

Spin transport in magnetic tunnel junctions with the insertion of [6]Cyclo-2,7-naphthylenes organic semiconductor

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Abstract

We studied magneto-transport properties of Co-balt-AlOx-permalloy magnetic tunnel junctions with the insertion of cyclic phenylene macrocycle [6]Cyclo-2,7-naphthylenes (CNAP) to investigate the effect of interfacial properties of π -conjugate organic molecule / ferromagnetic metal. Magnetoresistance ratio of the junction with no CNAP molecular layer was 2.1% at 300K, whereas the magnetoresistance ratio increased up to 5.6% at 300 K with insertion of the 3-nm-thick CNAP layer. The result is discussed in terms of spin polarization enhancement due to π -d hybridization at the interface of CNAP / NiFe.

1. Introduction

Recently, the hybrid nano-hetero structure consisting of organic semiconductors and magnetic materials attracted much attention to realize new functional devices. One issues is highly efficient spin-injection into the organic semiconducting layer [1-2], which is an important step to develop the spin-organic-light emission diode (spin-OLED) and flexible magnetic sensor [3-4]. Another issue is related to an organic/magnetic interface [4-7]. The π electron orbitals for an organic molecule can hybridize with d electron orbital for magnetic element, and this π - d hybridization enhances spin polarization [8], which could open new route to develop a devices showing a large magnetoresistance for applications, such as magnetic sensors. These topics are also quite interesting from the fundamental points of view since a new physics/chemistry is behind a numerous combination of organic/magnetic interface.

In this study we investigate the spin-dependent transport property of magnetic junctions including [6]cyclo-2,7-naphthylenes (CNAP) [9]. An illustration of molecular structure of CNAP is shown in Fig. 1(a). CNAP is a newly developed one of the cyclic phenylene macrocycle, so it has conjugated π -electron system and a shape with connection of six naphthylene molecules [10]. When this molecule is used in the organic light emission diode (OLED), it shows bipolar transport property and is profitable for practical OLED. Interesting point is that a molecular structure of CNAP is planar, so that it is likely form good interface. And also it has a high thermal stability, up to about 600°C,

which is close to the melting point of Aluminum metal, even though CNAP is organic molecule. This thermal stability can allow us to fabricate robust organic/magnetic metal interface.

2. Experimental procedures

The junction devices were prepared by the film deposition system which have various vacuum chambers for deposition of different materials. The stacking structure was glass substrate / Co (50) / AlOx (2 nm) / CNAP (0-15)/NiFe (30) (thickness is nm), as shown in Fig. 1(b) The Co electrode and Al-layer were deposited by sputtering technique, and the Al layer was then oxidized by oxygen plasma to form Al-O barrier. Subsequently, CNAP and NiFe layers were deposited by thermal and electron beam evaporation technique, respectively. The cross-type junction pattern with the junction area of $1.5 \times 2.0 \text{ mm}^2$ was formed using metal shadow masks for the deposition of each layer inside the vacuum chambers. In these process of device fabrication, each layer were deposited at room temperature and the devices were not exposed to the atmosphere.

Transport properties and magnetoresistance effects of the samples were characterized by a standard four probe method with different temperatures using Physical Property Measurement System (PPMS).

3. Experimental result and discussion

Figure 2(a) and 2(b) show the magnetoresistance curves for the junction devices without CNAP molecule and with the 3-nm-thick CNAP molecular layer, respectively. The junctions without the molecules shows tunnel magnetoresistance of $\sim 2\%$ at room temperature, which increases up to $\sim 6\%$ at low temperature. On the other hand, the junctions with the 3-nm-thick CNAP molecular layer showed magnetoresistance larger than that without CNAP layer, whose magnetoresistance ratio were about 10% at low temperature.

The CNAP molecular layer thickness dependence on magnetoresistance was also investigated. The magnetoresistance ratio exhibited a maximum values at CNAP layer thickness of about 3 nm and then reduced with further increasing the thickness of CNAP layer. Such trend are different from the junction with another organic molecules, as reported in Ref. 11-13. Resistance measurements for the

junctions with various temperature indicated that the transport mechanism is a carrier tunneling in thin region and a carrier hopping in CNAP layer. We discussed the magnetoresistance observed in the thinner region below.

In the case of incoherent spin-dependent tunneling transport dominated, the tunnel magnetoresistance ratio is expressed by

$$\text{MR ratio (\%)} = \frac{2P_1P_2}{1 - P_1P_2} \times 100, \quad (1)$$

according to the Jullie're's expression [14]. Here, P_1 and P_2 are the spin polarization values at Fermi level for each metallic magnet electrodes. Spin polarization at Fermi level is determined by the spin-dependent density-of-states at Fermi level at interface of electrodes. In general, the density-of-states at Fermi level at interface of molecule/magnetic metal can be modified by the hybridization of π -electron orbital for molecules and d -electron orbital for magnetic metals [8]. Thus, the enhanced MR in ultrathin CNAP inserted junctions might be originated from the enhancement of CNAP/NiFe interface spin polarization. Further studies are necessary to understand mechanism of enhancement and it will be discussed elsewhere [15].

4. Summary

We investigated spin-dependent transport properties of the magnetic tunnel junctions with the CNAP layer. The junctions with the a few nm thick CNAP layer shows MR ratio lager than that for the junctions without CNAP layer. This result suggested the CNAP/NiFe interface might have the high spin polarization even at room temperature.

Acknowledgements

This work was partially supported by ERATO Isobe Degenerate π -Integration Project (JST), The Murata Foundation, and WPI-AIMR Fusion research funding. We also thank Mr. H. Kiso and Y. Kondo for their helps with the device fabrications.

References

- [1] V.A. Dediu, *et.al.*, Nat. Mater. 8, 707 (2009).
- [2] X. Zhang *et. al.*, Nature Comm. 4, 1392 (2013).
- [3] T.D. Nguyen, *et.al.* Science 337, 204 (2012)
- [4] C. Barraud, *et.al.*, Appl. Phys. Lett. 96, 072502 (2010)
- [5] C. Barraud *et. al.*, Nat. Phys. 6, 615 (2010).
- [6] X. Zhang *et. al.*, Appl. Phys. Lett. 99, 162509 (2011)
- [7] K. V. Raman *et. al.*, Nature 493, 509 (2013)
- [8] M. Galbiati, *et.al.*, MRS Bulletin 39, 602 (2014).
- [9] W. Nakanishi *et. al.* Angew. Chem. 123, 5435 (2011)
- [10] M. Iyoda, J. Yamakawa, and M. J. Rahman, Angew. Chem. 50, 10522 (2011)
- [11] J.H. Shim, *et.al.*, Phys. Rev. Lett. 100, 26603(2008)
- [12] J.J.H.M. Schoonus, *et.al.*, Phys. Rev. Lett. 103, 146601 (2009).
- [13] G. Szulczewski, *et.al.*, Appl. Phys. Lett. 95, 202506 (2009)
- [14] M. Jullie're, Phys. Lett. A 54, 225 (1975)
- [15] K. Z. Suzuki *et al.* *submitted*.

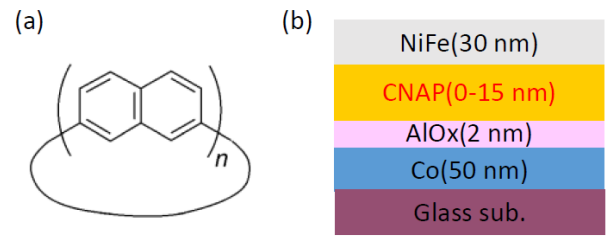


Fig. 1 (a) The molecular structure of [6]cyclo-2,7-naphthylenes (CNAP). (b) Stacking structure of devices.

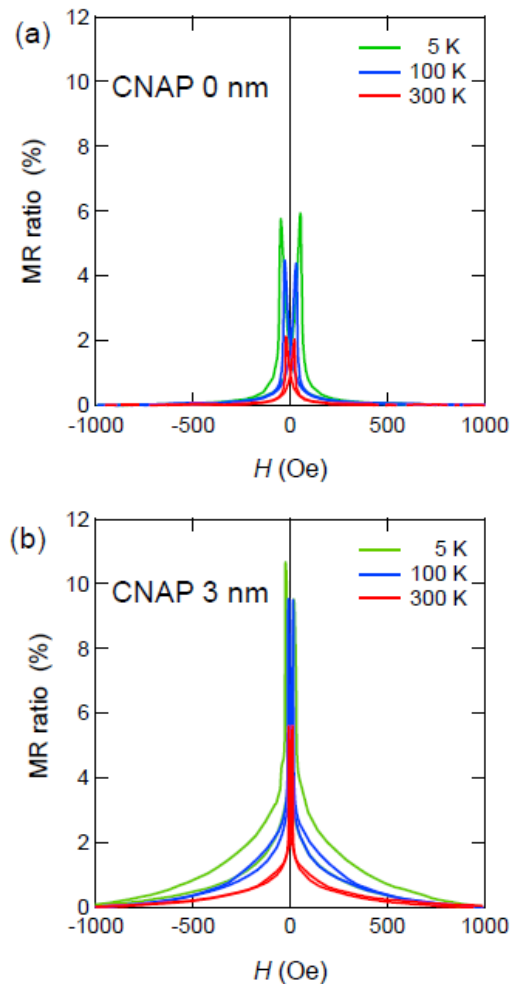


Fig. 2 Magnetoresistance curves measured at 5, 100, and 300K for the junction devices without CNAP molecule (a) and with the 3-nm-thick CNAP molecular layer (b).