

## **Supplemental Material: Resistive switching memory performance in oxide hetero-nanocrystals with well-controlled interfaces**

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## Section S1: The relationship between Fe<sub>3</sub>O<sub>4</sub> crystallinity and Fe deposition amount

To compare the crystallinities of Fe<sub>3</sub>O<sub>4</sub>/GeO<sub>x</sub>/Ge nanocrystals (NCs) with Fe coating layers of 6, 15, and 30 MLs, the analyses of 224<sub>Fe3O4</sub> spots in reflection high energy electron diffraction (RHEED) patterns of these NCs (Figs. S1(a)-(c)) were performed by fitting with Gaussian function. Figures S1(d)-(f) show the line profiles corresponding to the solid lines in Figs. S1(a)-(c), respectively. The full width at half maximum (FWHM) values of the 224<sub>Fe3O4</sub> fitted peaks in Fe<sub>3</sub>O<sub>4</sub>/Ge NCs with Fe coating layers of 6, 15, and 30 MLs were acquired to be 5.5, 4.7, and 3.9 nm<sup>-1</sup>, respectively, indicating that the crystallinity is enhanced with increasing the deposition amount of Fe coating layer. This relationship between Fe<sub>3</sub>O<sub>4</sub> crystallinity and Fe deposition amount is similar to the previously-reported result in Fe<sub>3</sub>O<sub>4</sub> NCs on Ge nuclei formed by Fe deposition at high temperature of 250°C [1], where it was reported that oxidation of Ge nucleus surface was prevented at the first stage of Fe<sub>3</sub>O<sub>4</sub> growth by Fe coating, resulting in the higher crystallinity of Fe<sub>3</sub>O<sub>4</sub>.

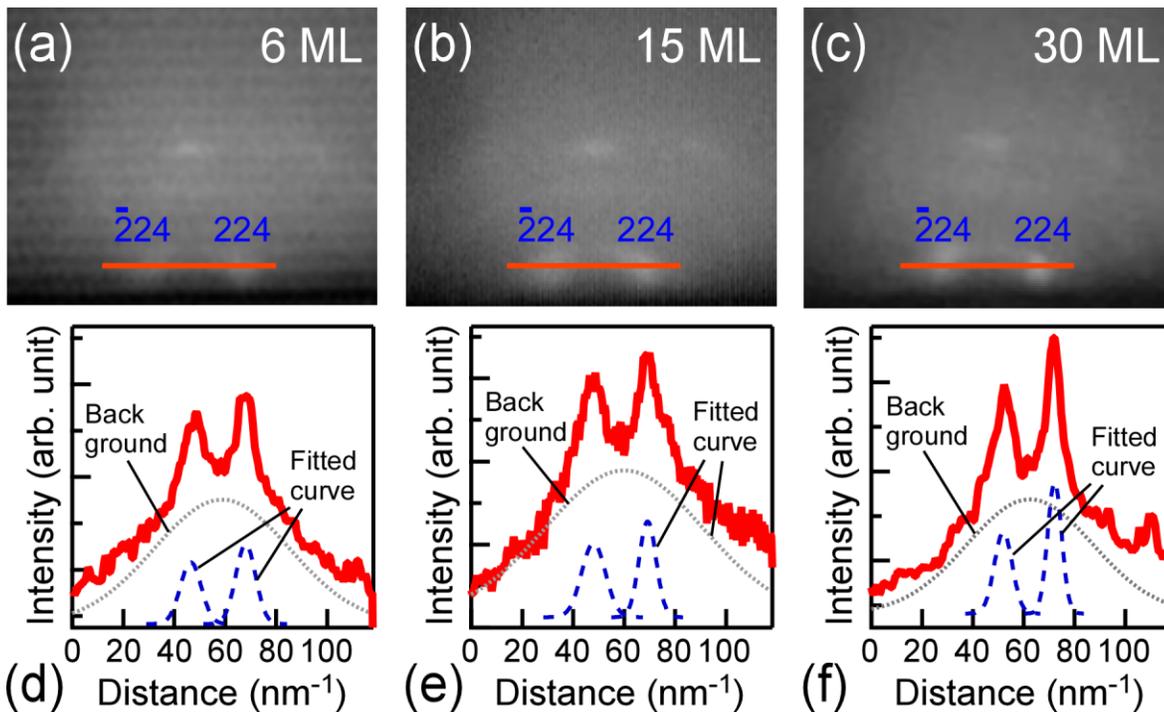


Figure S1 The RHEED patterns of Fe<sub>3</sub>O<sub>4</sub> NCs on Ge nuclei with Fe coating layers of (a) 6, (b) 15, and (c) 30 MLs, respectively. The profiles along the lines in (a), (b) and (c) are shown in (d), (e), and (f) respectively. The dotted and broken curves denote background and fitted ones, respectively.

## Section S2: The resistive switching variability of the NCs

The  $I_S$ - $V_S$  curves were acquired 15-20 times on each NC by C-AFM and measured NC number was 6-8 for each sample (total  $I_S$ - $V_S$  curves: 120 for each sample). The resistive switching probability value was defined as the switching observation number divided by measurement number. The resistive switching probability value measured on each NC is shown in Table S1. The average resistive switching probability value in one sample ( $P_{\text{switch}}$ ) was ~43, ~90, and ~3 % in as-grown NCs and NCs annealed at 250°C and at 400°C, respectively (Fig. S2). Note that NCs annealed at 250°C exhibited substantially higher  $P_{\text{switch}}$  of ~90 % than the other NCs. Besides, the standard deviations of the  $P_{\text{switch}}$  of individual NCs were estimated from Table S1 to be 0.09 in NCs annealed at 250°C, 0.26 in as-grown NCs. For reference, that in our previous  $\text{Fe}_3\text{O}_4$  NCs formed at high temperature is 0.3. This demonstrates that NCs annealed at 250°C had that the resistive switching uniformity was improved.

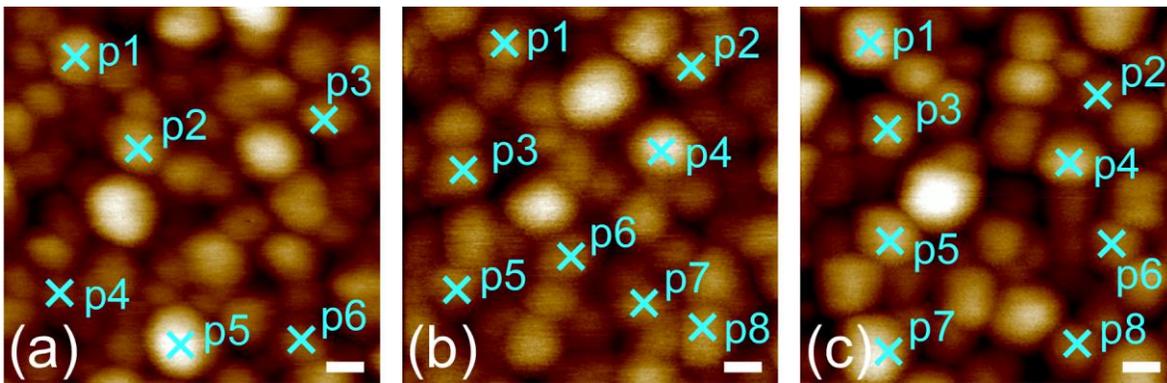


Figure S2 AFM images of (a) as-grown NCs and (b) NCs annealed at 250°C and (c) at 400°C. The  $I_S$ - $V_S$  measurement points are denoted by the cross marks in (a)-(c). Solid lines denote scale bars of 20 nm.

Table S1 Resistive switching probability measured on each NC in each sample.

	p1	p2	p3	p4	p5	p6	p7	p8
as-grown	45%	30%	45%	5%	50%	85%		
250	100%	87%	87%	93%	73%	87%	93%	100%
400	7%	0%	7%	0%	0%	7%	0%	0%

### Section S3: XPS measurement of Fe<sub>3</sub>O<sub>4</sub> NCs with the interfaces of Fe<sub>3</sub>O<sub>4</sub>/GeO<sub>x</sub>/Ge

The compositions of as-grown NCs and NCs annealed at 250°C and 400°C were precisely investigated by XPS measurements in the Fe2p region (Fig. S3). Other studies have reported that FeO and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> have satellite peaks near 715 or 720 eV, respectively, while Fe<sub>3</sub>O<sub>4</sub> has no satellite peaks [2]. The XPS spectra of as-grown NCs and NCs annealed at 250°C and 400°C displayed no satellite peaks, indicating that all the samples are Fe<sub>3</sub>O<sub>4</sub>. We also measured the XPS spectra around Ge3d to obtain the compositional information near the interface (Fig. S4). All the NCs had the peaks coming from oxidation states of Ge, indicating that GeO<sub>x</sub> was formed between Fe<sub>3</sub>O<sub>4</sub> and Ge nuclei through the oxidation of Ge nucleus interface. In the sample annealed at higher temperature (NCs annealed at 400°C), remarkable Fe-Ge peaks were also observed. The XPS spectra in the Ge3d region were deconvolved with Gaussian functions at the peak positions of Ge<sup>0</sup> (29.3 eV), Ge<sup>+</sup> (30.1 eV), Ge<sup>2+</sup> (31.1 eV), Ge<sup>3+</sup> (32.0 eV), Ge<sup>4+</sup> (32.6 eV), and Fe-Ge (29.8 eV) [3,4]. The integrated intensity ratios of Fe-Ge peak to the sum of all the peaks (Fe-Ge mixing ratio) were almost zero for as-grown (~0.6%) and NCs annealed at 250°C (~0.3%), while the ratio was high (17.4%) for NCs annealed at 400°C (Fig. 3(a) in main text). In NCs annealed at 400°C, this high Fe-Ge mixing ratio implies that Fe and Ge were mixed at the region near the interface, namely in GeO<sub>x</sub> interface layer, during high temperature annealing process. This demonstrates that as-grown NCs and NCs annealed at 250°C without high temperature annealing process have higher-quality GeO<sub>x</sub> than NCs annealed at 400°C.

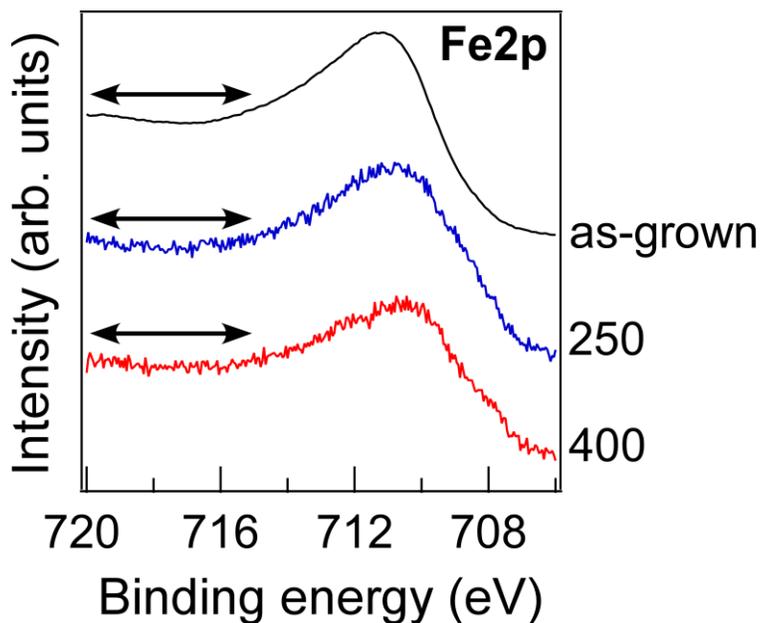


Figure S3 XPS spectra in the Fe2p region in as-grown NCs and NCs annealed at 250°C (250) and NCs annealed at 400°C (400). No satellite peaks near 715-720 eV.

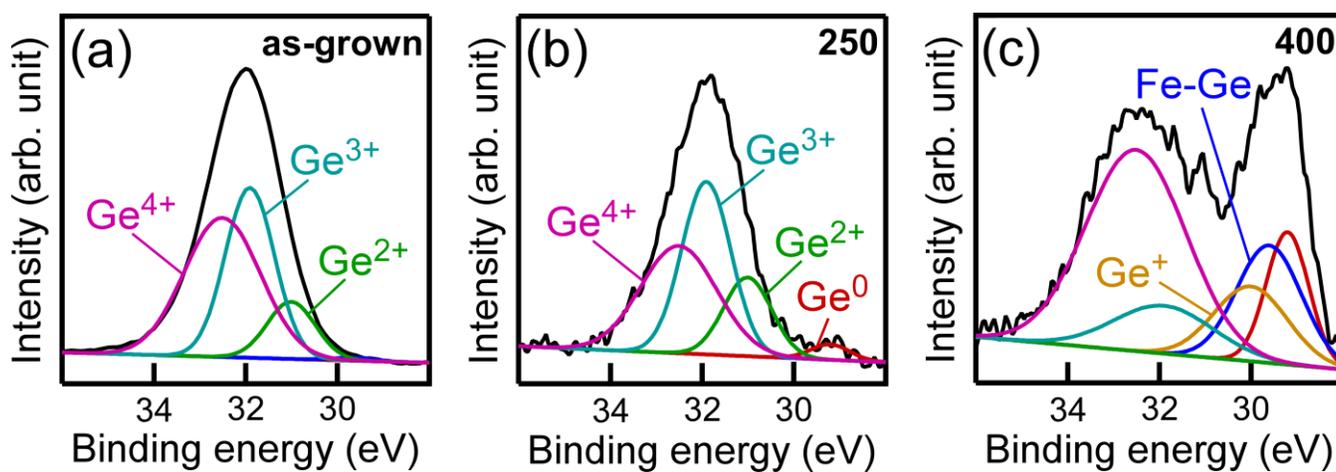


Figure S4 XPS spectra around Ge3d in (a) as-grown NCs and (b) NCs annealed at 250°C (250) and (c) at 400°C (400).

## References

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