Физика и техника полупроводников, 2016, том 50, вып. 5

Piezoresistive and posistor effects in polymer-semiconductor and polymer-ferropiezoceramic composites

© Havar A. Mamedov[+], Levent Parali[*], Mirza A. Kurbanov[•], Azad A. Bayramov[•],
Farida N. Tatardar[•], Israfil Sabikoğlu[‡]

[*] Celal Bayar University, Department of Electronics and Automation,
45400 Turgutlu, Manisa, Turkey
[+] Azerbaijan Technical University,
Baku, Azerbaijan
[•] Academy of Science of Azerbaijan, Institute of Physics,
Baku, Azerbaijan
[‡] Celal Bayar University, Faculty of Arts & Sciences, Departments of Physics,
45140 Manisa, Turkey
E-mail: levent.parali@cbu.edu.tr

(Получена 4 февраля 2015 г. Принята к печати 10 сентября 2015 г.)

In this study, piezoresistive and posistor effects in polymer-semiconductor and polymer-ferropiezoceramic composites have been investigated. The results show that composites based on crystallizable polymers, such as PVDF, HDPE, and PP dispersed by semiconductors and ferropiezoelectric fillers have piezoresistive and posistor properties, respectively. At low pressure, charge carriers tunneling through the located thin polymer among filler particles into the barrier define the conductivity of the composite. When pressure value is increased from 0 to 1 MPa, the thickness of the interlayer decreases and tunnel conductivity descends exponentially depending on barrier height. The piezoresistor sensitivity of a composite based on PVDF-70% vol + Si-30% vol is higher than a composite based on HDPE-70% vol + Ge-30% vol. Furthermore, the posistor properties of polymer composites dispersed by ferropiezoceramic are determined as the maximum resistance that varies significantly with temperature. Posistor effect in composites based on polymer + ferropiezoceramic is associated with the height of the barrier layer, which changes according to properties of filler, polymer, and dielectric permittivity of two-phase composites. The highest specific resistance related to HDPE-70% vol + $BaTiO_3$-30% vol composite was observed at ~ 403 K.

1. Introduction

Recently, the number of researchers investigating smart materials based on polymer-semiconductor, polymer-ferropiezoceramic and, especially, polymer sensor and publishing their results has improved dramatically [1–4]. The polymer-semiconductor and polymer-ferropiezoelectricy heterogeneous systems such as electrets, piezo, pyroelectrics, varistors, piezoresistors and posistors are areas for the creation of active dielectrics [5–8]. Polymer-semiconductor and polymer-ferropiezoelectric composites have piezoresistive a posistor effects, respectively, and they are widely applied in electronics and radio engineering devices such as current-voltage stabilizers, protection circuits, sensors, heaters, etc.

Piezoresistive composites are extensively used to detect strains caused by structural vibrations in macro-scale structures. The piezoresistive effect is described as the change of composite electrical resistance owing to external stress or composite deformation. As a sensor, this effect is commonly measured utilizing Wheatson bridge circuits. Several variations of Wheatson bridge are used under different circumstances. One of the configurations is shown in Fig. 1, *a* in which only two piezoresistor are implemented on the circuit. When sensor resistance is changed with piezoresistive effects, it causes changes in the voltage on the divider [9].

A posistor is actually a device called a Positive Coefficent Thermistor (PCT), it naturally exhibits very highly sensitivity over a narrow temperature band. Therefore, abrupt resistance growth of the $BaTiO_3$ — semiconductor composites in a narrow temperature range can be used for creation of a lot of sensor of high sensitivity [10]. When a given temperature (nominal response temperature) is exceeded, electrical circuit can be switched off through a relay, since the PCT have an extremely high ohmic value in the region of its response temperature. Used in many inrush current control circuits, a PCT is a resistor that starts with a relatively low resistance value at room temperature. When heated by a current flowing through it, its value quickly rises to a very high resistance. Generally, the posistor is an integrated solution that works as both current limit resistor and overcurrent fuse (Fig. 1, *b*) [11,12].

As a summary, the electrical resistance of a posistor composite alters according to temperature variations while the electrical resistance of a piezoresistive composite changes in accordance with applied stress and strain deformation [4]. The formation of a potential barrier on the interphase boundary in the above mentioned composite systems exhibits a piezoresistive or posistor effect [7]. The parameters of potential barriers formed on the interphase boundary are quite dependent on the structure and electrophysical properties of the components. Therefore, it is possible to produce both piezoresistive and posistor composites,

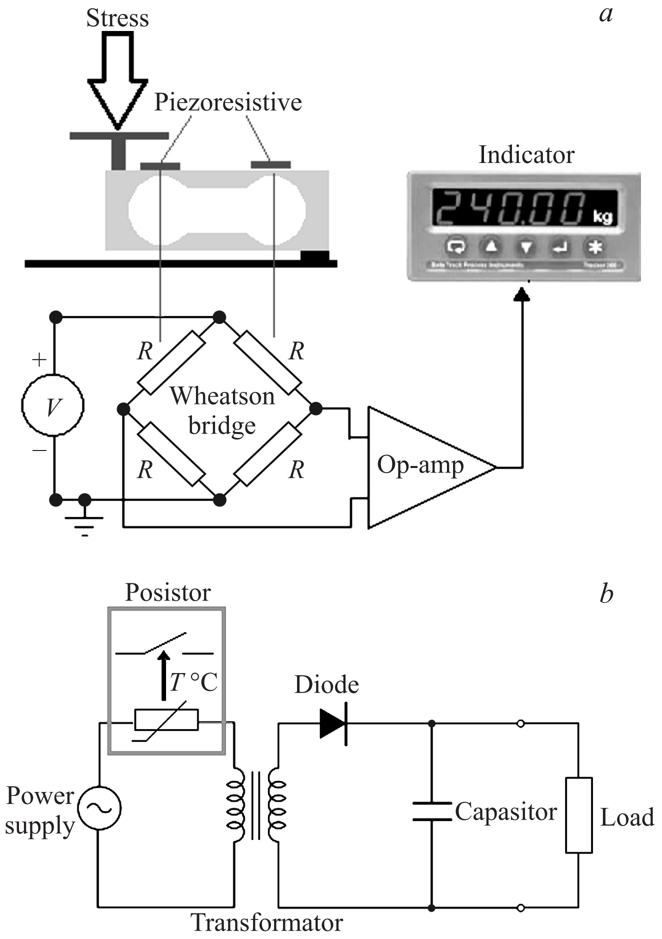

Figure 1. *a* — the stress measurement system based on piezoresistive as stress sensor. *b* — the overvoltage protection circuit with posistor.

which have various properties and structures using polymer matrixes, semiconductors, and ferropiezoelectric fillers.

The more effective piezoresistive and posistor composites like organic and inorganic dielectrics and semiconductors can be obtained through the synthesis of polymers with new chemical structures adding impurity semiconductive or ferropiezoelectric fillers into the polymer matrix. As polymer matrix, high density polyethylene (HDPE), polypropylene (PP), and polyvinylidene fluoride (PVDF) have some properties such as good workability, high plasticity, mechanical strengh, and low conductivity. Although HDPE and PP nonpolar polymers have almost identity electric characteristics, they have physicomechanical properties different from each other. PVDF polymer has high permittivity, also its conductivity is higher than that of polyolephines. Therefore, these polymers have been used to define the electrical and physicochemical characteristics of both the polymer-semiconductor and polymer-ferropiezoelectric composites [5,6,8]. As a consequence, excellent active composites with unique electrical and mechanical combinations can be created.

In this study, it is presented piezoresistive and posistor effects on polymer-semiconductor and polymer-ferropiezoceramic composites.

2. Experimental

Polymeric composites are known to be able to increase functionality by adding varying electrical properties to their mechanical response, which is typically achieved by suitable fillers [13–15]. Generally, the polymeric composites occur in at least two components as polymer and filler (dispersing agent) and their properties are associated with degree of crystallinity, structure and filler type, and content and orientation, which heavily depend on the specific processing conditions. Thus, the optimization protocols are fundamental for adaptation composites response [5,6,8]. The forming process of polymer composite includes three stages:

– choosing and preparation of suitable polymers and fillers.

– obtaining of homogeneous mixture.

– hot pressing of mixed composite (polymer + filler) under specific temperature and pressure.

The choice of composite components and the preparation of active materials are defined according to complex material properties such as high flexibility, mechanical and electrical strength, low electro-conductivity, compatibility of elements with various configurations, and high dielectric penetrability. In addition, it is necessary to consider the hermetization process, internal tension, and structural relaxation of the polymer matrix. In the study of polymers and their applications, polymer glass transition temperature is very important. The glass transition temperature should be high to provide stabile relaxing properties. These relaxing properties define working temperature range, stability, and composite fluidity. In this study, the thermo-plastic polyolefin polymers and fluoropolymer were chosen because they have excellent thermal, electrical and mechanical properties [16].

High-density polyethylene (HDPE), polypropylene (PP), and polyvinylidene fluoride (PVDF) were used as polymer matrix, Si and Ge as simple semiconductors, and $BaTiO_3$, PZT-5A, PZT-5H as ferropiezoceramics. Piezoresistive and posistor composites were obtained by the hot pressing method that involves high temperature and pressure simultaneously to implement the mixture of polymer-filler. Temperature-time and pressure regimes for composite formation are mainly dependent on the melting temperature of indicated polymers in composites. The melting temperatures of HDPE, PP and PVDF are 443, 475 and 473 K, respectively. Samples pressing in experimental works were carried out at 15 MPa. [5,6,8].

3. Results and discussions

Recently years, many researches have studied piezoresistive and posistor effects on various composite [17–24].

Especially, Knite et al. [17] have found that the experimental results for tensile strain are in good agreement with theoretical equations derived from the change of the particle separation on polyisoprene — carbon black composites under applied stress. In 2007, they examined the piezoresistivity of the polyisoprene-multiwall carbon nanotube composite for sensing strain [18]. However, the carbon black or metal powders have some significant disadvantages. The properties of the carbon black predominantly depend on its synthesis method, preparation, and treatment conditions. All these factors adversely affect to produce stable piezoresistive and posistor composites. Additionally, these conditions complicate to define the effects of both carbon black and metal powders into composite [25]. Therefore, the polycrystalline semiconductors (Si, Ge) as semiconductors filler have been chosen due to fact that they have widely varied electrical characteristics such as conductivity, carrier density, and mobility [25].

The measurement method of piezoresistive effect in a composite can be described as the change of electric resistance values in the sample under the action of mechanical stress. Firstly, the change in voltage between 1 and 100 was applied to inserted sample into plugs of press, and then variable current values of piezoresistor composite were measured under pressure conditions between 0 and 10 MPa. The coefficient of pressure sensibility was defined by the following equation:

$$K = \frac{\lg(\rho_0/\rho)}{P - P_0}, \tag{1}$$

where ρ_0 and ρ are specific resistances of sample at P_0 and P pressures, respectively. The error of pressure measurement is ±2% while the error of a specific resistance measurement is ±5%.

The resistance changes of HDPE + Si composite as 1st curve and PVDF + Si composite as 2nd curve, which included 30 vol% content of filler under the 1 V are shown in Fig. 2. It can be seen that the resistance changes of these composites nonlinearly decrease while the pressure values increase from 0 to 4 MPa. The piezoresistor sensitivity of the composite based on PVDF is higher than the composite based on HDPE. Although the resistance values of these composites change quickly in the range of 0–2 MPa, they alter slowly in the range of 2–4 MPa. The resistance changes of HDPE + Ge composite as 1st curve, PVDF + Ge composite as 2nd curve, HDPE + Si composite as 3rd curve, and PVDF + Si composite as 4th curve in the range of 0–4 MPa according to the volumes of filler are shown in Fig. 3. The resistance values of these composites increase quickly until 30 vol% filler, after which they decrease slowly.

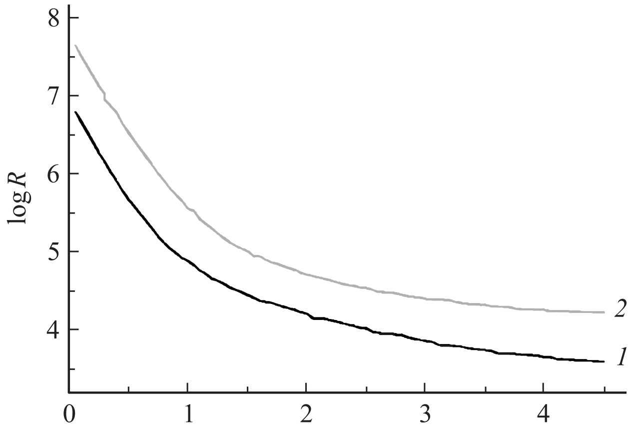

Figure 2. The resistance changes of HDPE + Si (1st curve) and PVDF + Si (2nd curve) composites on pressure. Φ = 30 vol%.

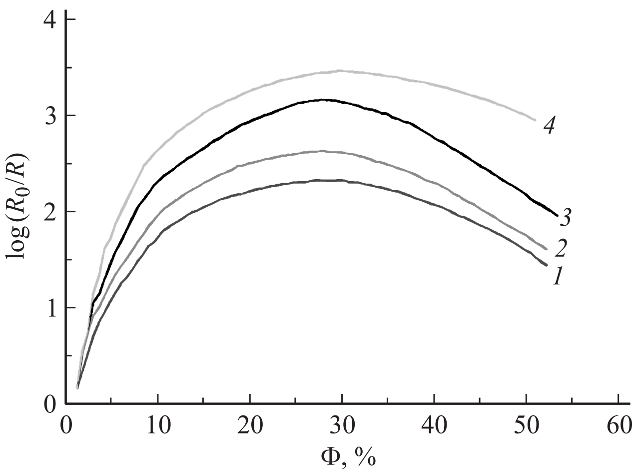

Figure 3. The resistance changes of HDPE + Ge (1st cure), PVDF + Ge (2nd cure), HDPE + Si (3rd cure), PVDF + Si (4th cure) composites according to contents of filler (Si, Ge).

It can be said that at low pressure, the conductivity of the composite is defined by charge carriers tunneling through located thin polymer among filler particles into the barrier. When pressure value is increased from 0 to 1 MPa, the thickness of interlayers decreases and tunnel conductivity descends exponentially depending on barrier width. Therefore, resistance of the composite is strongly dependent on pressure. The deformation of the composite increases at higher pressure due to the presence of more pressed particles, and the composite conductivity is generally expressed by contact resistance among particles. Although the contact resistance of the composite decreases in the pressure ranges 0–1 MPa, the reduction of composite resistance changes slowly at pressures over 1 MPa.

All investigations into these composites show that the sensitivities of composites decrease while the pressure value increases. The sensitivity coefficient of HDPE + 10 vol% Si and HDPE + 30 vol% Si samples are shown in Fig. 4, and the sensitivity coefficient was determined by the following equation:

$$B = \frac{\lg(R_1/R_2)}{P_2 - P_1}, \tag{2}$$

where R_1 and R_2 are resistances of composite at P_1 and P_2 pressure, respectively.

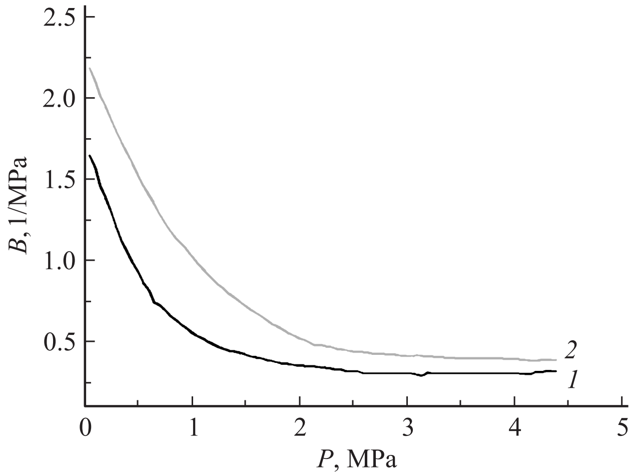

Figure 4. Dependence of sensitivity coefficient of HDPE + Si on pressure: *1* — $\Phi = 10\,\text{vol\%}$, *2* — $\Phi = 30\,\text{vol\%}$.

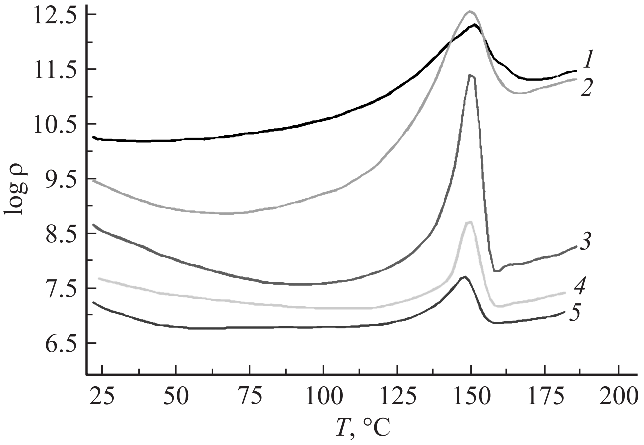

Figure 5. Temperature dependences of specific resistance of HDPE + BaTiO$_3$: *1* — $\Phi = 10\,\text{vol\%}$, *2* — $\Phi = 20\,\text{vol\%}$, *3* — $\Phi = 30\,\text{vol\%}$, *4* — $\Phi = 40\,\text{vol\%}$, *5* — $\Phi = 50\,\text{vol\%}$.

The posistor properties of polymer composites dispersed by ferropiezoceramic are determined as the resistance varies significantly with temperature. Most posistor composites are made of a doped polycrystalline ceramic containing barium titanate (BaTiO$_3$) and other compounds [26]. The specific resistance changes of the HDPE + BaTiO$_3$ composites, which have various filler contents according to temperature are indicated in Fig. 5. It can be seen that there is sharp growth in composite resistance with regard to filling degree in certain ranges of temperature. The maximum value of specific resistance related to HDPE + vol.30% BaTiO$_3$ composite was observed at ~ 403 K. The specific resistance (ρ_0) at room temperature, sensitivity ($\lg\rho/\rho_0$) and the maximum temperatures of various composites are shown in Table. PZT-5H and PZT-5A composites have different Curie's points. However, all of them have sharp resistance growth at melting temperatures of the crystal phase depending on the selected polyolefin.

In the posistor process, polymer composites are filled with semiconductors or ferropiezoceramic. Assimilating composite system can be regarded as a semi-conductive ceramic in which semi-conductive crystalline grains are distributed in the amorphous glassy phase of the same material. Crystalline grains of ferropiezoceramic, semiconductor and glassy phase have various conductivities, which differ by several orders of magnitude. The polymer + semiconductive filler have different conductivity and dielectric permittivity. As a result of this process, a barrier layer of volume charge is formed on the surface of crystalline grains. The electronic potential energy (φ) of the composite is determined by the following Poisson equation:

$$\varphi = \frac{e^2 N_s}{2\varepsilon_0\varepsilon_k} d, \tag{3}$$

where e is the electron charge density, N_s is the deep depletion region on the boundary, d is the width of the depletion layer, ε_0 is the permittivity of the vacuum, and ε_k is the dielectric constant. The conductivity of composite that is designated by φ and the height of potential barrier is proportional to a width of depletion layer — d, inversely proportional to composite dielectric constant — $\varepsilon_0\varepsilon_k$. Dependence of the specific resistance on the barrier height is exponential due to φ/kT [27]. The growth of barrier height (specific resistance) at the temperature over Curie's point decreases dielectric permittivity according to the Curie–Weiss law [7]. This model of barrier layer is used to explain not only anomaly of characteristic with positive temperature coefficient but also the dependence of specific resistance of semiconductive ceramic under applied voltage. If a U voltage performs among the barrier layer, the height of the barrier layer decreases, and it also leads to decreasing resistance. The growth of resistance under voltage distinctive appears at a temperature over Curie's point. The polymer composite filled with semiconductors or ferropiezoceramic is a double phase system, so component resistance differs strongly. The polymer-semiconductor composite occurs after mixing polymer matrix with low conductivity and semiconductive particles with high conductivity. The conductivity of semi-conductive particles is higher than that of the polymer matrix. The height of the barrier layer formed on the filler particles boundary depends on the dielectric permittivity of the material.

The anomalously sharp increase of composite resistance is not explained by ferroelectric phase transition inside filler particles. This is because the maximum resistance variation of the composite at maximum temperature depends only on the type of polymer matrix. In addition, the growth of composite resistance is observed not only in ferroelectric fillers but also in semiconductor fillers such as silicon and germanium. It should be noted that the composite based on the crystallizing polymer that is filled with semiconductors or ferroceramics has as an anomaly a temperature close to the temperature of the maximum specific resistance. For instance, temperature variations of dielectric permittivity of HDPE + PZT-5H composite with various fillers are shown in Fig. 6. Increasing filler content leads to the growth in dielectric permittivity of the

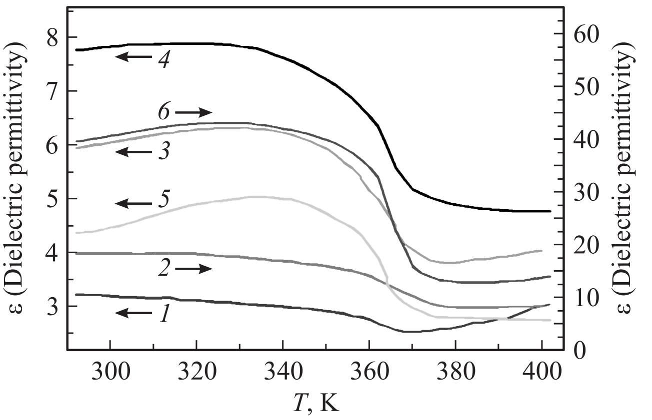

Figure 6. Temperature dependences of dielectric permittivity of HDPE + PZT-5H: *1* — $\Phi = 10$ vol%, *2* — $\Phi = 20$ vol%, *3* — $\Phi = 30$ vol%, *4* — $\Phi = 40$ vol%, *5* — $\Phi = 50$ vol%, *6* — $\Phi = 60$ vol%.

composite. After that, initial high dielectric permittivity values of the composite sharply decrease in the range from 373 to 403 K. The reduction of dielectric permittivity is observed at around 403 K for HDPE + PZT-5H, 433 K for PP + PZT-5H, respectively (Fig. 6) (Table). This indicates that the reduction of dielectric permittivity for composites based on both HDPE and PP does not connect with initial dielectric permittivity value and Curie's point of composite. In addition, this reduction of dielectric permittivity is also observed in composites with silicon fillers that are non-ferroelectric. The reduction of dielectric permittivity of composite may be associated with volume increases during the crystalline phase melting of polymer.

The dielectric permittivity of a composite material is determined by the Maxwell–Wagner theory:

$$\varepsilon_k = \frac{\varepsilon_1\big(\varepsilon_2 + 2\varepsilon_1 - 2\varphi(\varepsilon_1 - \varepsilon_2)\big)}{2\varepsilon_1 + \varepsilon_2 + \varphi(\varepsilon_1 - \varepsilon_2)}, \qquad (4)$$

where φ is volume fraction of contents, and ε_1 and ε_2 are dielectric permittivity of polymer matrix and filler, respectively. When the dielectric permittivity of a composite system is calculated using the Maxwell–Wagner theory, a significant discrepancy occurs between predicted and experimental values for dielectric permittivity. This discrepancy is due to the fraction of filler content within the two-phase composite [28].

This system consists of a continuous medium with dielectric permittivity ε_1 and statistically distributed spherical particles with dielectric permittivity ε_2. However, composites based on the crystallizable polymer with filler are concentrated in the inter-crystalline phase. Therefore, an experimental value of dielectric permittivity of composite is higher than when calculated using the Maxwell–Wagner equation. During the crystal phase melting of polymer, there is first a sharp growth in polymer values, then filler particles disperse under Brownian motion in all melting values. In conclusion, a dielectric permittivity of composite sharply decreases and becomes approximately equal to one calculated using the Maxwell–Wagner equation.

Specific resistance (ρ_0) at room temperature, sensitivity ($\lg\rho/\rho_0$) and maximum temperatures for various composites

80 vol% Polymer + 20 vol% Filler	$\lg\rho_0$ ohmmeter	Sensitivity $\lg\rho/\rho_0$	T_m Curie Point, K	Structure
PP+Si	3.3	6.7	433	*n*-type
PP+Ge	3.9	6.6	–	≪
HDPE+Si	3.5	8.1	403	≪
HDPE+Ge	3.2	7.2	–	≪
PP+BaTiO$_3$	10.2	3.2	433	Tetragonal
HDPE+BaTiO$_3$	9.5	3.7	403	≪
HDPE+PZT-5H	11.0	4.4	403	≪
PP+PZT-5H	11.6	1.5	433	≪
HDPE+PZT-5A	12.0	3.1	403	Rhombohedral
HDPE+Si	3.8	8.7	403	*p*-type

4. Conclusions

Results obtained from investigation of the piezoresistive and posistor effects in polymer-semiconductor and polymer-ferropiezoceramic composites show that composites based on the crystallizable polymers, such as PVDF, HDPE and PP dispersed by semiconductors and ferropiezoelectric fillers have piezoresistive and posistor properties, respectively. The positive temperature coefficient values of these composites depend on the type of polymer and filler, filler level, filler particle sizes, applied voltage and pressure, and other factors. Posistor effect in these composites is identified with barrier layer on the filler particles boundary. The height of the barrier depends on properties of filler, polymer, and dielectric permittivity of the composite. During the crystal phase melting of polymer, the volume expansion sharply increases and leads to spasmodic decreasing of dielectric permittivity increasing the barrier layer height and the growth of composite resistance.

Acknowledgements: This work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan Grant No: EIF-BGM-2-BRFTF-1-2012/2013-07/01/1-M-06.

References

[1] S. Choi, Z. Jiang. Sensors Actuators A: Phys., **128**, 317 (2006).

[2] I.M. De Rosa, F. Sarasini. Polymer Testing **29**, 749 (2010).

[3] P. Peng, S. Sezen, R. Rajamani, G. Erdman. Sensors Actuators A: Phys. **158**, 10 (2010).

[4] R. Haj-Ali R, H. Zemer, R. El-Hajjar. J. Aboudi, Int. J. Solids and Struct., **51**, 491 (2014).

[5] J.M.E. Lines, A.M. Glass (Clarendo Press-Oxford, London, 1977).

[6] I.S. Rez, Y.M. Poplavko. Radio I S. Moscow (1989) [in Russian].

[7] M.A. Kurbanov, M.G. Shakhtakhtinsky. Institute of Physics Azerbaijan National Academy of Sciences. Int. Conf., Bakü, Azerbaijan, (2005).

[8] M.K. Kerimov, M.A. Kurbanov, A.A. Bayramov, A.I. Mamedov. Matrix Nanocomposites and Polymers with Analytical Methods/Book, 3. Book ed. by: John Cuppoletti (INTECH Open Access Publisher, 2011) p. 375.

[9] M. Kalantari, J. Dargahi, J. Kovecses, M. Mardasi, S. Nouri, IEEE/ASME Trans. on Mechatronics, **17**, 572 (2012).

[10] L.A. Bashkirov, N.Y. Shishkin, O.I. Kurbachev, O.A. Chebotar, I.M. Zharsky. Sensors and Actuators B. **55**, 65 (1999).

[11] Z.G. Zhou, Z.L. Tang, Z.T. Zhang, W. Wlodarski. Sensors Actuators B: Chem., **77**, 22 (2001).

[12] Murata Manufac. Co. Ltd., PTC Thermistor (POSISTOR) Application Manual (2014).

[13] B. Adhikari, S. Majumdar. Progr. Polymer Sci., **29**, 699 (2004).

[14] M. Knite, V. Teteris, A. Kiploka, I. Klemenoks. Adv. Eng. Mater., **6**, 742 (2004).

[15] J. Zavickis, M. Knite, K. Ozols, G. Malefan. Mater. Sci. Eng. C. **31**, 472 (2011).

[16] V.V. Vasilyev, M.Yu. Tarnopol'skii. Composition Materials. Handbook. (Mashinostroenie, Moscow, 1990).

[17] M. Knite, V. Teteris, A. Kiploka, J. Kaupuzs. Sensors Actuators A: Phys., **110** 142 (2004).

[18] M. Kinite, V. Tupureina, A. Fuith, J. Zavickis, V. Teteris. Mater. Sci. Eng. C, **27** 1125 (2007).

[19] N. Serra, T. Maeder, P. Ryser. Sensors Actuators A: Phys., **186**, 198 (2012).

[20] M. Hussain, Y.H. Choa, K. Niihara. Compos. A: Appl. Sci. Manuf. **32**, 1689 (2001).

[21] L.H. Wang, T.H. Ding, P. Wang. Compos. Sci. Technol., **68** 3448 (2008).

[22] L.H. Wang, F.F. Ma, Q.S. Shi, H.H. Liu, X.T. Wang. Sensors Actuators A: Phys., **165**, 207 (2011).

[23] L.H. Wang, Y.Y. Han. Compos. A: Appl. Sci. Manuf. **47**, 63 (2013).

[24] L. Chen, G.H. Chen, L. Lu. Adv. Funct. Mater. **17**, 898 (2007).

[25] M.K. Kerimov, M.A. Kurbanov, I.S. Sultanahmedova, I.A. Faradzhzade, F.N. Tatardar, H.S. Aliyev, F.F. Yahyaev, U.V. Yusifova. Semiconductors **44**, 904 (2010).

[26] A.M. Slipenyuk, M.D. Glinkchuk, V.V. Laguta, I.P. Bykov, A.G. Bilous, O.I. Yunov. Ferroelectrics **288**, 243 (2003).

[27] L. Chun Hung, L. Yuh Yih, T. Tseung. J. App. Phys. **74**, 3383 (1993).

[28] M.E. Hossain, S.Y. Liu. Acta Mech., **225**, 197 (2014).

Редактор К.В. Емцев