Organic conductors and semiconductors are promising electronic materials due to their lightweight, easy application over larger areas and on a variety of substrates, and the potential for low cost fabrication. Various applications of these materials include organic light emission diode (OLED), transistors, solar cells, sensors, etc. The electronic properties of these materials can be modified easily using chemical tuning of their structure. The materials can be processed using self-assembly, monolayer deposition, etc., to achieve devices in nanodimensions. Recent reports have demonstrated that spin valves can be fabricated.

Thin organic films of a thickness of a few nanometers (a monolayer) are the source of high expectations for being useful components in many practical and commercial applications such as sensors, detectors, displays, and electronic circuit components. The Langmuir-Blodgett (LB)-technique is one of the most promising techniques for preparing such thin films as it enables (i) the precise control of the monolayer thickness, (ii) homogeneous deposition of the monolayer over large areas, and (iii) the possibility to make multilayer structures with varying layer composition. An additional advantage of the LB technique is that monolayers can be deposited on almost any kind of solid substrate.

Pyrrole is one of the most used monomers for preparation of electroconductive polymeric materials. Indeed it offers several advantages such as the easy accessibility, the polymerizability, both by chemical or electrochemical oxidation, the good specific conductivity, and chemical stability. Moreover, its variety of derivatives are building blocks of microstructured polypyrrole (PPy) for fabricating microdevices including reactors, actuators, and sensors. Here, the insulating \( \pi \)-conjugated molecular pyrrole derivative 3-hexadecyl pyrrole (3HDP) [Fig. 1(a) shows its molecular structure] will be used as the spacer layer. By sputtering, LB technique, ultraviolet (UV) lithography, etc., we will sandwich the organic film between two ferromagnetic layers forming a spin valve structure junction to obtain superior electronic transport.

The spin valve structure we used is Ta(5 nm)/Cu(20 nm)/Py(5 nm)/IrMn(10 nm)/Co_{60}Fe_{20}B_{20}(4 nm)/organic spacer layer/Co_{60}Fe_{20}B_{20}(4 nm)/Py(20 nm)/Cu(20 nm)/Ta(5 nm). It has fixed bottom ferromagnetic electrode and top free electrode. The metallic multilayer is deposited with three-chamber high vacuum magnetron sputtering system on the Si/SiO\(_2\) substrate (base vacuum better than \(10^{-7} \) Pa). First, the bottom electrode is deposited. Then, the samples are taken out from the chamber with vacuum break for the cover of spacer layer by LB technique. Figure 1(b) is the high magnification scanning electronic microscope (SEM) image of one-layer 3HDP film extended by LB technique on ferromagnetic Co_{60}Fe_{20}B_{20} film. It shows uniform surface on nanometer scale with cluster structure at the air-molecular interface. After immediately drying the film by dry N\(_2\), the samples were transferred to the main chamber again for the top electrode deposition. After that, the films are patterned to junctions of different sizes by UV optical lithography, ion etching, etc., for measurement.

The magnetoresistance of the fabricated devices was measured by sending a current through the two electrodes by four-probe method. Figure 2 showed the typical magnetoresistance curve under bias voltage up to 1 V. The MR value decreased when the LB-film layer increased. The telegraph noise and the layer dependent MR value suggest that the spin-polarized transport signals can be degraded by localized states in the molecular barriers and barrier quality.

**FIG. 1.** (a) The molecular structure of 3-hexadecyl pyrrole. (b) The high magnification SEM image of one-layer molecular LB film on Co_{60}Fe_{20}B_{20} film. It shows uniform surface on nanometer scale with cluster structure at the air-molecular interface.
sistance (MR) loop obtained at room temperature marked by (a) for one-layer spacer junction with size of $5 \times 10^2 \mu m^2$ and (c) for three-layer spacer junction of $15 \times 30 \mu m^2$ in size. They showed obvious spin valve switching behavior with outside magnetic field changing. But the resistance area product (RA) and the MR values are not uniform and the curves showed degradation possibly due to the not ideal spacer layer. Small coercivity force less than 10 Oe can be observed during the resistance change for one-layer and three-layer LB-film spacers, similar to magnetic tunnel junctions (MTJs) of similar structure with Al$_2$O$_3$ barrier we fabricated and the work of Kauffer. Namely, the resistance changing corresponds to the switching of the free ferromagnetic layer. There is a consistent spin transportation in the molecular layer.

The junction with Al$_2$O$_3$ barrier we fabricated has barrier thickness of about 1.2 nm; about 35% MR value is obtained under the similar bias voltage of about 1 mV and MR values of 60% at room temperature, 80% at low temperature observed after annealing. So the polarity (P) of the Co$_{0.05}$Fe$_{2.0}$B$_{2.0}$ we used can reach 0.53 from Julliere’s formulas. The largest MR value we have measured is 20% in one-layer spacer junction under the similar bias voltage of about 1 mV [Fig. 2(a)]. This is $4/7$ of that of as deposited Al$_2$O$_3$ barrier junction, from which we conclude that the electron spin is capable of maintaining a high degree of polarization during the process passing though the spacer layers. Other junctions with smaller MR have nice switching behavior and better curve shape with more or less telegraph noise. For three-layer junctions, only the highest MR value of 6% is observed and still with degradation of curves. Figure 2(c) gave a curve with smaller MR value and smaller degradation. It shows obvious time-dependent telegraph noise signals suggesting the existence of localized states in the barriers as that in self-assembled molecular (SAM) layer. The origin of these states could be formed in the physical process of molecular and top-layer deposition, by chemical reactions between the monolayer and the metals, or by stress.

For two-layer samples, no working junctions were obtained by optical lithography method. Only about 0.2% MR value is detected at room temperature from a $100 \times 100 \mu m^2$ junction by metal mask method [Fig. 2(b)]. And it shows large coercivity. We guess that there must be a bad spacer layer with too many defects in it. Only the anisotropy magnetoresistance (AMR) signal is detected. For identification, the $M-H$ hysteresis loops are measured with vibrating sample magnetometer (VSM) at room temperature (Fig. 3). The samples with one-layer and three-layer spacers showed good character in free layer and pinned layer though there is little difference on magnetic moment coming from the intermixing layer at the interface of organic and free layer formed by sputtering ferromagnetic particles into the gap of molecular clusters. The two-layer spacer sample shows rather large coercivity value just like single layer high coercivity magnetic material. It means that the top and bottom ferromagnetic layers coupled together strongly through the bad quality even-layer LB film which is formed under the solution and easily destroyed when the sample is taken out of the solution.

The character and quality of the LB-technique spacer layer are further characterized by measurement of the $I-V$ curve for special size junction of $5 \times 10^2 \mu m^2$. For one-layer samples, linear behavior is observed under a rather big voltage to 1 V though they are slightly different in resistance (Fig. 4). Slightly tunneling behavior is observed in junctions with three-layer spacer (inset of Fig. 4). So the diffusive transport behavior should dominate for spin transportation in such single layer organic material instead of tunneling which can be due to the potential barrier at the interfaces for multilayer film spacer. With the layer increasing, the junction resistance increased, and the observed MR value decreased. It is possibly from the scattering of the spin by polarons and bipolarons in the organic molecular layer and also at the interface between the layers for three-layers spacer.

In conclusion, the magnetic/organic/magnetic spin valve structure has been fabricated with small $\pi$-conjugated molecular pyrrole derivative 3-hexadecyl pyrrole as the spacer layer by LB technique. The junctions exhibit MR value up to 20% at room temperature. This demonstrates that spin-flip scattering and spin-orbit processes can be weak enough in molecular layers that these structures may prove useful in...
applications involving electron-spin manipulation. However, we also find a strong layer dependence of the MR value. It means that the spin polarization decreases by scattering from the polarons, bipolarons, and the interface between the organic layers when the current diffused into the organic spacer layer. The presence of telegraph noise suggests the existence of localized states within the not ideal organic spacer layer. An improved procedures for extending the thin organic film on magnetic surface and depositing molecular top contacts are likely increase the MR. A better understanding of the spin transport behavior in small molecular organic films is still needed.

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