Supplementary Information

Improving MgO/Fe Insulator-Metal Interface Structure through Oxygen-Precoating of Fe(001)

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Cleaning process of Fe(001) whisker single crystal surface.

A Fe(001) whisker single crystal was cleaned via Ar^+ sputtering process (see Fig. S1a) with the evolution of temperature between room temperature and 350, 500, 600 degrees Celsius. The cleaned surface showed the squared bcc(001) symmetry spots in the low-energy electron diffraction (LEED) images (see Fig. S1b).

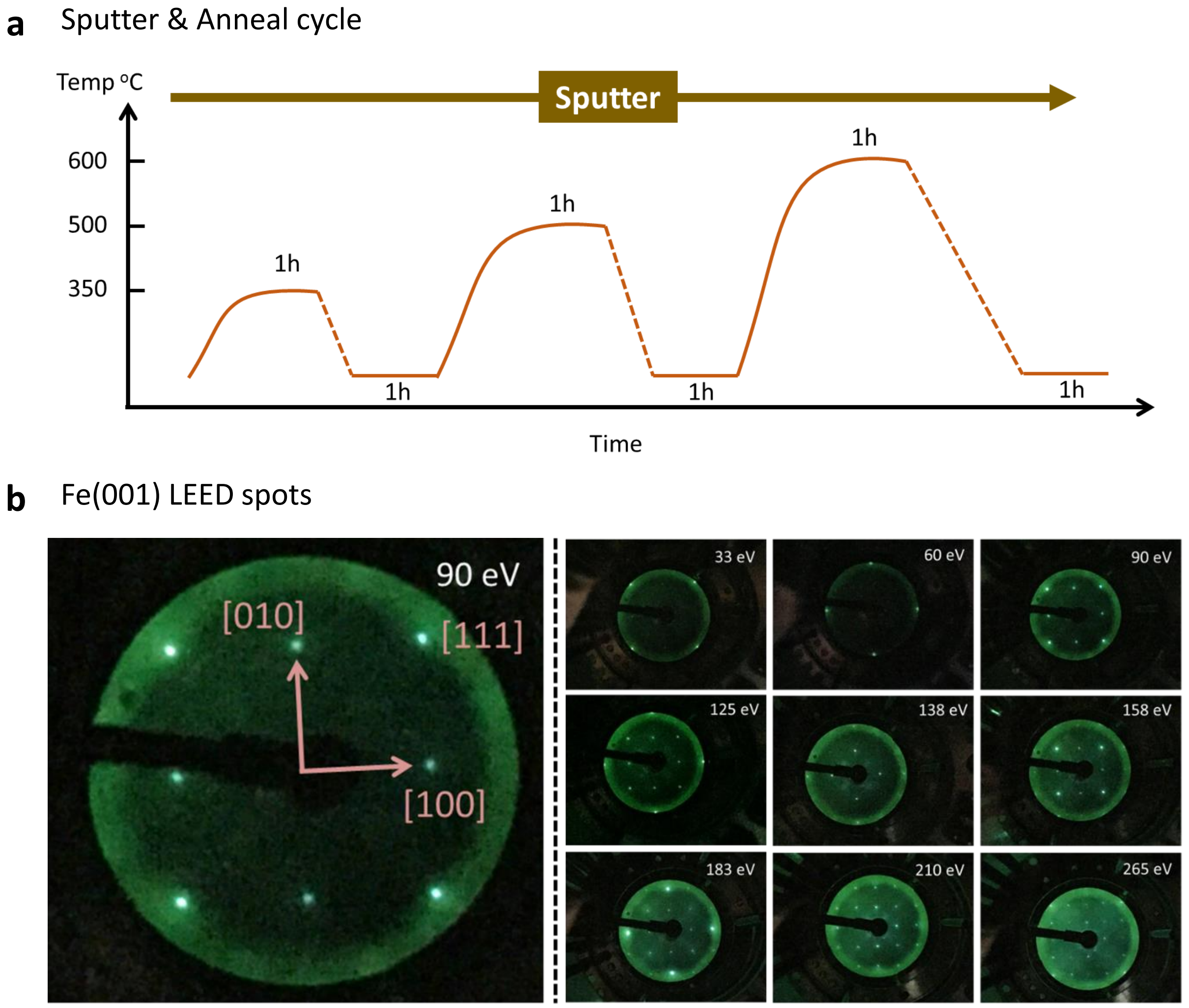

Figure S1. (a) UHV cleaning cycles of the Fe(001) whisker surface using Ar^+ sputtering at different substrate temperatures. (b) LEED images on the cleaned Fe(001) surface at 300 K in UHV.

Magnesium evaporation control

A magnesium rod (length 50 mm, diameter 1.6 mm, purity 99.95%) was set in the electron bombardment type evaporator (see Fig. S2a). The top of the Mg rod was heated by the accelerated hot electrons (HV 0.5 kV, EC 3-4 mA) from the tungsten filament. The Mg deposition rate was controlled by monitoring the quartz crystal microbalance and the evaporated Mg flux (see Fig. S2b). Figure S2c-e shows STM results of 1.5 ML Mg films deposited on the O/Fe(001). The absorbed Mg atoms thermally diffused on the surface and the 1st Mg layer grew in a step flow mode. However, the second Mg layer started to grow before the first Mg layer completely covered the substrate O/Fe(001) surface. This means that the Mg films grew in a layer-plus-island mode. Also, both first and second Mg layers have a height of ~0.15 nm.

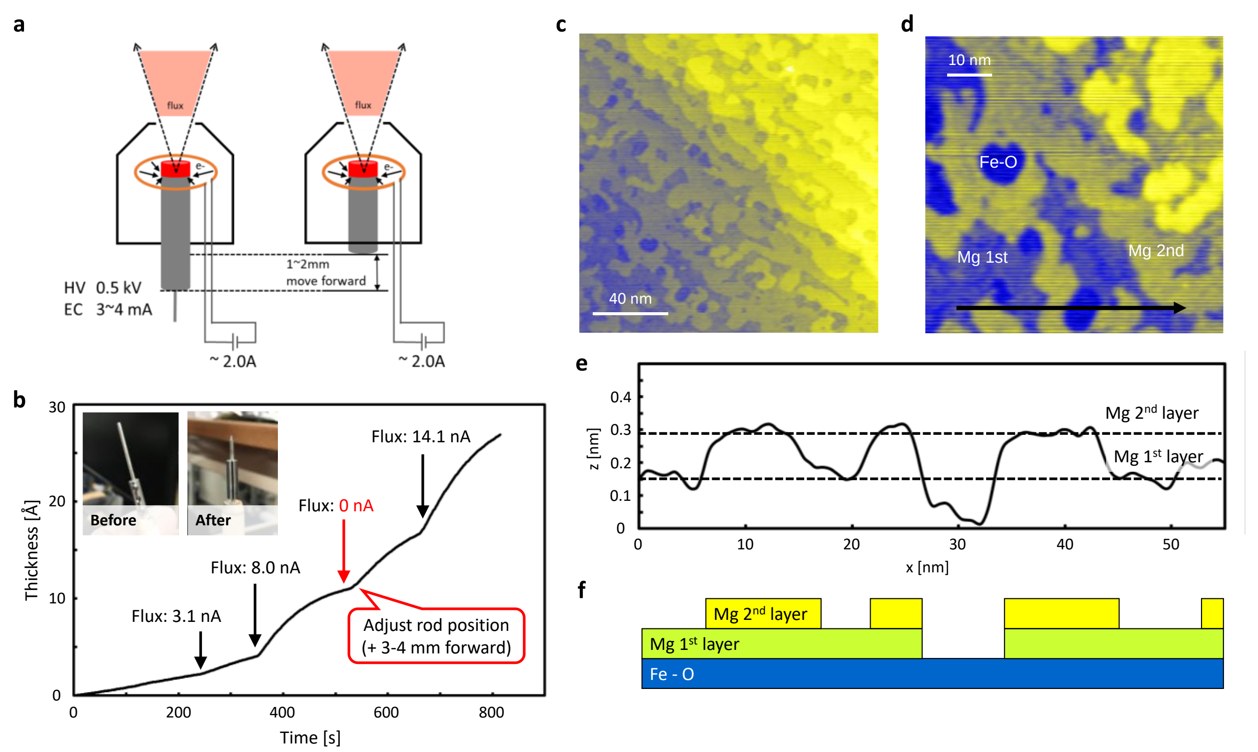

Figure S2. (a) A sketch of the magnesium (Mg) evaporator. A constant flux was provided by adjusting the rod position. (b) The Mg deposition rate obtained by the quartz crystal microbalance was controlled by the Mg flux of the evaporator. (c, d) STM topographic images obtained on the surface of the Fe(001)-whisker substrate covered by 1.4 ML Mg: (c) 100×100 nm^2, V_s = -1.0 V, I = 80 pA (d) 50×50 nm^2, V_s = -1.0 V, I = 100 pA. Blue -yellow contrast illustrates the low-high height scale. (e) Height profile along the arrow in (d). (f) The cross section view model corresponds to the height profile in (e).

Electronic structures of Mg films on Fe(001)-*p*(1×1)O

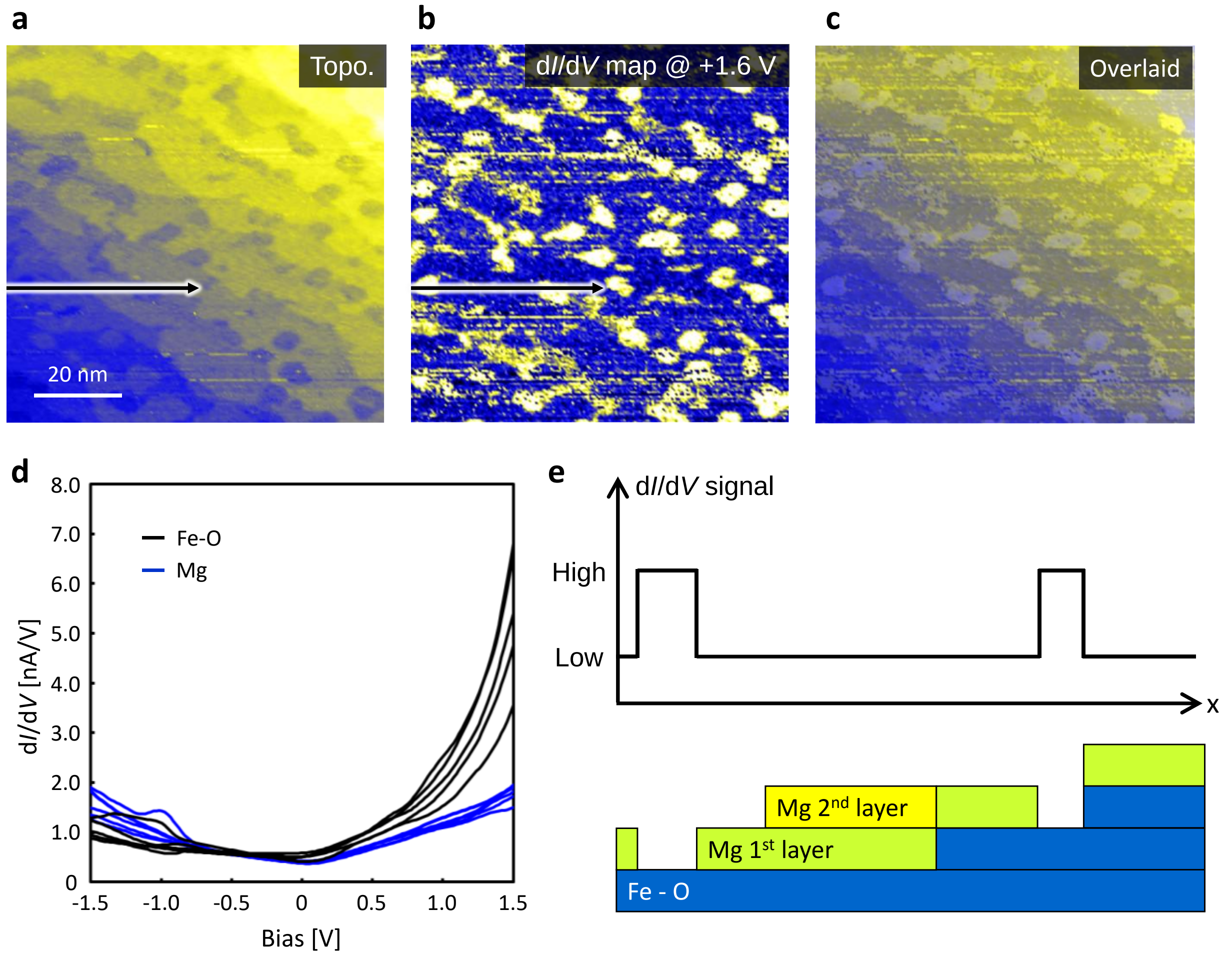

Figure S3. STM/STS results obtained on the 1.4 ML Mg films deposited on the O/Fe(001) substrate. (a, b) Simultaneously obtained (a) STM topographic image and (a) d*I*/d*V* map at +1.6 V: 100×100 nm^2, V_s = -1.0 V, *I* = 520 pA. In (a), blue -yellow contrast illustrates the low-high height scale. In (b), blue -yellow contrast illustrates the low-high differential tunneling conductance (d*I*/d*V*) scale. (c) Overlaid image of (a) and (b). (d) d*I*/d*V* curves obtained at the substrate O/Fe(001) area (black lines) and the Mg films (blue lines). (e) Comparison between d*I*/d*V* signal and the cross section view model of the Mg films on O/Fe(001).

Line profiles in d*I*/d*V* maps across the atomic defect in the MgO nanoisland

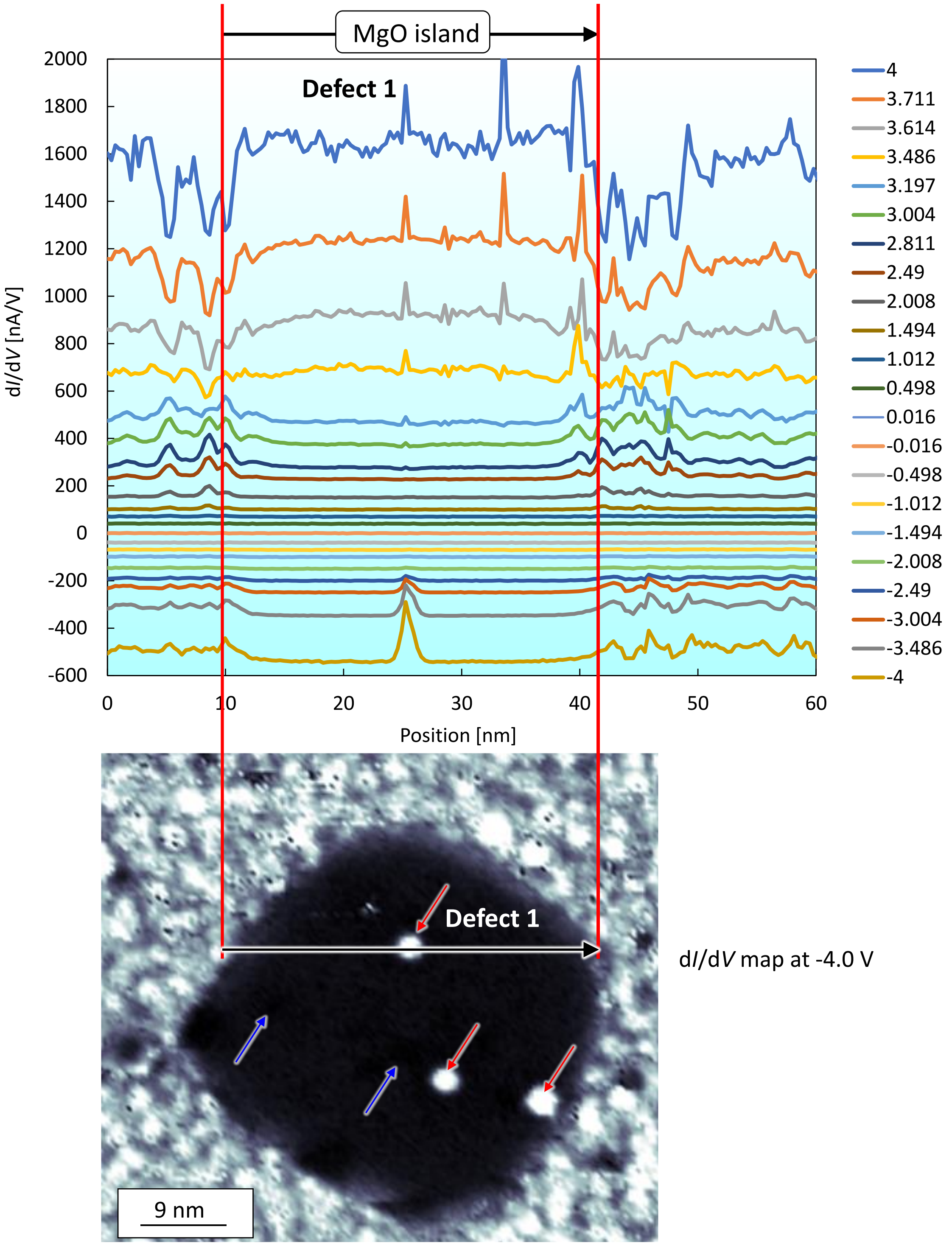

Figure S4. Line profiles along the black arrow in the d*I*/d*V* maps at various bias voltages between +4 and -4 V (V_s = +4.0 V, *I* = 1 nA), which across the regularly shaped MgO nanoisland. Defect 1 and 2 positions are marked by red and blue arrows, respectively.

DFT calculations of CuPc DOS

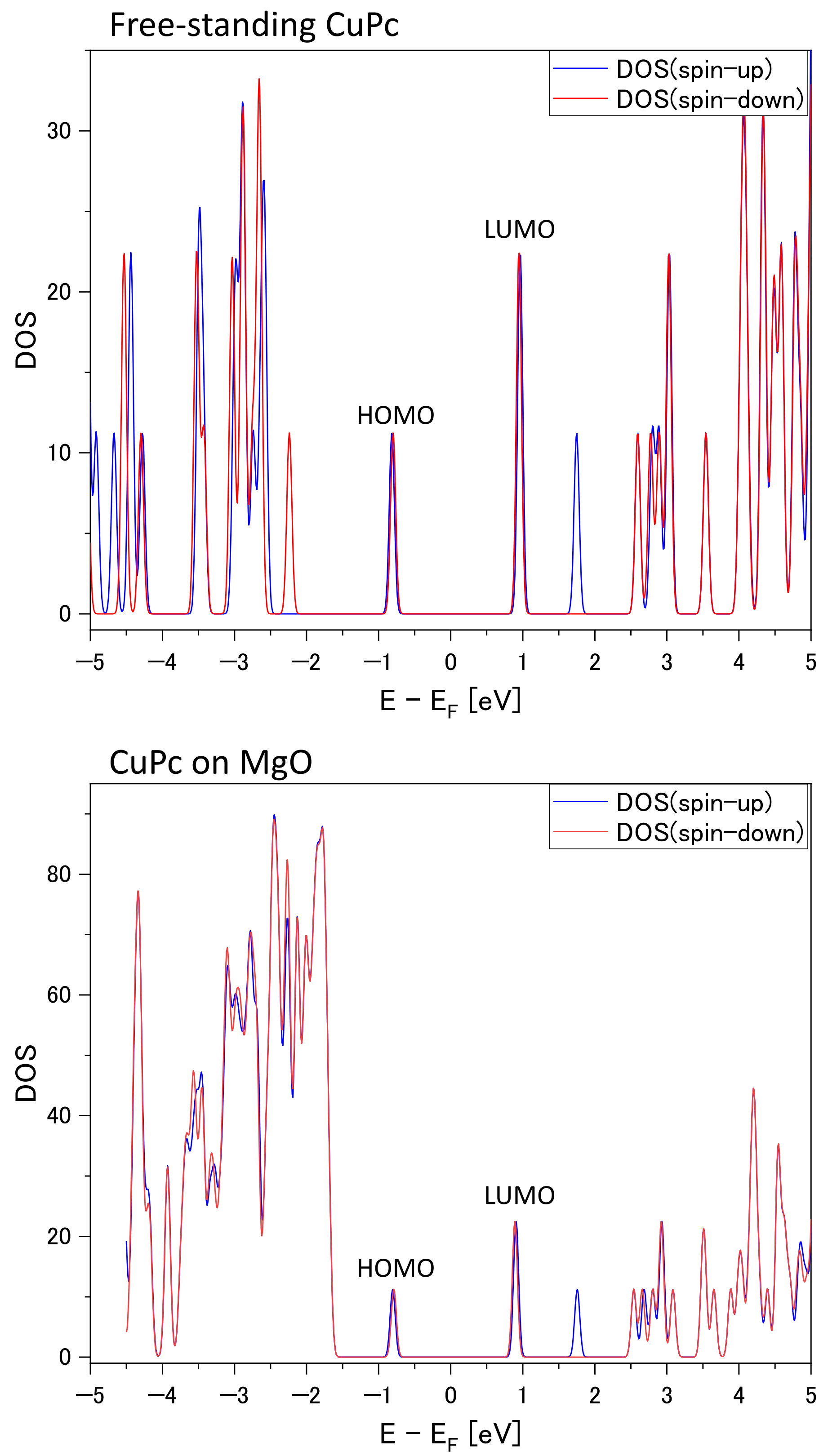

Figure S5. DFT calculation results of CuPc DOS. Upper and lower panels denote free-standing CuPc and CuPc adsorbed on MgO surface, respectively.