St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 2024. Vol. 17. No. 4
Научно-технические ведомости СПбГПУ. Физико-математические науки. 17 (4) 2024

Original article
UDC 538.955-405
DOI: https://doi.org/10.18721/JPM17409

VERTICAL SPIN VALVE PERFORMANCE OF NiFe/Co-PANI/NiFe SYSTEM

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Abstract. The organic materials are found to be potent candidates for spintronics applications. Here, we have presented a cobalt-loaded polyaniline (Co-PANI)-based spin valve with NiFe alloy as ferromagnetic contacts. The spin valve signal was observed at temperatures from 10 K to 300 K. The *IV* curve of the spin valve exhibited a linear relationship, which showed that Co-PANI behaved like metal in this valve. The highest value of the magnetoresistance (MR) was found to be 8.13% at 10 K, whereas it decreased to 3.32 % at 300 K. Similarly, the bias current effect showed that the highest value of MR was 3.46 % for 10 A, which reduced down to 0.93% for 40 A.

Keywords: polymeric composites, magnetic materials, spin-valve, organic spintronics

For citation: Nemade K. R., Maheshwary P. B., Vertical spin valve performance of NiFe/Co-PANI/NiFe system, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (4) (2024) 106–113. DOI: https://doi.org/10.18721/JPM.17409

Научная статья
УДК 538.955-405
DOI: https://doi.org/10.18721/JPM.17409

ПОКАЗАТЕЛИ РАБОТЫ ПОДВЕСНОГО СПИНОВОГО КЛАПАНА СИСТЕМЫ NiFe/Co-PANI/NiFe

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Аннотация. Установлено, что органические материалы являются перспективными для применения в спинтронике. В работе представлен спиновый клапан на основе полианилина, допированного кобальтом (Co-PANI), с железоникелевым сплавом в качестве ферромагнитных контактов (система NiFe/Co-PANI/NiFe). Сигнал от спинового клапана наблюдался в температурном диапазоне от 10 К до 300 К. Вольтамперная характеристика этого устройства была линейной, что указывало на поведение материала Co-PANI, свойственное металлу. Наивысшее значение магнетосопротивления, которое составило 8,13 %, было достигнуто при температуре 10 К; затем значение снижалось до 3,32 % при 300 К. Аналогично проявилось и влияние тока смещения: наибольшее значение магнетосопротивления, равное 3,46 %, было получено при токе 10 А, а затем оно снизилось до 0,93 % при 40 А.

Ключевые слова: полимерный композит, магнитный материал, подвесной спиновый клапан, органическая спинтроника

Ссылка при цитировании: Немаде К. Р., Махешваре П. Б. Показатели работы подвесного спинового клапана системы NiFe/Co-PANI/NiFe // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 17. № 4. С. 106–113. DOI: https://doi.org/10.18721/ JPM.17409

Introduction

The organic materials are found to be more appropriate for spintronics application due to their outstanding characteristics that is a long spin relaxation time of spin polarized electrons. Similarly, the small spin-orbit coupling is another virtue of organic materials, which make it promising alternative over existing inorganic spintronics [1]. Organic spintronic device technology has a range of versatile applications, such as magnetic-field sensing, logic devices, oscillators, light emitting device and memory. In current decade, the field of organic spintronics is prospering gradually and some significant reports are summarized here.

Z. H. Xiong et al. [6] critically studied the use of a spin valve made of organic materials. The spin valve is a device with multilayer structure consisting of magnetic and nonmagnetic materials, known as a spacer. In this device, the electrical resistance depends on the spin of electrons passing through the device, which can be controlled by an external magnetic field. This study underlined that spin-polarized carrier injection, transport and detection are the key processes in the spintronics, which can be easily achieved in the organic spintronic materials [2].

The first tunable organic magnetoresistance effect in polyaniline (PANI) modified with poly(p-phenylene-2,6-benzobisoxazole) synthesized by a surface-initiated polymerization was reported by H. Gu et al. [3]. The organic magnetoresistance effect in the PANI modified with poly(p-phenylene-2,6-benzobisoxazole) varied from 1.2 to 5.1, and –34.8 % for the values of fibers 5, 10, 30, and 60 wt. %, respectively. The result of investigation showed the magnetoresistance to be tunable in polyaniline [3]. H. Gu et al. critically reviewed giant magnetoresistance characteristics of nanostructured polyaniline. The giant magnetoresistance effect in conducting polymers, especially in polyaniline, has deserved close attention due to easy and cost-effective synthesis techniques, good transport properties and high giant magnetoresistance signals relative to other organic spintronic materials. N. Tanty et al. [4] reported the low temperature transport properties and magnetoresistance measurements of polyaniline-carbon nanotube composite. The result of this study showed that the transition from positive to negative magnetoresistance was achieved at a higher concentration of multi-walled carbon nanotubes. Using the wave function shrinkage effect and quantum interference effect, N. Tanty et al. demonstrated the transition in magnetoresistance from positive to negative one. A. L. Lin et al. [5] studied the magnetoresistance phenomenon in polyaniline-iron oxide nanoparticle organic hybrid composite. The material under study showed a positive magnetoresistance of 85.7 % at room temperature. The polyaniline-iron oxide exhibited memory effect, i. e., the device could maintain its resistive state even when the power being switched off [6]. But a serious problem associated with organic spintronics materials arises when spin is injected into medium. Since ferromagnetic contacts and organic semiconductors do not match in impedance, the spin current through the interface disappears immediately [7].

Inspiring by the challenges associated with organic spintronics technology, we decided to study the spin-valve effect in the cobalt-loaded polyaniline (Co-PANI) composite from a magnetoresistance (MR) perspective. Similarly, we analyzed the effect of temperature and bias current on the spin-valve performance.

Experimental

In the present work, cobalt-containing polyaniline (Co-PANI) was prepared using the *ex-situ* procedure. The starting materials polyaniline (PANI), $CoCl_2 \cdot 6H_2O$ and other chemicals were purchased from Sigma-Aldrich and used without further treatment. In the preparation of Co-PANI composite, 0.5 % by weight $CoCl_2 \cdot 6H_2O$ was added in 30 ml of double distilled water under constant magnetic stirring for 10 min. Similarly, 5 g of PANI was added in 30 ml of double distilled water and kept for probe-sonication (30 min). After completion of ultrasonic treatment of the probe with a dose of PANI, the solution of $CoCl_2\cdot 6H_2O$ was added in the solution of PANI under constant magnetic stirring. After this step, the final suspension was again left for probe sonication (30 min). Finally, the solution was filtered and washed with deionized water. The resulting final product was dried at 60°C in an oven.

The structural study of Co-PANI composite was performed using X-ray diffraction (XRD) analysis with Rigaku Miniflex XRD set up CuK_α radiation ($\lambda = 1.5406$ Å). The surface morphology of Co-PANI composite was analyzed by field emission scanning electron microscopy (FE-SEM) on the SEM setup of ZEISS SIGMA operating at 5 kV ETH voltage. Raman spectroscopy was applied to study the chemical structure of composites. The Bruker RFS 27 Raman spectrometer was used for Raman analysis. To explore the ferromagnetism in the Co-PANI composite, Vibrating Sample Magnetometer (VSM) technique was used and the data recorded using VSM set up (Quantum Design Model-PAR 155).

In the process of fabrication of the Co-PANI-based spin-valve device, first pre-patterned NiFe electrode (bottom FM) 50 nm in thickness deposited by electron-beam lithography on SiO_2/Si substrate was taken. The Co-PANI composite ~1.2 μm thick was transferred to this bottom electrode by spin coating technique. After this step, in the second run of electron-beam lithography, NiFe (Top FM) electrode was deposited on the Co-PANI layer of the same thickness. Fig.1,*a* shows the schematic of the Co-PANI-based spin valve.

Next, the characteristics of the spin valve were measured using a four-terminal setup to analyze the performance of the spin valve. In this study, the bias current was applied perpendicular to the device, whereas magnetic field employed in-plane at 45° to the direction of NiFe electrodes. The all measurements of the Co-PANI composite-based spin valve were investigated on the physical properties measurements system made by Quantum Design. The measurement design and optical micrograph of the spin valve is shown in Fig. 1,*b*.

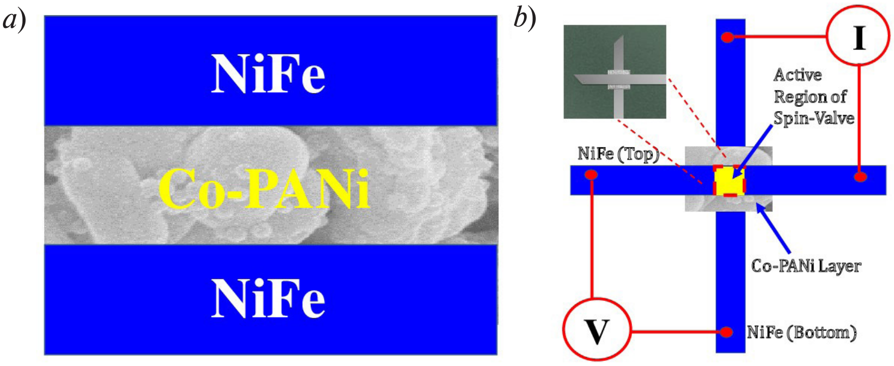

Fig. 1. Schematic (*a*) and measurement (*b*) structures of the Co-PANI-based vertical spin-valve device with optical micrograph

Results and discussion

Fig. 2,*a* depicts the XRD pattern of the Co-PANI composite. This pattern that exhibits noisy behavior with some sharp peaks, indicates that the composite is in the semi-crystalline state. Fig. 2,*b* shows the Raman spectrum of the Co-PANI composite. The C–N stretching band of semiquinoid form of PANI appears in the region of 1222 cm^{-1}. The weak broad hump around 1140 cm^{-1} may arise due to a vibration mode. The band that appears around 1390 cm^{-1} is attributed to the C–N stretching vibration from benzenoid. The band at 1650 cm^{-1} is outcome of the C=N stretching from quinoid (*Q*) structure. The degree of protonation of PANI improves in the presence of metal oxide, this may be due to metal oxide extract electron from PANI [8]. Fig. 2,*c* shows the SEM image of the Co-PANi composite. This image shows that the composite sample has irregular morphology. More detailed observation of the SEM image shows that spherical Co nanoparticles appear on the PANI surface. Fig. 2,*d* shows the typical hysteresis loops observed for PANI and Co-PANI composite samples. The area with the hysteresis loop significantly increased for the Co-PANi composite. This is attributed to larger magnetization of Co nanoparticles and interfaces formed between Co nanoparticles and PANI.

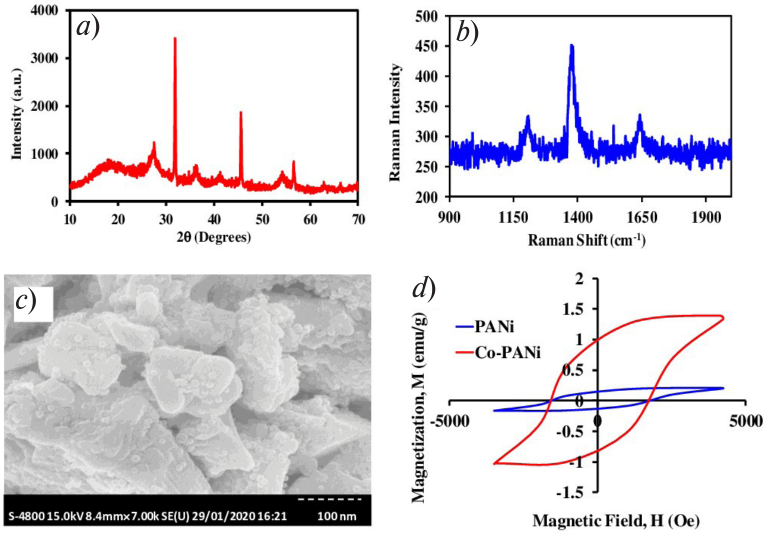

Fig. 2. The XRD pattern (*a*), Raman spectrum (*b*), SEM image (*c*) of the Co-PANI composite and hysteresis loops observed for the PANI and Co-PANI composite samples (*d*)

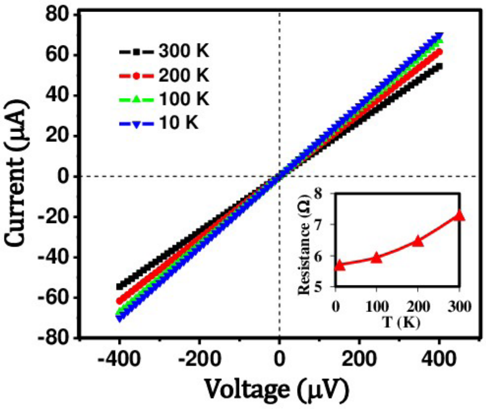

Fig. 3. Current-voltage characteristics of the spin valve at different temperatures from 10 K to 300K. *Inset*: the resistance curve as a function of temperature at zero magnetic field

Fig. 3 depicts the current-voltage (*IV*) characteristics of NiFe/Co-PANI/NiFe spin valve recorded at temperatures 10, 100, 200 and 300 K. The linear *IV* curve reveals the Ohmic nature of contacts occurs between NiFe and Co-PANI [9]. Next, the inset of Fig. 3 shows the variation of resistance with temperature. It can be seen that the resistance increases with increasing temperature, which indicates that Co-PANI behaves like metal in the spin-valve device. In other words, the thin layer of the Co-PANI reveals conductive property and no tunneling characteristics present in the thin layer of the Co-PANI [10].

In the present research, spin-valve effect in the Co-PANI-based device was analyzed by studying the magnetoresistance ratio (MR, %). It is defined as

$$\mathrm{MR} = [(R_{ap} - R_p)/R_p]\cdot 100\ (\%),$$

where R_{ap} is the resistance depending on magnetic field, R_p is the resistance bound up with parallel alignment of magnetizations [11].

Fig. 4,*a* shows the MR signal of NiFe/Co-PANI/NiFe spin valve that includes the bistable resistance state, where the high state and low state are associated with the antiparallel and parallel magnetization configurations between FM electrodes, respectively. Measurements of MR in the spin-valve show the highest value MR = 8.13 % at 10 K and the lowest value MR = 3.32 % at 300 K.

Further, Fig. 4,*b* shows the variation of MR of spin-valve and the spin polarization as a function of temperature (from 10 K to 300 K). The necessary values of the spin polarization were estimated using the relation

$$MR = (2P_1P_2)/(1 - P_2P_2),$$

where P is the spin-polarization [12].

In our case, both FM contacts were NiFe, therefore $P_1 = P_2$. It is observed that both MR and the spin polarization monotonically reduce with increasing temperature. The decrease in MR magnitude with increasing temperature is associated with several processes such as inelastic scattering with phonons, surface states and thermal smearing of electrons in FM metals [13]. Finally, the effect of bias current on MR of spin-valve was investigated for current values 10, 20, 30 and 40 μA at room temperature 300 K. Fig. 4,*c* shows the MR recorded for different values of bias currents. It is clearly observed that the amplitude of MR decreases with increasing the bias current. The highest value of MR was found to be MR = 3.46 % for 10 μA and it decreased monotonically with increasing the bias current. Fig. 4,*d* shows the variation of MR and the spin-polarization with the bias current value. It is observed that both quantities decrease monotonically with the bias current. The decrease in MR with the current bias is associated with accumulation of the spin excitations at the interfaces between NiFe and Co-PANI. Moreover, the generated localized states at interfaces act as a metal layer in the vertical spin valve [14].

Table shows the MR values reported in literature about spin valves based on organic

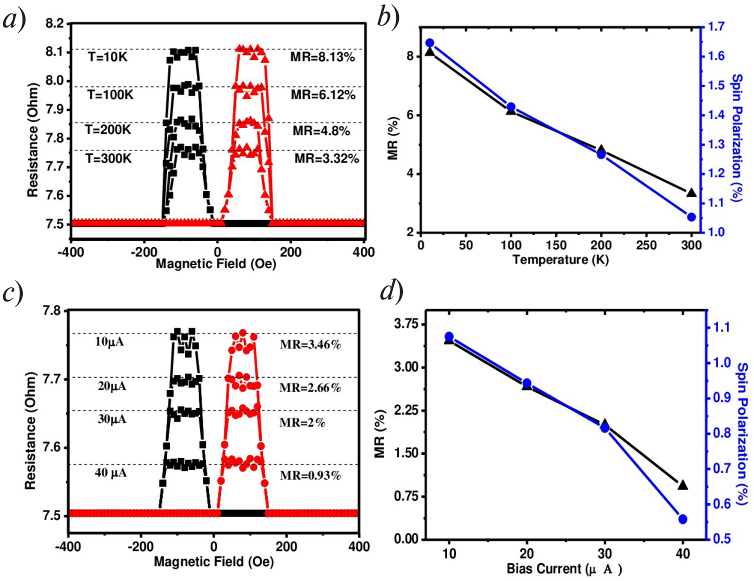

Fig. 4. The data obtained for the spin valve:
a – the temperature dependence of the MR; *b* – variation of the MR and spin polarization as a function of temperature; *c* – the bias current dependence of the MR; *d* – variation of the MR and spin polarization as a function of bias current

Table

MR values reported in literature about spin valves based on organic semiconductors with various ferromagnetic electrodes

Organic semiconductor	FM electrode	*T*, K	MR, %	Reference
Copper (II)-phthalocyanine	Fe/Co	40	6.4	[15]
Bathocuproine	Co/NiF	Room	3.5	[16]
Polymer-P(NDI2OD-T2)	LSMO/Co/Al		6.8	[17]
Co-PANI	NiFe/NiFe	10 300	8.13 3.32	This work

semiconductors with various ferromagnetic (FM) electrodes. The results obtained in the present investigation motivate further research. The main accomplishment of the present study is that the MR can be tuned to a specific value by controlling the temperature or bias current.

Conclusions

In conclusion, we have successfully demonstrated the spin-valve effect in the Co-PANI layer sandwiched between NiFe as FM electrodes. The findings in the present work shows that magnetoresistance (MR) is sensitive to the temperature and bias current of a spin-valve device. It was observed that MR decreased with increasing temperature. Similarly, the MR also decreased with increasing the bias current. Current-voltage characteristics of the spin valve revealed that semiconducting Co-PANI layer sandwiched between NiFe as FM electrodes, behaved like a metal layer. The present study showed that PANI based spin valves were expected to be an attractive category of materials due to their ease of preparation for spintronics application, that open up new opportunities for spintronics technology.

Acknowledgements

The authors are thankful very much to the Chief Director of Indira College, Kalamb Dist. Yavatmal for providing necessary facilities.

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Received 22.09.2023. Approved after reviewing 03.06.2024. Accepted 03.06.2024.

Статья поступила в редакцию 22.09.2023. Одобрена после рецензирования 03.06.2024. Принята 03.06.2024.