Large exchange bias in polycrystalline MnN/CoFe bilayers at room temperature

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Spinelectronics is becoming an increasingly important future technology for the realization of nonvolatile, fast, low-power computer memory and is already well-established in hard disk drive read heads and magnetic sensors\cite{1,2}. The often required magnetic films that do not respond to external magnetic field, the so-called fixed layers, are achieved by pinning them to an antiferromagnet via the exchange bias effect, which causes a shift of the magnetic loop\cite{3}. In the present letter we report on the new polycrystalline exchange bias system MnN/CoFe, which shows exchange bias of up to 1480 Oe at room temperature. The corresponding interfacial exchange energy is $J_S = 0.38 \text{erg/cm}^2$ and the maximum blocking temperature at which the exchange bias vanishes is about 300$^\circ$C. Thus, the bilayers show exchange bias properties that partly excel those of standard PtMn/CoFe, IrMn/CoFe, or NiMn/NiFe bilayers\cite{4,5}, however without the need for noble metals or other critical materials.

The key component in spinelectronic devices, a magnetoresistive element using either the giant magnetoresistance (GMR) or tunnel magnetoresistance (TMR), is comprised of two magnetic films: a free sense-layer and a fixed reference layer. The ferromagnetic free layer is free to follow external magnetic fields or can be switched by a current via the spin transfer torque. The reference layer has to be stable against external fields to allow for different magnetic alignments of the two layers, which give rise to the magnetoresistance. Usually the fixed layer is obtained by pinning a thin ferromagnetic film (FM) to an antiferromagnetic film (AFM). The exchange bias (EB) associated with this pinning shifts the magnetic hysteresis of the free layer to fields that are not encountered during normal device operation. The antiferromagnet has to meet a number of criteria to be suitable for integration into such stacks:

1. Temperature stability: the temperature at which the exchange bias of the AFM/FM stack vanishes (the so-called blocking temperature) has to be significantly larger than the device operation temperature.

2. Exchange bias and coercive fields: the exchange bias field has to be significantly larger than the coercive field to allow for a clear separation of the parallel and antiparallel magnetic states of the GMR or TMR stack.

3. Ease of manufacturing: processing with industry-standard magnetron sputtering onto Si wafers is desired, hence polycrystalline systems have to meet the above criteria. High annealing temperatures above 300$^\circ$C and deposition at elevated temperature should also be avoided for integration with semiconductor technology.

4. Environmental safety and price: for large-scale application the price of the material will play a crucial role. Also, use of unsafe or otherwise critical materials should be avoided.

The criteria 1 to 3 are mostly met by the commonly used antiferromagnets PtMn and IrMn\cite{6,7}, although PtMn requires high temperature annealing to form the antiferromagnetic phase. However, criterion 4 is obviously violated: Pt and Ir are rare, expensive, and mining for them causes considerable environmental pollution\cite{8}. Thus, alternatives to these noble-metal based systems are needed. Other antiferromagnets, such as FeMn and NiMn have poor corrosion resistance or the ratio of exchange bias and coercive fields is not ideal for application\cite{9}.

In the present letter we report on a new exchange bias system that is as good as present standard systems, however not needing expensive precious metals or other critical materials. Our system is based on the antiferromagnet MnN. It crystallizes in the $\theta$-phase of the Mn-N phase.
The MnN thickness was 30 nm. The samples were annealed at 325 °C for 15 min. Dotted lines are guides to the eye throughout this letter.

To investigate the suitability of MnN as an antiferromagnet for exchange bias applications, we prepared film stacks of Ta 10 nm / MnN tMnN / CoFe tCoFe / Ru 2 nm on thermally oxidized Si wafers by (reactive) dc magnetron sputtering at room temperature. The MnN films were prepared in an atmosphere of Ar 60% : N2 40% at a working pressure of 1.5 · 10−3 mbar with a rate of 0.1 nm/s. The sputter deposition system operated at a base pressure of 2 · 10−7 mbar. Subsequent post annealing and field cooling in a magnetic field of 6.5 kOe was done in a vacuum furnace. Magnetic characterization of the stacks was performed using the longitudinal magneto-optical Kerr effect (MOKE) at room temperature. X-ray diffraction on the films showed that the MnN has [100] texture on Ta with a = 4.21...4.30 Å, i.e. the tetragonal c-axis is in the film plane.

In Figure 1 we show a magnetic loop of an optimized MnN/CoFe bilayer with tMnN = 30 nm and tCoFe = 1.5 nm. It shows high exchange bias and a reasonably low coercive field with a squareness of S = Msat/M(HEB) ≈ 0.63. The small asymmetry of the curve arises from a quadratic contribution to the MOKE. The ferromagnet is fully saturated at zero external field. In the follow-

The Néel temperature of this compound is about 660 K [9–11]. The Néel transition is accompanied by a tetragonal-to-cubic structural transformation caused by magnetostriction.

dependence of the exchange bias field and coercive field on the film thicknesses. a, The dependence of HEB and HC on the MnN thickness. The CoFe thickness was 2.0 nm. b, The dependence of HEB and HC on the CoFe thickness. The MnN thickness was 30 nm. The samples were annealed at 325 °C for 15 min. Dotted lines are guides to the eye throughout this letter.

FIG. 3. Dependence of the exchange bias field on annealing temperature and duration. The samples with MnN 30 nm / CoFe 1.9 nm were annealed and field cooled at temperature T A for different times tA. a, Samples successively heated for tA with increasing temperature T A. b, Same data, parametrized with annealing temperature T A.

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ing we discuss the variation of various stack parameters to identify the optimum deposition and post-annealing conditions for the MnN/CoFe stacks to maximize the exchange bias field and simultaneously minimize the coercive field of the CoFe.

Figures 2a and 2b display the variation of the exchange bias field $H_{EB}$ and the coercive field $H_C$ with the film thicknesses $t_{MnN}$ and $t_{CoFe}$. For the MnN thickness variation a clear maximum of $H_{EB}$ was observed at $t_{MnN} = 30$ nm. Below $t_{MnN} = 12$ nm no exchange bias was detected, and below $t_{MnN} = 7$ nm the coercive field was not even enhanced. The maximum of the exchange bias is found for much larger AFM thickness as compared to IrMn (7 nm) or PtMn (20 nm).

The CoFe thickness variation, shown in Fig. 2b has a maximum at $t_{CoFe} = 1.5$ nm and the usual $t_{CoFe}$ dependence for larger CoFe thickness. At lower thickness, the exchange bias drops sharply. The hyperbolic part allows to determine the interfacial exchange energy $J_S = t_{CoFe} M_{CoFe} H_{EB} = 0.38 \text{ erg/cm}^2$ using the saturation magnetization of $M_{CoFe} \approx 1700 \text{emu/cm}^2$ for our Co$_{70}$Fe$_{30}$ composition. This exchange energy is significantly larger than that of typical IrMn/CoFe stacks and is comparable to that of NiMn/NiF or PtMn/CoFe. Chemically well ordered Mn$_3$Ir in contact with CoFe was shown to provide $J_S > 1 \text{ erg/cm}^2$. However, ordered Mn$_3$Ir requires careful temperature control during deposition and needs an additional high temperature annealing.

As shown in Figure 3a, a broad range of annealing and field cooling conditions is available to obtain high exchange bias with the MnN/CoFe stack. The exchange bias depends on both the annealing temperature and the annealing time. With increasing temperature, less time is required to have the highest exchange bias. The same data are shown in Figure 3a with a different parametrization. Here one can see that annealing at 275°C gives an exchange bias above 1000 Oe with annealing times between 5 and 240 min. If necessary for the remainder of the film stack, lower or higher annealing temperatures between 225 and 325°C can equally well be chosen when the annealing time is adapted accordingly. The drop of the exchange bias at high annealing temperatures and long annealing times indicates thermal degradation of the bilayer due to diffusion.

The blocking temperature of the AFM/FM stack is a crucial parameter for device operation. In fact, such a stack does not have a single blocking temperature. Rather, there is a typically broad distribution of blocking temperatures, which depend on the grain sizes of the involved films. To quantify this distribution for our films, we performed reversed field cooling experiments. In a first step, the exchange bias was set by field cooling from 300°C to room temperature in a field of 6.5 kOe and the magnetic loop was measured. Thereafter, the sample was field cooled from successively increasing temperatures $T_r$ in a reversed magnetic field of $-6.5 \text{kOe}$ and magnetic loops were taken at room temperature. The results from this procedure are shown in Fig. 4a. While the coercive field remains essentially unaffected as expected, the exchange bias field goes through zero at about 140°C and is not completely restored after reversed field cooling from 300°C. This small degradation is in line with the annealing time dependencies discussed earlier (cf. Figure 3). The zero of the exchange bias field marks the point at which exactly half of the film volume has reversed due to reversed field cooling, i.e. the corresponding AFM/FM grains were unblocked at the reversal temperature $T_r$. Thus, it marks the median blocking temperature $\langle T_B \rangle$.

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From the $H_{EB}(T_r)$ dependence we obtain the volume fraction of unblocked grains, the so-called unblocked ratio $UBR(T_r)$ as

$$UBR(T_r) = 100 \% \cdot \left[ \frac{H_{EB}(RT) - H_{EB}(T_r)}{2H_{EB}(RT)} \right],$$

which represents the cumulative distribution function of the blocking temperature. Consequently, the blocking temperature distribution is obtained by taking the derivative $dUBR(T)/dT$. $UBR(T_r)$ and its derivative

**FIG. 4. Exchange bias and coercive field of a MnN/CoFe stack in a reversed field cooling experiment.** a. The sample with MnN 30 nm / CoFe 1.9 nm was set by field cooling from 300°C (after 15 min annealing) and then successively reverse field cooled for 15 min per point with increasing temperature. b. Derived unblocked ratio and distribution. The distribution is obtained by differentiating the unblocked ratio, which describes the fraction of antiferromagnetic grains that are above their blocking temperature at the respective temperature. The dashed line represents a fit of two Gaussians to the distribution.
are shown in Figure 4b. The blocking temperature distribution shows two maxima, one at around 125°C and another one at 250°C. This bimodal distribution is rather unusual for exchange bias systems and its origin is the subject of further studies we conduct. It probably indicates the existence of at least two different populations of AFM/FM coupled grains with two different grain size distributions or may be related to the in-plane orientation of the crystallographic c-axis with respect to the exchange bias field. The blocking temperature distribution goes almost to zero at 300°C, indicating the maximum blocking temperature in this system. By fitting two Gaussians to the blocking temperature distribution we extract the full width at half maximum (FWHM) of the two peaks to be 94 K (larger peak) and 71 K (smaller peak), respectively.

Finally, we investigated the films for effects of repeated magnetic reversal, the so-called training effect. By repeatedly switching the MnN/CoFe stacks for up to 150 times, we found that the training effect is negligible in this system. Only in some cases, the first loop exhibited about 5% larger exchange bias and coercive fields than all following loops.

Our findings demonstrate that MnN is a useful antiferromagnet for exchange biasing in spin-electronic devices. The MnN/CoFe system has large exchange bias, reasonably large blocking temperature and is cheap in terms of materials and processing cost.

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1 Gregg, J. F., Petej, I., Jouguelet, E. & Dennis, C. Spin electronics—a review. J. Phys. D: Appl. Phys. 35, R121 (2002).
2 Chappert, C., Fert, A., & Nguyen Van Dau, F. The emergence of spin electronics in data storage. Nature Materials 6, 813 (2007).
3 Nozières, J. & Schuller, I. K. Exchange bias. J. Magn. Magn. Mater. 192, 203 (1999).
4 Berkowitz, A. E. & Takano, K. Exchange anisotropy a review. J. Magn. Magn. Mater. 200, 552-570 (1999).
5 Nozières, J. P. et al. Blocking temperature distribution and long-term stability of spin-valve structures with Mn-based antiferromagnets. J. Appl. Phys. 87, 3920 (2000).
6 Ali, M. et al. Antiferromagnetic layer thickness dependence of the IrMn/Co exchange-bias system. Phys. Rev. B 68, 214420 (2003).
7 Rickart, M., Guedes, a., Ventura, J., Sousa, J. B. & Freitas, P. P. Blocking temperature in exchange coupled MnPt-CoFe bilayers and synthetic antiferromagnets. J. Appl. Phys. 97, 10K110 (2005).
8 Glaister, B. J., Mudd, G. M. The environmental costs of platinumPGM mining and sustainability: Is the glass half-full or half-empty? Minerals Engineering 23, 435 (2010).
9 Otsuka, N., Hanawa, Y. & Nagakura, S. Crystal Structure and Phase Transition of Mn3N2 Studied by Electron Diffraction. Phys. Status Solidi (a) 43, K127 (1977).
10 Suzuki, K. et al. Crystal structure and magnetic properties of the compound MnN. J. Alloys Compd. 306, 66 (2000).
11 Leineweber, A., Niewa, R., Jacobs, H. & Kockelmann, W. The manganese nitrides α-Mn3N2 and θ-Mn6N5+x: nuclear and magnetic structures. J. Mater. Chem. 10, 2827 (2000).
12 Trudel, S. et al. Note: Probing quadratic magneto-optical Kerr effects with a dual-beam system. Rev. Sci. Instrum. 81, 026105 (2010).
13 Tsunoda, M., Imakita, K., Naka, M. & Takahashi, M. L12 phase formation and giant exchange anisotropy in Mn3Ir/CoFe bilayers. J. Magn. Magn. Mater. 304, 55 (2006).
14 Reck, R. A. & Fry D. L., Orbital and Spin Magnetization in Fe-Co, Fe-Ni, and Ni-Co. Phys. Rev. 184, 492 (1969).

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AUTHOR CONTRIBUTIONS

M.M. designed the research and wrote the manuscript. M.D. performed experimental work and data analysis.

COMPETING FINANCIAL INTERESTS

The authors declare that they have no competing financial interests.