

# Tuning of magnetism in ferromagnetic thin films by reversing the functional groups of molecular underlayer

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(Received 13 April 2010; accepted 2 June 2010; published online 28 June 2010)

We demonstrate a molecular approach of tuning the magnetic properties of ferromagnetic (FM) thin films by reversing the functional groups of the organic underlayer. For the CoFe/Langmuir–Blodgett (LB) film system, we find that the coercivity of CoFe thin films (from 4 to 10 nm) made on hydrophobic surfaces is significantly enhanced whereas that on hydrophilic surfaces remains unchanged, as compared with the films directly on glass substrates. These findings suggest an alternative way for tuning the magnetic properties of the FM layer by LB film in which the functional groups play an important role. © 2010 American Institute of Physics.

[doi:10.1063/1.3457907]

The emerging fields of spintronics and organic electronics have led to an interdisciplinary area where the primary focus is to investigate the spin transport in spintronic devices involving organic materials.<sup>1–5</sup> Some technologically important issues such as the spin polarization of tunneling current through organic molecules and the detection of spin-polarized carriers inside organic materials have been addressed within the scope of organic spintronics.<sup>6–9</sup> Despite their vantage in spin-transport properties, the magnetic properties of such spintronic devices should also be taken into concern because they could be influenced by the inclusion of organic materials. Inorganic molecules such as H<sub>2</sub> were found to change the spin reorientation transition behavior in ferromagnetic (FM) ultrathin films.<sup>10</sup> More recently, the impact of evaporated organic molecules and coated polymers upon the magnetic properties of FM thin films have also been reported.<sup>11,12</sup>

Molecular spintronics, on the other hand, is a fast-developing subarea of spintronics related to organic spintronics with specific interest in materials structure that involves single molecule or molecular monolayer.<sup>13–15</sup> The concept of molecular spin valve has been realized in molecular spintronics in which FM/molecular monolayer interface was encountered.<sup>13</sup> Once again the mutual interaction between the two materials through the interface plays an essential role in the device's performance. Some interesting phenomena regarding the impact of the molecular monolayer have been reported, including the shift in magnetic properties in dilute magnetic semiconductors (DMS) driven by self-assembled monolayer (SAM),<sup>16,17</sup> and the suppression of ferromagnetism due to the FM/SAM interaction.<sup>18</sup> In this paper we report our experimental study of two FM thin films made onto Langmuir–Blodgett (LB) film containing a molecular monolayer. The results show that the coercivity of the FM film is tunable by the functional groups of the LB film. The molecular underlayer also impacts the covering FM layer in the ways of morphology and magnetism.

The schematics of the bilayer system used for this study is illustrated in Fig. 1. The structure consists of a molecular monolayer on Corning glass substrate and a covering FM layer. The organic molecular monolayer is fabricated by the standard LB process in a KSV Mini-Through System.<sup>19</sup> The material for the LB film is stearic acid (SA, available from Aldrich) which is a long-chain amphiphilic molecule containing different functional groups from one end to the other. Depending on which end is attached to the substrate, two types of molecular surface, i.e., hydrophobic surface (h.o.s.) and hydrophilic surface (h.i.s.), can be constructed on glass substrate by a dipping/pulling-out-of-solvent process. After drying several hours in air, the substrate holding the LB film is transferred into a sputtering chamber (base pressure on the order of  $5 \times 10^{-8}$  mbar) for the capping of the FM layer. Two FM materials, CoFe and NiFe (permalloy) as hard and soft magnets respectively, are chosen for the top FM layer. The sample's surface morphology and roughness are characterized by atomic force microscopy (AFM), whereas the magnetic hysteresis loops are measured by magneto-optical Kerr effect (MOKE).

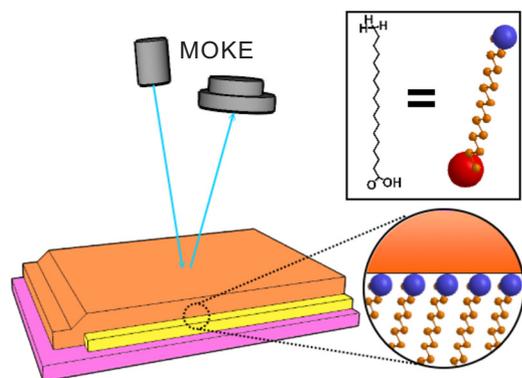


FIG. 1. (Color online) Schematics of the FM-LB bilayer system. The zoom-in picture illustrates the interface between the FM film and the functional groups of the LB molecular monolayer. The inset shows the scheme of the SA molecule in which the blue (small) ball and red (big) balls represent the methyl and carboxylic functional group, respectively.

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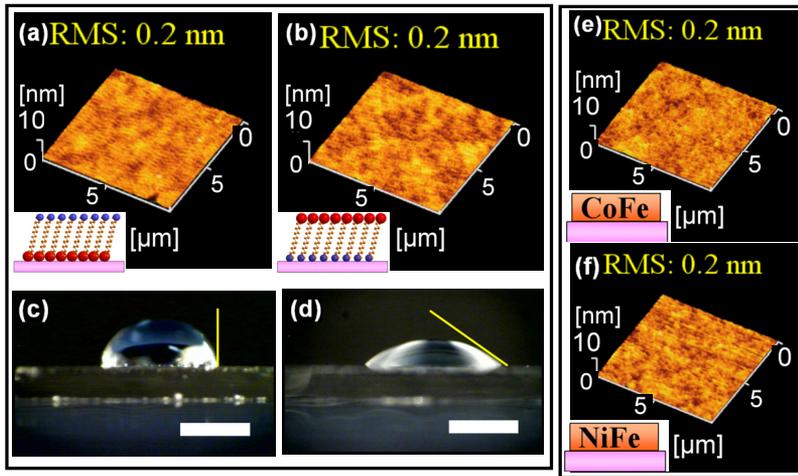


FIG. 2. (Color online) Surface morphologies of LB and FM thin films. (a) and (b): The AFM images of h.o.s. and h.i.s. The contact angles between a water drop and the h.o.s. and h.i.s. surfaces are shown in (c) and (d), respectively, where the scale bar is set by 1 mm. [(e) and (f)] The AFM images of 4 nm CoFe and NiFe thin films on glass substrates.

Figures 2(a) and 2(b) display the AFM images of the LB films of different molecular orientation (without the top FM layer). In both cases, the topological information indicates that the LB films are rather smooth with an rms roughness around 0.2 nm within the scanning area of  $10 \times 10 \mu\text{m}^2$ . The ordering of the LB films is checked by the contact angle between a water drop and the surface of the molecular monolayer, as indicated in Figs. 2(c) and 2(d). To obtain the fundamental morphological information of the FM films, we also measured the surfaces of 4 nm CoFe and NiFe films deposited directly on glass substrates, and the results are shown in Figs. 2(e) and 2(f). These images indicate that the FM films are flat with an rms roughness around 0.2 nm within the same areal scale. Varying the FM layer thickness from 3 to 30 nm does not significantly change the surface morphology or roughness, so long as the films are made on pure glass substrates.

The magnetic hysteresis loops of 3 nm CoFe on three different surfaces, namely, h.o.s., h.i.s., and pure glass, are shown in Fig. 3(a). The curves overlap one another with nearly identical coercivity. As the CoFe films are made thicker (6 nm), the coercivity of the film on h.o.s. is significantly enhanced whereas those of the other two remain unchanged, as indicated in Fig. 3(b). A brief note here: we have tried to vary the relative orientation between the applied magnetic field and the sample surface from parallel to perpendicular geometry, and have confirmed that the magnetization of our samples is not only in the lateral (in-plane) direction but also along the long side of the rectangular shape (measured  $25 \times 8 \text{ mm}^2$ ).

To investigate whether the coercivity enhancement is morphologically induced, AFM scans are performed on the surfaces of 6 nm CoFe films covering h.o.s. and h.i.s., and the images are shown in Fig. 3(c). Compared with the CoFe film deposited directly on glass substrate, the films with molecular underlayer are rougher, evidencing that the clusterlike morphology is originated from the molecular underlayer. The results indicate that clusters have developed as the films are grown thicker but there is no significant morphological difference between the FM films made on differently oriented molecular underlayers.

For a more systematic analysis, we have varied the thickness of the FM layer deposited on three different surfaces. Figure 3(d) shows the coercivity change with respect to the thickness variation, whereas the inset indicates the

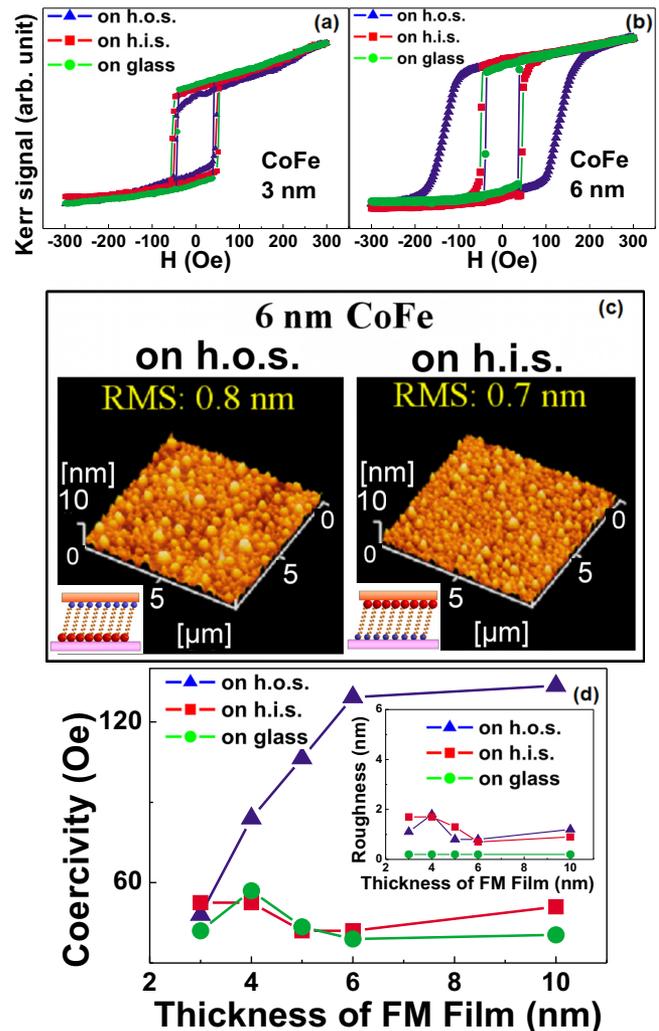


FIG. 3. (Color online) Magnetic and surface characterizations of CoFe thin films on LB molecular underlayer. (a) and (b) show the hysteresis loops of 3 nm and 6 nm CoFe on three different surfaces, respectively. (c) shows the AFM images of 6 nm CoFe on h.o.s. and h.i.s., taken within the area of  $10 \times 10 \mu\text{m}^2$ . (d) shows the plot of coercivity vs the thickness of CoFe for three kinds of underlayer, and the corresponding changes of roughness are indicated by the inset.

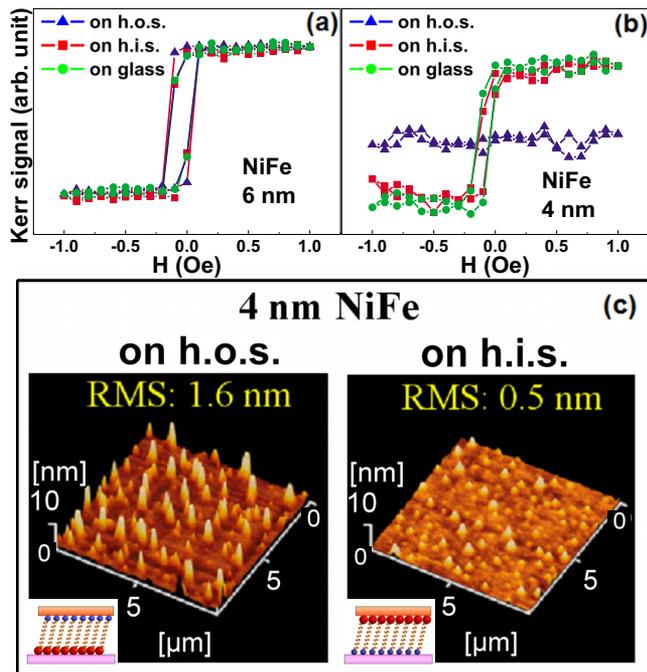


FIG. 4. (Color online) Magnetic and surface characterizations of NiFe thin films on LB molecular underlayer. (a) and (b) show the hysteresis loops of 6 nm and 4 nm NiFe on three different surfaces, respectively. (c) shows the AFM images of 4 nm NiFe on h.o.s. and h.i.s.

corresponding roughness changes. Two conclusions can be drawn at this point: (1) the coercivity increases with the FM layer thickness (from 4 to 10 nm), provided that this coercivity increase is seen only in the samples with h.o.s. underlayer; and (2) the organic underlayer results in the roughening of the covering FM layer but the degree of roughening is indifferent to the types of the underlayer. The morphology also shows no significant difference between the FM films on different organic surfaces at various thicknesses, as indicated by the AFM images. Due to the facts that there is no obvious morphological difference between the CoFe films on different kinds of molecular surfaces [see Fig. 3(c)], and that the surface morphology of pure LB films is also similar regardless of the molecular orientation [see Figs. 2(a) and 2(b)], morphological effect is less likely to be the cause that enhances the coercivity. Further experiments such as the characterization of crystalline structure, ordering of LB film, and magnetic domain structure are under consideration to reveal the actual mechanism responsible for this enhancement.

As for the NiFe (permalloy) films, the LB molecular underlayer has no impact on their coercivity at the thicknesses of 5 and 6 nm [see Fig. 4(a)]. But in the consequence of FM thickness variation, we found that the room-temperature ferromagnetism of permalloy thin film on h.o.s. vanishes when its thickness is reduced to 4 nm, as indicated by the MOKE results in Fig. 4(b). Figure 4(c) displays the AFM images of 4 nm NiFe films on h.o.s. and h.i.s. surfaces. Apparently morphology plays an essential role here. The surface of the film on h.o.s. is rougher with an rms roughness much larger than that on h.i.s., suggesting the origin of the FM vanishing is morphological. Similar results have been

reported in NiFe films by other researchers using less reactive functional group (methyl group) of SAM.<sup>18</sup> They attribute the vanishing of ferromagnetism to morphological disorder that interferes with the ferromagnetic behavior. The AFM results of our thicker NiFe films with h.o.s. and h.i.s. underlayers also display the morphological difference of similar degree, suggesting that the h.o.s. has a profound impact on the growth of the covering NiFe layer.

In conclusion, we have used a single type of organic molecules to create two different functional-group surfaces and to study the morphology and magnetism of the FM films, including CoFe and NiFe, deposited thereafter. AFM results reveal that the hydrophobic and hydrophilic molecular surfaces have similar and different impacts on the morphologies of CoFe and NiFe, respectively. MOKE results indicate that the h.o.s. causes coercivity variation in CoFe and magnetic suppression in NiFe, whereas the latter is considered morphologically related. These findings suggest that in designing future state-of-the-art molecular spintronic devices, functional group could be a key parameter in tuning the structural and magnetic properties of the participant FM materials.

This work was supported in part by the National Science Council of Taiwan under Grant No. NSC 98-2120-M-002-010.

- <sup>1</sup>Z. H. Xiong, D. Wu, Z. V. Vardeny, and J. Shi, *Nature (London)* **427**, 821 (2004).
- <sup>2</sup>V. Dediu, M. Murgia, F. C. Matocota, C. Taliani, and S. Barbanera, *Solid State Commun.* **122**, 181 (2002).
- <sup>3</sup>V. A. Dediu, L. E. Hueso, I. Bergenti, and C. Taliani, *Nature Mater.* **8**, 707 (2009).
- <sup>4</sup>S. Sanvito, *Nature Mater.* **6**, 803 (2007).
- <sup>5</sup>Z. V. Vardeny, *Nature Mater.* **8**, 91 (2009).
- <sup>6</sup>T. S. Santos, J. S. Lee, P. Migdal, I. C. Lekshmi, B. Satpati, and J. S. Moopera, *Phys. Rev. Lett.* **98**, 016601 (2007).
- <sup>7</sup>J. H. Shim, K. V. Raman, Y. J. Park, T. S. Santos, G. X. Miao, B. Satpati, and J. S. Moopera, *Phys. Rev. Lett.* **100**, 226603 (2008).
- <sup>8</sup>A. J. Drew, J. Hoppler, L. Schulz, F. L. Pratt, P. Desai, P. Shakya, T. Kreouzis, W. P. Gillin, A. Suter, N. A. Morley, V. K. Malik, A. Dubroka, K. W. Kim, H. Bouyanfif, F. Bourqui, C. Bernhard, R. Scheuermann, G. J. Nieuwenhuys, T. Prokscha, and E. Morenzoni, *Nature Mater.* **8**, 109 (2009).
- <sup>9</sup>M. Cinchetti, K. Heimer, J.-P. Wüstenberg, O. Andreyev, M. Bauer, S. Lach, C. Ziegler, Y. Gao, and M. Aeschlimann, *Nature Mater.* **8**, 115 (2009).
- <sup>10</sup>R. Vollmer, Th. Gutjahr-Löser, J. Kirschner, S. van Dijken, and B. Poelsema, *Phys. Rev. B* **60**, 6277 (1999).
- <sup>11</sup>W. Xu, J. Brauer, G. Szulczewski, M. S. Driver, and A. N. Caruso, *Appl. Phys. Lett.* **94**, 233302 (2009).
- <sup>12</sup>T. P. I. Saragi, C. Schmidt, K. Schultz, T. Weis, J. Salbeck, and A. Ehresmann, *J. Magn. Magn. Mater.* **321**, 2204 (2009).
- <sup>13</sup>J. R. Petta, S. K. Slater, and D. C. Ralph, *Phys. Rev. Lett.* **93**, 136601 (2004).
- <sup>14</sup>A. R. Rocha, V. M. García-Suárez, S. W. Bailey, C. J. Lambert, J. Ferrer, and S. Sanvito, *Nature Mater.* **4**, 335 (2005).
- <sup>15</sup>L. Bogani and W. Wernsdorfer, *Nature Mater.* **7**, 179 (2008).
- <sup>16</sup>T. C. Kreutz, E. G. Gwinn, R. Artzi, R. Naaman, H. Pizem, and C. N. Sukeik, *Appl. Phys. Lett.* **83**, 4211 (2003).
- <sup>17</sup>I. Carmeli, F. Bloom, E. G. Gwinn, T. C. Kreutz, C. Scoby, A. C. Gossard, S. G. Ray, and R. Naaman, *Appl. Phys. Lett.* **89**, 112508 (2006).
- <sup>18</sup>S. N. Ahmad, S. G. Rao, S. A. Shaheen, D. Magana, and G. F. Strouse, *Appl. Phys. Lett.* **92**, 112511 (2008).
- <sup>19</sup>D. K. Schwartz, *Surf. Sci. Rep.* **27**, 245 (1997).