

Perpendicular Magnetic Anisotropy in $\text{Fe}_2\text{Cr}_{1-x}\text{Co}_x\text{Si}$ Heusler Alloy

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Perpendicular magnetic anisotropy (PMA) was achieved in annealed $\text{Fe}_2\text{Cr}_{1-x}\text{Co}_x\text{Si}$ (FCCS) Heusler alloys with different Co composition x . The Co composition is varied to tune the Fermi level in order to achieve both higher spin polarization and better thermal stability. The PMA is thermally stable up to 400°C for FCCS with $x = 0, 0.3, 0.5$, and 350°C for FCCS with $x = 0.7, 0.9, 1$. The thickness of FCCS films with PMA ranges from 0.6 nm to 1.2 nm. The annealing temperature and FCCS thickness are found to greatly affect the PMA. The magnetic anisotropy energy density K_U is $2.8 \times 10^6 \text{ erg/cm}^3$ for 0.8 nm Fe_2CrSi , and decreases as Co composition x increases, suggesting that the PMA induced at FCCS/MgO interface is dominated by the contribution of Fe atoms. There is a trade-off between high spin polarization and strong PMA by adjusting Co composition.

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I. INTRODUCTION

MgO-based magnetic tunnel junctions (MTJs) has attracted great interest due to large tunneling magnetoresistance (TMR) effect [1]-[2] and potential applications in magnetoresistive random access memory (MRAM). Compared with both types of MTJs with in-plane and perpendicular magnetization of ferromagnetic electrodes, the later ones show more advantages in high thermal stability and low critical current for spin-transfer torque induced magnetization switching [3]-[4]. However, the conventional perpendicular magnetic anisotropy (PMA) materials, including rare-earth/transition metal alloys [5]-[6], Co/(Pd, Pt, Ni) multilayers [7]-[8], and $L1_0$ -ordered (Co, Fe)Pt alloys [9]-[10] were limited for further application so far due to low spin polarization and high damping constant. Therefore, PMA materials with high spin polarization, low damping constant and good lattice matching with MgO are desired for spintronic devices. Recently, interfacial perpendicular anisotropy induced by MgO interface was shown as an efficient way to realize PMA for conventional magnetic storage materials, such as CoFeB [11]. However, the damping constant of CoFeB increases sharply as its thickness decreases (less than 1.8 nm) [12], which will lead to the increase in the intrinsic critical switching current density. Therefore, materials with high spin polarization and low damping constant are promising PMA candidates for MTJs at sub-50 nm dimension.

Recently, full Heusler alloys have attracted much attention as PMA materials, such as Co_2FeAl [13]-[14] and $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ [15]. In this study, we focus on a new material, Fe-based full Heusler alloys $\text{Fe}_2\text{Cr}_{1-x}\text{Co}_x\text{Si}$ (FCCS) since FCCS have been predicted to have high spin polarization and good thermal stability [16]. The Co composition is adjusted to tune the Fermi level to the center of minority band gap to enhance the spin polarization and thermal stability. In our previous studies, we have implemented full Heusler alloy FCCS thin films as bottom ferromagnetic electrode with in-plane magnetization in MTJs [17]-[18]. Full Heusler

alloys have low magnetocrystalline anisotropy due to cubic crystalline structure, so it is difficult to realize PMA in Heusler alloys thin films with large thickness (larger than 2 nm). Therefore, we fabricated ultrathin FCCS full Heusler alloy films faced to MgO layer and demonstrated that the PMA results from interfacial perpendicular anisotropy between FCCS and MgO. The post-annealing temperature dependence, thickness dependence and Co composition dependence of PMA in ultrathin FCCS films were also investigated.

II. EXPERIMENTAL RPOCEDURE

All samples were prepared by an ultrahigh vacuum magnetron sputtering system with base pressure of 10^{-7} Pa. The stack structure is MgO (001) substrate/ Cr (40 nm)/ $\text{Fe}_2\text{Cr}_{1-x}\text{Co}_x\text{Si}$ (t nm)/Mg (0.3 nm)/MgO (2.5 nm)/Ru (3 nm), with $t = 0.6 - 1.4$ nm and $x = 0, 0.3, 0.5, 0.7, 0.9, 1$, respectively. The FCCS films with different x were prepared by co-sputtering technique using Fe_2CrSi and Fe_2CoSi sputtering targets. The composition was controlled by adjusting the input power of each sputtering target at a constant deposition rate. Prior to the deposition, the MgO substrate was pre-heated at 600°C for 1 hour. The Cr buffer layer was *in-situ* annealed at 700°C for 30 minutes after deposition at room temperature in order to achieve a very flat surface. Then FCCS film was deposited on Cr at room temperature, followed by *in-situ* annealing at 400°C to promote chemical ordering. The MgO layer was grown by RF sputtering in a plasma oxidation chamber at room temperature. To prevent over-oxidation of FCCS film by MgO layer, a thin Mg layer of 0.3 nm was inserted before MgO deposition. The post-annealing effect was investigated by *ex-situ* post-annealing at various temperatures ranging from $T_a = 250^\circ\text{C}$ to 400°C in high vacuum in the presence of an out-of-plane magnetic field of 1 Tesla. Alternating gradient magnetometer (AGM) was used to characterize the magnetic properties. X-ray Photoelectron Spectroscopy (XPS) was employed to analyze the interface property.

III. RESULTS AND DISCUSSION

No apparent PMA is observed for all the as-deposited FCCS samples regardless of t and x . It is noted that PMA in FCCS films only occurs after post-annealing, which could be due to the formation of better interface between FCCS and MgO, and improved quality of MgO layer after post-annealing [18]-[21]. Figure 1(a) shows the post-annealing temperature T_a dependence of $\text{Fe}_2\text{Cr}_{0.3}\text{Co}_{0.7}\text{Si}$ film with a thickness of 0.8 nm. There is a clear transition from in-plane magnetic anisotropy to PMA after post-annealing at 250°C. The perpendicular M - H loops show sharp magnetization reversal and the PMA is stably maintained with T_a up to 350°C, suggesting that the structure has a good thermal stability. However, at $T_a = 400^\circ\text{C}$, the squareness of perpendicular M - H loop degrades for FCCS films with $x = 0$ (shown in Fig. 1(b)), 0.3, 0.5 due to Cr diffusion into FCCS film, while in-plane magnetic anisotropy are observed for FCCS films with $x = 0.7, 0.9, 1$ (shown in Fig. 1(c)). This indicates that the PMA in FCCS films with lower Co composition have better thermal stability. For Heusler alloys with a chemical form of X_2YZ , the transition metals X and Y occupy simultaneously X sites when the Y atom is more electronegative than the atoms X [22]-[24]. Therefore, in Fe_2CrSi , when Cr is partially replaced by Co, some Co atoms do not directly occupy the sites of Cr (Y), but the sites of Fe (X), pushing Fe to the Y sites. As Co composition increases, less Fe atoms occupy X sites. Our experimental results suggest that the observed PMA in FCCS strongly depends on Fe occupation in the Fe sites and becomes the strongest when the Fe sites are occupied by Fe atoms. Figure 1(d) shows the T_a dependence of saturation magnetization (M_S) and coercivity (H_C) of perpendicular M - H loops for $\text{Fe}_2\text{Cr}_{0.3}\text{Co}_{0.7}\text{Si}$ sample. The initial increase in M_S with T_a could be attributed to the improved FCCS chemical ordering from disordered $A2$ or partially ordered $B2$ to fully ordered $B2$ or $L2_1$ [25]. As T_a further increases, the M_S decreases slightly due to oxidation at the interface and then largely at $T_a = 400^\circ\text{C}$ due to Cr diffusion into FCCS film. The H_C of perpendicular M - H loops is

increased with T_a up to 350°C, and then decreases at $T_a = 400^\circ\text{C}$. Considering that there is an optimum oxidation for the PMA in ferromagnet/oxide structure [26], there may also be similar behavior at the FCCS/MgO interface that the optimum oxidation occurs at post-annealed of 350°C, resulting in the largest H_C with sharp magnetization reversal. Therefore, T_a of 250°C can be considered as the critical temperature for the transformation of magnetic easy axis from in-plane direction to out-of-plane direction, and T_a of 350°C as the best thermal treatment for FCCS films with PMA.

PMA is observed in FCCS ultrathin films with different Co composition x and thickness $t = 0.6 - 1.2$ nm but disappears at $t \geq 1.4$ nm. Figure 2(a) shows the perpendicular M - H loops of $\text{Fe}_2\text{Cr}_{0.3}\text{Co}_{0.7}\text{Si}$ films with different thickness. Figure 2(b) shows the thickness dependence of H_C and ratio of remanent magnetization (M_r) over M_S . The H_C decreases from 645 Oe to 92 Oe as t increases, and the best square shape with sharp magnetization reversal is given at $t = 0.8$ nm.

The Co composition x dependence of PMA for FCCS is shown in Fig. 3. The monotonic increment of M_S with x can be attributed to more valence electrons of Co than Cr. The M_S values of 0.8 nm-thick FCCS films are close to those of $B2/L2_1$ -ordered epitaxial FCCS films with a thickness of 30 nm [18], suggesting that FCCS ultrathin films have high chemical ordering which may result in high spin polarization. Magnetic anisotropy energy density (K_U) is estimated by $K_U = M_S H_k / 2$, where H_k is perpendicular anisotropy field. The calculated K_U is 2.8×10^6 erg/cm³ for Fe_2CrSi , 2.3×10^6 erg/cm³ for $\text{Fe}_2\text{Cr}_{0.7}\text{Co}_{0.3}\text{Si}$, and further decreases as Co composition increases. The K_U values are comparable to the conventional PMA materials, CoFeB/MgO structure [27], and Heusler alloy $\text{Co}_2\text{FeAl}/\text{MgO}$ structure [13], which would be high enough to secure good thermal stability for devices at sub-50 nm dimensions. The decline trend of K_U versus Co composition is expected, since the PMA induced at FCCS/MgO interface should be determined mainly by the contribution of Fe

atoms rather than Co atoms [28]. The increase of Co composition would lead to less Fe atoms at the interface, because more Co atoms occupy the Fe position. As a result, Fe_2CrSi has the strongest PMA. However, we have demonstrated that $\text{Fe}_2\text{Cr}_{0.3}\text{Co}_{0.7}\text{Si}$ is expected to have the highest spin polarization [18]. Therefore, there is a trade-off between strong PMA and high spin polarization by adjusting Co composition in FCCS films.

The origin of PMA in FCCS/MgO remains unclear. As the PMA is only observed in an ultrathin FCCS layer, it must be originated from the interface at the FCCS/MgO. So far, three main contributions to the interfacial PMA have been identified: 1) the hybridization between ferromagnetic Fe- or Co-3*d* and O-2*p* electron orbitals at the interface of FCCS/MgO; 2) the elastic stress due to the lattice distortion arising from the mismatching of FCCS and MgO lattice constants; 3) the breaking of crystal symmetry at the interface. The atomic structure of ferromagnetic materials, such as Fe and Co, is $3d^n4s^2$ ($n = 6$ and 7 , respectively). The localized 3*d* electrons are responsible for the spontaneous magnetization of these ferromagnets. The origin of PMA is related to the anisotropy of these orbitals. In a bulk ferromagnet, the 3*d* orbitals degenerate in a first approximation (the chemical environment is roughly spherical). The presence of an interface breaks this quasispherical symmetry so that the energy of 3*d* orbitals pointing toward the interface is different from the energy of the 3*d* orbitals with planar symmetry. At the FCCS/MgO interface, one can expect that the predicted charge transfer between Fe-/Co- and O in optimally oxidized FCCS/MgO interface increases the asymmetry of the Fe/Co 3*d* bands, reducing the energy of the 3*d* orbitals responsible for the out-of-plane anisotropy and creating a splitting between in-plane and out-of-plane *d* orbitals. Thus, this strong band splitting could lead to strong PMA [26], [29]. The Co and Fe 2*p* spectra are shown in Fig. 4 for $\text{Fe}_2\text{Cr}_{0.7}\text{Co}_{0.3}\text{Si}$ film post-annealed at 350°C, while the rest FCCS films with different Co composition have similar observation. The main peaks of CoO 2*p*_{3/2}, CoO 2*p*_{1/2}, Fe_2O_3 2*p*_{3/2}, and Fe_2O_3 2*p*_{1/2} have been detected, indicating that the

$\text{Fe}_2\text{Cr}_{0.7}\text{Co}_{0.3}\text{Si}$ film is partially oxidized. Our results are consistent to those reported in Ref. [30]. The charge transfer between Co/Fe and O at the FCCS/MgO interface may be responsible for the observed PMA. As discussed above, there is a slight decrease in K_U when more Fe is substituted by Co. This change in PMA is attributed to the hybridization of the atomic orbitals. This indicates that the PMA induced at FCCS/MgO interface should be dominated by the contribution of Fe atoms rather than Co atoms, which is consistent with the result reported in Ref. [28].

It is noteworthy that we deposited 0.3 nm Mg layer between FCCS and MgO barrier to prevent the over oxidation of FCCS, since the over-oxidized FCCS surface may act as additional scattering centers for spin polarized tunneling electrons, which could reduce the spin polarization [31]. On the other hand, Fe-O and Co-O bonding can induce strong PMA. Hence, Mg layer thickness should be optimized to achieve both high spin polarization and strong PMA.

IV. CONCLUSION

In summary, we have observed the strong PMA in the annealed FCCS/MgO structure with different Co composition x for achieving high spin polarization and good thermal stability. There is a trade-off between strong PMA and high spin polarization in FCCS by adjusting Co composition. Our results show that Heusler alloy FCCS with strong PMA are applicable for perpendicular MTJ applications.

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Figure captions:

Figure 1 Hysterisis loops at room temperature for (a) 0.8 nm $\text{Fe}_2\text{Cr}_{0.3}\text{Co}_{0.7}\text{Si}$ sample at different post-annealing temperature T_a , (b) 0.8 nm Fe_2CrSi sample at $T_a = 400^\circ\text{C}$, and (c) 0.8 nm Fe_2CoSi at $T_a = 400^\circ\text{C}$. (d) Saturation magnetization, M_S and coecivity, H_C as a function of T_a for 0.8 nm $\text{Fe}_2\text{Cr}_{0.3}\text{Co}_{0.7}\text{Si}$ sample.

Figure 2 (a) Perpendicular hysterisis loops at room temperature for $\text{Fe}_2\text{Cr}_{0.3}\text{Co}_{0.7}\text{Si}$ with different thickness t . (b) Coecivity, H_C and the ratio of remanent magnetization over saturation magnetization, M_r/M_S as a function of $\text{Fe}_2\text{Cr}_{0.3}\text{Co}_{0.7}\text{Si}$ thickness t .

Figure 3 Saturation magnetization, M_S and magnetic anisotropy energy density, K_U versus Co composition x .

Figure 4 Co and Fe 2p XPS spectra for the 350°C annealed $\text{Fe}_2\text{Cr}_{0.7}\text{Co}_{0.3}\text{Si}$ sample.

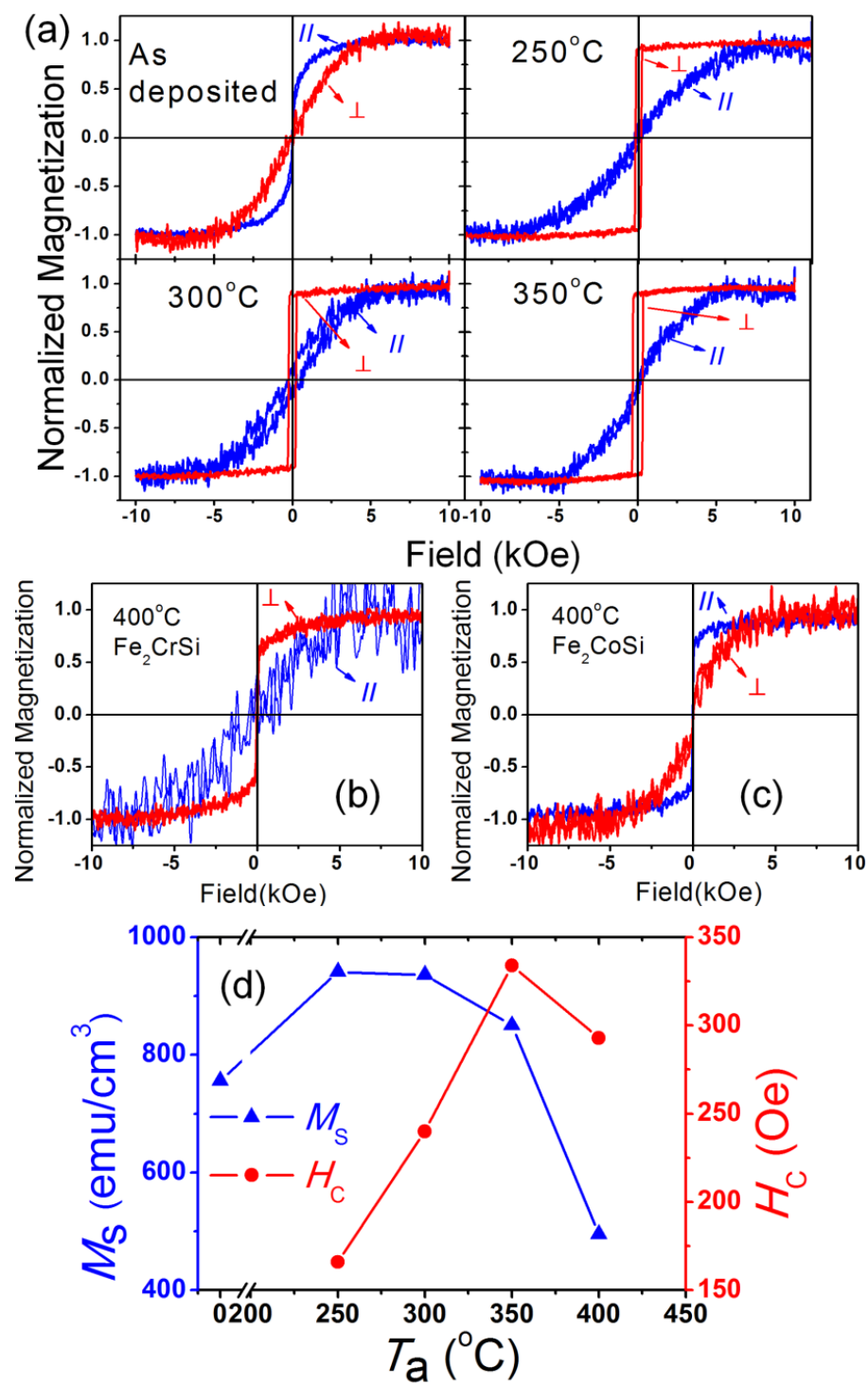


Figure 1

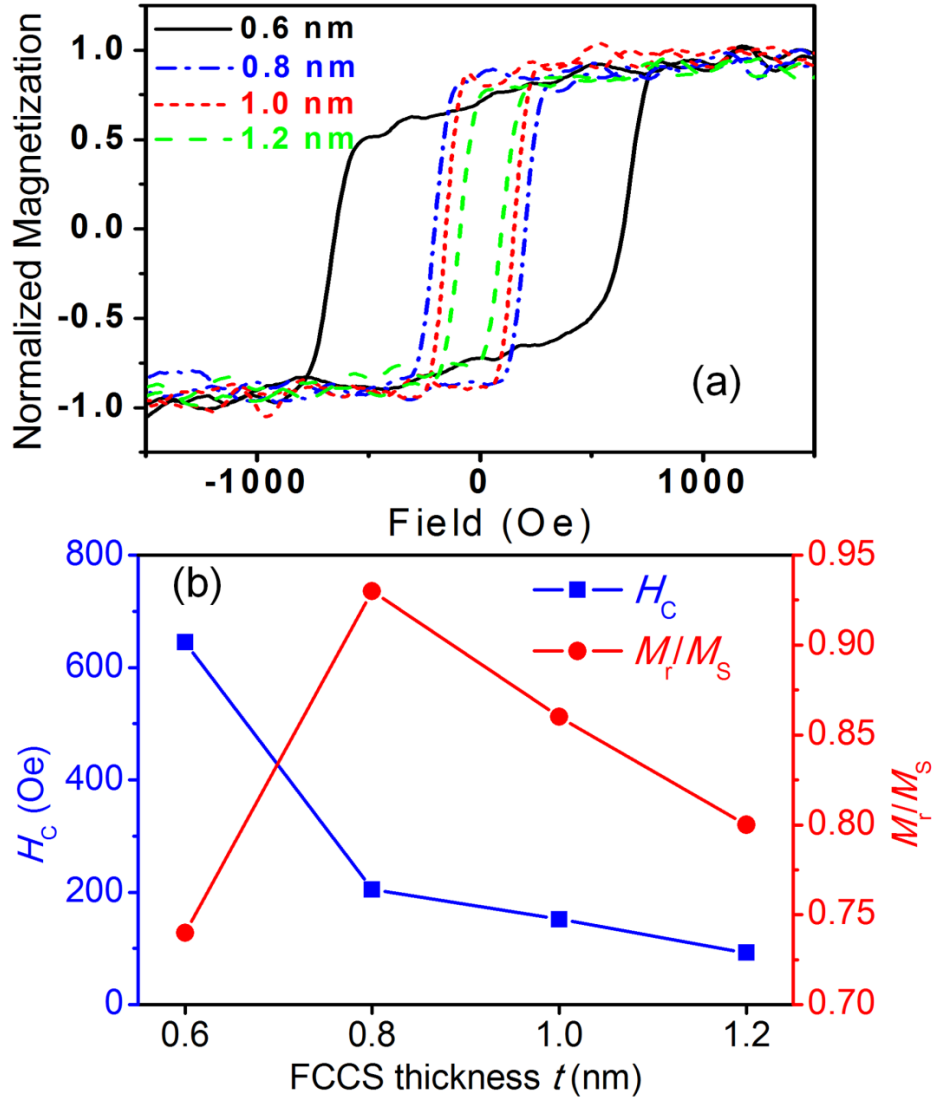


Figure 2

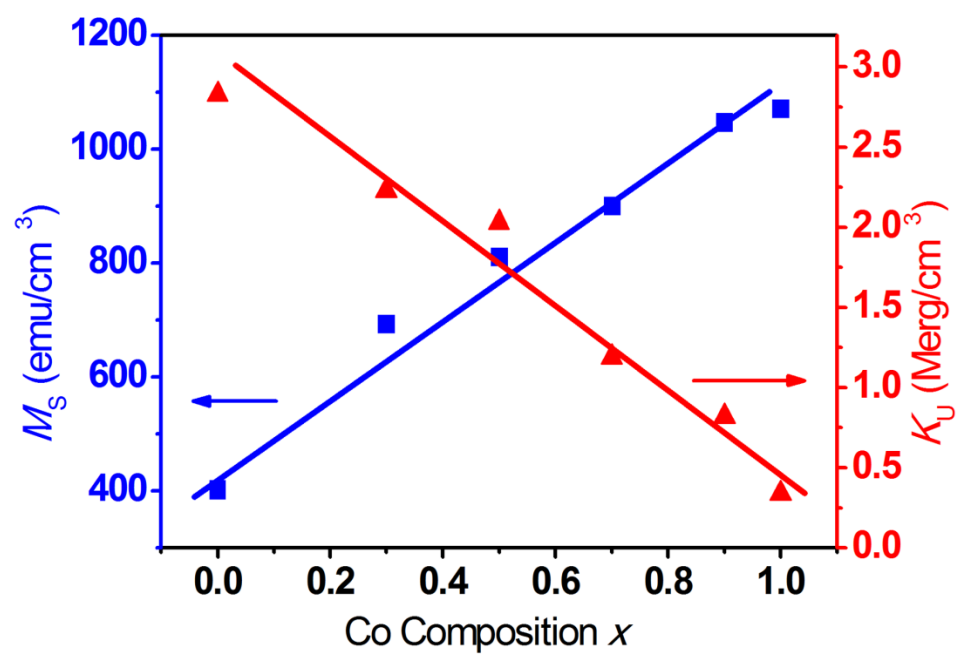


Figure 3

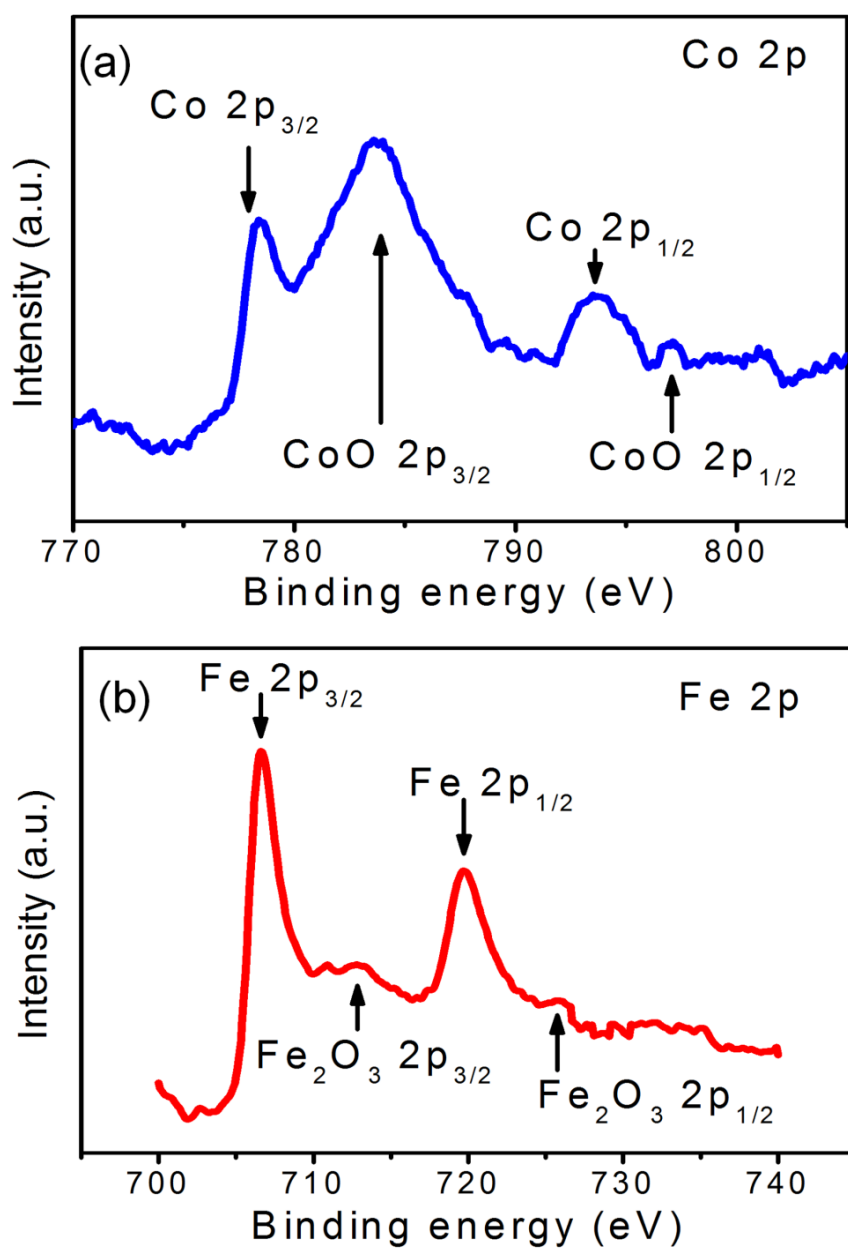


Figure 4