Supporting Information

**Ion-Irradiation-Induced Cobalt/Cobalt Oxide Heterostructures: Printing 3D Interfaces**

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December 2, 2019

S.1
Sample preparation

CoO and Co$_3$O$_4$ samples were RF-sputter deposited from a CoO target. The oxygen content of the samples was controlled by allowing oxygen gas to flow through the sputtering chamber in chosen quantities. XPS spectra for the CoO and Co$_3$O$_4$ samples fabricated for this report are shown in figure 1. Spectra from standard Co$_3$O$_4$ and CoO are indicated by the black and red lines respectively. The smaller peaks or “satellites” observed are known as shake-up satellites and they arise from an interaction between a photoelectron and a valence electron. Through the interaction, a photoelectron can excite a valence electron to a higher energy level and in doing so, lose a few electron volts of its kinetic energy [1]. This will create a satellite peak associated with a core-level peak of photoelectrons. The strength of the satellite peaks in this spectrum provides information on the oxide phase present, strong satellite peaks imply the CoO oxide phase, whereas weak satellite peaks are characteristic of Co$_3$O$_4$ [2]. For samples deposited with 2 % oxygen gas relative to the entire gas flow, the CoO phase is formed. Using a higher oxygen content results in the Co$_3$O$_4$ oxidation state.

![XPS spectra of CoO and Co$_3$O$_4$ normalized to 1. The black and red lines are the expected spectra from CoO and Co$_3$O$_4$ respectively.](image)

Figure S.1: XPS spectra of CoO and Co$_3$O$_4$ normalized to 1. The black and red lines are the expected spectra from CoO and Co$_3$O$_4$ respectively.

For the multilayer films, Co was DC sputtered. For the realization of CoO(0.8nm)/Pt(0.8nm)$_5$, each Co(0.4nm) deposited layer was subsequently exposed to ambient conditions for 3 minutes resulting in the CoO(0.8nm) layers.
**X-ray diffraction analysis of CoO/Pt multilayers**

X-ray diffraction (XRD) measurements were performed on as-grown as well as irradiated, extended [CoO(0.8 nm)/Pt(0.8 nm)]₅ multilayers at room temperature using a Cu-Kα radiation as shown in fig. S2. The as-grown sample shows only the substrate and the CoO/Pt multilayer related superstructure peak. For a better guidance, we calculated the weighted average of the CoO/Pt and Co/Pt peak positions based on the relative amount of the corresponding atoms and included them in the figure. After irradiation, superstructure peak shifts to higher angles closer to the expected Co/Pt peak position. Accordingly, the observed shift is attributed to the formation of metallic Co [3]. On the other hand, a small peak indicated as "X" becomes visible. According to a previous study, this peak could be attributed to nanocrystalline PtO (101) formation [4]. Moreover, oxidation of Pt requires certain conditions such as energy, surface area, etc., and it does not easily happen under ambient conditions. Therefore, even if oxidation of Pt occurs, it should occur internally (i.e., a 0.8 nm thick Pt layer can only capture oxygen from the neighboring CoO, not from air) provided that irradiation supplies the necessary conditions and the Pt cap should remain the same. However, at this point, it could be a speculation and we believe that a more detailed work has to be done to assign this peak to a certain structure.
Figure S.2: Room temperature XRD patterns of as-grown and irradiated extended $\text{[CoO(0.8nm)/Pt(0.8nm)]}_5$ multilayers. The black arrows show the angles where the corresponding crystal structure should have a peak. Dashed lines show calculated weighted averaged peak positions for CoO/Pt (blue) and Co/Pt (purple) multilayers.

**Distribution of protons**

The multilayer system used in this work was irradiated with 0.3 keV protons under normal incidence. SRIM simulations (see figure S.3) show the projected lateral (a) and longitudinal (b) range. A Gaussian-like depth profile is expected throughout the CoO/Pt stack. Deviations occur due to density changes between CoO and Pt layers. The lateral deviation from the incidence axis of incident protons was calculated to be around 3 nm. This means, according to SRIM, that oxygen can be potentially displaced within 3 nm (probably less due to ion stopping energy losses) underneath the irradiation mask in this multilayer system. However, in order to make any conclusions on lateral resolution, dose dependency of the magnetic response in our system has to be investigated. In a previous study, a dose dependent lateral resolution of the proton irradiation induced magnetic patterning via oxygen reduction was explored considering similar conditions for CoO/Pd multilayers. They found that the lateral resolution for device fabrication (i.e., device-to-device distance) was around 7 nm, while the lateral straggle was around 3 nm. The lateral ranges that we found from SRIM simulations are in agreement with that study [5].
However, in order to define the lateral resolution, dose dependence of magnetization recovery for different irradiation mask dimensions should be studied.

Figure S.3: (a) Projected lateral range of energetic protons incident on the [CoO/Pt]$_5$ system used in this study simulated using SRIM. Simulations for 0.1, 0.3, and 0.5 keV irradiation energies are presented. The lowest and highest energies are shown for comparison to the energy used in this work (0.3 keV). (b) Normalized depth distribution of proton concentration calculated by SRIM simulations.

**Perpendicular magnetic anisotropy (PMA) in extended multilayer films**

The M-H loops of figure S.4 were measured at 300 K with the field out-of-plane for the following un-patterned stacks: Si/SiO$_2$/Ta(3nm)/Pt(3nm)/[CoO(0.8nm)/Pt(0.8nm)]$_5$/Pt(2.7nm) and Si/SiO$_2$/Ta(3nm)/Pt(3nm)/[Co(0.4nm)/Pt(0.8nm)]$_5$/Pt(2.7nm), oxide and metallic, respectively. The reason we have 0.4 nm Co in the metallic sample is that we estimated that the oxidation step during Co deposition produces CoO layers that are almost twice as thick as the Co layers in the metallic reference.
The oxide extended sample was irradiated with 0.3 keV H\(^+\) under a fixed dose of 10\(^{17}\) cm\(^{-2}\) (blue data set). Non-irradiated oxide (red) and metallic (green) references were measured for comparison. After proton irradiation, partial PMA is observed in comparison to the non-irradiated oxide, which directly indicates Co metal formation in the CoO/Pt layers. Conversely, the remanence and coercivity (H\(_c\)) of the irradiated multilayer is rather small when compared to the non-irradiated metallic reference where H\(_c\) = 23 mT. This is attributed to damaged Co/Pt interfaces after irradiation. It was shown previously that 30 keV He\(^+\) irradiation of Co/Pt multilayers yields decreased coercivity, arising from interfacial atomic intermixing of Co and Pt. Moreover, in the event of substantial interfacial damage, the samples’ easy axis can switch to in-plane [6]. In the case of 0.3 keV protons, the ion energy is too small to displace Co or Pt, making Co/Pt intermixing unlikely; however, it is probable that the reduced H\(_c\) arises from an interfacial roughening caused by displaced O atoms or the possible formation of PtO.

Saturation magnetizations of approximately 0.71 and 0.35 MA/m for the metallic and irradiated oxide systems were measured, respectively. The latter M\(_s\) was calculated under the assumption that there was no volume change in the CoO layers after irradiation and does not correlate with the metallic reference, implying that the film was only partially reduced of O. For a clearer comparison of the most significant results upon irradiation, please see the table S.1.

Figure S.4: Out-of-plane M-H loops measured by SQUID VSM at room temperature.
Table S.1: A short summary of the main magnetic properties of reference samples as well as some of the selected irradiated samples

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>$M_s$ (MA/m)</th>
<th>Exchange Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co/Pt]$_5$ ref (OOP)</td>
<td>0.71</td>
<td>Not applicable</td>
</tr>
<tr>
<td>[CoO/Pt]$_5$ irradiated (OOP) - extended film</td>
<td>0.35 (~50% of Co ref)</td>
<td>No exchange bias</td>
</tr>
<tr>
<td>[CoO/Pt]$_5$ irradiation through a 500nm mask (OOP)</td>
<td>0.41 (~58% of Co ref)</td>
<td>Exchange bias</td>
</tr>
<tr>
<td>Co(3 nm)/Pt Reference sample (IP) - extended film</td>
<td>1.10 (~1% of Co ref)</td>
<td>No exchange bias</td>
</tr>
<tr>
<td>CoO(6 nm) / Pt irradiation through a 500nm mask (IP)</td>
<td>0.012 (~10% of Co ref)</td>
<td>No exchange bias</td>
</tr>
</tbody>
</table>

In table 1, a short summary of the most important magnetic parameters extracted from certain samples are given in order to support the information given in the main manuscript.

**Magnetic field dependent magnetization measurements of irradiated single CoO and Co$_3$O$_4$ films**

![Figure S5](image)

Figure S5 In-plane magnetic field dependent magnetization curves of a) proton-irradiated extended CoO films and b) proton-irradiated extended Co$_3$O$_4$ films. The colors in a) and b)
correspond to same irradiation doses. M-H curves for films irradiated with protons at ion dose of $1 \times 10^{17}$ ions.cm$^{-2}$ through striped irradiation masks are given for c) CoO, and d) Co$_3$O$_4$.

Figure S.5 shows the room temperature field dependent magnetization curves of the irradiated, extended (a and b) and masked (c and d) cobalt oxide films as under in-plane applied magnetic field. Saturation magnetization given in figures 1 a) and 2 f) have been extracted from these measurements.

**Anomalous Hall Effect (AHE)**

AHE measurements were carried out at room temperature on the same multilayer films discussed in figure S4. A current was applied across the unpatterned films and the transverse resistance ($R_{xy}$) was measured as a function of applied field ($\mu_0H$), across a distance of approximately 4 mm, as shown by the schematic in figure S.6 (a). The AHE curves are shown in figure S.6 (b). This data correlates well with the M-H loops of figure S4. As expected, no AHE was observed in the non-irradiated oxide reference. The metallic reference has squareness close to unity displaying strong anisotropic behavior, whereas the irradiated sample shows only partial PMA in comparison. Hall resistance, however, was measured at half that of the metallic reference, again implying that oxygen was only partially removed.

Figure S.6: (a) Schematic representation of a sample surface contacted with a current source and measuring probes spaced approximately 2 mm apart. The external field is applied out-of-plane. (b) AHE curves for the same multilayer films from the previous section (same color scheme).
References


[4] M. Sarno, E. Ponticorvo Much enhanced electrocatalysis of Pt/PtO2 and low platinum loading Pt/PtO2-Fe3O4 dumbbell nanoparticles
