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Magnetoresistance in Ferromagnet/Wide Band Gap Polymer Structures

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Abstract

The appearance of spintronics of polymeric materials is an important step in the development of spintronics. In the scope of this trend, it seems important to consider the possibilities of the non-traditional polymer functional materials – the polymers with a wide band gap. The results of study of the conductivity change in magnetic field for CPP (current perpendicular to the plane) geometry are presented in the current work with respect to the heterostructures containing a layer of such polymer material. Reversible electronic conductivity switching, driven by an external magnetic field, exists in the asymmetric system of Ni/polydiphenylenephthalide (film)/non-ferromagnetic metal. It is possible to change the sign of magnetoresistive phenomena by changing the magnitude of the external influence and (or) the initial electronic state of the polymeric material. The value of the threshold magnetic field for the switching of conductivity depends on the initial magnetic state of the charge-injecting ferromagnetic electrode. The phenomenon of the electronic conductivity switching of wide band gap polymer film, driven by an external magnetic field, has the character of resonance tunnelling and takes place providing that there is coincidence of the energy level of permitted states in the charge-injecting electrode and the thin energy band of coherent charge transfer in the middle of the band gap of the polymer film. The electronic conductivity switching is closely connected with partial spin polarization of current that is injected from the ferromagnet to the polymer. Evidence of spin transport is obtained in the symmetric structure of the CPP type of spin valve with polymeric spin-transport layer thickness no less than 800 nm. Theoretical models of these phenomena are discussed and the conclusion is drawn that the use of polymers with a wide band gap is certainly promising as the functional materials of spintronics.

Keywords

Polymer Electronics, Spintronics, Magnetism, Magnetic Materials, Conductivity Switching

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1. Introduction

New approaches in spintronics have recently appeared, as can be seen in [1]. A new experimentally revealed effect is described, that is huge magnetoresistance. The work is based on theoretical premises [2]. The approach is that relaxation processes in the ferromagnet on the non-ferromagnetic/ferromagnetic border are taken into account for the first time. Thus, damped spin precession in the ferromagnetic material around the direction of the magnetic field leads to the change of magnetic flux through the interface. Electromotive force is induced as the result of the flux change according to Faraday's law, and this fact in turn has an influence on the electrostatic barrier potential in the non-ferromagnetic/ferromagnetic interface. This effect together with the Coulomb blockade in the MnAs nanoparticles enables us to observe a great change in the resistance of the structure – huge magnetoresistance at low

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temperatures (3 K). Inorganic semiconductors: MnAs, GaAs are used to reveal this huge magnetoresistance in [1].

Simultaneously, some fundamentally new phenomena are being studied in the organic semiconductors: an abnormally long mean free path for the spin orientation [3] and organic magnetoresistance (OMAR) [4–6]. OMAR is a fundamentally new type of magnetoresistance because the objects of study in this case are polymeric semiconducting materials, not containing inclusions of transition and d-elements. Just the inclusions of transition elements or elements with an initial magnetic order are traditional for magnetoresistance objects. OMAR reveals polymers according to the spin-orbital interactions in the molecule. Organic magnetoresistance can be decreased by increasing the percentage of the component with strong spin-orbital interaction [6].

Thus, two independent treatments have been registered in recent studies on spintronics: new methods of obtaining magnetoresistance in inorganic semiconducting structures, and work with polymer semiconducting materials that are revealing unusual magnetoresistive properties. Note that in both cases the research is talking about fundamentally new phenomena taking place in a constant magnetic field. The work in [1] (huge magnetoresistance) uses great magnetic fields (up to 10 kiloGauss) and low temperatures (3 K). As a rule, low magnetic fields (near 200 mT) and room temperature are needed for experiments on magnetoresistance with organic semiconductors [4–6]. Still, the magnetoresistive changes there are very small (~5 %).

The question arises, is it possible to combine the advantages of experiments [1] (huge value of magnetoresistance) and [6] (controlled variable effect, low magnetic fields, room temperature)? In order to obtain a structure possessing such qualities, it is necessary to find a material that is able to undergo abrupt resistance changes. Such materials include organic dielectrics. A semiconducting type of conductivity is typical for any dielectric material, because it surely has defect levels in the band gap. If the band gap is too wide, then the possible conductivity is determined only by the states inside the band gap. And if the quantity of the defect levels can abruptly increase (for example, with structure transition), then the conductive change will be very big. Thus, dielectric polymeric materials are capable of great changes of conductivity. This refers to those materials that can undergo the switching of conductivity under certain conditions [7]. From this point of view, it is reasonable to consider a polymer layer with a wide band gap placed on a ferromagnetic electrode (substrate) to obtain a managed large magnetoresistance, as described in [1,2], in low constant magnetic fields and at room temperature.

2. Research Significance

Polymers with a wide band gap possess a number of unique features, and these polymers have been studied for some time [8]. The most striking feature of the sufficiently thin layers of such polymers appears to be their ability to switch conductance to 6–8 orders with changes in the boundary conditions [7,8]. Besides, data are available for the conductivity switching of such polymeric layers on substrate (electrode) with a magnetic order when the magnetic phase transition of the substrate takes place [9]. All these data indicate good prospects for the use of such materials as the layers for heterostructures with the resistance controlled by the magnetic field. This work presents the results of study on managing the conductivity of heterostructures containing a layer of polymer with a wide band gap, with the aid of weak magnetic fields.

3. Samples and Measurement Procedure

Conductivity measurements for heterostructures were performed in Auto Scan Mode of the magnetic field, with automatic fixing of numerical values and simultaneous printing of the results on the computer monitor. The direction of current flow was normal to the layers of the heterostructure, while the direction of the external magnetic field was normal or parallel to the sample surface. All measurements were performed at room temperature and atmospheric pressure. Experiments were conducted on heterostructures of ferromagnet/polymer/non-ferromagnetic metal, non-ferromagnetic metal/polymer/non-ferromagnetic metal and ferromagnet/polymer/ferromagnet. As ferromagnetic substrates, either nickel polycrystalline plate of 1–2 mm thickness and area of 0.25 cm^2 (nickel purity more than 99.9%), or polycrystalline cobalt were used. Plates of single crystal nickel or nickel films, obtained by the vacuum deposition method on the glass or chromium sublayer, were used as substrates also. Copper or brass plates were used as non-ferromagnetic substrates. A polymer layer was deposited on the substrate by the method of centrifugation of the solution in cyclohexanone. Non-conjugated polymer polydiphenylenephthalide (poly 3.3'-phthalidiliden-4.4'biphenylene, PDP) was used as the polymer with a wide band gap. Solid homogeneous polymer films of 0.3–0.8 μm thickness were obtained after oven drying at a temperature of 423 K. The second non-ferromagnetic contact was performed as copper (brass) spring, copper film or silver paste. The value of the bias electric voltage was 1 V as a rule.

Multilayer film heterostructures of the

glass/chromium/nickel/PDP/nickel type were also studied. The film electrode thickness obtained by vacuum deposition was ~1 μm. The polymer layer thickness was up to 1.2 μm. The experimental setup is shown in Fig. 1. The lower two-layer film chromium/nickel had a selected direction and increased magnetic rigidity in the initial state [10]. The upper nickel film was soft magnetic electrode and did not have a selected direction in the initial state.

Magnetostriction of the substrate was measured by the bridge method with a semiconducting linear strain gauge of samarium sulfide of SmS–O–VL series (SMS-Tenzotherm, PhTI St Petersburg), intended for measurements in the magnetic field.

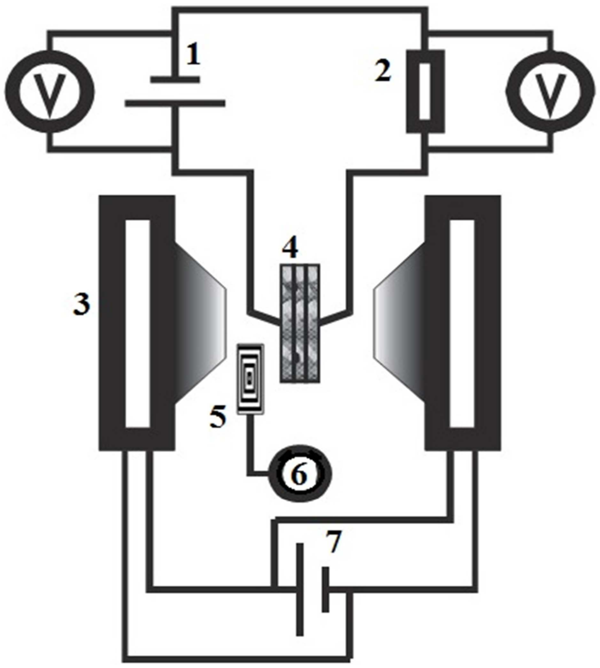

Figure 1. Experimental setup. 1 – voltage source for measurement circuit, 2 – ballast resistance, 3 – magnet, 4 – sample, 5 – Hall sensor, 6 – teslameter, 7 – voltage source for the magnet, V – voltmeters.

4. Experimental Results

4.1. Huge Magnetoresistance Effect on the Ferromagnet/Polymer Heterostructures

Huge magnetoresistive effects in the structure of ferromagnet/ electroactive polymer/ non-magnetic metal have been found in a number of studies. These effects are an abrupt change of resistance of the structure when the external magnetic field reaches a certain magnitude (Fig. 2, Fig. 3).

The dependence of the current flowing through the experimental sample on the magnitude of the external magnetic field is presented in Figure 2. The initial state of the sample with H = 0 corresponds to high conductivity. The conductivity of the sample remained virtually unchanged with increase of the magnetic field to H ~ 150 mT. Above this value, current change of a fluctuating nature with increasing oscillation amplitude according to the increase of the magnetic field was registered in the electric circuit. Upon reaching H = 210 mT, there was a decrease in the current and the sample was practically transformed into a low-conducting state. The relative variation of the current in this case was ~ 10^4 times. The consequent increase in the external magnetic field up to 300 mT did not lead to a change in the current flowing through the sample.

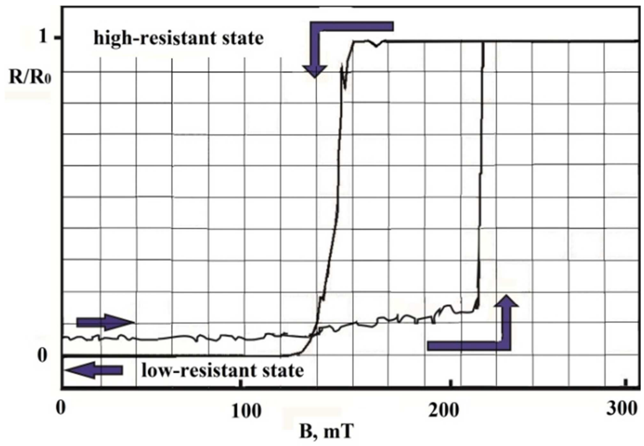

Figure 2. Huge magnetoresistance effect for Co/PDP/Cu heterostructure. Reversible change of the external magnetic field at a speed of 10 mT/s from 0 to 300 mT. Arrows show the direction of the external magnetic field change. R_0 is the resistance of the structure for the dielectric state of the film. The dielectric (high-resistance) state has resistance R_0 ~ 10^8 Ohm/μm across the polymer film.

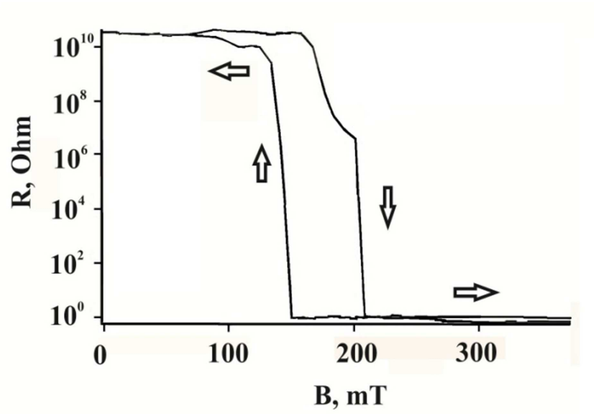

Figure 3. The dependence of the resistance of Ni/PDP/Cu heterostructure on the external magnetic field. Arrows show the direction of the magnetic field change. T = 300 K.

When the magnetic field decreased, the sample underwent a transition to the initial high-conductive state, but the magnetic field for reverse transition was less than that for direct transition. It was ~ 148 mT, and hysteresis was observed. It is assumed that the hysteresis of the conductivity switching was due to the hysteresis of magnetization reversal of the ferromagnetic substrate. Hysteresis loop of the polymer conductivity switching was wider for magnetically hard substrates Co than for magnetically soft Ni (compare fig. 2 and fig. 3).

The sign of the magnetoresistance depends on the conductivity state that the polymer film possessed at the beginning of the experiment [11]. To select the initial resistance, it is sufficient to apply small uniaxial pressure perpendicular to the plane of the sample [12]. If the film had high resistance (R ~ 10^8 Ohm), then a negative magnetoresistive effect is registered (Fig. 3). If the film had low resistance (R ~ 10 Ohm), then the magnetoresistance is positive, that is, with increase of the external magnetic field, conductivity decreased and resistance increased (Fig. 2).

Besides additional external factors leading the system to a pre-threshold state (pressure, voltage), it is necessary to take into account the actual electrical state of the polymer film; the degree of occupancy of the traps in the polymer layer is also important.

4.1.1. Influence of Magnetostriction

The role of magnetostriction in the manifestation of electronic conductivity switching is investigated for the nickel/PDP/copper system [13]. Magnetostrictive strain measurements were carried out by the bridge method with smooth variation of the magnetic field. The rate of the change of the magnetic field corresponded to that for resistivity switching measurements.

Linear magnetostriction change curves were obtained for strain gauge orientation parallel to the magnetic field (longitudinal magnetostriction) and normal to the magnetic field for two directions (transversal magnetostriction for magnetic field orientation in the plane of the sample, and also normal to the plane of the sample). Basic galvanomagnetic effects were excluded by repeating the measurements with the opposite direction of the current through the strain gauge. The final curve was constructed as the average of the curves for the opposite direction of the current. The value of the signal from the measuring bridge was recorded with continuous increase of the external magnetic field and its subsequent decrease (as in the experiments in Figs. 2, 3). Magnetostrictive strain grew at low fields up to 70–100 mT, regardless of the relative orientation of the magnetic field and the strain gauge. Thereafter, the curves reached the saturation region, and significant changes of deformations were not observed. Fig. 2 and Fig. 3 show that the magnetic field region, where there is an effect of electronic conductivity switching, does not coincide with the area of significant magnetostriction. Therefore, magnetostrictive ferromagnetic substrate deformation cannot be the cause of the conductance switching effect in the Ni/polymer/Cu structure.

Magnetostrictive deformations directed perpendicular to the plane of the substrate should be particularly discussed. In [13] it was not possible to measure these directly using strain gauges, as the nickel plate was too thin (around 1 mm). Basically, the deformation caused by the transverse magnetostriction can initiate conductivity switching due to changes in pressure on the polymer. The high sensitivity of the electrical conductivity of thin films of polydiphenylenephthalide to uniaxial pressure applied perpendicular to the film surface is well known [7]. Moreover, a slight external pressure is required for the manifestation of the effect of conductivity switching in the magnetic field [12]. Deformations of the substrate can affect the conductivity switching of the structure. However, it is also known that nickel has negative magnetostriction [14], i.e., the layer thickness decreases along the magnetic field. Therefore, in this case, the increase of the magnetic field caused a decrease of pressure of the electrode on the polymeric film.

The sample was in the low-conductive initial state in the embodiment of the electronic conductivity switching presented in [13]. Therefore, the decrease in pressure can only lead to a decrease in conductivity, and not increase it, in accordance with all the known experience accumulated to date [7]. There is no evidence to show that an increase of conductivity is possible with decreasing pressure in metal/polymer/metal type structures.

It has been found that the phenomenon of the appearance/disappearance of the electronic conductivity switching controlled by a magnetic field on the nickel/polymer boundary is not correlated with a significant change of magnetostrictive deformations. This conclusion is based on the fact that transversal (magnetic field orientation normal to the linear strain gauge) and longitudinal (magnetic field orientation parallel to the linear strain gauge) magnetostrictions do not change practically in the plane of the substrate in the range of magnetic fields provoking transition [13]. The role of the longitudinal magnetostriction perpendicular to the plane of the sample also cannot be considered defining, so the sign of conductivity switching varies in the same sample, depending on the initial conditions, whereas the sign of the longitudinal magnetostriction of the substrate does not change.

There are a number of additional facts which indirectly indicate the negligible effect of magnetostriction on the electronic conductivity switching. For example, there is a study of such switching for a multilayer film structure with a nickel electrode with thickness ≈200 nm. It is well known that the magnetostriction coefficient of the film material is less than that of the bulk one. However, the threshold magnetic field is of the same order of magnitude as for the film substrate and for the bulk.

Thus, the results can be interpreted as a lack of correlation between the magnetostriction in the ferromagnetic substrate, and huge magnetoresistance occurring in the ferromagnet/polymer/non-magnetic metal structure. In this regard, it may be confirmed that the change of magnetostrictive deformations of ferromagnetic substrate in the plane, which is a layer of a polymer, cannot be the cause of any significant effect on the conductivity of the polymer film.

4.1.2. Experiment with Copper Interlayer

Already in [15] it has been shown theoretically that there are different conditions for electrons with different spin orientations (different resistance of the interface) to overcome the boundaries between ferromagnetic and non-ferromagnetic metal. Therefore, it seemed logical to investigate the effect of partial spin polarization of charge carriers in the ferromagnet on the existence of an electronic switch controlled by a magnetic field [16].

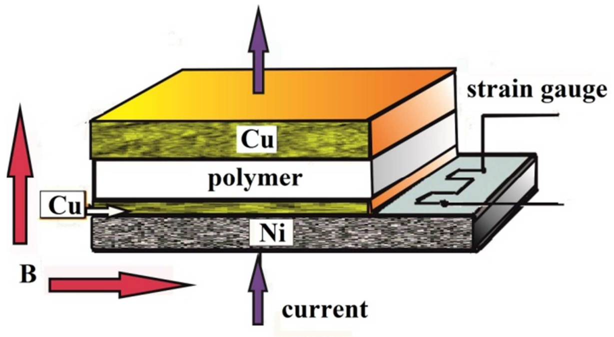

Figure 4. Multi-layer structure for the determination of the spin-polarized states' influence on magnetoresistance.

The initial conductivity of the polymer film was determined by external pressure. The magnetic field varied smoothly (10 mT/s), and the current passing through a ballast resistance of 200 kOhm was recorded. The ballast resistance was connected in series with the working cell. The bias voltage did not exceed 1.5 V. Introduction of a depolarizing layer (Cu) between the ferromagnet and organic transport layer changed the degree of spin polarization of the conduction electrons. The introduction of this depolarizing layer was produced by the use of thermal diffusion vacuum deposition on the surface of the nickel substrate (Fig. 4).

The electronic magnetoresistive switching of conductivity vanishes when the copper interlayer becomes thick enough (more than 10 nm). The strain gauge for measurements of magnetostriction of the ferromagnetic substrate is shown also.

The results of experiments carried out in [16] show that the magnetoresistance of a system of ferromagnet/copper/polymer/copper can be observed under the condition that the thickness of the copper layer separating the ferromagnetic surface and polymer does not exceed a certain value. In the context of this work, this thickness was 10 ± 2 nm. This value was defined by atomic force microscopy method as the boundary for the manifestation of the effect. The appearance of the magnetoresistance at a lower copper layer thickness can be explained by the incomplete depolarization of electrons with a copper layer.

4.1.3. Switching Threshold Control

For a ferromagnet/PDP/non-ferromagnetic metal structure, the change in the value of the threshold of conductivity switching in an external magnetic field when the initial magnetic state of substrate ferromagnetic wafer changed has been shown in [17].

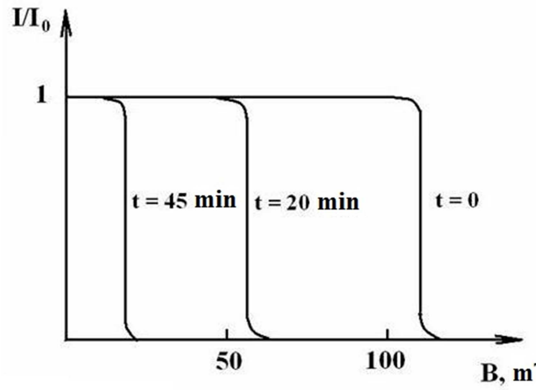

Figure 5. Change of threshold field for resistance switching t is the time of exposure in the external magnetic field normal to the plane surface, I is the current through the polymer; I_0 is the initial current for the high-conductive state.

Changing of the magnetic field threshold is explained by the appearance of residual magnetization after exposure in a non-saturating magnetic field perpendicular to the plane of the substrate and, consequently, a change of the initial state of magnetization reversal in the future.

Figure 5 shows a typical dependence of the electronic conductivity switching in the Ni/PDP/Cu structure from the time of thermal annealing of the nickel electrode. Here, thermomagnetic annealing means the exposure of ferromagnetic polycrystalline plate in a non-saturating magnetic field perpendicular to the plane of the structure at room temperature. In this case, the magnetoresistive ratio is positive, so that the influence of the magnetic field led to a sharp increase of the resistance of the structure at a threshold field. Increasing the annealing time leads to a decrease of the threshold field. The longest time did not exceed 60 minutes, as the magnetoresistive effect disappeared at longer intervals of exposure.

The sign of conductivity switching for the polymer film depended on the initial state of the film: i.e., it had been defined by the initial conditions for charge injection into the polymer.

In a ferromagnetic electrode there is certainly some initial domain structure of a labyrinth type. This form of domain is associated with the heterogeneity of the structure in polycrystalline samples or films. Single crystals of the correct structure form on the surface the so-called surface domains whose shape is associated with surface defects. The equilibrium domain configuration minimizes the sum of energies of the exchange interaction (orientation of domains towards an "easy" crystallographic direction), of the magnetoelastic component (orientation of domains according to the elastic stresses and defects in the sample, surface domains) and of the demagnetizing field (closure domains).

The direction perpendicular to the plane is "hard" in a flat plate, due to the shape anisotropy, i.e., complete reorientation of domains in this direction is only possible in very significant fields, repeatedly exceeding the saturation field for a continuous medium. The reason for this is the flat shape of the electrode and the resulting significant demagnetizing fields. Therefore, when the external field is perpendicular to the plane of the electrode plate, a ferromagnet is certainly in a non-saturated state at the available magnitudes of magnetic field– up to 500 mT. Change in the energy state of a ferromagnetic electrode due to increased residual magnetization can lead to a change of the potential barrier formed at the ferromagnet/polymer interface. This may affect the value of the external magnetic field required for switching.

Small changes in the magnetic anisotropy in the given conditions lead to significant changes in conductivity switching fields. Note also not only the relatively small amount, but also the high reversibility of the described changes of state of the sample obtained in the experiment. Therefore, such a method of controlling the magnitude of the switching field can be applied in both scientific and industrial practice.

To estimate the potential barrier change in the magnetic field [11], the current–voltage characteristics method was used [18]. When the bias voltage is V = 1 V, the tunnelling current for the low-conductive state without magnetic field is I_{0mT} = 1.13 μA; if the external magnetic field is 250 mT then the tunnelling current is I_{250mT} = 0.6 μA. According to

[18, 11], $I_0/I_{250} = 1.88 = [\exp(e\varphi_{b250}/kT)]/[\exp(e\varphi_{b0}/kT)] = \exp[(e/kT)\cdot(\varphi_{b250} - \varphi_{b0})]$.

Here φ_{b250} is the tunnel barrier height in the interface in the external magnetic field of 250 mT; φ_{b0} is the tunnel barrier height in the interface without the external magnetic field; T = 295 K; e is the electron charge; k is the Boltzmann constant.

The tunnel barrier change is

$$\varphi_{b250} - \varphi_{b0} = \ln(1.88)\cdot kT/e = 0.016 \text{ eV}.$$

This estimation indicates that the potential barrier in the ferromagnet/polymer interface really changes in the external magnetic field.

4.2. Valve Effect

The angular dependence of the resistance on the direction of the external magnetic field has been obtained with the magnetic field parallel to the plane of the structure. Structure of Cr/Ni/PDP/Ni with the current normal to its plane in dependence on the external magnetic field direction. The measured value is the voltage on the ballast resistor (200 kOhm). Two types of experiments were conducted:

1. Ray scanning (reversible increasing of the magnetic field oriented towards a definite direction from 0 to 250–350 mT). Automatic change of the external magnetic field with a speed no greater than 10 mT/s from 0 to maximal meaning and back was performed in turn for different directions in steps of 20 degrees (18 points for complete revolution). After that, an angular diagram was drawn for three shears – three values of the external field: 0, 120 mT, and 250 (350) mT, and the points were taken one from each scan.

2. Round measurements for different fields. The field value was exhibited in steps of 50 mT, then the angle dependence was measured in the definite magnetic field. Angle dependence is the dependence of the value of current flowing through the experimental structure normally to the plane of the layers on the external magnetic field direction in the plane of the structure, in steps of 20 degrees. Increase of the reversible magnetic field in the defined direction for ~ 5 mT was set automatically for each point [19].

3. Conductivity switching only for the selective direction of the external magnetic field parallel to the direction selected for the current flow in the valve structure.

Ray scan results indicated the presence of the selected sector of directions for all the selected values of the external magnetic field. The preferred direction here means the orientation direction of the external magnetic field in the plane of the structure, when a current flowing perpendicular to the plane of the structure is at maximum. For circular measurements in different fields, when the rotation of the sample was carried out at a given value of the external magnetic field in the plane of the structure, the preferred direction in large fields changes the orientation. The results of the experiment of the first type are shown in Fig. 6. The field slice is 120 mT. The polymer layer thickness is 750 nm.

Thus, the angular dependence of the resistance on the direction of the external magnetic field is detected in the examined structures to be symmetrical with the configuration of the spin valve "current perpendicular to the plane". This dependence is characterized by the selected area for orientation directions of the external magnetic field, in preference to the current flow.

For the results shown in [19], the sector for highlighted areas was much narrower than in Fig. 6, at ~ 30 degrees.

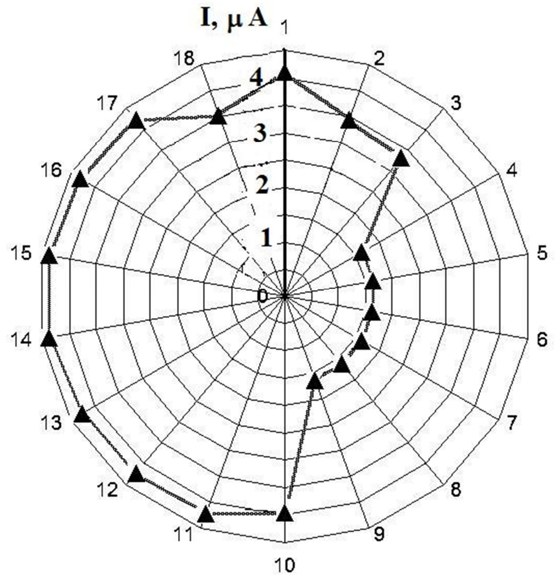

Figure 6. Dependence of the current through the spin-valve CPP heterostructure vs. in-plane magnetic field direction. Magnetic field is taken to be 120 mT. The type of original experiment: magnetic field is scanning from 0 to 350 mT for each direction, the speed of the magnetic field change is 10 mT/s.

5. Discussion

There are several important features of the electronic conductivity switching that is observed in the Ni (Co)/PDP/Cu structure:

1. Room temperature of the experiment.

2. Presence of only one ferromagnetic electrode.

3. Large relative resistive change:

$$((R_2\text{-}R_1)/\ R_2 \sim 10^{(6\text{–}8)})$$

4. The magnetoresistive effect can be both positive and negative. The sign of the effect depends on the initial conductivity state of the sample.

5. The effect is revealed at values of the external magnetic field of 50–500 mT.

It has been established that common electronic switching conduction properties are not dependent on the method of manufacturing a ferromagnetic layer of the Ni(Co)/polymer/Cu structure. The resistance of the polymer film is about 100 MOhm in the dielectric state and about 10 Ohm in the quasi-metallic state. The most convincing argument against primitive explanation of the experiments on the conductivity switching of PDP film in magnetic field is the possibility of obtaining the magnetoresistive effect of both signs at the same fixation of a sample (Fig. 3).

Consider the process of charge transport in the heterostructure ferromagnet/polymer (FM-P) [20]. The polymer used is an organic insulator with a band gap of 4.2 eV. However, a narrow gap of permitted states forms in the middle of the band gap after a certain exposure (for example, low external pressure). Formation of the gap is due to the trapping of electrons by the transport side groups of the polymer molecules. A transport zone is formed when these trapped electrons become numerous, due to overlap of their wave functions. The external magnetic fields used (up to 0.5 T) cannot create a charge transport zone, therefore additional action is needed to control the electrical resistance change of the FM-P heterostructure in the magnetic field (additional mechanical pressure or additional electric field). In this case, the thermal smearing of the band edges is irrelevant, since the transport corridor is formed in the middle of the forbidden band. Magnetization reversal of a ferromagnet changes the shape of the potential barrier in the interface. Evaluations [11] showed that when an external magnetic field is switched on, the potential barrier is lowered by ~ 0.01 eV. Abrupt change in the electrical resistance of the structure occurs at a certain value of the magnetic field (usually in the zone of proximal paraprocess). This process is similar to resonant tunnelling. Huge magnetoresistance on the array of paramagnet nanoparticles [1] is the effect closest in nature to the huge magnetoresistance on FM-P type heterostructures. Thus, the main factor for the emergence of a huge magnetoresistance for FM-P type structures is the possibility of change of the potential barrier in the magnetic field, leading to changes in charge tunnelling. At the FM-P interface, reversal magnetization takes place as a change in the energy of the magnetic subsystem of a ferromagnet and as relaxation processes. However, in [1] reducing the thermal smearing of the energy of carriers in the array of nanoparticles requires very low temperatures. At the same time, to overcome disorientation in the statistical array of nanoparticles, [1] requires very significant magnetic fields. Huge magnetoresistance in FM-P structures is revealed at room temperature. The large value of sharp and reversible transition of magnetoresistance in the magnetic field in combination with the small size of the required magnetic fields, and the relative simplicity of the manufacturing technology of metal-polymer structures make this effect promising for use. The glass/chromium/nickel/PDP/nickel structure type with CPP configuration and magnetic field in the plane of the structure is found to demonstrate:

A valve effect. Conductivity switching only for the selective direction of the external magnetic field parallel to the direction selected for the current flow in the valve structure.

Confirmation of inequality of the directions of current flow in experiments with ray scanning of the external magnetic field (Fig. 10).

The experimental results indicate that spin-dependent tunnelling exists in the FM-P structure. Results of the study of current–voltage characteristics for the FM-P interface [11] also show that the direction of current through the structure has a large influence on the charge transport through the polymer, i.e., as concerns the impact of the presence of partial spin polarization of the charge carriers. However, the model of spin-dependent tunnelling describes the behaviour of charge carriers only near metal/polymer interfaces and does not explain the effect of the valve in the hard ferromagnet/PDP/soft ferromagnet structure. Let us consider a possible means of charge transport through the polymer layer with conservation of spin. To explain this phenomenon, one can assume ballistic charge transport, as in [19], or one can use a model [21] suggesting the presence of magnetic order induced by external magnetic field in quasi-one-dimensional conductive channels. Quasi-one-dimensional channels contain paramagnetic oxygen, that is, the induced magnetic order is fundamentally possible. In the case of using such a model [21], the charge transport pattern reduces to the double-barrier tunnelling magnetic nanocontact for which the resonance conditions are possible. These resonant conditions lead to the switching of conductivity when the external magnetic field is oriented exclusively in the preferred direction.

For the general explanation of conductivity switch in the wideband polymer layer one can also attract the model for the system of one-dimensional quantum conductors [22]. Here the small shift of Fermi level leads to the great switching of conductivity. But the details of such theory application need the additional research.

6. Conclusions

Reversible electronic switching of conductivity controlled by external magnetic field exists in the asymmetric structure of ferromagnet/ polydiphenylenephtalide (film)/non-ferromagnetic metal. The sign of the electronic switching of conductivity is determined by the initial metastable state of the polymer film. Linear magnetostriction of the ferromagnetic electrode is not essential for the manifestation of the effect. Electronic switching of conductivity is closely connected with partial spin polarization of the current that is injected from the ferromagnet to the polymer. The threshold field value for switching of conductivity depends on the initial magnetic state of the ferromagnetic electrode-injector. Switching of conductivity as a rule takes place in the region of near-paraprocess, where change of the zone structure of the ferromagnetic electrode begins. Moreover, a potential barrier at the interface varies due to external magnetic field [11]. In the presence of a small residual potential barrier at the ferromagnet–polymer interface in an asymmetric structure, slight magnetoresistive tunnelling phenomena are possible and, in particular, the dependence of the CPP “current perpendicular to the plane” structure’s resistivity from the direction of the magnetic field in the plane on the structure is characteristic for tunnelling anisotropic magnetoresistance [11]. The additional effect which brings the system to be close to the switching threshold can play the role of the parameter controlling the type of magnetoresistive effect.

Conductivity switchings controlled by the magnetic field with the external magnetic field orientation perpendicular or parallel to the plane of the structure were obtained in the symmetric structure of the spin-valve CPP. The selected direction for conductivity switching exists for external magnetic field orientation parallel to the plane of this structure. The angular dependence of the current on the direction of the magnetic field of “directivity pattern” type was obtained in the plane of the structure for a polymer interlayer thickness no less than 750 nm. This is proof of the possibility of spin transport for a spin-valve structure with a charge transport layer made from polymer material with a wide band gap.

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