Sn_{0,9}Sb_{0,1}O_2$. Встановлено, що при вимірюванні методом триточкового згинання значення коефіцієнта тензочутливості плівок залежить від знака залишкових напружень на межі плівка—підкладка. Спостережений ефект можна пояснити суттєвим впливом процесів перебудови шляхів протікання заряду на зміну величини електроопору при деформуванні.