Artificially engineered Heusler ferrimagnetic superlattice exhibiting perpendicular magnetic anisotropy

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To extend density limits in magnetic recording industry, two separate strategies were developed to build the storage bit in last decade, introduction of perpendicular magnetic anisotropy (PMA) and adoption of ferrimagnetism/antiferromagnetism. Meanwhile, these properties significantly improve device performance, such as reducing spin-transfer torque energy consumption and decreasing signal-amplitude-loss. However, materials combining PMA and antiferromagnetism rather than transition-metal/rare-earth system were rarely developed. Here, we develop a new type of ferrimagnetic superlattice exhibiting PMA based on abundant Heusler alloy families. The superlattice is formed by [MnGa/Co2FeAl] unit with their magnetizations antiparallel aligned. The effective anisotropy (Ku eff) over 6 Merg/cm² is obtained, and the SL can be easily built on various substrates with flexible lattice constants. The coercive force, saturation magnetization and Ku eff of SLs are highly controllable by varying the thickness of MnGa and Co2FeAl layers. The SLs will supply a new choice for magnetic recording and spintronics memory application such as magnetic random access memory.

Nanometer ferromagnets have been widely used in storage media, non-volatile memory and logical devices based on spintronics, where the magnetization is manipulated by magnetic field, spin-polarized current, and electric field. As demanded by cell minimization, ferromagnets employed for information storage experienced a transition from in-plane to perpendicular magnetization in last decades. Several types of ferromagnets with perpendicular magnetic anisotropy (PMA) were developed to fulfill this request, including tradition/noble metal alloys/multilayers (e.g, FePt, CoPt alloys), rare-earth/transition metal alloys, newly developed CoFeB thin films, and recent promising tetragonal Heusler alloys. The high Ku eff is necessary to overcome the thermal fluctuation as cell lateral size minimization. Additional advantages are the low energy consumption of the spintronics-devices manipulated by spin-transfer torque (STT) and the simplified head structure for Hard disk drive storage. Beyond the stability requested for individual cells, the long-range static magnetic interaction between neighboring magnetic units becomes critically important as the density increasing when facing the integration of devices. As the bit distance decreases, a collective behavior occurs as a result of the dipolar interaction. Ferrimagnetic/antiferromagnetic materials were proposed as recording media, owing to the fact that the distance between ferrimagnetic especially antiferromagnetic islands can be drastically reduced without fearing of the information stored on one island affecting that of neighboring islands compared to ferromagnets. In addition, the antiferromagnetic bit has a low signal amplitude loss compared with usual ferromagnets. Beyond being proposed for recording media, antiferromagnetic and ferrimagnetic composites have drawn intensive attention recently, owing to their abundant domain phase-diagram, special dynamics process and unusual FMR model. In addition, the double magnetic sub-lattice makes them one of the candidate for all optical switching media. Nowadays, the perpendicular magnetized ferromagnetic composite are mainly based on transition-metal/rare-earth system, such as Dy-Co and Tb-Fe alloy/multilayers, and ferrimagnetic/nonmagnetic multilayers with interlayer antiferromagnetic coupling. However, the fabrication and investigation on perpendicularly magnetized ferrimagnetic composites based on 3d metal without noble and rare-earth elements is rarely been reported, owing to the significant challenge of developing easily-to-built ferrimagnetic composites with systematically controllable parameters.

Here, using the Heusler alloys Mn₆₂Ga₃₈ (MnGa) and Co₅₀Fe₂₃₇Al₂₆₃ (CFA), we design a new ferrimagnetic superlattices (SLs) exhibiting PMA for magnetic recording and spintronics devices application. The MnGa and CFA alloys used for SLs architecture are L₁₀ ordered PMA ferromagnet and cubic soft ferromagnet, respect-
cube. Mn$_{x}$Ga$_{100-x}$ is a promising tetragonal Heusler alloy exhibiting hederally coordinated with both the Fe and Co atoms, at the corners of a tetragonal variant of the L2$_1$ Heusler unit cell, which is stretched by Co$_2$FeAl, shown in Figure 1a, has an L2$_1$ structure, where Fe and Al atoms occupy two interpenetrating fcc lattices with an NaCl-type structure.$^{31}$ The Co atoms form a simple cubic lattice, and they are tetrahedrally coordinated with both the Fe and Co atoms, at the corners of a cube. Mn$_{x}$Ga$_{100-x}$ is a promising tetragonal Heusler alloy exhibiting PMA.$^{18–20}$ The L1$_0$ structure stable for $x = 50–65$, is a highly distorted tetragonal variant of the L2$_1$ Heusler unit cell, which is stretched by $\sim 25\%$ along the c axis. The structure of Mn$_{x}$Ga$_{100-x}$ can be regarded as periodic atomic planes of Mn and Ga along the c direction. As the Mn content increases, parts of the Ga atoms are replaced by Mn atoms, and the moments of the substituted Mn atoms are antiparallel to those of the original Mn atoms along the c direction.$^{30}$

**Results**

**Ordered structure with flexible lattice constants of SLs.** The periodic layered SLs illustrated in Figure 1b are formed by [MnGa/CFA] units with the magnetizations of the MnGa and CFA layers antiparallel to each other owing to the antiferromagnetic interfacial exchange coupling between them. Figure 1c shows the typical transmission electron microscope (TEM) cross-sectional image of [MnGa(3.0 nm)/CFA(1.5 nm)]$_5$ SL deposited on an MgO(001) single-crystal substrate buffered with a 40-nm-Cr layer. Well crystallized structure is shown in the sample, where the MnGa and CFA layers have the same in-plane lattice constant, indicated by the continuous vertical lattice line. The clear alternative Energy Dispersive X-ray (EDX) spectroscopy peaks of Mn (MnGa) and Co (CFA) shown in Figure 1d indicate the periodic layered structure formed in the SL sample.

To study the structure and magnetic properties systematically, four series of SLs with different thickness of CFA ($t_{\text{CFA}} = 0.5, 1.0, 1.5$, and 2.0 nm) were fabricated on MgO(001) substrate, which are denoted as CFA05, CFA10, CFA15 and CFA20, respectively. The thickness of the MnGa layer ($t_{\text{MnGa}}$) in each series varies from 1.0 to 6.0 nm (see method). The lattice parameters of the SLs were determined by in-plane and out-of-plane X-ray diffraction (XRD) using a Cu K$_\alpha$ source with $\lambda = 1.5418$ Å. Figure 2a shows the in-plane 20 patterns of the CFA05 samples. The single (200) peaks indicate the same in-plane lattice constant ($a$) for MnGa and CFA in each sample, which is consistent with the TEM result. As $t_{\text{MnGa}}$ increases, diffraction peaks of SLs shift to higher angle gradually, implying that the $a$ value decreases as $t_{\text{MnGa}}$ increases. The out-of-plane 20 patterns of CFA05 SLs are shown in Figure 2b. The (004) peaks of SLs marked in the square shift from 61.81$^\circ$ to 51.75$^\circ$ gradually, corresponding to the increase in lattice constant $c$ of the SLs as $t_{\text{MnGa}}$ increases. The diffraction peaks of (200) and (004) of SLs shown in Figures (a) and (b) indicates well-ordered structure formed in SLs, where MnGa and CFA layers have L1$_0$ and B$_2$ ordering.$^{20–38}$ Detailed XRD patterns of all SL samples are shown in supporting information (Figures S1 to S5).

Owing to the in-plane lattice mismatch between the MnGa and CFA materials, the lattice constants of SLs strongly depend on the thickness of the MnGa and CFA layers. The $a$ and $c$ values of SLs calculated from the XRD patterns are summarized in Figures 2c and d, respectively. Generally, the SLs lattice exhibits a transition from CFA-dominated to MnGa-dominated as $t_{\text{MnGa}}$ increase for each series. Here, the $a$ values of SLs are calculated in the frame of tetragonal cell as a reference of MnGa cell, where $a = \sqrt{2}/2$ times of the cubic cell ($a$'). For each series, $a$ decreases as $t_{\text{MnGa}}$ increases and exhibits a dramatic change at certain $t_{\text{MnGa}}$, which possibly correspond to the transition of the SLs from cubic to tetragonal. The $c$ values of SLs exhibit a monotonic increase with $t_{\text{MnGa}}$ in each series and SLs with thinner $t_{\text{CFA}}$ have larger $c$. As the MnGa layer is thick enough, such as 4 and 6 nm for the CFA05 and CFA15 series, the $c$ of SLs are almost same as that of the MnGa alloys.

**Ferrimagnetism and PMA nature of SLs with widely tunable parameters.** Typical $M(H)$ loops in the perpendicular direction for CFA15 SLs are plotted in Figure 3a. For $t_{\text{MnGa}} \approx 2.0$ nm, the SLs exhibits PMA indicated by square-shaped $M(H)$ loops. It is noted that both the $H_c$ and $M_s$ of SLs strongly depend on $t_{\text{MnGa}}$ and exhibit a non-monotonic dependence. The perpendicular $M(H)$ loops of the

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**Figure 1 | Formation and structural information of SLs.** (a), Schematic picture of L2$_1$ Co$_2$FeAl (up) and L0$_0$ MnGa (down) alloys. (b), Illustration of ferrimagnetic SLs, where the magnetizations of the CFA and MnGa layers are antiparallel aligned. (c), (d), Cross-sectional TEM image (c) and EDX spectrum (d) of [MnGa(1.5 nm)/CFA(3 nm)]$_5$ SL on an MgO(001) substrate. The gray, red, green and purple lines in (d) correspond to the EDX intensity of the Mg, Mn, Co, and Cr elements, which correspond to the MgO, MnGa, CFA and Cr layers, respectively.
four series of SLs are shown in supporting information (Figures S6 to S9). Figure 3b shows the perpendicular and in-plane \( M(H) \) loops for the \([\text{MnGa}(6 \text{ nm})/\text{CFA}(1.5 \text{ nm})]_5\) sample. A linear \( M(H) \) loop in the in-plane direction indicates a well PMA, and the effective anisotropy \( K_u^{\text{eff}} \) calculated from \( H_s M_s/2 \) is 6.8 Merg/cm\(^3\), where \( H_s \) is the saturation field of the in-plane \( M(H) \) curve.

The \( M_s \) of SLs as a function of \( t'_{\text{MnGa}} \) \( (t'_{\text{MnGa}} \text{ is effective thickness of MnGa layer with consideration of additional MnGa layer deposited on the top of SLs, see method}) \) for the four SL series are shown in Figure 3c. For each series, \( M_s \) firstly decreases in the CFA-dominated regime as \( t_{\text{MnGa}} \) increases, owing to the fact that the increase in the antiparallel-aligned magnetization of MnGa decreases the net magnetization of SLs. As \( t'_{\text{MnGa}} \) increases further in the MnGa-dominated regime, \( M_s \) increases as \( t'_{\text{MnGa}} \) increases, owing to the magnetization of MnGa being in the same direction as the MnGa layers. Based on the antiparallel alignment of magnetizations of MnGa and CFA layers, the \( M_s \) of SLs can be described by the following formula.

\[
M_s = \left( \frac{t'_{\text{MnGa}}}{t_{\text{CFA}}} - M_{\text{CFA}}/t_{\text{CFA}} \right) / \left( t'_{\text{MnGa}} + t_{\text{CFA}} \right)
\]

The fits are shown by the solid lines in Figure 3c; the fitted magnetizations of MnGa and CFA layers are \( 460 \) and \( 1105 \) emu/cm\(^3\), respectively, which are comparable to the values of bulk MnGa and CFA materials\(^{18,38} \) (see supporting information Figure S10). It is noted that, the magnetization of SLs is zero for certain \( t_{\text{MnGa}} \), so-called compensational points. At these points, the magnetizations of...
the CFA and MnGa layers have the same magnitude with antiparallel configuration, the SLs are antiferromagnetic composites. $K_{u,\text{eff}}$ of the SLs estimated from $H_{M/2}$ are plotted in Figure 3d. Generally, SLs with small $t_{\text{CFA}}$ and large $t'_{\text{MnGa}}$ exhibit a high $K_{u,\text{eff}}$, the phase-diagram of $K_{u,\text{eff}}$ as a function of $t_{\text{CFA}}$ and $t'_{\text{MnGa}}$ is shown in the supporting information (Figure S12). For a density of 1 Tbit/inch$^2$, the smallest volume $V$ for the stability condition $K_{u,\text{eff}}V/k_{B}T \geq 60$ to be satisfied at room temperature is 800 nm$^3$ if considering the distance between neighboring bits is the same as the bit diameter, for $K_{u,\text{eff}}$ of 3 Merg/cm$^3$. This volume corresponds to a nano-pillar with a height equal to its diameter with dimensions of 10.5 nm. Assume the PMA of SLs originates from the MnGa layers, the $K_{u,\text{eff}}$ of the SLs can be described by:

$$K_{u,\text{eff}} = (K_{u,\text{MnGa}}t'_{\text{MnGa}} - 2\pi M_{\text{CFA}}^2 t_{\text{ICFA}})/(t_{\text{CFA}} + t'_{\text{MnGa}})$$

(2)

where $K_{u,\text{MnGa}}$ denotes the effective uniaxial anisotropy of the MnGa layer in SLs. From the fits shown with the solid lines, the $K_{u,\text{MnGa}}$ and $M_{\text{CFA}}$ are $\sim 8$ Merg/cm$^3$ and $\sim 1100$ emu/cm$^3$, respectively (see support information Fig. S12). It is reasonable to attribute the smaller $K_{u,\text{MnGa}}$ compared with the bulk material to the structural change of the MnGa layer in SLs. In particular, the $K_{u,\text{MnGa}}$ is 6 Merg/cm$^3$ for the CFA20 series owing to the cubic-like lattice of the SLs.

In each series, $H_{c}$ shows a maximum value near compensational points marked by the dotted line in Figure 3e. $H_{c}$ decreases to zero as $t'_{\text{MnGa}}$ decrease to zero, where the PMA of SLs disappears. On the other side, $H_{c}$ saturates to that of single-MnGa-layer when $t'_{\text{MnGa}}$ is thick enough, where the property of SLs is dominated by the MnGa. Here, simply based on the Stoner-Wohlfarth description, the coercivity is proportional to the uniaxial anisotropy field $H_{c}$ of continuous film depend on nucleation field, in addition to $K_{u,\text{eff}}$ only. It shows that the non-monotonic $t'_{\text{MnGa}}$ dependent of $H_{c}$ can be well described by the Stoner-Wohlfarth model.

**Formation of SLs on SiO$_2$ amorphous substrate.** For materials designed for application, fabrication on different substrates, especially on amorphous substrates, is essentially important. Here, we demonstrate the formation of textured SLs on an amorphous substrate. The SLs with periodic CFA/MnGa layers were deposited on SiO$_2$ substrate at room temperature, buffered with Ta(10 nm)/Cr(5 nm)/MgO(2 nm) and capped with 5-nm-Ta layer, as shown in Figure 4a. Post annealing at 400 °C was performed for 10 min in vacuum to crystallize the SLs. Three series of SLs (cfa12, cfa15 and cfa20) were fabricated, where $t_{\text{CFA}} = 1.2, 1.5, \text{and } 2.0$ nm, respectively. Square-shaped out-of-plane $M(H)$ loops of cfa15 SLs are observed, as shown in Figure 4b. This indicates that the SLs exhibit PMA owing to the textured structure formed on SiO$_2$ substrate. Up to now, tetragonal MnGa layers were only achieved on single crystal substrates such as GaAs(001) SiTiO$_3$(001) and MgO(001) owing to the metastable nature of the tetragonal order. The ordered structure of SLs well formed on the amorphous substrate is likely induced by the crystalline structure of the CFA layer. The $t_{\text{MnGa}}$ dependence of $M_{u,\text{eff}}$, $K_{u,\text{eff}}$, and $H_{c}$ of the SLs for the three series are summarized in Figure 4c, where the solid lines are the fits based on formula (1), (2), and (3), respectively. The $M_{\text{CFA}}$ and $M_{\text{CFA}}$ in these SLs from the fit of $M_{u,\text{eff}}$ are $\sim 460$ and $\sim 1100$ emu/cm$^3$, which is consistent with that for the SLs deposited on MgO(001) substrate.

**Discussion**

The magnetism of Mn-Ga alloys originates from the Mn atoms, which have a half-filled d shell. This makes the exchange interaction involving Mn-Ga thin film more sensitive to the interfacial environment and more flexible to being tuned. An antiferromagnetic exchange coupling at the MnGa/Cu$_2$FeAl interface was achieved when the structure was annealed at 400 °C, owing to the Co atoms...
Co$_2$FeAl and Mn-Ga films were Co$_{50}$Fe$_{23.7}$Al$_{26.3}$ (CFA) and Mn$_{62}$Ga$_{38}$ (MnGa), analyzed with inductively coupled plasma mass spectrometry. The stoichiometric compositions of the Co$_x$FeAl and Mn-Ga films were Co$_{0.9}$Fe$_{3.7}$Al$_{5.3}$ (CFA) and Mn$_{52}$Ga$_{38}$ (MnGa), analyzed with inductively coupled plasma mass spectrometry. [MnGa($t_{\text{MnGa}}$)/CFA($t_{\text{CFA}}$)]$_5$/MnGa($t_{\text{MnGa}}$) SL stacks were fabricated using an ultrahigh-vacuum sputtering system with a base pressure of less than 1 mTorr. The Cu$_3$Ga$_2$Mn$_6$O$_9$ substrate with structure of [MnGa($t_{\text{MnGa}}$)/CFA($t_{\text{CFA}}$)]$_5$/MnGa($t_{\text{MnGa}}$) was deposited on top to prevent contamination and oxidation of the SLs. The SLs deposited on the SiO$_2$ substrate were fabricated under the same conditions with a buffer layer of Ta(5.0 nm)/Cr(5.0 nm)/MgO(001) single-crystal substrate, with a 40-nm-Cr as the buffer layer of MgO(2.2 nm)/Ta(2.0 nm)/MgO(001) single-crystal substrate, with a 40-nm-Cr as the buffer layer of MgO(2.2 nm)/Ta(2.0 nm)/MgO(001) single-crystal substrate, with a 40-nm-Cr as the buffer layer of MgO(2.2 nm)/Ta(2.0 nm)/MgO(001) single-crystal substrate, with a 40-nm-Cr as the buffer layer of MgO(2.2 nm)/Ta(2.0 nm)/MgO(001) single-crystal substrate, with a 40-nm-Cr as the buffer layer.
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**Author contributions**

Q.M. conceived the idea and designed the experiments. Q.M. fabricated and measured the samples with the help of S.M. Q.M., S.M., X.Z., and T.M. discussed the results. Q.M. analyzed the results and wrote the manuscript with the help of all authors. The study was performed under the supervision of S.M. and T.M.

**Additional information**

**Supplementary information** accompanies this paper at http://www.nature.com/scientificreports

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