Supporting Information

Room-temperature electrochemical reduction of epitaxial magnetite films to epitaxial iron films

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Materials and Methods

1. Electrodeposition and electrochemical reduction of Fe₃O₄ films on Au single crystals.

All the Fe₃O₄ films were electrodeposited onto gold single-crystalline substrates from a stirred solution of 87 mM Fe(III), 100 mM triethanolamine (TEA), and 2 M NaOH at 80 °C by applying -1.065 V vs. Ag/AgCl using a Brinkmann PGSTAT 30 Autolab potentiostat controlled with GPES software (version 4.9). The Fe₃O₄ films used to do the reduction experiments were electrodeposited onto Au single crystals by passing about 0.3 C/cm² charge, resulting in a film thickness of about 600 nm. The Fe₃O₄ films deposited on the Au(110) single crystal that used to do the linear sweep voltammetry were electrodeposited by passing about 0.1 C/cm² charge, and were about 200 nm thick.

The pre-deposited Fe₃O₄ films on Au single-crystalline substrates were electrochemically reduced to Fe films in the solution containing only 2 M NaOH at room temperature by applying -1.22 V vs. Ag/AgCl using the Autolab potentiostat. This potential is on the positive edge of the cathodic peaks for film reduction that are shown in Figure 1 of the main text. The cathodic current density during reduction was typically 1-2 mA/cm². The Fe films used to do the X-ray characterization in Figure 2 were fully reduced from the pre-deposited Fe₃O₄ films by applying -1.22 V until the monitored cathodic current reached the plateau, which usually took less than 1 hour. The partially reduced Fe₃O₄ films were produced by applying -1.22 V constant potential until 1 C/cm² charge passed.

2. X-ray diffraction characterization.

X-ray diffraction (XRD) experiments and texture analysis for all the pre-deposited Fe_3O_4 and the Fe films after reduction on Au single crystals were done using a high-resolution Philips X-Pert MRD X-ray diffractometer with a $\text{CuK}\alpha 1$ radiation source ($\lambda = 0.154056 \text{ nm}$). The θ - 2θ scans were obtained using the line focus mode with a hybrid monochromator consisting of a Göbel X-ray mirror and $\text{Ge}[220]$ 2-bounce, 2-crystal monochromator as the primary optic and a 0.18° thin film collimator as the secondary optic. Scans were run from 5° to 100° or 110° based on the 2θ value. The texture analysis was operated in point focus mode using a $2 \text{ mm} \times 2 \text{ mm}$ crossed slit collimator with a Ni filter as the primary optic and a 0.27° parallel plate collimator with flat graphite monochromator as the secondary optic. All the pole figures were run by first setting the diffraction angle, 2θ , for a plane that is not parallel with the surface of the material. The tilt angle, χ , was then varied from 0° to 90° in 3° increments, and at each tilt angle the azimuthal angle was rotated from $\varphi = 0^\circ$ to 360° with increments of 3° .

3. Direct electrodeposition of Fe/Fe₃O₄ heterojunctions on Au single crystals.

In this case, both the Fe and Fe_3O_4 layers in the Fe/Fe₃O₄ heterojunction were electrodeposited from a stirred solution of 87 mM Fe(III), 100 mM triethanolamine (TEA), and 2 M NaOH at 80°C . The Fe layer was first electrodeposited on Au single crystals by applying a constant potential of -1.35 V vs. Ag/AgCl until 1 C/cm^2 charge passed. After the Fe deposition, the surface of the Au single crystal was completely covered by a shiny iron layer. Then, the Fe_3O_4 layer was electrodeposited on top of the pre-deposited Fe layer by applying a constant potential of -1.065 V vs. Ag/AgCl until 0.5 C/cm^2 charge passed. The out-of-plane and in-plane orientations of the

directly deposited Fe and Fe₃O₄ layer layers were determined by X-ray θ -2 θ scans and pole figures, as shown in Figure S1.

4. Special Fe/Fe₃O₄ heterojunctions produced by partially reducing pre-deposited Fe₃O₄ films.

The pre-deposited Fe₃O₄ films on Au(100), Au(110) and Au(111) single crystals were partially reduced by applying a constant potential of -1.20 V vs. Ag/AgCl in 2 M NaOH at room-temperature. X-ray θ -2 θ scans of all three partially reduced Fe₃O₄ films are shown in Figure S2, which confirm that part of the Fe₃O₄ films has been reduced to Fe. The unreduced Fe₃O₄ layers have the same out-of-plane orientations as the as-deposited Fe₃O₄ films shown in Figure 2 in the main text and the orientations of the formed Fe layers are controlled by the Au substrates instead of the precursor Fe₃O₄ films. Therefore, three different types of Fe/Fe₃O₄ heterojunctions were produced: Au(100)/Fe(100)/Fe₃O₄(111), Au(110)/Fe(211)/Fe₃O₄(110), and Au(111)/Fe(110)/ Fe₃O₄(111).

These Fe/Fe₃O₄ heterojunctions are special because in this situation the orientations of both the Fe and Fe₃O₄ layer are controlled by the Au substrate. This property is not likely obtainable by direct deposition techniques in which the orientation of the upper layer is usually controlled by the directly contacted bottom layer. For example, if we first electrochemically deposit Fe on the Au single crystal, then electrochemically deposit Fe₃O₄ on the pre-deposited Fe layer, the orientation of the Fe₃O₄ layer will be controlled by the Fe layer instead of Au substrate. This is

proved by the X-ray diffraction θ - 2θ scans and pole figure measurements (Figure S1) on the directly deposited Fe₃O₄/Fe heterojunctions on Au single crystals. The directly deposited Fe layer has the same out-of-plane orientation as the Fe layer reduced from precursor Fe₃O₄ (Figures. S1 & S2). However, the orientations of the directly deposited Fe₃O₄ layers on the pre-deposited Fe layer are different from those directly deposited Fe₃O₄ on Au. In the situation of directly deposited Fe₃O₄/Fe heterojunctions on Au(100), the produced Fe₃O₄/Fe heterojunction is Fe₃O₄(100)/Fe(100)/Au(100). On Au(110), the Fe₃O₄ layer has two different out-of-plane orientations, (110) and (311). On Au(111), the Fe₃O₄ layer also has both (111) and (100) out-of-plane orientations. Thus, by partially reducing pre-deposited Fe₃O₄ films on single-crystalline Au substrates, we are able to produce singly oriented Fe₃O₄/Fe heterojunctions on Au(110) & Au(111), which are not producible by direct deposition.

5. Determination of the in-plane orientation of Fe films reduced from Fe₃O₄ films using X-ray pole figures.

The in-plane orientations of the Fe films after reduction on Au(100), Au(110), and Au(111) single crystals were measured by the X-ray pole figures as shown in Figures S3e, S3e', and S3e'' (also in the main text Figures. 2g-i). The in-plane orientations of the Fe films could be solved by comparing the measured X-ray pole figures with the corresponding stereographic projection generated using CaRIne 3.1 software. A stereographic projection is a plot which shows the angular relationships of the faces in the crystal based on its crystallographic structure. The (110) pole figure of the Fe film on Au(100) in Figure S3e shows four equally spaced ($\Delta\phi = 90^\circ$) peaks

appearing at a tilt angle, χ , of 45° , which matches with the interplanar angle between the $\{110\}$ and $\{100\}$ planes of Fe. Four peaks indicate that there is only one (100) domain of Fe. A Fe(100) stereographic projection probing Fe(110) type reflections is shown in Figure S3a which matches with the Fe(110) pole figure in Figure S3e except that there is another broad peak at the center in the pole figure. This peak is due to the high-angle tail of the Au(200) peak at the 2θ angle of 44.431° . Because the Au(200) peak is broad at the base as shown in Figure 2a in the main text, the high-angle tail of the Au(200) peak extends past 44.671° , which is the 2θ angle used in this Fe(110) pole figure. The Au(100) stereographic projection of Au probing the Au(200) type of reflection is shown in Figure S3c. If we overlap the stereographic projections of Fe in Figure S3b and the stereographic projections of Au in Figure S3c (as shown in Figure S3d), the combined projections match the measured Fe(110) pole figure of the Fe film. Based on the matched stereographic projection, the in-plane orientation relationship of the Fe film and the Au substrate can be determined using the CaRIne software to point out any two orthogonal directions in the Fe and Au. Combining the out-of-plane orientation relationship based on the θ - 2θ scan (Figure 2a in the main text) with the in-plane orientation relationship based on the pole figure (Figure 2g), the epitaxial relationship for the Fe film on Au(100) is Fe(100)[001]//Au(100)[011].

On the Au(110) single crystal, the (110) pole figure of Fe (Figure 2h) shows two peaks at both $\chi \approx 30^\circ$ and 54° which are due to $[211]$ orientation of the Fe film. The presence of two peaks at $\chi \approx 54^\circ$ indicates two antiparallely aligned $\{211\}$ domains of Fe on Au(110) which matches with the corresponding stereographic projections in Figures. S3a' and S3b'. Because the peaks

from these two domains overlap with each other at $\chi \approx 30^\circ$, there are only two peaks at $\chi \approx 30^\circ$. Similar to the situation in the Fe(110) pole figure on Au(100), the two more intense peaks at tilt angle of 45° arise from the Au(110) substrate and match well with the angle between the (110) and (200) planes of Au. Because the difference between the 2θ values of Au(200) and Fe(110) is only 0.24° , the reflection of the (110) plane of Au is very intense. This causes the four peaks from the reflection of the in-plane [211] orientation of the Fe film at $\chi \approx 73^\circ$ (which are shown in the stereographic projection in Figure S3b') to be absent because the intensity of the high tilt angle reflections are too low compared with the strong reflection of (110) plane of Au substrate. Therefore, the epitaxial relationships for the two Fe domains on Au(110) are Fe(211)[01 $\bar{1}$]/Au(110)[001] and Fe(211)[01 $\bar{1}$]/Au(110)[00 $\bar{1}$].

The (211) pole figure of Fe film on Au(111) shown in Figure 2i is more complicated than the first two. It appears to have 6 “elongated” peaks at $\chi \approx 30^\circ$, 6 peaks at $\chi \approx 54^\circ$, and 9 weak peaks at $\chi \approx 73^\circ$, 3 of which are more intense than the others. These tilt angles are matched with the interplanar angles of {211} and {110} for Fe. The presence of 6 peaks at $\chi \approx 54^\circ$ suggests there are three {110} domains of Fe that are rotated by $\Delta\phi = 120^\circ$ relative to each other. By comparing the (211) pole figure of Fe on Au(111) with the Fe(110) stereographic projection probing the (211) types of reflections (Figs. S3a'' and S3b''), it reveals that the 6 “elongated” peaks at $\chi \approx 30^\circ$ are actually 12 peaks, each two of which are close to each other. The three stronger peaks at $\chi \approx 72^\circ$ and the one peak at the center are, again, due to the high-angle tail of the Au(222) peak. There should also be 12 peaks from the reflection of {110} planes of Fe at $\chi \approx 73^\circ$. However,

some of them are absent because of the low intensity of the reflection at high tilt angle.

Therefore, the epitaxial relationship for three domains of Fe film on the Au(111) substrate are

$\text{Fe}(110)[1\ \bar{1}\ 0]//\text{Au}(111)[\ \bar{1}\ \bar{1}\ 2]$, $\text{Fe}(110)[\ 1\ \bar{1}\ 0]//\text{Au}(111)[2\ \bar{1}\ \bar{1}]$, and $\text{Fe}(110)[1\ \bar{1}\ 0]//\text{Au}(111)[\ \bar{1}\ 2\ \bar{1}]$.

6. SEM images of the precursor Fe_3O_4 film and the Fe film reduced from the precursor Fe_3O_4 film.

The SEM images of the precursor Fe_3O_4 film and the Fe film reduced from the precursor Fe_3O_4 film as shown in Figure S4 were taken on the Hitachi S4700 FE-SEM with an accelerating voltage of 15 kV. The precursor magnetite film has the crystal size about 200-300 nm. After the reduction, the Fe film has the crystal size about of 100-150 nm.

7. Hysteresis loops of the as-deposited Fe_3O_4 film and the Fe film after reduction on Au(110).

The hysteresis loops of the as-deposited Fe_3O_4 film and the Fe film after reduction on a Au(110) single crystal are measured in the Quantum Design Physical Property Measurement System (PPMS, San Diego, CA) using the VSM mode. The Au(110) single crystal used in this experiment has a diameter of 5 mm and a thickness of 1 mm.

Supporting Figures

Figure S1. X-ray θ - 2θ scans and pole figure measurements of electrochemically deposited $\text{Fe}_3\text{O}_4/\text{Fe}$ heterojunctions on Au single crystals. X-ray θ - 2θ scans of $\text{Fe}_3\text{O}_4/\text{Fe}$ on (a) Au(100), (d) Au(110) and (g) Au(111). Fe(110) pole figures of $\text{Fe}_3\text{O}_4/\text{Fe}$ on (b) Au(100) and (e) Au(110) and Fe(211) pole figure of $\text{Fe}_3\text{O}_4/\text{Fe}$ on (h) Au(111). Fe_3O_4 (311) pole figures of $\text{Fe}_3\text{O}_4/\text{Fe}$ on (c) Au(100), (f) Au(110), and (i) Au(111). (Peaks marked with a red star are from Au.)

Figure S2. X-ray θ - 2θ scans for partially reduced Fe_3O_4 films on (A) Au(100), (B) Au(110) and (C) Au(111) single crystals. (Peaks marked with a red star are from Au.)

Figure S3. Fe(100) stereographic projection probing the Fe(110) reflection, Fe(211) stereographic projection probing the Fe(110) reflection, and Fe(110) stereographic projection probing the Fe(211) reflection are shown in **a**, **a'** and **a''** (**column a**), respectively. Single domain of Fe(100) stereographic projection probing Fe(110) type of reflection is shown in **b** which remains the same as the one in **a**. Overlapping of two antiparalleled domains of Fe(211) stereographic projection probing Fe(110) type of reflection is shown in **b'**. Overlapping of three 120° rotated domains of Fe(110) stereographic projection probing Fe(211) type of reflection is shown in **b''**. Au(100) stereographic projection probing Au(200) type of reflection, Au(110) stereographic projection probing Au(200) type of reflection, and Au(111) stereographic projection probing Au(222) type of reflection are shown in **c**, **c'** and **c''** (**column c**), respectively. The overlapping of corresponding Fe stereographic projection in **column b** and Au stereographic projection in

column c are shown in **column d**. The measured (110), (110), and (211) pole figures of Fe on Au(100), Au(110) and Au(111) are shown in **e**, **e'**, and **e''**, respectively.

Figure S4. Top-view SEM images of the Fe₃O₄ film (left) and the Fe film (right) reduced from the Fe₃O₄ film on Au(111).