ADVANCED MATERIALS

Towards Flexible Magnetoelectronics: Buffer-Enhanced and Mechanically Tunable GMR of Co/Cu Multilayers on Plastic Substrates**

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Magneto- as well as flexible electronics have emerged as two of the most rapidly developing technologies of the 21st century. Low processing costs and mechanical stretchability render flexible electronic devices[1–6] highly attractive for a variety of applications such as flexible circuit boards,[7] solar cells,[8] paper-like displays,[9] and sensitive skin.[10] The giant magnetoresistance (GMR) effect, discovered in 1988,[11,12] is broadly applied in read heads in hard disk drives or in nonvolatile memory devices,[13] and has helped to initiate the development of magnetoelectronics (also known as spintronics).[14] Magnetoelectronics on flexible substrates allows the direct integration of GMR devices onto bendable supports, which can be shaped into almost any arbitrary geometry.[15] However, only limited progress has been made over the last years towards flexible magnetoelectronics due to the relatively small GMR effect achievable on plastics.[15–18] The establishment of high-performance flexible magnetoelectronics would open straightforward access to practical magnetic field sensors,[15,17,18] as well as promising perspectives towards accurate fine-tuning of the GMR by substrate stretching or bending.

In this study, we show that the GMR effect of Co/Cu multilayers (MLs) on a flexible plastic substrate can be enhanced up to 200% by introducing an appropriate buffer layer. GMR values of Co/Cu MLs on buffered flexible substrates are even larger than those on thermally oxidized Si substrates due to an increased antiferromagnetic coupling fraction. Furthermore, we experimentally demonstrate to tune (increase or decrease) the GMR effect, by applying external tensile stress through substrate stretching.

The sample structure is schematically shown in Figure 1a. Following a 1 nm Co bottom layer directly deposited on oxidized Si substrates or on flexible plastic substrates, N periods of Co/Cu bilayers were deposited. Except where stated differently, the plastic substrate in this study is made out of polyester, and the notation $(Co/Cu)_N$ MLs denotes N periods of Co_1 nm/Cu_1 nm bilayers with a Cu thickness corresponding to the first antiferromagnetic (AFM) coupling maximum. Figure 1b shows a photograph of circularly bended $(Co/Cu)_{20}$ MLs deposited on a polyester substrate, which demonstrates the excellent bendability of Co/Cu MLs on polyester substrates.

As presented in Figure 1c, GMR values measured at room temperature in a magnetic field of 0.2 Tesla are 34.4, 27.3, and 28.1% for $(Co/Cu)_{20}$ MLs deposited on Si, kapton, and polyester substrates, respectively. GMR values are a little larger than in a previous report and require a comparable lower magnetic field of 0.2 Tesla to obtain similar values as observed for 1.5 Tesla.[16] Still, GMR values of Co/Cu MLs deposited on plastic substrates are lower than those of Co/Cu MLs deposited on thermally oxidized Si (SiO_2/Si, shortened as Si) substrates, which is caused by the large surface roughness of plastic substrates.[19,20] It should therefore be possible to improve the GMR effect of Co/Cu MLs on flexible plastic substrates by introducing suitable buffer layers to smoothen the rough surfaces.

The surface morphology and the roughness were characterized by Atomic Force Microscopy. As shown in Figure 2d, the root mean square roughness, Rq, of the bare polyester (P) substrate is one order of magnitude larger than that of oxidized Si substrate (Si). After spin-coating a 2 μm photoresist (PR) buffer layer, the surface roughness of the PR buffered plastic substrate (PR+P), and the Co/Cu MLs deposited on it, decreases down to a similar value obtained for the oxidized Si substrate. As more bilayers are deposited, the roughnesses measured for the multilayers on PR+P and bare oxidized Si substrates remain constant within the experimental error. For the multilayers on bare plastic substrates, a systematic decrease of the surface roughness with increasing number of Co/Cu bilayers is observed, because the bilayers, themselves, act as a buffer to improve the growth conditions for the following bilayers.[20]

Figure 2a shows GMR values of $(Co/Cu)_{10}$ MLs on Si, P, and PR+P substrates, respectively. $(Co/Cu)_{10}$ MLs on P have the lowest GMR, while MLs on PR+P experience the highest GMR, which is ∼100%, and 57% higher than those of MLs deposited on P and Si, respectively. Figures 2b and c investigate the effect of the number of (Co/Cu) bilayers N on several GMR values and GMR ratios. From Figure 2b we find that for each N, GMR values of Co/Cu MLs deposited on bare plastic

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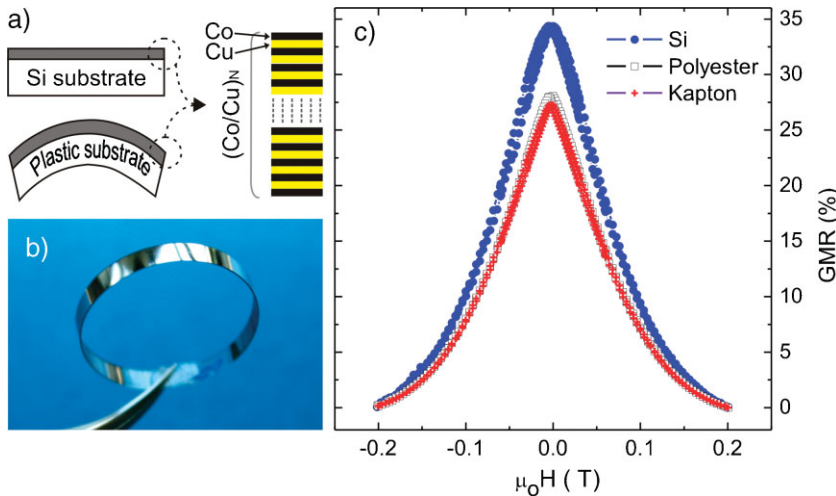Helmholtzstr. 20, 01069 Dresden (Germany)

Figure 1. a) Schematic illustration of $(Co/Cu)_N$ MLs deposited on Si and flexible substrates. b) A photographic image of circularly bended $(Co/Cu)_{20}$ MLs deposited on polyester substrate. c) GMR curves of $(Co/Cu)_{20}$ MLs deposited on polyester, kapton, and thermally oxidized Si substrates.

substrates are lower than those deposited on oxidized Si substrates. However, GMR values significantly increase after introducing a PR buffer layer and GMR values rise to even higher values than those achieved on Si substrates. The ratio between GMR values for various substrates is presented in Figure 2c as a function of the bilayer number N. With increasing N, the relative GMR enhancement decreases and approaches one as 50 bilayers are deposited.

It is not difficult to understand the GMR enhancement by PR buffering.[19,20] As shown in Figure 2d, after PR buffering, the surface roughness of the Co/Cu MLs decreases over one order of magnitude, which suggests that the interface roughness within the Co/Cu ML stack decreases after PR buffering and thus results in the enhancement of the GMR.[19] However, this cannot explain why the GMR values of Co/Cu MLs deposited on PR+P substrates are even larger than those of MLs deposited on Si because the surface roughness of MLs deposited on PR+P substrates are similar or even a little larger than those of MLs deposited on Si substrates.

Because only antiferromagnetically coupled regions of the MLs can contribute to the magnetoresistance, the antiferromagnetic coupling fraction (AFF) is generally used to quantify the fraction of MLs with antiparallel alignment of adjacent film magnetizations at a zero external magnetic field. The AFF is given by[20,21]

$$AFF = 1 - \frac{M_R}{M_S} \tag{1}$$

where M_R and M_S are the remnant and saturation magnetizations, respectively. Generally, M_R and M_S can be obtained from the magnetic hysteresis loops or magneto-optical-Kerr-effect (Moke) hysteresis loops.[20]
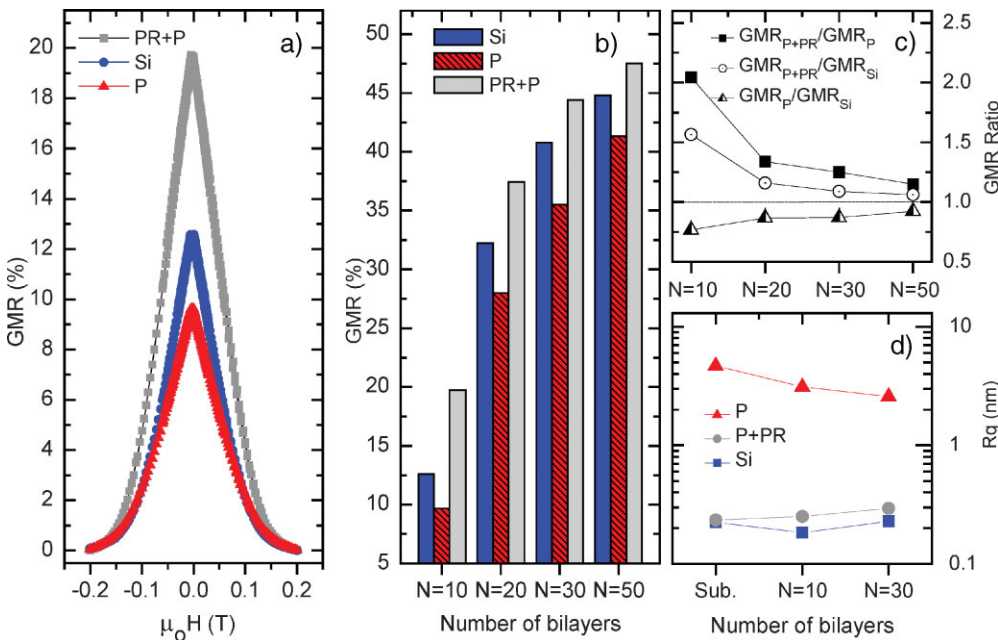
We measured Moke hysteresis loops of $(Co/Cu)_{10}$ MLs deposited on polyester and Si substrates with and without PR buffer layers, respectively. As checked from hysteresis loops in Figure 3a and b, the AFF of $(Co/Cu)_{10}$ MLs becomes larger after PR buffering for both plastic and Si substrates. The AFF values can be directly calculated from Moke hysteresis loops using Equation 1. The substrate effect on the AFF and GMR of $(Co/Cu)_{10}$ MLs is shown in Figure 3c. There is a good correlation between the AFF and GMR for $(Co/Cu)_{10}$ MLs deposited on various substrates. AFF values of $(Co/Cu)_{10}$ MLs on P, Si, PR+P, and PR+Si are 0.102, 0.132, 0.238, and 0.25, respectively. The AFF value of MLs on PR+P is 2.33, and

Figure 2. a) GMR curves of $(Co/Cu)_{10}$ MLs deposited on Si, Polyester (P), Photoresist buffered Polyester (PR+R) substrates. b) GMR comparison of $(Co/Cu)_N$ MLs on various substrates with different numbers of bilayers. c) GMR ratio of $(Co/Cu)_N$ MLs deposited on Si, P, and PR+P substrates. d) Root mean square roughness, Rq, of Si, P, PR+P bare substrate and Co/Cu films on corresponding substrates.
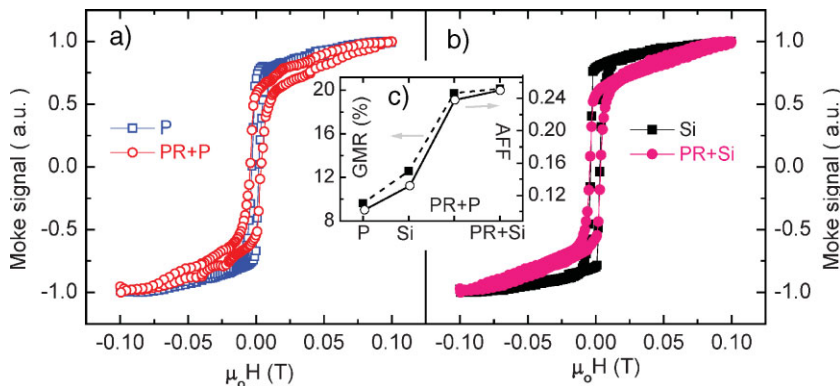
Figure 3. Moke hysteresis loops for (Co/Cu)$_{10}$ MLs deposited on a) P and PR+P substrates and b) Si and PR+Si substrates. c) Effect of substrate on the GMR and AFF.

1.80 times larger than those of MLs deposited on bare polyester and bare oxidized Si substrates, respectively. Both the AFF and GMR of MLs on PR+Si substrate are the highest. This implies that the PR buffer layer is effective to increase the AFF not only for the plastic substrate but also for the oxidized Si substrates and thus enhance the GMR effect.

As discussed above, we can conclude that the PR buffer layer can improve the interface quality and increase the anti-ferromagnetic coupling fraction of Co/Cu MLs, which leads to the increase of the GMR effect. This may be used to explain why the GMR of Co/Cu MLs deposited on plastic substrates significantly increases after PR buffering, and why the GMR of Co/Cu MLs deposited on PR-buffered plastic substrate is even larger than that of MLs deposited on Si substrate.

Previous experimental and theoretical investigations have shown that for Fe/Cr and Co/Cu MLs, a small variation of the thickness of nonmagnetic spacer-layers will dramatically change the GMR effect especially around the AFM coupling maximum due to the Ruderman–Kittel–Kasuya–Yosida (RKKY) oscillatory feature of the exchange coupling strength.[22–29] In the following, we show that Co/Cu MLs deposited on plastic substrates also reveal a similar oscillatory feature with varying Cu thickness. We investigate the influence of externally applied stress on the GMR of MLs deposited on flexible plastic substrates.

In order to check the oscillatory feature, we prepared a series of (Co_1 nm/Cu_t nm)$_{30}$ MLs on polyester substrates with various thicknesses t near the critical thickness corresponding to the first AFM coupling maximum (t_{AFM}) ranging from 0.89–1.06 nm. As shown in Figure 4, GMR of (Co_1 nm/Cu_t nm)$_{30}$ MLs deposited on polyester substrates shows an oscillatory behavior, which is similar to previous reports for MLs deposited on oxidized Si substrates.[26–29] It should be noted that GMR values of present Co/Cu MLs on polyester substrates also strongly vary with the Cu thickness especially near t_{AFM}. For example, a variation of the Cu thickness near t_{AFM} on the order of 1–3% causes a change of the GMR on the order of 10–50%. This suggests that the GMR effect with the Cu thickness near t_{AFM} can probably be tuned by changing the Cu spacer thickness through substrate stretching. As

schematically shown in the bottom inset in Figure 5a and b, an applied uniaxial tensile stress leads to a remnant strain (ε) along the longitudinal direction of the sample with a width (w_0) of 3 mm and a length (L_0) of 60–70 mm. We assume that the decrease in width is negligible compared to the change in the layer thickness under a small strain less than 3%, i.e., $w_\varepsilon \approx w_0$. Obeying the volume conservation for the Cu spacer layer before and after a strain, $L_\varepsilon w_\varepsilon t_\varepsilon = L_0 w_0 t_0$, where t_0 and t_ε are the thicknesses of Cu layer before and after strain respectively, and considering $L_\varepsilon = L_0 (1 + \varepsilon)$, we obtain

$$t_\varepsilon = t_0/(1 + \varepsilon) \qquad (2)$$

That means, a remnant tensile strain ε of 1–3% leads to a reduction of Cu thickness between 0.99–2.9%, which may significantly change the strength of the interlayer exchange coupling and thus the GMR effect.

Figure 5 experimentally demonstrates that the GMR of Co/Cu MLs deposited on polyester substrates can be adjusted (increased or decreased) by stretching samples. The variation of GMR with increasing strain can be explained by the change in the Cu thickness (and thus the coupling strength) as shown in Figure 4. In Figure 5a, when the initial Cu thickness is thicker than t_{AFM} (region III), the GMR of Co/Cu MLs rises with increasing strain. The top inset in Figure 5a shows that the GMR of MLs obviously increases after stretching ($\varepsilon = 2.7\%$),
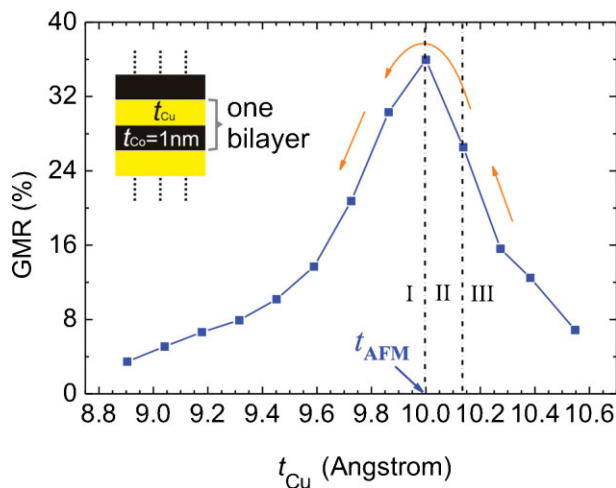

Figure 4. GMR values as a function of Cu thickness for (Co_1 nm/Cu_t nm)$_{30}$ MLs deposited on polyester substrates. t_{AFM} denotes the critical Cu thickness at the first anti-ferromagnetic coupling maximum. Region I (or III) denotes region where Cu thickness is thicker (or thinner) than t_{AFM}, and region II denotes region where the Cu thickness is a little thicker but very near t_{AFM}. The arrows indicate the expected trend of the GMR when decreasing the Cu thickness. The inset schematically shows the sample structure with a Co thickness of ~1 nm and a Cu thickness of t nm as used for different samples.
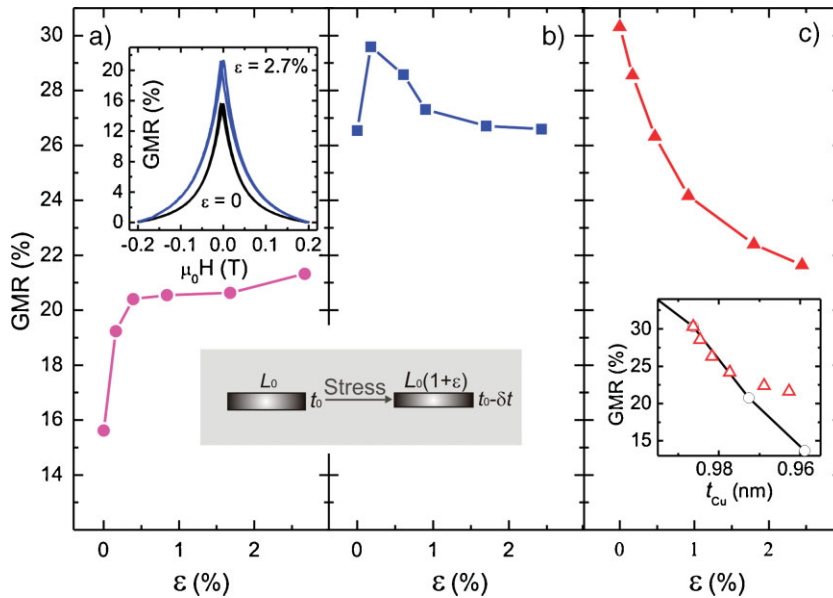
Figure 5. Strain-dependent GMR of (Co_1 nm/Cu_t nm)$_{30}$ MLs deposited on polyester substrates under 0.2 Tesla with various initial Cu spacer thicknesses of $t_{Cu} = 1.027$ nm (a), $t_{Cu} = 1.014$ nm (b), and $t_{Cu} = 0.986$ nm (c). The top inset in (a) shows the GMR curves before (0) and after strain (2.7%). The bottom inset in (a) and (b) schematically shows the Cu thickness decreases under an external tensile strain. The bottom inset in (c) shows the GMR depending on the Cu thickness calculated from Equation 2 (open triangle symbols) in comparison with the experimental data directly taken from Figure 4 (solid line with open circle symbols).

because in this case the decrease in the Cu thickness leads to an increase in the AFM coupling strength. However, when the initial Cu thickness is thinner than t_{AFM} (region I), increasing strain leads to a decrease of the AF coupling strength resulting in a smaller GMR. This case is shown in Figure 5c. If the initial Cu thickness is a little thicker than but very near t_{AFM} (region II), increasing strain leads to an initial increase and then decrease the GMR, and this behavior is indeed observed in Figure 5b. Our results demonstrate that the GMR effect can be accurately controlled by substrate stretching, which seems to induce a change of the Cu spacer layer thickness and therefore alters the strength of the interlayer exchange coupling.

The bottom inset in Figure 5c shows the Cu thickness dependent GMR in comparison with the experimental data directly taken from Figure 4 (solid line with open circle symbols), where the Cu thickness is calculated from Equation 2 (open triangle symbols). As long as the strain is less than 1%, both curves agree well with each other; while for larger strain values the curve drifts apart. Thus, it is difficult to explain quantitatively the variation in GMR only by considering the strain-induced t_{Cu}, especially when the applied strain is sufficiently large. For example: i) Strain may modify the Fermi surface with respect to the bulk and hence also the periods of the oscillatory coupling, which then leads to the variation of GMR values.[30] Such an effect was taken to explain the GMR variation of Co/Cu multilayers subject to high pressure.[31] ii) Structural defects, e.g., micro-cracks, could be formed in the MLs when the strain is sufficiently large (e.g., $\varepsilon > 1\%$), which may enhance the

spin-independent scattering and generally result in a decrease in GMR values.[32] It is noticeable, though, that in Figure 5a, we observe a GMR increase with increasing strain, which is hard to explain by the generation of defects. Detailed theoretical analyses as well as further experimental investigations are necessary to clarify the mechanisms in stretched GMR multilayers.

Finally, we carried out bending experiments for Co/Cu MLs on polyester substrates. For this purpose we fixed one end of a Co/Cu MLs/polyester stripe with a width of 3 mm and a length of 70 mm and bended the other end of the stripe elastically into a semi-circular shape with a diameter of ∼45 mm. One end of the stripe was then released and the sample unbended to its initial straight state to complete a full bending/unbending cycle. There were no changes in both the resistance and magnetoresistance measurements before and after 1000 bending/unbending cycles. In addition, our Co/Cu MLs on plastic substrates can easily be cut into arbitrary irregular shapes and geometries without changing the GMR effect, which render these structures interesting candidates for, e.g., fully flexible and high performance magnetic-field sensors.

In conclusion, the GMR effect of Co/Cu MLs deposited on photoresist-buffered flexible substrates is enhanced up to 115–200% for (Co/Cu)$_N$ MLs (with N ranging from 50 to 10) compared to those directly deposited on bare plastic substrates. Using nowadays available ultra-smooth plastic substrates (RMS roughness <1–2 nm), similar or even better GMR values might be achievable. These GMR values are even higher than those of MLs deposited on oxidized Si substrates. The performance enhancement is explained by a decrease of the interface roughness and an increase of AFF values. We also demonstrate that the GMR effect can be mechanically tuned and explained by varying the Cu thickness by applying an external stress. Bending experiments confirm excellent flexibility and stability of our structures. Considering the low-cost, full flexibility, and large GMR effect, Co/Cu MLs on plastic substrates constitute a promising technology towards a new generation of flexible magnetoelectronics.

Experimental

Deposition of Co/Cu MLs: The Co/Cu MLs samples in this study were deposited by dc magnetron sputtering of Co and Cu targets, respectively. The base pressure of the sputter system was 1×10^{-5} Pa. Argon with a purity of 99.998% was introduced as a working gas. The sputter pressure was 0.5 Pa and the deposition rate of Co was fixed at ∼0.05 nm s^{-1}, while the deposition rate of Cu was adjusted in the region of 0.02–0.12 nm s^{-1} by changing the power for the Cu target. Various

thicknesses of Cu layers can be obtained by adjusting the deposition time and/or the power of the Cu target.

Several series of $(Co/Cu)_N$ MLs with various bilayer number N were prepared on thermally oxidized Si (Si), photoresist (PR) buffered Si (PR+Si), kapton, bare polyester (Soennecken, Germany) and PR buffered polyester (PR+P) substrates. In order to make comparison for the GMR of $(Co/Cu)_N$ MLs deposited on various substrates, we deposited MLs on various substrates in a single run to exclude the effects from different deposition conditions.

Preparation of Photoresist Buffer Layer: AR-P 3510 positive photoresist (Allresist, Germany) was spin-coated on plastic or oxidized Si substrates at a rotation speed of 3500 rpm. Then the PR-buffered substrates were put on a hot plate to perform a soft baking at 95 °C for 1 minute. The thickness of the buffer layer is about 2 μm.

GMR Measurement: A conventional four-point technique and a current-in-plane configuration were used to measure the GMR of Co/Cu MLs at room temperature under 0.2 Tesla. The GMR ratio was calculated by $(R_0 - R_H)/R_H$, where R_0 is the maximum resistance near zero magnetic field, and R_H is the resistance at the high magnetic field (0.2 T).

Moke Hysteresis Loop Measurement: The Moke hysteresis loops were measured in a home-made Moke system in an in-plane configuration under a maximal magnetic field of ± 0.1 T.

Characterization of Strain Dependence of GMR: The remnant tensile strain was performed by an Instron 8562 testing machine. The Co/Cu MLs deposited on a plastic substrate with a thickness of 0.1 mm, a width of 3 mm, and a length of 60–70 mm is prepared for experiments. The strain control mode and a strain rate of $1 \times 10^{-4}\,\mathrm{s}^{-1}$ were used. Firstly, we measure the GMR of the Co/Cu MLs before strain; then perform a loading and unloading cycle to get a certain remnant tensile strain, and take out the sample to measure the GMR; perform a larger remnant strain and measure corresponding GMR again; repeat the procedure and finally to obtain the strain dependence of GMR in a strain range of 0–3%.

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