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Anomalous enhancement in interfacial perpendicular magnetic anisotropy through uphill diffusion

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We observed interfacial chemical sharpening due to uphill diffusion in post annealed ultrathin multilayer stack of Co and Pt, which leads to enhanced interfacial perpendicular magnetic anisotropy (PMA). This is surprising as these elements are considered as perfectly miscible. This chemical sharpening was confirmed through quantitative energy dispersive x-ray (EDX) spectroscopy and intensity distribution of images taken on high angle annular dark field (HAADF) detector in Scanning Transmission Microscopic (STEM) mode. This observation demonstrates an evidence of miscibility gap in ultrathin coherent Co/Pt multilayer stacks.

The perpendicularly magnetized free electrodes have become a great deal of attention in perpendicular magnetic recording media, perpendicular spin valves (p-SVs), and magnetic tunnel junctions (p-MTJs) for highly efficient spin-torque-transfer devices. One of the stringent requirements to fabricate these devices is the thermal stability of the free electrode up to 350°C. As the free electrode consists of ultrathin multilayer stacks of Co and Pt or Pd, the interfacial degradation due to perfect miscibility in nature at such a high temperature becomes a major concern. In fact, this degradation causes a change in the slope of the compositional gradient at the interfaces and results in a decrease in effective perpendicular magnetic anisotropy (PMA)^{1–5}. More recently, though few studies have claimed enhanced PMA on annealing with or without additional interfacial layer^{6–9}, the origin of this is yet to be justified.

With the advancement of characterization techniques, thermal energy driven intermixing phenomena were studied extensively in miscible (e.g., Cu/Ni) multilayer systems by atom probe tomography¹⁰ with reasonably thicker layers (> 2 nm). Experimental observations of interface sharpening on thermal annealing in miscible system were attributed to change in the localized concentration gradient at the cost of intermixing¹⁰. This phenomena was well explained theoretically by using Monte-Carlo simulation with the modification of Fick's first law: $j = -D(C)\text{grad}C$, where $D(C)$ is the diffusion coefficient, which strongly depends on local composition and C is the concentration^{11,12}. However, in case of ultrathin multilayers, where the thickness of each layer is constrained to few monolayers, quantification of intermixing is a real challenge due to formation of coherent structure with lattice strain. In such coherent system, thermally driven atomic diffusion is a complex phenomena and the mechanism of which is still under scientific debate.

In this report, we present the anomalous enhancement of PMA in ultrathin Co/Pt multilayers upon annealing at 350°C in vacuum. Detailed structural studies revealed that uphill diffusion among the layers sharpens the compositional gradient which in turn enhances the PMA. This observation is unexpected owing to the fact that the Co and Pt are reported as miscible^{1–5}. We believe that ultrathin Co/Pt layer grown at room temperature has higher coherent lattice strain with localized defects and annealing causes relaxation of strain by re-ordering elements within layers through uphill diffusion.

Results and Discussion

The Co/Pt multilayer stacks (3 bi-layers with a modulation length varying from 0.4–3.0 nm) were fabricated by magnetron sputtering with a base pressure of $\sim 7.0 \times 10^{-9}$ mbar and annealed at a temperature of 350°C for duration of 1 hr. The structural characterization of the samples was carried out by x-ray diffraction (XRD) and



the periodicity of the structure was confirmed by x-ray reflectometry (XRR). The magnetic properties of the multilayer stacks were examined by vibrating sample magnetometry (VSM). Structure and chemistry across the layers were studied using High Resolution Scanning Transmission Electron Microscopy (HRSTEM) and Energy Dispersive X-ray (EDX) spectroscopy.

The in-plane and out-of-plane M-H loops for two multilayer stacks with modulation lengths 0.4 and 2.4 nm are presented in Fig. 1(a) and (b), respectively. These figures also include the M-H loops of multilayer stacks measured after annealing. For smaller modulation length of 0.4 nm, out-of-plane M-H loop for as grown sample exhibited sharp magnetization reversal, while in-plane shows a linear reversible behaviour below the saturation field and effective anisotropy energy per unit volume, K_{eff} for the film was estimated around 5.5×10^6 erg/cm³. Surprisingly, post-annealing at 350°C yielded similar M-H loops (see fig. 1(a)) indicating the thermal stability. Similar observations have been made recently on ultrathin Co/Pd multilayers^{8,9} and have been attributed to the formation of an ordered-alloy-like fcc (111) superlattice structure¹³ with complete suppression of interdiffusion. However, for higher modulation length, it has been reported¹⁻⁵ that the post annealing at temperatures such as 350°C causes the atomic diffusion at the interface, which deteriorates the chemical composition gradient and hence the PMA of the multilayer stack. Interestingly, contradictory to these observations, post-annealing in our multilayer stacks with higher modulation lengths has induced an enhancement in PMA (see Fig. 1 (b), also see fig.S1 and S2 in supplementary pages for data related to samples having different modulation lengths). Further insight has been provided in the inset (II) of Fig 1 (b), where, $t_{Co} \cdot K_{eff}$ (erg/cm²) is plotted against Co layer thickness, t_{Co} (nm). It is surprising to see that the enhancement in PMA is more significant for higher t_{Co} in such a miscible system, which is very much similar to the observed behaviour reported in immiscible Co/Au system¹⁴. The inset (II) of Fig. 1(b) also indicates that the thermal stability factor

($t_{Co} \cdot K_{eff} A/k_B T$) is highest for $t_{Co} \sim 0.5$ to 0.6 nm due to higher $t_{Co} \cdot K_{eff}$ values. The origin of this enhancement in PMA on annealing is given below.

Basically, the magnetic anisotropy is defined by two competitive interaction mechanisms, i.e., the magnetic dipolar and the spin-orbit interaction¹⁵. In magnetic thin films, the dipolar interaction develops a shape anisotropy which lies within the film plane. Theoretically, it was predicted that a two dimensional sheet of Co monolayer always has in-plane anisotropy¹⁶, however the presence of a Pt monolayer on both sides of Co layer converts the magnetic anisotropy from in-plane to out-of-plane due to asymmetric spin-orbit interaction at the interface as predicted by Néel¹⁷. Other than Néel's anisotropy, the magneto-elastic anisotropy has important contribution towards PMA due to misfit strain between two layers with different atomic constituents. In our previous report on Co/Pt MLs¹⁸, the effect of strain on magnetic anisotropy was discussed in detail for $0.2 \text{ nm} < t_{Co} < 1.8 \text{ nm}$. The interfacial anisotropy originated from both Néel's and magneto-elastic anisotropy plays an important role in contributing PMA. In practical case, the total effective magnetic anisotropy is nothing but the resultant of shape and interface anisotropies. Further, if the Co layer thickness lies within few monolayers, the interface anisotropy becomes comparable to and even dominates over the shape anisotropy, which results in out-of-plane anisotropy ($K_{eff} > 0$). In our investigations, annealing enhances PMA, indicating an improvement in interfacial anisotropy.

To understand this increment in PMA after annealing, structural investigations were carried out. Figures 1 (c) and (d) show XRR spectra and XRD patterns of both as-deposited and annealed samples, respectively. The observed sharpening in XRR interference fringes for annealed sample indicates the increase in compositional gradient. XRD patterns showed the following features: (i) presence of a single peak at $2\theta = 40.9^\circ$ due to formation of coherent Co/Pt(111) structure¹⁸, (ii) a decrease in FWHM of (111) reflection (FWHM = 1.238° and 1.114° before and after annealing, respectively), suggest-

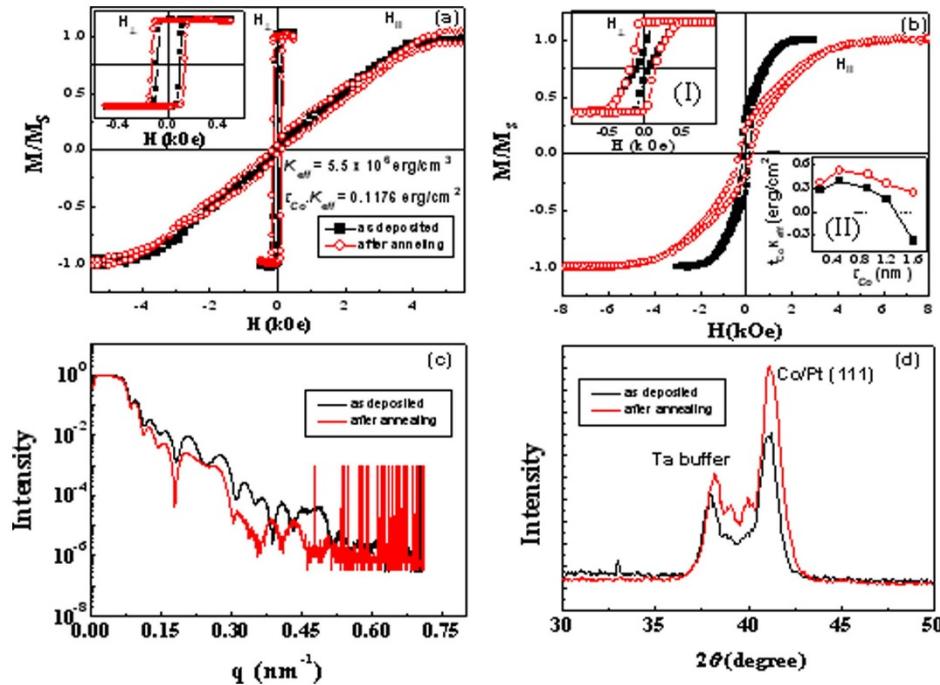


Figure 1 | Magnetic and structural characterization of Co/Pt multilayers stack. The out-of-plane (H_{\perp}) and in-plane (H_{\parallel}) M-H hysteresis curves of MLs Si/Ta (4 nm)/[Pt (t_{Pt})/Co (t_{Co})]₃/Pt(2 nm) with (a) $t_{Co} = 0.2$ nm and $t_{Pt} = 0.2$ nm, (b) $t_{Co} = 1.2$ nm and $t_{Pt} = 1.2$ nm in as-deposited and annealed samples. Inset of (a) and inset (I) of (b) show magnified version of out-of-plane M-H curves. The inset (II) in (b) shows values of $t_{Co} \cdot K_{eff}$ against t_{Co} with constant $t_{Pt} = 1.2$ nm. (c) and (d) present x-ray reflectometry spectra and x-ray diffraction pattern of as-grown and annealed sample with $t_{Co} = 1.2$ nm and $t_{Pt} = 1.2$ nm.



ing better crystallinity, and (iii) the shift of the coherent peak towards Co (111), indicating strain relaxation in Co on annealing, which implies the reduction in magneto-elastic anisotropy (also, see Figs. S3 and S4 in supporting information section). Similar strain relaxation on annealing has been reported by Y. Tamura et al.¹⁹, but with a decrease in PMA. Therefore, we infer that enhanced Néel's anisotropy is the only contributor to improve PMA in the system.

Further insight related to structure and chemistry was carried out by HAADF-HRSTEM. We have chosen the multilayer with $t_{Co} \sim 1.2$ nm and $t_{Pt} \sim 1.2$ nm for HRSTEM studies, as, the value of $t_{Co} \cdot K_{eff}$ is very close to the zero. Due to coherent lattice structure of Co/Pt multilayer stack, it is hard to distinguish the individual atomic layers from images taken in TEM mode (figs. S6 (a) and (b)). Nevertheless, as the atomic numbers of Pt (78) and Co (27) are far apart, hence HAADF imaging in STEM mode had been carried out (low magnification images in figs. S6 (c) and (d)). Figures 2(a) and (b) are the HRSTEM images of as-grown and annealed stacks, respectively; clearly revealing a layered structure. Both samples contain seven alternate bright and dark layers (numbered as 1 to 7, from outermost to the layer on substrate). Darker and brighter layers in these HAADF-STEM images represent Co and Pt rich respectively. In as-grown stack, within dark layers few small regions with relatively brighter contrast have been observed. One such regions from each of the dark layers (within white boxes) presented in Figs. 2(c)–2(e). The 3D intensity distribution of the imaged regions encompassed within white boxes in Figs. 2(c)–2(e) are presented in Figs. 2(f)–2(h), respectively. Since these regions are few atomic columns wide, i.e., they most likely contain more high Z elements. However, such regions were not been observed in the annealed sample.

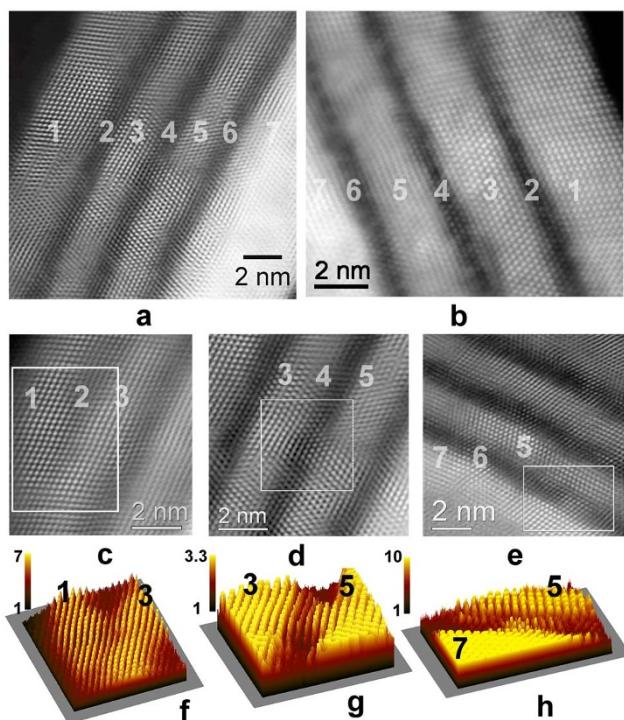


Figure 2 | HAADF-HRSTEM images of as grown (a) and annealed (b) samples showing all the layers while tilted in $<110>$. (c), (d), (e) show the relatively brighter contrast small regions (within white boxes) within dark layers 2, 4 and 6 respectively of as grown sample. (f), (g), (h) are the three dimensional intensity distributions of the regions enclosed within white boxes in Fig. 2 (c), (d) and (e) respectively. Each of the intensity distribution is normalized with respect to the minimum intensity value of the corresponding imaged region.

To quantify relative elemental distribution among the individual layers, EDX quantification was done under similar experimental conditions for both as-grown and annealed stacks. To avoid specimen drift and to keep beam-spreading below the width of the smallest individual layer all EDX spectra were recorded for 100s with a probe diameter ~ 0.1 nm respectively which leads to a compromise in s/n ratio. To compensate that, the spectra were recorded from 20 different positions at each layer over a distance around 500 nm along the length of the layers. Calculated beam-spreading²⁰ on layer 7 (for both samples) were well below 1 nm where determined specimen thickness along electron beam^{21,22} varied between 5–15 nm. Since layer 7 is the farthest layer from the edge of wedge shaped sample, so, no EDX spectra picked up information from adjacent layers. Quantification has been carried out with calculated k-factors of the elements which accurately measures relative compositional changes of each layer between two samples. Average values of the compositions with standard deviations for both the stacks are plotted in Fig. 3 (a) and (b). In both the samples, layers 2, 4 and 6 contained relatively higher Co than others, as expected from HAADF-STEM images. Comparing Fig. 3(a) and (b) it is revealed that after annealing, concentration of Co decreased in Pt-rich layers (3 and 5) while increased in Co-rich layers (2, 4 and 6). This infers to only one possibility that annealing resulted in uphill diffusion of Co giving increased chemical sharpening, as indicated in the XRR spectra. Further, standard deviations of composition in dark layers of as-grown stack are larger than that of the annealed one. As discussed earlier in this report, this may correspond to the brighter contrast regions within dark layers in as-grown stack, which vanished after annealing.

Using the intensity distribution of HAADF-HRSTEM images, 1-D distribution of both elements, Co and Pt, across the layers has been determined. Line profiles, (averaged over few nm along the length of the layers) taken across the layers, were used to determine the elemental distribution (method in supplementary section) by assuming that layers 1 (i.e., Pt cap layer) and 7 (i.e., Pt layer nearest to Ta buffer) contain Pt only and the TEM sample is wedge shaped. One line profile from each sample are shown in Figs. 3 (c) and (d). The profiles indicated a periodic distribution of Co and Pt within the stack. Moreover, these profiles reveal the improved chemical sharpening in annealed stacks, further confirming the uphill diffusion on annealing.

Though this observed uphill diffusion in Co/Pt multilayer stacks is surprising, there are some reasons which can interpret this anomaly. First, the Co-Pt binary bulk phase diagram may be incomplete and there exists a miscibility gap. The other possibility, perhaps more likely, is the coherent lattice strain in ferromagnetic material along with magnetic exchange interaction can alter the diffusion mechanism in large extent. It has been suggested that in Co-Pt alloy system, the magnetic interaction energy may introduce a positive energy of mixing which can cause clustering of ferromagnetic atoms²³. This phenomenon along with the observed coherency strain in multilayer stacks can drive Co-atoms towards higher concentration resulting in uphill diffusion and leading to enhancement in the PMA.

Interfacial chemical sharpening as a result of uphill diffusion in post annealed ultrathin multilayer stack of Co and Pt results in enhancement of interfacial perpendicular magnetic anisotropy (PMA). Since these elements are considered as perfectly miscible in bulk phase so this surprising result may lead to redraw the phase diagram of two miscible elements (magnetic-non-magnetic) for nano scale regime and offers valuable information for futuristic memory device technology.

Methods

The Co/Pt multilayer films with structure Ta (4 nm)/[Pt (t_{Pt})/Co (t_{Co})]₃/Pt(2 nm) were deposited on Si (100) substrates by DC magnetron sputtering with a base pressure of $\sim 7 \times 10^{-9}$ mbar. During the deposition, Ar pressure in the chamber was

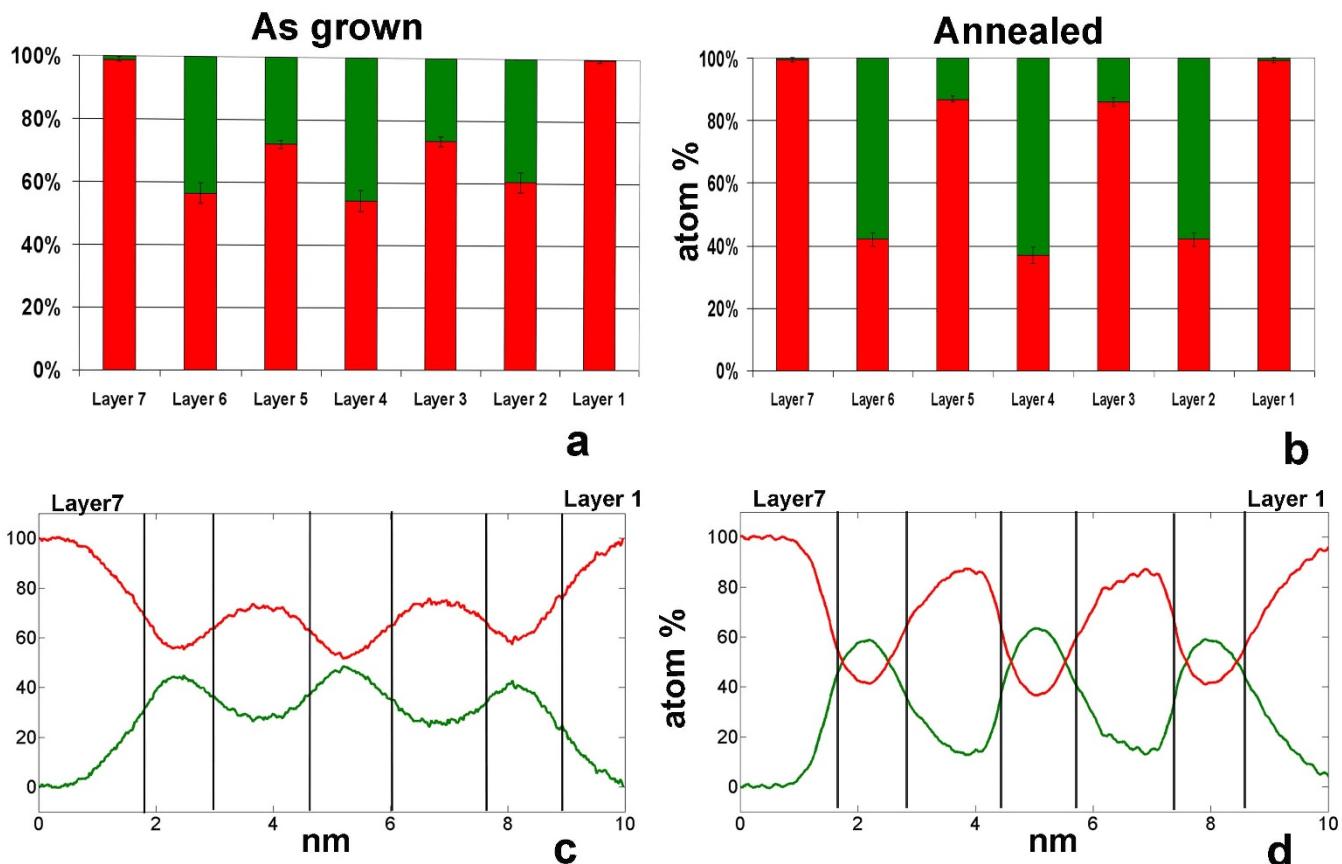


Figure 3 | EDX spectroscopic quantifications within each layers of as grown and annealed samples are plotted respectively in (a) and (b). Average concentration of each layer (Pt in red and Co in green) is plotted with standard deviation. The atomic distribution (averaged over 2 nm along the length of the layers) of Pt (red) and Co (green) across the layers in as grown and annealed samples are plotted in (c) and (d), respectively.

maintained at 5×10^{-3} mbar. The growth rates of Co, Pt, and Ta were 1.2, 2.6, and 1.3 Å/s, respectively.

The samples were then annealed in $\sim 7 \times 10^{-9}$ mbar at 350°C for 1 hr. The magnetic parameters of both as deposited and annealed samples were obtained from in-plane and out-of-plane hysteresis loops measured at room temperature using vibrating sample magnetometer (VSM). To prepare samples for experiments using STEM both as grown and annealed multilayer film samples were cut using Microsaw MS3 (Technoorg Linda, Hungary) with a dimension of 0.5 mm \times 1.5 mm to make sandwich which was then placed within the 1 mm \times 1.8 mm slot of Titanium 3 slots grid (Technoorg Linda, Hungary) and fixed with G1 epoxy (Gatan Inc, USA). Then grinding and dimpling were done to bring down the specimen thickness to a residual value of 10 to 15 μ m, and finally Ar+ ion-beam thinning was performed. By means of double-sided ion-beam etching at small angles ($<6^\circ$) assisted by liquid N2 cooling and low energies (acceleration voltage: 2.5 kV; beam current $< 8 \mu$ A), substantial heating of the TEM foils and consequently the introduction of artifacts were avoided. A FEI-TITAN microscope operated at 300 kV equipped with FEG source, EDX detector, Cs (spherical aberration coefficient) corrector for condenser lens systems and a high angle annular dark field (HAADF) detector was used to perform S/TEM experiments. Sample was tilted to $<110>$ zone axes to make the growth direction of multilayer structure perpendicular to the electron beam. For imaging in STEM mode semi convergence angle of electron probe incident of the specimen and camera length were maintained 17.8 mrad and 128 mm respectively during the experiments and all images were taken with HAADF detector. All images were filtered with similar low pass filter in Fourier space to increase signal to noise ratio. All energy dispersive x-ray (EDX) spectrums data were taken in spot mode for 100 seconds keeping other experimental parameters same as high resolution Z contrast imaging which was acquired for a dwell time of 20 microseconds. EDX quantification was done using TIA software.

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Author contributions

T.D. and S.B. performed the TEM experiments and analysis. P.D.K. and P.C. performed the magnetic, XRD and XRR experiments and analysis. S.C.P. was involved in the initial stage of STEM experiments. H.C.B. was involved in the analysis of the PMA data and paper writing.

Additional information

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