Single Phase $L1_0$-Ordered High Entropy Thin Films with High Magnetic Anisotropy

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The high entropy composition space offers a huge number of material systems to explore, with potential to exhibit desirable magnetic properties such as high magnetic anisotropy without the use of rare-earths. Here we demonstrate design and fabrication approaches to achieve single-phase high entropy films with high magnetic anisotropy.

***Index Terms*—high entropy alloy, magnetic anisotropy, rapid thermal annealing.**

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I. Introduction

High entropy alloys (HEA) containing 5 or more elements may exist as stable phases by virtue of their high configurational entropy, opening a new and potentially important route for material discovery [1]. While the search for new rare-earth-free high anisotropy materials has mostly exhausted the pool of binary and ternary alloy compositions, entropy-stabilization affords a vast number of unique and unexplored electronic structures which may be favorable to high magnetic anisotropy. Conventional HEAs exhibit uniform chemical disorder and cubic crystal structures, whereas long-range chemical order and lower symmetry crystal structures play important roles in magnetic anisotropy. Here we apply design and fabrication strategies to realize non-equiatomic HEAs with intermetallic sublattices and uniaxial symmetry, and probe their magnetic properties throughout the high entropy composition space.

II. $L1_0$-Ordered (FeCoNiMnCu)Pt

Rapid thermal annealing (RTA) of transition metal alloy films on Si/SiO_2 has been shown to be an effective means of inducing high anisotropy phase formation in disordered solid solution precursors, in part due to the substrate-induced strain [2-6]. FeCoNiMnCu thin films sputtered on thermally oxidized Si/SiO_2 substrates at room temperature exhibit limited crystal growth, as observed from X-ray diffraction (XRD), and are magnetically soft with a coercivity on the order of 10 Oe. Application of substrate heating during deposition leads to separation of an Fe-rich body-centered-cubic (*bcc*) phase and Cu-rich face-centered-cubic (*fcc*) phase due to the large positive binary mixing enthalpy of Fe-Cu. In contrast, the films treated with RTA at 600 °C for 30 s exhibit a single *fcc* phase, demonstrating the advantage of the RTA method in suppressing growth of secondary phases in HEAs. Simultaneously, the films exhibit a nearly 40-fold increase in coercivity, as illustrated by first-order reversal curve (FORC) measurement [6, 7] in Fig. 1, indicating the stabilization of sizeable magnetic anisotropy in the HEA film.

To facilitate lower-symmetry chemical order and crystal structure in combination with strong spin-orbit coupling, we have included 50 at.% Pt in the film in search of highly anisotropic $L1_0$ ordering. After RTA treatment, the film exhibits a single $L1_0$ phase with (001) orientation and high $L1_0$ order parameter S = 0.8 extracted from XRD, indicating the formation of a highly ordered superlattice arrangement. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM), shown in Fig. 2a-b, illustrates the 4-fold and 2-fold symmetry along the [001] and [110] zone-axis, respectively, as well as the chemical ordering apparent by the Z-contrast between FeCoNiMnCu and Pt sites. The films exhibit a coercivity increase by 3 orders of magnitude after RTA, illustrated by the emergence of high field features in the FORC distributions, shown in Figs. 2c-f. The bimodal distribution in the out-of-plane direction reflects the domain wall nucleation and pinning reversal mechanisms and distribution of grain size. An effective uniaxial anisotropy of 2×10^6 erg/cm^3 is extracted from the hysteresis loops, consistent with predictions based on the effective valence electron concentration (VEC) [8-11].

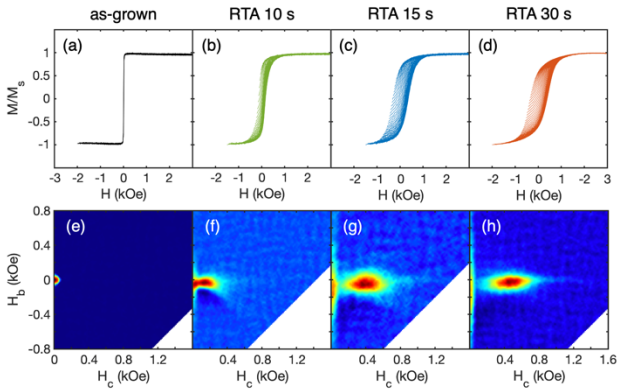

Fig. 1. (a-d) Families of FORCs and (e-h) the corresponding FORC distributions (a,e) after sputtering at 350 °C, and after subsequent RTA at 600 °C for (b,f) 10 s, (c,g) 15 s, and (d,h) 30 s.

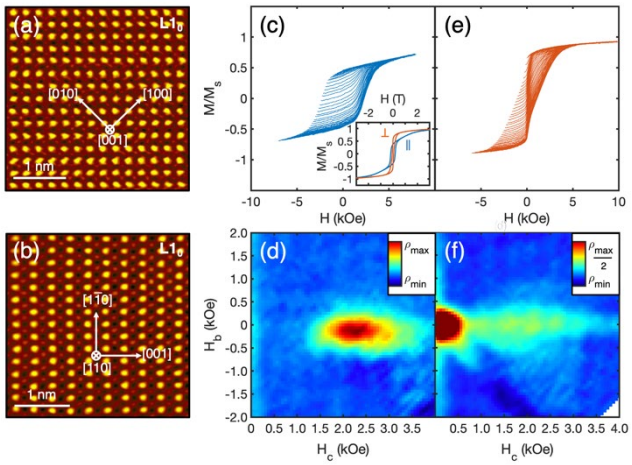

Fig. 2. HAADF-STEM of (FeCoNiMnCu)Pt film along (a) [001] and (b) [110] zone axes of $L1_0$ structure. Family of FORCs and corresponding FORC distributions for (c,d) in-plane and (e,f) out-of-plane directions.

III. C16 Phase High Entropy Borides

The introduction of boron (B) into high entropy systems is a promising approach to promote chemical order and uniaxial crystal structures [12]. Here we show the fabrication of a high entropy boride with C16 tetragonal structure, which has not been previously demonstrated. The binary magnetic C16 borides exhibit negative anisotropy constants, which is undesirable for permanent magnets and magnetic recording media, however previous studies have shown that the mixing of Fe and Co on the transition metal sublattice leads to a flipping of the sign of the anisotropy from negative to positive [13]. Larger anisotropy values may exist within the parameter space, but may not be accessible via single element substitution without the use of 4*d* or 5*d* metals [14]. In our work, we explore the composition space of a quinary boride system in search of high anisotropy using only 3*d* metals.

To rapidly explore the C16 phase composition space for high magnetic anisotropy, we deposited $(Fe_xCo_yNi_zMn_{1-x-y-z})_2B$ films on Si/SiO_2 wafer using a combinatorial co-sputtering method which results in a composition gradient across the substrate. The combinatorial samples were treated with RTA at 600 °C for 60 s and the coercivity and saturation magnetization were extracted from the measured hysteresis loops. XRD of the RTA-treated boride film confirms the C16 tetragonal structure, with lattice constants a = 5.06 Å and c = 4.21 Å for the equiatomic composition, and no secondary phases. The magnetic properties of 98 unique compositions were measured, and the maximum H_c of 720 Oe was found in $(Fe_{0.41}Co_{0.18}Ni_{0.14}Mn_{0.27})_2B$, while the maximum M_s of 590 emu/cm^3 was found in $(Fe_{0.26}Co_{0.39}Ni_{0.22}Mn_{0.13})_2B$. Density functional theory (DFT) calculations of K_u and M_s were carried out and show good qualitative agreement with experiments.

IV. MnAl-Based High Entropy Alloys

Finally, we have studied the magnetic properties of $FeCoNiMnAl_x$ (x = 0, 0.25, 0.50, 1.0, 1.5) films. FeCoNiMn and $FeCoNiMnAl_{0.25}$ exhibit *fcc* structure from XRD, with low M_s. Upon increasing the Al content to x = 0.50, a large enhancement of M_s, by over 3-fold, is observed, coinciding with a transformation from the *fcc* to *bcc* structure. DFT calculations on the magnetic ground state predict a switching of Mn from antiferromagnetic to ferromagnetic upon the *fcc* to *bcc* transformation, and the calculated M_s matches well with the experimental trend. Experimental confirmation of this mechanism is obtained via XMCD measurement, which reveal the exchange splitting of the Mn *d*-band in the *bcc* phase films.

In addition, after field-cooling to 5 K in 500 Oe applied field, we find a large exchange bias of 565 Oe and 930 Oe in the *fcc* phase films with x = 0 and x = 0.25, respectively. The exchange bias is dramatically suppressed to ~0 Oe in the *bcc* phase films, revealing the origin of exchange bias effect in the antiferromagnetic order of Mn.

These results demonstrate sensitive control over the magnetic order and functional properties such as the magnetic anisotropy and exchange bias in HEA films by tuning of the composition. They also illustrate the promise of HEAs for discovery of novel magnetic materials.

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