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Citation: *J. Appl. Phys.* **111**, 07B515 (2012); doi: 10.1063/1.3676207

View online: <http://dx.doi.org/10.1063/1.3676207>

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## Self-assembly of Fe nanocluster arrays on templated surfaces

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(Presented 2 November 2011; received 23 September 2011; accepted 9 November 2011; published online 5 March 2012)

The growth of Fe nanoclusters on the Ge(001) and MoO<sub>2</sub>/Mo(110) surfaces has been studied using low-temperature scanning tunneling microscopy (STM) and X-ray magnetic circular dichroism (XMCD). STM results indicate that at low coverage Fe atoms self-assemble on both surfaces into well-separated nanoclusters, which nucleate at equivalent surface sites. Their size, shape, and the observed spatial separation are dictated by the substrate and depend on preparation conditions. Annealing the Fe nanoclusters on Ge(001) at 420 K leads to the formation of linear nanocluster arrays, which follow the Ge dimer rows of the substrate, due to cluster mobility at such temperature. In turn, linear Fe nanocluster arrays are formed on the MoO<sub>2</sub>/Mo(110) surface at room temperature at a surface coverage greater than 0.5 monolayer. This is due to the more pronounced row pattern of the MoO<sub>2</sub>/Mo(110) surface compared to Ge(001). These nanocluster arrays follow the direction of the oxide rows of the strained MoO<sub>2</sub>/Mo(110) surface. The Fe nanoclusters formed on both surfaces show a superparamagnetic behavior as measured by XMCD.

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### I. INTRODUCTION

Self-assembled atomic or molecular nanostructures are an important topic in modern surface science and nanotechnology.<sup>1–5</sup> A major reason for this attention is the prospect of controlling atomic scale structures on surfaces, which can lead to mass fabrication of usable systems and novel devices. A promising approach toward the control of self-assembly is the use of preformed surface templates onto which particular nanostructures can be arranged in a well-ordered fashion.<sup>5–7</sup> Surfaces such as the Ge(001)–(2 × 1) reconstructed surface and the MoO<sub>2</sub>/Mo(110) surface exhibit well-defined nanorows formed by Ge dimers and Mo oxide, respectively.<sup>8,9</sup> Such surfaces are suitable templates for the growth of well-ordered, uniformly sized metal nanoclusters.<sup>10,11</sup> In the present work we use the Ge(001)–(2 × 1) reconstructed surface and the MoO<sub>2</sub>/Mo(110) surface as templates for the growth of ordered arrays of Fe nanoclusters. We employ scanning tunneling microscopy (STM) and X-ray magnetic circular dichroism (XMCD) to study the nucleation, structure, and magnetic properties of the Fe nanoclusters. The results obtained provide important information on Fe nanoclusters grown on the Ge(001) surface and the oxidized Mo(110) surface and will be of value for the development of spin-electronics.

### II. EXPERIMENTAL

STM experiments were performed at 78 K, using a commercial instrument from Createc, in an ultrahigh-vacuum

system ( $5 \times 10^{-11}$  mbar). An electrochemically etched monocrystalline W(100) tip<sup>12</sup> was used to record STM images in constant current mode. The voltage  $V_b$  corresponds to the sample bias with respect to the tip. The Ge(001) surface was cleaned by cycles of Ne<sup>+</sup> ion sputtering at an energy of 0.6 keV and annealing at 925 K for 40 min. The Mo(110) surface was prepared by *in situ* annealing at 1300 K in an oxygen atmosphere of  $1 \times 10^{-6}$  mbar, followed by high temperature flashes at 2200 K. The sample was oxidized at 1250 K in an oxygen atmosphere of  $5 \times 10^{-7}$  mbar for 2 min. The quality of both substrates was verified by low-energy electron diffraction and STM before the deposition of Fe. Fe was deposited from an electron-beam evaporator at a rate of 0.1 monolayer (ML) per minute. The substrate was kept at room temperature (RT) during deposition. After deposition, the sample was transferred into the STM and cooled down to 78 K. XMCD measurements were performed at the D1011 beamline at MAX-lab, Sweden. Fe 2p X-ray absorption (XA) spectra were recorded using sample drain current. The relative intensities of the spectra were normalized to the same continuum jump at the photon energy of 745 eV. The photon energy resolution was set to 200 meV at the Fe L<sub>3</sub>-edge ( $\approx 710$  eV). For XMCD measurements a switchable magnetic field of 0.05 T was applied.

### III. RESULTS

The Ge(001)–(2 × 1) surface reconstruction exhibits dimer rows, which are formed through the pairing of nearest-neighbor surface atoms.<sup>8</sup> These rows are oriented along the  $[1\bar{1}0]$  crystallographic direction. At low coverage (0.05 ML–0.50 ML) Fe forms uniformly sized, well-separated nanoclusters on the

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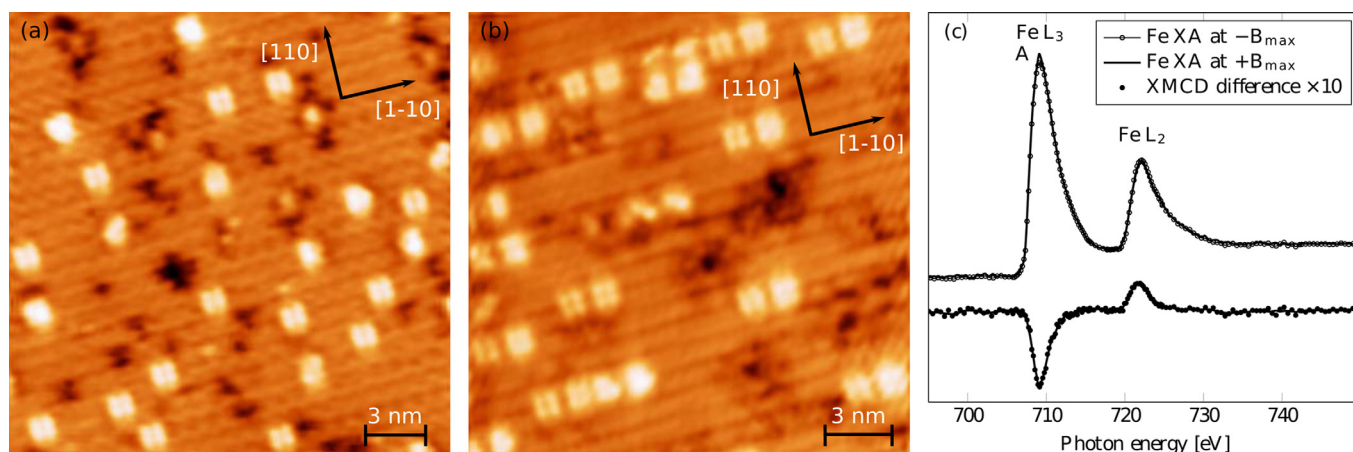


FIG. 1. (Color online) STM images of (a) 0.2 ML of Fe on Ge(001),  $V_b = 1.5$  V,  $I_t = 1.60$  nA,  $24$  nm  $\times$   $24$  nm,  $78$  K and (b) 0.3 ML of Fe on Ge(001) annealed at  $420$  K for  $30$  min to form linear nanocluster arrays,  $V_b = 1.5$  V,  $I_t = 1.60$  nA,  $20$  nm  $\times$   $20$  nm,  $78$  K. (c) Fe  $2p$  XA spectra measured at  $150$  K from  $0.3$  ML of Fe nanocluster arrays on Ge(001) with the magnetic field of  $0.05$  T applied in two opposite directions ( $-B_{max}$  and  $+B_{max}$ ). The XMCD spectrum is multiplied by a factor of  $10$  for clarity.

Ge(001) surface at RT (Fig. 1(a)). Each individual nanocluster consists of  $16$  Fe atoms<sup>11</sup> and its size is equal to  $9 \text{ \AA} \times 9 \text{ \AA}$ . They have an apparent corrugation height of  $(1.1 \pm 0.1) \text{ \AA}$ , which does not depend on the bias voltage. It is clear from Fig. 1(a) that these nanoclusters follow the  $[1\bar{1}0]$  direction of the Ge dimer rows, although the separation between the clusters varies throughout the image. Further deposition of Fe does not lead to the formation of ordered nanocluster arrays, but only to a higher density of nanoclusters of the same size. However, annealing the Fe nanoclusters on the Ge(001) surface at  $420$  K for  $30$  min leads to the formation of linear nanocluster arrays. These arrays are elongated along the  $[1\bar{1}0]$  direction of the Ge dimer rows (Fig. 1(b)) and were found to be up to  $15$  nm in length. The temperature of  $420$  K has been chosen due to the observation that, for temperatures higher than  $430$  K, interdiffusion of Fe and Ge seems to take place.<sup>13</sup> The Fe nanocluster arrays have a corrugation height of  $(1.1 \pm 0.1) \text{ \AA}$ , the same as the single nanoclusters prior to annealing. In the  $[110]$  direction, these nanostructures are  $9 \text{ \AA}$  wide. An individual nanocluster array consists of several Fe nanoclusters aligned along the  $[1\bar{1}0]$  direction of the Ge dimer rows. The separation

between the nanoclusters forming the arrays is approximately  $4 \text{ \AA}$ . This suggests that the cluster-cluster interaction is weaker than the interatomic interaction within a single cluster.

In order to study the magnetic properties of the Fe nanocluster arrays, XMCD measurements at RT and at  $150$  K were carried out at normal and grazing X-ray incidence. The XA spectra from Fe nanocluster arrays on the Ge(001) surface shown in Fig. 1(c) were measured at  $150$  K at grazing X-ray incidence with the magnetic field aligned along the  $[1\bar{1}0]$  direction of the Ge substrate. The spectra have a shape typical of the XA spectrum of a metal (one asymmetric peak A), indicating that no significant intermixing occurs at the Fe/Ge(001) interface, which is in agreement with previous studies.<sup>14</sup> The XMCD spectrum shown in Fig. 1(c) results from the subtraction of the XA spectrum taken at the maximum magnetic field ( $+B_{max}$ ) applied in one direction from the other spectrum taken at the maximum magnetic field ( $-B_{max}$ ) applied in the opposite direction. Grazing X-ray incidence XMCD measurements for the Fe nanocluster arrays show very small dichroism at RT and a prominent difference between the two opposite magnetic directions at

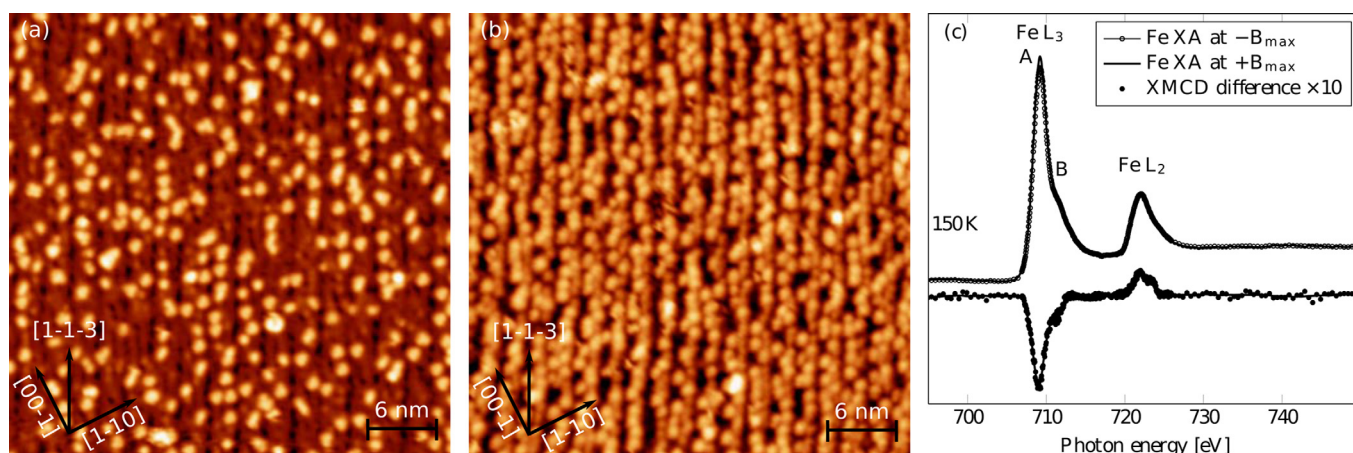


FIG. 2. (Color online) STM images of (a)  $0.3$  ML of Fe on  $\text{MoO}_2/\text{Mo}(110)$ ,  $V_b = -0.5$  V,  $I_t = 1.10$  nA,  $40$  nm  $\times$   $40$  nm,  $78$  K and (b)  $0.7$  ML of Fe on  $\text{MoO}_2/\text{Mo}(110)$ ,  $V_b = 1.2$  V,  $I_t = 1.00$  nA,  $40$  nm  $\times$   $40$  nm,  $78$  K. (c) Fe  $2p$  XA spectra measured at  $150$  K from  $0.7$  ML of Fe nanocluster arrays on  $\text{MoO}_2/\text{Mo}(110)$  with the magnetic field of  $0.05$  T applied in two opposite directions ( $-B_{max}$  and  $+B_{max}$ ). The XMCD spectrum is multiplied by a factor of  $10$  for clarity.



150 K. This indicates a superparamagnetic behavior of the Fe nanocluster arrays on Ge(001) similar to the one observed for the separated nanoclusters.<sup>11</sup> Furthermore, no magnetic hysteresis loop with remanence was observed at 150 K, in comparison to the ferromagnetic response of larger clusters and nanorods.<sup>3,15–17</sup> This suggests that the nanocluster array size is still too small to provide a ferromagnetic response.

MoO<sub>2</sub> grows on the Mo(110) surface in the form of an O-Mo-O trilayer, exhibiting well-ordered oxide nanorows separated by 2.3 nm.<sup>9</sup> These rows are oriented along the  $[\bar{1}\bar{1}\bar{3}]$  crystallographic direction of the Mo(110) surface. Deposition of 0.3 ML of Fe on the MoO<sub>2</sub>/Mo(110) surface leads to the formation of small nanoclusters, which have a round shape and are 6 Å in diameter (Fig. 2(a)). Most of these nanoclusters are found as individual structures on the surface. However, some of them form larger structures with rectangular, triangular and square shapes, consisting of two, three, and four small nanoclusters, respectively. All these nanostructures are located on top of the oxide rows, with a variable separation between them. In the case of higher Fe coverage (0.6 ML–0.9 ML) the separation between nanoclusters on the MoO<sub>2</sub>/Mo(110) surface becomes much smaller. It is clear from Fig. 2(b) that at such coverage the Fe nanoclusters self-assemble into linear nanocluster arrays. These arrays follow the  $[\bar{1}\bar{1}\bar{3}]$  direction of the substrate oxide rows.

The XA spectra from the Fe nanocluster arrays on the MoO<sub>2</sub>/Mo(110) surface were measured at RT and 150 K at normal X-ray incidence and grazing X-ray incidence. Figure 2(c) shows the grazing X-ray incidence spectra taken at 150 K with the magnetic field applied along the  $[\bar{1}\bar{1}\bar{3}]$  direction of the substrate oxide rows. The Fe L<sub>3</sub> spectra exhibit two structures: The main asymmetric peak A and a high-energy shoulder B. The latter indicates that some intermixing occurs at the Fe/MoO<sub>2</sub> interface, resulting in bonding between some of the Fe atoms and the top O layer of the substrate. However, the energy and the shape of the main peak A are typical for the XA spectrum of Fe metal. Grazing X-ray incidence XMCD measurements for the Fe nanocluster arrays show very small dichroism at RT and a prominent difference between the two opposite magnetic directions at 150 K (Fig. 2(c)). The same results were obtained for the separated nanoclusters on MoO<sub>2</sub>/Mo(110). This indicates a superparamagnetic behavior of both Fe nanocluster arrays and separated Fe nanoclusters on the MoO<sub>2</sub>/Mo(110) surface. No magnetic hysteresis loop with remanence was observed at 150 K, similar to the case of Fe/Ge(001). This suggests that the individual nanoclusters

within the array are still too well-separated from each other to result in a ferromagnetic response of the whole system.

#### IV. CONCLUSION

The results obtained show that the Ge(001) and the MoO<sub>2</sub>/Mo(110) surfaces are suitable templates for the growth of well-ordered, uniformly-sized Fe nanoclusters and nanocluster arrays. At low coverage, Fe self-assembles into small clusters, which are well separated on both surfaces. On the Ge(001) surface, Fe nanocluster arrays that follow the Ge dimer rows can be formed only by annealing the Fe/Ge(001) system at 420 K, due to cluster mobility at such temperature. In contrast, linear Fe nanocluster arrays that follow the Mo oxide rows are spontaneously formed on the MoO<sub>2</sub>/Mo(110) surface at RT if the Fe coverage exceeds 0.5 ML. The observed Fe nanoclusters and nanocluster arrays show a superparamagnetic behavior as measured by XMCD.

#### ACKNOWLEDGMENTS

This work was supported by Science Foundation Ireland (Grant Nos. 06/IN.1/I91 and 07/RFP/MASF185).

- <sup>1</sup>J. V. Barth, G. Costantini, and K. Kern, *Nature* **437**, 671 (2005).
- <sup>2</sup>K. Zhu, D. Wang, and J. Liu, *Nano Res.* **2**, 1 (2009).
- <sup>3</sup>Y. Hu, Z. Zhang, Q. Zhou, W. Liu, Z. Li, and D. Meng, *Nano Res.* **3**, 438 (2010).
- <sup>4</sup>S. A. Krasnikov, C. M. Doyle, N. N. Sergeeva, A. B. Preobrajenski, N. A. Vinogradov, Y. N. Sergeeva, A. A. Zakharov, M. O. Senge, and A. A. Cafolla, *Nano Res.* **4**, 376 (2011).
- <sup>5</sup>S. A. Krasnikov, S. I. Bozhko, K. Radican, O. Lübben, B. E. Murphy, S.-R. Vadapoo, H.-C. Wu, M. Abid, V. N. Semenov, and I. V. Shvets, *Nano Res.* **4**, 194 (2011).
- <sup>6</sup>H. J. W. Zandvliet, *Phys. Rep.* **388**, 1 (2003).
- <sup>7</sup>J. Wang, M. Li, and E. I. Altman, *Phys. Rev. B* **70**, 233312 (2004).
- <sup>8</sup>R. E. Schlier and H. E. Farnsworth, *J. Chem. Phys.* **30**, 917 (1959).
- <sup>9</sup>K. Radican, N. Berdunov, G. Manai, and I. V. Shvets, *Phys. Rev. B* **75**, 155434 (2007).
- <sup>10</sup>J.-L. Li, J.-F. Jia, X.-J. Liang, X. Liu, J.-Z. Wang, Q.-K. Xue, Z.-Q. Li, J. S. Tse, Z. Zhang, and S. B. Zhang, *Phys. Rev. Lett.* **88**, 066101 (2002).
- <sup>11</sup>O. Lübben, S. A. Krasnikov, A. B. Preobrajenski, B. E. Murphy, and I. V. Shvets, *Nano Research* **4**, 971 (2011).
- <sup>12</sup>A. N. Chaika, S. S. Nazin, V. N. Semenov, S. I. Bozhko, O. Lübben, S. A. Krasnikov, K. Radican, and I. V. Shvets, *Europhys. Lett.* **92**, 46003 (2010).
- <sup>13</sup>P. Ma and P. R. Norton, *Phys. Rev. B* **56**, 9881 (1997).
- <sup>14</sup>M. Cantoni, M. Riva, G. Isella, R. Bertacco, and F. Ciccacci, *J. Appl. Phys.* **97**, 093906 (2005).
- <sup>15</sup>P. Torelli, S. Benedetti, P. Luches, L. Gragnaniello, J. Fujii, and S. Valeri, *Phys. Rev. B* **79**, 035408 (2009).
- <sup>16</sup>S. Baker, C. Binns, K. W. Edmonds, M. J. Maher, S. C. Thornton, S. Louch, and S. S. Dhesi, *J. Magn. Magn. Mater.* **247**, 19 (2002).
- <sup>17</sup>A. Kleibert, K.-H. Meiwes-Broer, and J. Bansmann, *Phys. Rev. B* **79**, 125423 (2009).