Effect of thermal deformation on giant magnetoresistance of flexible spin valves grown on polyvinylidene fluoride membranes*

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We fabricated flexible spin valves on polyvinylidene fluoride (PVDF) membranes and investigated the influence of thermal deformation of substrates on the giant magnetoresistance (GMR) behaviors. The large magnetostrictive $Fe_{81}Ga_{19}$ (FeGa) alloy and the low magnetostrictive $Fe_{19}Ni_{81}$ (FeNi) alloy were selected as the free and pinned ferromagnetic layers. In addition, the exchange bias (EB) of the pinned layer was set along the different thermal deformation axes α_{31} or α_{32} of PVDF. The GMR ratio of the reference spin valves grown on Si intrinsically increases with lowering temperature due to an enhancement of spontaneous magnetization. For flexible spin valves, when decreasing temperature, the anisotropic thermal deformation of PVDF produces a uniaxial anisotropy along the α_{32} direction, which changes the distribution of magnetic domains. As a result, the GMR ratio at low temperature for spin valves with EB$\parallel \alpha_{32}$ becomes close to that on Si, but for spin valves with EB$\parallel \alpha_{31}$ is far away from that on Si. This thermal effect on GMR behaviors is more significant when using magnetostrictive FeGa as the free layer.

Keywords: giant magnetoresistance, flexible spin-valves, thermal expansion

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1. Introduction

Flexible giant magnetoresistance (GMR) spin valves,[1,2] which typically include a free ferromagnetic (FM) layer and a pinned FM layer separated by a nonmagnetic (NM) conductive layer,[3] play an important role in wearable devices due to their high sensitivity, light weight, and mechanical deformability.[4,5] When spin valves are used in various temperatures, the magnetic anisotropy of FM layers would intrinsically decrease with temperature increasing, which is harmful to the thermal stability of magnetic devices.[6–14] On the other hand, the thermal deformation of flexible substrates usually changes the magnetic anisotropy of FM layers due to the inverse magnetostrictive effect of magnetic materials, thus destabilizing the magnetotransport properties of spin valves.[15] Obviously, the thermal effect on the magnetotransport behaviors is critically important and needs to be considered for developing flexible magnetoelectronic or spintronics devices.[16,17]

Recently, a few works have been conducted to investigate the temperature dependence of magnetic anisotropy of magnetic films and to promote the thermal stability of magnetic devices.[18,19] To obtain a good thermal stability in high frequency applications, Phuoc *et al.* realized an increment of magnetic anisotropy with temperature in FeCoHf thin films fabricated by a gradient-composition deposition technique.[10] Shin *et al.* exhibited a control of the direction and uniformity of magnetic anisotropy in magnetostrictive $Fe_{72}Si_{14}B_{14}$ film by means of the inverse magnetostriction with an inner stress induced by the difference of the thermal expansion between the magnetic layer and the conductive layer.[12] In addition, the magnetic tunnel junction (MTJ), which requires a good thermal stability well beyond room temperature for the application in information storage, has also been studied in detail.[14] These previous studies focused on the films prepared on rigid substrates which usually induce an insignificant and isotropic mechanical strain under thermal deformation. In contrast, a number of flexible substrates possess a large and anisotropic thermal deformation. The investigation on magnetic devices grown on a flexible substrate which displays a significant thermal deformation is interesting but rare.

It is well known that β-phase polyvinylidene fluoride

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(PVDF) possesses a large anisotropic thermal expansion coefficient ($\alpha_{31} = -13$ ppm/k, $\alpha_{32} = -145$ ppm/k).[20] Because the coefficient along the α_{31} direction is smaller than that along the α_{32} direction, an in-plane uniaxial compressive strain is generated along the α_{31} direction by cooling PVDF membrane and transferred to magnetic layers grown in it, which results in the change of magnetic anisotropy via the inverse magnetostrictive effect. On the other hand, $Fe_{81}Ga_{19}$ (FeGa) alloy which exhibits the largest magnetostriction ($\sim$ 350 ppm for the typical bulk) among the various alloys not containing rare earth elements has been extensively applied as engineering materials in strain sensors and actuators.[21–24] The combination of FeGa alloy and PVDF membrane is a model system to investigate the influence of thermal deformation on the magnetic properties of magnetic films. Previously in FeGa/PVDF films we realized the enhancement of magnetic anisotropy with increasing temperature by utilizing the anisotropic thermal deformation of PVDF.[15] In this work, we investigated the effect of thermal deformation on the GMR behaviors of flexible spin valves grown on PVDF. The large magnetostrictive FeGa alloy and the low magnetostrictive FeNi alloy were selected as the free and pinned FM layers, and the exchange bias (EB) was set along the α_{31} or α_{32} axes of PVDF. With temperature decreasing, the anisotropic thermal deformation of PVDF produces a uniaxial anisotropy along the α_{32} direction, which could enhance the GMR ratio for spin valves with EB$\parallel \alpha_{32}$, but decrease the GMR ratio for spin valves with EB$\parallel \alpha_{31}$. This effect of thermal deformation on GMR behaviors becomes obvious when using magnetostrictive FeGa as the free layer.

2. Experimental

Spin valves with a structure of Cu(10 nm)/FM1(free layer, 5 nm)/Cu(2.5 nm)/FM2 (pinned layer, 5 nm)/IrMn(15 nm) [Fig. 1(a)] were fabricated at $T = 290$ K on flexible PVDF membranes and rigid Si wafers by using a magnetron sputtering system with a base pressure of 5.0×10^{-8} Torr. $Fe_{81}Ga_{19}$ (FeGa) and $Fe_{19}Ni_{81}$(FeNi) were selected as the FM1 and FM2 layers in a spin valve of SV-FM1/FM2. Before deposition, a negative photoresist (AR-P5350) layer was spin-coated on PVDF membranes to reduce the surface roughness. As shown in Fig. 1(b), the surface roughness can be decreased from 32.6 nm to 0.3 nm. A magnetic field of approximately 1000 Oe was provided by a permanent magnet to induce the exchange bias between the FM2 and antiferromagnetic layers. All samples were protected from oxidation by a 5-nm Ta layer. The surface morphology of the samples was characterized by atomic force microscopy (AFM) using Vecoo Dimension 3100V. The magnetic hysteresis loops and the magneto-transport characterizations for the spin valves were performed using a physical property measurement system (PPMS, Model-9). The GMR ratio is defined as the change of sample resistance under an external magnetic field.

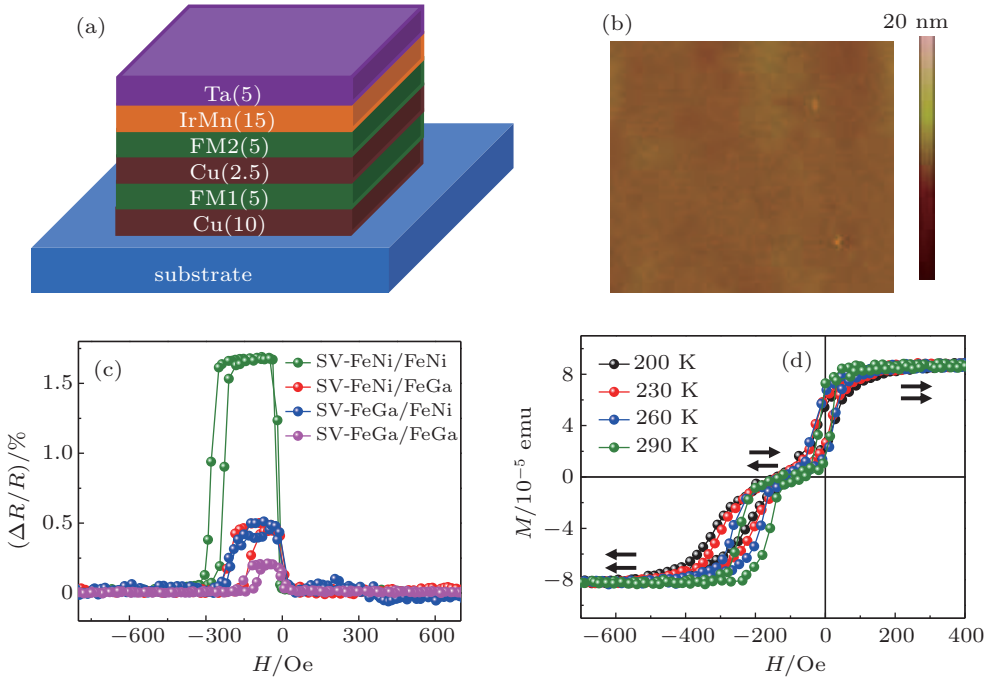


Fig. 1. (color online) (a) Schematic diagram of the spin-valve structures. (b) Topography (5 μm×5 μm) of a PVDF membrane after being spin-coated with a negative photoresist (AR-P5350) layer. (c) GMR curves for SV-FeNi/FeNi, SV-FeNi/FeGa, SV-FeGa/FeNi, and SV-FeGa/FeGa prepared on Si. (d) Hysteresis loops under various temperatures for SV-FeGa/FeGa prepared on PVDF with EB$\parallel \alpha_{31}$. The arrows indicate the parallel or antiparallel alignment of magnetic moments in the free and pinned layers.

3. Results and discussion

The rigid spin valve with the small magnetostrictive FeNi alloy used as both the free and pinned layers, i.e., SV-FeNi/FeNi, prepared on Si displays a GMR ratio about 1.78%, as shown in Fig. 1(c). When an FeGa layer is used as the free or pinned FM layers, that is SV-FeNi/FeGa and SV-FeGa/FeNi, both spin valves show a reduced GMR ratio of about 0.6%. When FeGa layers are used as both the free and pinned FM layers, i.e., SV-FeGa/FeGa, the GMR ratio is further decreased to 0.2%, which indicates that the presence of the FeGa/Cu interface leads to the significant reduction of the GMR ratio. When such spin-valve structures are grown on flexible PVDF, the hysteresis loops of flexible spin valves display an obvious temperature dependent behavior due to the large thermal deformation of PVDF. Taking the flexible SV-FeGa/FeGa with EB$\|$ α_{31} as an example, the magnetization curve shows two separate hysteresis loops, corresponding to the FeGa free layer and the FeGa/IrMn EB bilayer. With sweeping magnetic field, the magnetizations of the two FeGa layers can be changed between the parallel and antiparallel alignments, as shown in Fig. 1(d). In addition, the squareness of the minor loop of the FeGa free layer obviously decreases from 0.65 to 0.28 when cooling the sample from 290 K to 200 K. Correspondingly, the squareness of the EB minor loop of the FeGa pinned layer decreases from 0.63 to 0.35, and the EB field $H_{\rm eb}$ increases from 204 Oe to 284 Oe. The temperature dependence of loop squareness can be understood by considering the anisotropic thermal deformation of PVDF membranes. For polycrystalline magnetic films, the magnetic domains do not strictly orient along the uniaxial magnetic anisotropy, but have a distribution around this direction.[15,25,26] The tensile strain along the α_{32} direction caused by the anisotropic thermal deformation of PVDF on cooling the samples produces an additional uniaxial magnetic anisotropy along the α_{32} axis. For EB$\|$ α_{31}, the additional anisotropy would induce a broad distribution of domain orientations and decrease the loop squareness measured along the α_{31} axis. In contrast, for EB$\|$ α_{32}, the anisotropy along the α_{32} axis would result in a narrow distribution of domain orientations and increase the loop squareness measured along the α_{32} axis.

Prior to studying the effect of thermal deformation of flexible PVDF substrate on the GMR behaviors of spin valves, the intrinsic temperature dependence of GMR behaviors needs to be considered. Figure 2(a) shows the GMR curves measured at different temperatures for the reference SV-FeNi/FeNi prepared on rigid substrate. The GMR ratio intrinsically increases from 1.78% to 2.86% and the corresponding magnetic field sensitivity

$$S = \frac{1}{R_0}\frac{\mathrm{d}R}{\mathrm{d}H}\bigg|_{\mathrm{d}^2R/\mathrm{d}H^2=0},$$

which is determined by the slope of the minor loop of the free layer, increases from 0.06%/Oe to 0.15%/Oe when the temperature decreases from 290 K to 200 K. In addition, the squareness of GMR curves was often used to indicate the change of magnetic anisotropy,[27] and the squareness of the minor GMR curves for the pinned FeNi layer remains around 0.89 regardless of the variation of temperature, which indicates that due to the small and isotropic thermal expansion of silicon substrates ($\approx$ 2 ppm/K),[28] the contribution of mechanical strain on the magnetic anisotropy can be neglected. However, the spontaneous magnetization of ferromagnetic materials increases with temperature deceasing, which leads to the intrinsic increase of the GMR ratio. For this kind of SV-FeNi/FeNi grown on flexible PVDF, the GMR ratio increases from 0.94% to 1.46% for the configuration of EB$\|$ $\alpha_{31}$and increases from 1.4% to 2.2% when EB$\|$ α_{32}, as respectively shown in Figs. 2(b) and 2(c). Obviously, the GMR ratios for the three kinds of SV-FeNi/FeNi prepared on both Si and PVDF display the similar temperature dependence, as shown in Fig. 2(d). However, because of the different surface roughnesses, the GMR ratio of spin valve grown on Si is a little larger than that prepared on PVDF. For flexible SV-FeNi/FeNi with EB$\|$ α_{31}, the magnetic field sensitivity is close to 0.03%/Oe, but shows a slight decrease with temperature reducing. Corresponding, the squareness of the minor GMR curves for the pinned FeNi layer decreases from 0.69 to 0.62 when the temperature is reduced from 290 K to 200 K. As compared to the reference SV-FeNi/FeNi on Si, the thermal deformation of PVDF induces a uniaxial anisotropy along the α_{32} direction, which reduces the magnetic field sensitivity and the squareness of GMR curves for flexible SV-FeNi/FeNi with EB$\|$ α_{31}. For flexible SV-FeNi/FeNi with EB$\|$ α_{32}, the magnetic field sensitivity is close to 0.06%/Oe and slightly increases with temperature reducing and the squareness of the minor GMR curves for the FeNi pinned layer increases from 0.78 to 0.93 for the temperature varying from 290 K to 200 K due to the thermally induced uniaxial anisotropy along the α_{32} direction. Due to the very small coercivity of the FeNi free layer, the squareness of the FeNi free layer obtained by using the GMR curves has a considerable error. Roughly, for SV-FeNi/FeNi grown on Si, the squareness of the FeNi free layer remains around 0.96 regardless of the variation of temperature. For flexible SV-FeNi/FeNi with EB$\|$ α_{31}, the squareness of the FeNi free layer decreases from 0.61 to 0.53 when the temperature is reduced from 290 K to 200 K. For flexible SV-FeNi/FeNi with EB$\|$ α_{32}, the squareness of the FeNi free layer correspondingly increases from 0.81 to 0.87. The changes of squareness with temperature are similar to that of the FeNi pinned layer. Our experimental observations demonstrate that for spin valves using the low magnetostrictive FeNi alloy, the thermal deformation of flexible substrate shows a slight influence on the magnetic field sensitivity and the squareness of GMR curves.

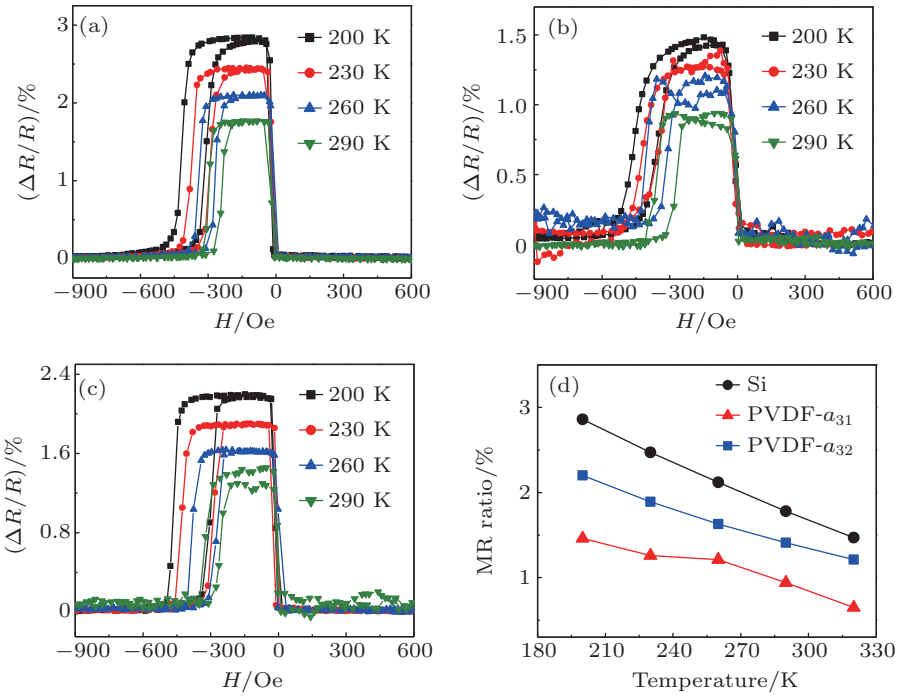


Fig. 2. (color online) GMR curves for SV-FeNi/FeNi prepared on (a) Si, (b) PVDF with EB$\|$ α_{31}, and (c) PVDF with EB$\|$ α_{32} with temperatures varied from 290 K to 200 K. (d) The temperature dependence of GMR ratio summarized from panels (a)–(c).

When the magnetostrictive FeGa alloy is used as free layers in spin valves, the GMR behaviors show an enhanced temperature dependence. For rigid SV-FeGa/FeNi prepared on Si, as shown in Fig. 3(a), the GMR ratio intrinsically increases from 0.45% to 0.64% when cooling the sample from 290 K to 200 K. The magnetic field sensitivity correspondingly increases from 0.01%/Oe to 0.02%/Oe and the squareness of GMR curves increases from 0.58 to 0.64 for the FeGa free layer, and increases from 0.67 to 0.72 for the FeNi pinned layer. In contrast, for the flexible SV-FeGa/FeNi prepared on flexible PVDF with EB$\|$ α_{31}, with decreasing temperature from 290 K to 200 K, the GMR ratio increases from 0.36% to 0.47% and the magnetic field sensitivity decreases from 0.009%/Oe to 0.004%/Oe, as shown in Fig. 3(b). Correspondingly, the squareness of the minor GMR curves decreases from 0.64 to 0.30 for the FeGa free layer and from 0.65 to 0.38 for the FeNi pinned layer. In case of EB$\|$ α_{32}, the GMR ratio increases from 0.4% to 0.63% and the magnetic field sensitivity increases from 0.011%/Oe to 0.021%/Oe for the temperature varying from 290 K to 200 K, as shown in Fig. 3(c). The corresponding squareness of GMR curves increases from 0.87 to 0.96 for the FeGa free layer, and increases from 0.59 to 0.87 for the FeNi pinned layer. In comparison with the FeNi free layer in SV-FeNi/FeNi, the FeGa free layer in SV-FeGa/FeNi shows a more pronounced temperature effect due to the larger magnetostriction of FeGa. Moreover, the squarenesses of GMR curves for both SV-FeNi/FeNi and SV-FeGa/FeNi show the similar temperature dependence caused by the thermal deformation of PVDF substrates, which indicates that both FeGa and FeNi are positive magnetostrictive. It should be noted that, the squarenesses of the minor GMR curves for the FeGa free layer for the three kinds of SV-FeGa/FeNi are different. At 290 K, they are 0.68, 0.64, and 0.87 for SV-FeGa/FeNi grown on Si, on PVDF with EB$\|$ α_{31}, and on PVDF with EB$\|$ α_{32}, respectively. This also can be interpreted by the anisotropic thermal deformation of PVDF substrates. During deposition of magnetic film even at an ambient temperature, the sample temperature would be slightly enhanced due to the illumination of atomic flux. After deposition, the sample is cooled to room temperature. Thus, a uniaxial anisotropy along the α_{32} direction is induced, which leads to a reduced squareness of the minor GMR curves for the FeGa free layer for the sample with EB$\|$ α_{31} and an enhanced squareness of the FeGa free layer when EB$\|$ α_{32}. Additionally, with the decrease of the temperature, the enhanced uniaxial anisotropy along the α_{32} direction can result in a broad distribution of magnetic domain orientations in the FeGa layer for EB$\|$ α_{31}, but lead to a narrow distribution of magnetic domains when EB$\|$ α_{32}. The distribution of domain orientations has a significant influence on the parallel and antiparallel magnetic configurations. As a result, with temperature decreasing, the GMR ratio for spin valves with EB$\|$ α_{32} becomes close to that on Si, but for spin valves with EB$\|$ α_{31} the value is far away from that on Si, as shown in Fig. 3(d). As compared to the flexible SV-FeNi/FeNi, the thermal deformation of PVDF substrates displays a more remarkable influence on the temperature dependence of GMR ratio of SV-FeGa/FeNi due to the utilization of magnetostrictive FeGa layer.

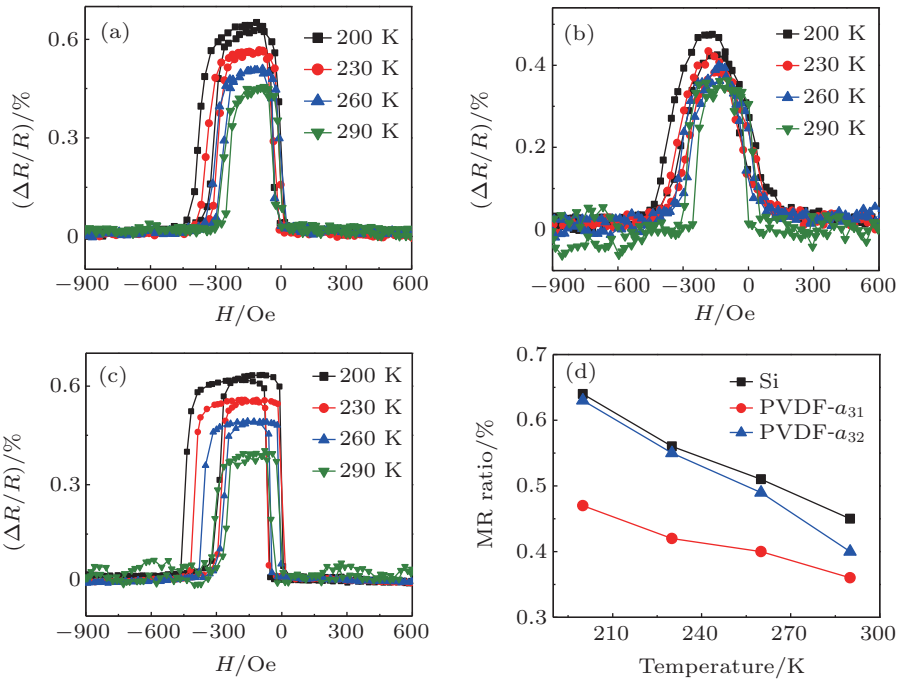


Fig. 3. (color online) GMR curves for SV-FeGa/FeNi prepared on (a) Si, (b) on PVDF with EB$\|$ α_{31}, and (c) on PVDF with EB$\|$ α_{32} under different temperatures varied from 290 K to 200 K. (d) The temperature dependence of GMR ratio summarized from panels (a)–(c).

4. Conclusions

In conclusion, we have systematically investigated the effect of thermal deformation of flexible PVDF substrate on the spin-valve structures where the large magnetostrictive FeGa and the low magnetostrictive FeNi alloys were selected as the free layer and the pinned layers. For flexible SV-FeNi/FeNi, the anisotropic thermal deformation of PVDF shows a slight influence on the magnetic field sensitivity and the squareness of GMR curves, but not on the GMR ratio. When the magnetostrictive FeGa layer is used as the free layer, i.e., SV-FeGa/FeNi, the thermal deformation of PVDF displays a more remarkable influence not only on the magnetic field sensitivity and the squareness of GMR curves, but also on the GMR ratio.

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