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| Highlights    | • The spin transport in pigment-red PTCDA films has been achieved at room temperature.  
• The spin diffusion length in PTCDA films has been estimated to be about 14 ± 2.0 nm at RT.  
• A PTCDA film is used not only for protection but also as a spintronic material. |
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Spin-pump-induced spin transport in a thermally-evaporated pigment-red film

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Abstract:

We report the spin transport properties in a pigment-red (perylene-3,4,9,10-tetracarboxylic dianhydride: PTCDA) film prepared by thermal evaporation. In a palladium(Pd)/PTCDA/Ni\textsubscript{80}Fe\textsubscript{20} tri-layer sample, a pure spin-current is generated in the PTCDA layer by using the spin-pumping driven by the ferromagnetic resonance of the Ni\textsubscript{80}Fe\textsubscript{20} film. The generated spin current is absorbed into the Pd layer, converted into a charge current with the inverse spin-Hall effect in Pd, and
detected as an electromotive force. This is clear evidence for the spin transport in a PTCDA film, and it is confirmed that a PTCDA film is useful not only as a robust protection layer material but also as a spintronic material.
1. Introduction

Carbon-based molecular materials for the wide possibility of spintronic applications have attracted much attention [1-18]. Those are expected as good spin transport materials originating from the weak spin-orbit interaction in the materials. Recently, the spin transport in a thermally-evaporated pentacene film which shows photoconductivity has been achieved at room temperature [7]. This means, under an assumption that the spin transport in pentacene films is mainly driven by a charge transport in the films, it is expected to switch the spin current in the molecular materials through the visible light irradiation, by utilizing the photoconductivity [7-9]. It is also expected to produce spin-related functions through the visible light irradiation, by controlling the excited $\pi$-electron states in molecular materials [10]. Moreover, to control the spin transport property by applying a pressure may be realized by utilizing the flexibility and the spin-orbit interaction differences derived from the molecular structure differences [12]. In these attractive examples, improvement of the physical durability of the molecular materials is an indispensable issue to develop the molecular spintronics as similar to the case of the conventional molecular electronics.

In the conventional $\pi$-conjugated molecular electronics, a copper-phthalocyanine (CuPc) molecular film [14-17] and a perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) molecular film [17-19] are usually used to overcome the above physical durability problem. The CuPc and
the PTCDA are respectively called as a pigment-blue and a pigment-red, which are robust materials due to the rigid molecular frames. These pigment films are easily formed by thermal evaporation in a vacuum. In particular, a PTCDA film is known as durable even in high-dense plasma like the sputtering method which is a standard technique to form thin films [19]. Thus, even in spintronics, PTCDA films will probably be useful. At present, the spin physics and/or applications in PTCDA molecular films have not been studied much yet [17,18]. With a magnetic tunnel junction structure, the spin transport phenomenon in PTCDA films has been demonstrated by using a spin-polarized charge current [18], where the PTCDA film thickness was only 2 nm. This means that the spin transport mechanism in PTCDA films is still unclear because there are two possibilities of the spin transport mechanism [18]: one is due to a tunneling process through the PTCDA film (not a spin injection process), and another is due to a spin-injection process into the PTCDA films. Thus, to clarify the spin transport mechanism in PTCDA molecular films is necessary for future spintronic application. In this study, we demonstrate the spin transport in thermally-evaporated PTCDA films with the thickness of several tens of nanometers by using the spin-pumping, [4-9,12,20-24] at room temperature (RT). This is clear evidence for the spin transport in PTCDA films via a spin injection process, and it is confirmed that a PTCDA film is useful not only as a robust protection layer material but also as a spintronic material.
2. Experimental methods

Our sample structure and experimental set up are illustrated in Figure 1. The spin transport in a PTCDA film is observed as follows: in palladium(Pd)/PTCDA/Ni$_{80}$Fe$_{20}$ tri-layer samples, a spin-pump-induced pure spin current, $\vec{J}_S$, driven by ferromagnetic resonance (FMR) [20,21] of the Ni$_{80}$Fe$_{20}$ film is generated in the PTCDA layer via the $s$-$d$ coupling at the Ni$_{80}$Fe$_{20}$/PTCDA interface. This $\vec{J}_S$ flows in the PTCDA layer, and is then absorbed into the Pd layer. The absorbed $\vec{J}_S$ is converted into a charge current due to the inverse spin-Hall effect (ISHE) [23] in the Pd layer, and detected as an electromotive force, $\vec{E}$, [4-9,12,22-24] which is expressed as,

$$\vec{E} \propto \theta_{\text{SHE}} \vec{J}_S \times \vec{\sigma}, \quad (1)$$

where $\theta_{\text{SHE}}$ is the spin-Hall angle which is the conversion efficiency from a spin current into a charge current in the material (in this case, Pd), and $\vec{\sigma}$ is the spin-polarization vector of the $\vec{J}_S$. That is, if the electromotive force due to the ISHE in Pd is detected under the FMR of the Ni$_{80}$Fe$_{20}$ film, it is clear evidence for the spin transport in a PTCDA film.

There are studies with a ferrimagnetic insulator Y$_3$Fe$_5$O$_{12}$ (YIG) as the spin injector for the similar experiments in this field [5,11]. If we can repeatedly prepare the good quality YIGs, the YIGs would be better than Ni$_{80}$Fe$_{20}$ in physical property studies because in the similar experiment method, extrinsic electrical signals from Ni$_{80}$Fe$_{20}$ itself is easily overlapped due to the electrical
conductivity [25]. However, to prepare good YIGs with reproducibility is generally hard, and the hardness to form the good YIGs is an indispensable bottleneck, especially for future industrialization. In this study, thus, Ni$_{80}$Fe$_{20}$ is used as the spin injector and such extrinsic signals [25] are carefully extracted.

Electron beam (EB) deposition was used to deposit Pd (Furuuchi Chemical Co., Ltd., 99.99% purity) to a thickness of 10 nm on a thermally-oxidized silicon substrate, under a vacuum pressure of $<10^{-6}$ Pa. Next, PTCDA molecules (Tokyo Chemical Industry Co., Ltd.; sublimation grade) were thermally evaporated through a shadow mask, under a vacuum pressure of $<10^{-6}$ Pa. The deposition rate and the substrate temperature during PTCDA depositions were set to 0.1 nm/s and RT, respectively. The PTCDA layer thickness ($d$) was varied between 15 and 60 nm. Finally, Ni$_{80}$Fe$_{20}$ (Kojundo Chemical Lab. Co., Ltd., 99.99%) was deposited by EB deposition through another shadow mask, under a vacuum pressure of $<10^{-6}$ Pa. During Ni$_{80}$Fe$_{20}$ depositions, the sample substrate was cooled with a cooling medium of -2°C, to prevent the deposited molecular films from breaking. For a control experiment, samples with a Cu layer instead of the Pd layer were prepared, where the Cu has smaller $\theta_{\text{SHE}}$ than Pd originating from the spin-orbit interaction difference.

An X-ray diffraction (XRD) spectrometer (Rigaku, Ultima IV) to evaluate the PTCDA film structure was used. The x-ray wavelength was 0.154 nm (Cu-K\(\alpha\)) and a general out-of-plane scan
was implemented. A microwave TE$_{011}$-mode cavity in an electron spin resonance system (JEOL, JES-TE300) to excite the FMR in a Ni$_{80}$Fe$_{20}$ film, and a nano-voltmeter (Keithley Instruments, 2182A) to detect electromotive forces from the samples were respectively used. Leading wires for detecting the output voltage properties were directly attached at both ends of the Pd (or Cu) layer with silver paste. All of the measurements were performed at RT.

3. Results and discussion

Figure 2 shows XRD spectra of PTCDA films prepared under various conditions. $\Theta$ is the incident beam angle to the sample film plane. The diffraction peaks in the range between $2\Theta = 29^\circ$ and $35^\circ$ are derived from the Si/SiO$_2$ substrates. We compared the PTCDA film thickness difference (50 or 100 nm) and the underlayer difference (on a Pd film the thickness of 10 nm formed on a thermally oxidized Si substrate, or directly on a thermally oxidized Si substrate (no Pd films)). PTCDA films generally have monoclinic structure [26,27]. In the case the PTCDA film thickness is 50 nm directly formed on the substrate (spectrum no. 4), the (102) diffraction peak of PTCDA films [26,27] has broadly and weakly been observed, while not appeared in the case the PTCDA film thickness is 100 nm (spectrum no. 2). In the case that the PTCDA film is 50 nm formed on Pd (spectrum no. 3), the (102) peak is almost disappeared. That is, our PTCDA
films on Pd are hardly crystallized. Although we haven’t considered the relationship between the
film structure and the spin-dependent property in PTCDA films yet, the film structure will be
improved near future in order to study the relationship, for example, by utilizing a self-assembly-
monolayer technique as similar to the case of the conventional molecular electronics.

Figure 3(a) shows the FMR spectrum of a sample with a Pd layer and with the $d$ of 30 nm at
an external magnetic field orientation angle ($\theta$) to the sample film plane of $0^\circ$. The applied
microwave power is 200 mW. $H$ is the strength of the external static magnetic field. The FMR
field ($H_{FMR}$) of the Ni$_{80}$Fe$_{20}$ film is 1,049 Oe at a microwave frequency ($f$) of 9.45 GHz. The $4\pi M_s$
of the Ni$_{80}$Fe$_{20}$, where $M_s$ is the saturation magnetization of the Ni$_{80}$Fe$_{20}$ film, is estimated to be
8,806 G with the FMR conditions in the in-plane field:

$$\frac{\omega}{\gamma} = \sqrt{H_{FMR}(H_{FMR} + 4\pi M_s)}, \quad (2)$$

where $\omega$ and $\gamma$ are the angular frequency ($2\pi f$) and the gyromagnetic ratio of $1.86 \times 10^7$ G$^{-1}$s$^{-1}$ of
Ni$_{80}$Fe$_{20}$, respectively [7,22,24]. Fig. 3(b) shows the output voltage properties of the same sample
as used in Fig. 3(a); the circles represent experimental data and the solid lines are the curve fit
obtained using the equation [7,22-24]:

$$V(H) = V_{Sym} \frac{\Gamma^2}{(H-H_{FMR})^2+\Gamma^2} + V_{Asym} \frac{-2\Gamma(H-H_{FMR})}{(H-H_{FMR})^2+\Gamma^2}, \quad (3)$$

where $\Gamma$ denotes the damping constant (56 Oe in this study). The first and second terms in eq. (3)
correspond to the symmetry term to $H$ due to the ISHE, and the asymmetry term to $H$ due to the
anomalous Hall effect and/or other effects showing the same asymmetric voltage behavior relative to the $H$, respectively [7,22-24]. $V_{\text{Sym}}$ and $V_{\text{Asym}}$ correspond to the coefficients of the first and second terms in eq. (3). In the Fig. 3(b), output voltages are observed at $H_{\text{FMR}}$ at $\theta$ of 0 and 180°. Notably, the output voltage changes their signs between $\theta$ values of 0 and 180°. This sign inversion of voltage in Pd associated with the magnetization reversal in Ni$_{80}$Fe$_{20}$ is characteristic of ISHE [7,22-24].

As a control experiment, we tested samples with a Cu layer instead of the Pd layer. Fig. 3(c) shows the FMR spectrum of a sample with a Cu layer and with the $d$ of 30 nm at the $\theta$ of 0°. The applied microwave power is 200 mW. Fig. 3(d) shows output voltage properties of the same sample as used in Fig. 3(c), where tiny electromotive forces compared with Fig. 3(b) were observed at $\theta$ values of 0 and 180°. This must come from the $\theta_{\text{SHE}}$ difference between Pd and Cu due to the spin-orbit interaction difference. As another control experiment, we studied the microwave power ($P$) dependence of the electromotive forces in a sample with a Pd layer and with the $d$ of 30 nm at the $\theta$ of 0°; the results are shown in Fig. 4. The $V_{\text{Sym}}$ increases in proportion to the increase in $P$. The above results suggest that the dominant origin of the electromotive force at the $H_{\text{FMR}}$ observed for the sample with a Pd layer (see Fig. 3(b)) is due to the ISHE in Pd. That is, spin-pump-induced spin transport in an evaporated PTCDA film has been achieved at RT. This is clear evidence for the spin transport in PTCDA films via a spin injection process.
Figure 5 shows the $d$ dependences of (a) $4\pi M_s$ in samples calculated via eq. (2) and of (b) $V_{\text{Sym}}$ estimated via eq. (3). To increase the reliability, a lot of samples were tested. Circles and a triangle were the experimental data. With increasing $d$, $V_{\text{Sym}}$ due to the ISHE in Pd seems to decrease with large deviation while $M_s$ slightly decreases. The electrical resistance of the Pd layer in samples is almost constant which means the Ni$_{80}$Fe$_{20}$ and Pd layers seem not to be directly connected within the measurement range. Meanwhile, when the current-voltage (I-V) properties between the Ni$_{80}$Fe$_{20}$ and Pd layers of several Pd/PTCDA/Ni$_{80}$Fe$_{20}$ tri-layer junction samples were measured, the followings were found: samples with the $d$ of 50 nm showed non-linear I-V properties and the resistivity values were like almost insulator. However, one junction sample with the $d$ of 30 nm showed a linear I-V property with one-tenth the resistivity of samples with the $d$ of 50 nm. This indicates the existence of pin-holes in PTCDA films in samples with thinner $d$ than 30 nm. For samples with thinner $d$, Pd and Ni$_{80}$Fe$_{20}$ may connect via pin-holes, not via the PTCDA layers, and the existence of the pin-holes in PTCDA films may cause more deviation of $V_{\text{Sym}}$ in samples than those with the thicker $d$ because the $V_{\text{Sym}}$ in samples with thinner $d$ includes extrinsic signals from the Ni$_{80}$Fe$_{20}$ itself [25]. Another reason of the $V_{\text{Sym}}$ deviation might be due to random networks of $\pi$-electron orbit in PTCDA films originating from the poor crystallinity.

Thus, as similar to the previous study [7], we estimated the spin diffusion length ($\lambda_s$) in PTCDA films with deviation, as follows: First, the datum of a sample with the $d$ of 15 nm (plotted by a
triangle in Fig. 5(b)) was excluded in the estimation of the $\lambda_s$. Next, two fitting curves as shown in the dotted lines in Fig. 5(b) for evaluation of the $\lambda_s$ in PTCDA films with estimation deviation were drawn under an assumption of an exponential decay of the spin current [4-7,22] in PTCDA films which means that the spin current in PTCDA films is diffusive: One is the fit for the longest $\lambda_s$ (~16 nm) by using relatively-small value data set. Another is the fit for the shortest $\lambda_s$ (~12 nm) by using relatively-large value data set. Thus, the $\lambda_s$ in PTCDA films was estimated to be 14±2.0 nm at RT.

We discuss the validity of the $\lambda_s$ estimation of our PTCDA films with the reported values in other molecular materials studied at RT by using a spin-pump-induced spin current [4-9,12]. The estimated $\lambda_s$ value of 14±2.0 nm in PTCDA films at RT is comparable or short to the reported spin diffusion lengths of other “low-molecular-weight” molecular films prepared by thermal evaporation: ~13 nm for C$_{60}$ fullerene [12], ~25 nm for C$_{84}$ fullerene [12], ~35 nm for TIPS-pentacene [9], ~42 nm for “normal” pentacene [7], and ~50 nm for Alq$_3$ [5]. Polymer films, such as PBTTT and PEDOT:PSS films, tend to possess longer spin diffusion lengths than “low-molecular-weight” molecular films: ~150 nm for PBTTT [4], and ~150 nm for PEDOT:PSS [6]. A polyaniline film, which is a conductive polymer film, has an extremely long spin diffusion length at RT of ~590 nm [12]. It is noticed that the relationship between the film crystallinity and the spin diffusion length in molecular films in all estimation of those reference values has not
been studied yet. Although the spin diffusion length of several tenth nm may be enough for spintronic application because the recent nanotechnology has been much evolved, it is significant for developing the molecular spintronics to investigate the relationship between the film crystallinity and the spin diffusion length in molecular films. This will be studied in near future by using the samples with molecular films having good crystallinity.

Finally, we compare our pigment-red PTCDA study with a pigment-blue CuPc study [14]. The spin transport distance in a CuPc film is estimated to be ~1 nm in pure spin injection process and ~35 nm in contaminated spin injection process through an inelastic process by using a two-photon photoemission process [14]. Although the evaluation method is different to each other, the spin diffusion lengths in PTCDA and CuPc films have been estimated to be comparable. Thus, when the two kind pigments are used as physically durable and spin-transporting materials, the two pigments can separately be used on the viewpoint of an optical reason (for example, the energy band gap difference), and it is probably same as the case of conventional molecular electronics.

4. Conclusions

Spin transport properties of thermally-evaporated pigment-red PTCDA films were studied at
RT by using the spin-pumping for the spin injection and using the ISHE in non-magnetic metals for the spin detection methods. We achieved the spin transport in PTCDA films; the spin diffusion length in PTCDA films was estimated to be 14±2.0 nm at RT. It was confirmed that a PTCDA film is useful not only as a protection layer material but also as a spintronic material, which paves a way to developing molecule-based spintronic devices.

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Fig. 1. (a) Bird’s-eye-view and (b) top-view illustrations of our sample and an orientation of external applied magnetic field $\vec{H}$ with an angle ($\theta$) to the sample film plane. $\vec{J}_S$ and $\vec{E}$ correspond to the spin current generated in the PTCDA film by the spin-pumping and the electromotive forces due to the ISHE in Pd, respectively.
**Fig. 2.** X-ray diffraction spectra for PTCDA films prepared by various conditions. The spectrum 1, 2, 3 and 4 are respectively for the PTCDA film with the thickness \(d\) of 100 nm formed on a Pd film, for the PTCDA film with the \(d\) of 100 nm directly formed on a Si/SiO\(_2\) substrate, for the PTCDA film with the \(d\) of 50 nm formed on a Pd film, and for the PTCDA film with the \(d\) of 50 nm directly formed on a Si/SiO\(_2\) substrate. \(\Theta\) is the incident x-ray beam angle to the sample film plane. The diffraction peaks in the range between \(2\Theta = 29^\circ\) and \(35^\circ\) are derived from the Si/SiO\(_2\) substrates.
Fig. 3. (a) FMR spectrum and (b) output voltage properties of a sample with a Pd layer. (c) FMR spectrum and (d) output voltage properties of a sample with a Cu layer. $\theta$ is the static magnetic field ($H$) angle to the sample film plane. $H_{\text{FMR}}$ is the ferromagnetic resonance field. The PTCDA film thickness is 30 nm and the applied microwave power is 200 mW.
Fig. 4. (a) Microwave power \((P)\) dependence of electromotive force generated in a sample with the PTCDA film thickness of 30 nm and (b) an analysis result obtained with eq. (3). \(V_{\text{Sym}}\) corresponds to the coefficient of the first term in eq. (3). The dashed line in (b) is a linear fit.
Fig. 5. Dependences of (a) $4\pi M_s$ ($M_s$: saturation magnetization), calculated by eq. (2), and of (b) $V_{\text{Sym}}$ estimated by eq. (3), on the PTCDA film thickness ($d$). Circles and a triangle are the experimental data. The dotted lines in (b) are curve fits under an assumption of an exponential decay of the spin current in PTCDA films.
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