Morphological and Interfacial Studies of Fe Clusters on SrTiO$_3$ (001) Surfaces*

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Fe clusters grown on SrTiO$_3$ (001) surfaces were studied with UHV-TEM/STM combined system. Fe clusters have two types of epitaxial orientation relationships: one with a simple cube-on-cube with $45^\circ$ orientation and the other with a higher index interface plane. The second one grows in twins. It was deduced that the clusters with the first orientation relationship have truncated pyramid shapes and stronger bonding energy and that the second one have near-roundish shapes with weaker bondings. The clusters influence each other so that their orientations deviate. [DOI: 10.1380/ejssnt.2015.85]

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I. INTRODUCTION

Nano-sized clusters and particles are attracting much attention for both fundamentally and technologically due to their unique properties [1-5]. Metal clusters on oxide substrates are of particular interest due to their applicability in nanomagnetism, catalysis, and so on. Self-assembling of metal clusters on oxide substrates is an effective and simple technique to fabricate these structures, and many approaches are being investigated to achieve a narrow size distribution and an ordered spatial arrangement. These include controlling the compositions, structures and reconstructions, flatness and patterning, polarity of oxide surfaces [6-10]. And in either way, structure and properties of the interface are the utmost important to those systems.

SrTiO$_3$ (STO) is one of the most widely used substrate materials for these purposes, with the perovskite structure composed of repeated stackings of individual TiO$_2$ and SrO layers along the [001] direction. Efforts have been made to grow metal clusters of controlled sizes and morphologies on its surface by using chemical etching, controlling geometry, fabricating reconstructions and buffer layers, using ion-bombardment and so on [11-15]. Some of these methods are adequately effective for controlled nanoparticle growth. For example, Silly et al. successfully controlled shapes of nanoparticles by tuning STO (001) substrate reconstruction and the substrate temperature during deposition [12]. Sun et al. also controlled shapes of nanoparticles on a reconstructed STO (001) substrate and utilized them to catalyse carbon nanotubes [15]. However, since these studies image nanoparticles with STM, the exact interfacial structures, which affect the properties of nanoparticles farthest, are not obtained directly. Since interface interaction significantly affects the size and morphology of a cluster [16-18], cross sectional observation is greatly required for clarification of precise interfacial structure.

In the present study, interfacial structures of Fe clusters on a STO (001) surface as well as their morphologies and arrangements are investigated by using ultrahigh vacuum (UHV)-transmission electron microscopy (TEM)/scanning tunnelling microscopy (STM) combined system. The system enables in-situ observation of clusters from both horizontal and vertical directions by combining STM plan-view observation and TEM plan-view and profile-view observations. The formation of Fe/STO interface was achieved by depositing Fe clusters on clean STO substrates that are annealed under UHV. They were transferred to either microscope without exposing to air for further observation from different directions. Multiaxial observation reveals the interfacial structure along with their morphology. Several interfacial structural models of the clusters are proposed.

II. EXPERIMENTS

The experiments were performed in a UHV-TEM/STM Integrated Characterization System (UTSICS), which is a combination of UHV sample preparation chambers and UHV microscopes (STM: JSPM-4500XT, TEM: JEM-2000VF) with base pressure of $\sim 10^{-8}$ Pa [19]. The specimens were prepared from SrTiO$_3$ (001) wafers (La-doped, 5 at.%). Bulk samples were used for STM observation, and ion-milled thin samples for TEM observation. After chemically cleaned in NH$_4$-HF buffer solution (BHF, pH $\sim 4.5$) for 5 min [20], they were annealed in the cleaning chamber of UTSICS at about 1100 K for 30 min. by electron bombardment at 5 kV. Then they were transferred either to STM or to TEM to confirm the cleanness of the surfaces.

Fe clusters were deposited in a deposition chamber of UTSICS by electron beam at room temperature (RT). The deposition rate was about 0.01 nm/s. The vacuum during deposition was kept below $5 \times 10^{-8}$ Pa. The samples were transferred to the microscopes again for further observation.

Fe clusters were formed on both plan-view and profile-view surfaces [21]. Profile view surfaces are made at the very edge of the thinnest part of TEM samples. With a (001) substrate, the plan-view surface is the same (001) STO and the profile-view surfaces are perpendicular to this, typically (110) STO and (100) STO planes. Fe clusters grown on plan-view surfaces are observed with STM and TED. Those on profile-view surfaces are observed with high resolution TEM (HR-TEM).

STM images were taken in constant current mode with positive sample bias of 1.0-2.0 V. Electrochemically etched W tips were used. TEM images and transmission electron microscopy images were acquired with a JEOL JEM-2000VF microscope using a Schottky field emission gun with a 40 nm tungsten tip. The voltage was 100 kV and a LaB$_6$ filament was used. The samples were transferred to the microscope without exposing to air for further observation from different directions.
FIG. 1. Fe clusters on STO (001). a) TEM plan-view image of Fe clusters on STO (001), and b) corresponding diffraction pattern showing several types of crystallographic orientations.

III. RESULTS AND DISCUSSION

A. TEM observation

Depending on preparation methods and conditions, various surface reconstructions are known to be formed on STO (001) [22-29]. The influential factors are annealing temperature, ambient atmosphere particularly partial pressure of oxygen, surface sputtering condition before annealing, and so on. Especially, a surface becomes severely disordered during sputtering, leaving the uppermost layers with oxygen vacancies [24]. Thus the subsequent annealing induces oxygen diffusion and surface recrystallization at the same time, making various superstructures possible to appear. In the present study, TEM STO (001) substrates showed simple 1 × 1 structures after electron beam annealing in UHV [21]. Thus the surfaces are supposed to be TiO₂ terminated and be oxygen depleted due to UHV annealing.

Fe deposition onto these 1 × 1 surfaces leads to formation of clusters of various sizes and morphologies. Figure 1 shows TEM image and diffraction pattern of Fe clusters on a STO (001) substrate after RT deposition. In the electron diffraction (TED) patterns were taken with an accelerating voltage of 200 kV. High-resolution images were acquired with CCD camera (Gatan Orius SC200). Observation of the identical samples with both TEM and STM was not performed in the present study due to the experimental difficulties.

TEM image in Fig. 1a, nanoparticles on a STO (001) surface plane show moiré fringes of different directions and spacings. Each set of moiré fringes represents a nanoparticle. The interferences are derived from several lattice mismatches such as STO 220 and Fe 200 reflections (denoted as A in the figure), STO 310 and Fe 112 (B), and STO 300 and Fe 112 (C) for spacings 4.0 nm, 2.2 nm, and 1.2 nm, respectively. Their orientation relationships (ORs) are typically

OR 1 is a simple cube-on-cube with 45° orientation one. Thus the fringe set A represents translational fringes while those of B and C are from translational and slight rotational ones. In the image, sets of fringes are randomly distributed. The particle sizes range from 5 nm to 15 nm. This implies that there is no particular advantageous epitaxial relationship between the two. Also, the particle sizes are not affected by epitaxial relationships. Corresponding diffraction pattern in Fig. 1b shows the above relationships. The growth of two kinds of Fe crystalline planes is indicated. The spots arising from OR 1 (outlined by yellow lines) are aligned to the spots of STO \{110\}. Those of OR 2 are shown by blue lines. Another sets of spots, which are in a twin relationship with OR 2, are represented by green lines:

\[(001)_{\text{STO}} \parallel (001)_{\text{Fe}} \text{ and } [110]_{\text{STO}} \parallel [100]_{\text{Fe}}, \quad \text{(OR 1)}\]
\[(001)_{\text{STO}} \parallel (012)_{\text{Fe}} \text{ and } [110]_{\text{STO}} \parallel [121]_{\text{Fe}}, \quad \text{(OR 2)}\]

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\[(001)_{\text{STO}} \parallel (012)_{\text{Fe}} \text{ and } [110]_{\text{STO}} \parallel [121]_{\text{Fe}}, \quad \text{(OR 3)}\]

Only one crystal plane, Fe (112), is aligned to STO (110) in either case. Most of their spots appear as arcs rather than points, which indicates a deviation of growth direction of each particle from the exact epitaxial ones. It should be noted that the fringes exhibit the existence of dislocations and strain inside particles as extra fringes, bending, and changes of their spacings.

From above results, possible interface structures are schematically drawn in Fig. 2. Both OR 1 and 2 are
modeled in both top and side views. They have epitaxial and non-stoichiometric orientation relationships so misfit dislocations appear at certain positions. For Fe deposition on TiO$_2$-terminated surfaces, only OR 1 has been reported so far [30, 31]. OR 1 is a reasonable relationship for bcc metals due to the low interface energy caused by the registry of metal adatoms on the O sub-lattice on the TiO$_2$-terminated STO (001) surface [32]. This does not apply for OR 2(3) with their inclined atomic arrangements as evident in Fig. 2. However, since the surface energies of {001)$_{Fe}$ and {012)$_{Fe}$ are remarkably close (1.54 and 1.59 J/m$^2$ for {001)$_{Fe}$ and {012)$_{Fe}$, respectively) [33], coexistence of OR 1 and OR 2(3) must become enable. The imperfect surface plane of STO due to oxygen depletion might allow this relatively corrugated plane to appear at the interface.

The clusters were also observed from the vertical direction. Some of them are placed on the edge {100} planes with their low index crystal planes perpendicular to the field of view. These clusters are shown in the TEM images in Fig. 3. In Fig. 3a, two small clusters are seen, overlapping with each other. They are outlined with white lines for clarity. Right hand side of them happened to sit on a half slope (STO (110) plane). Both of them have OR I as specified in the image. Their non-stoichiometry interfaces are recognized. Their widths are roughly 4 nm and their heights are about 2 nm. They seem to possess modified Wulff (Winterbottom) construction [33]. It describes thermally equilibrium shape of particles on a support. In the present case, not all clusters reach equilibrium shape, but some do, as the ones here. For the bcc structure, the least energy surfaces are {100} and {110}. In the image, both clusters have (001) surfaces on the top, which size is about 1 nm. Winterbottom theory gives the equilibrium shape of small crystal particles placed on solid substrates. It describes the dependence of the particle shape upon the anisotropy of the surface energy of the particle and upon the binding between the particle and the substrate. Using the surface energies and the bonding energy across the interface, the interface free energies in the present case can be written as

$$\gamma_{\text{int}} = \gamma_{\text{Fe}} + \gamma_{\text{STO}} - \gamma_{\text{bonding}}$$

(1)

where $\gamma_{\text{int}}, \gamma_{\text{Fe}}, \gamma_{\text{STO}},$ and $\gamma_{\text{bonding}}$ denote the interface free energy between the particle and the substrate, the anisotropic surface energy of the Fe cluster, the surface free energy of the STO substrate, and the free energy associated with bonding across the interface, respectively. In the case of the clusters in the image, less than half of the cluster is exposed above the substrates surface. According to the Winterbottom theory, this occurs when the interface energy is between the substrates surface energy and the substrate surface energy plus the particle surface energy [33]:

$$-\gamma_{\text{Fe}} < (\gamma_{\text{int}} - \gamma_{\text{STO}}) < 0.$$  

(2)

By applying the surface energy values [34, 35] to equations (1) and (2), one can estimate range of interfacial bonding energy as 1.54 < $\gamma_{\text{bonding}}$ < 3.08 (J/m$^2$) for clusters with OR 1 interfaces.

In Fig. 3b, other Fe clusters are shown. Although the image resolution is not high enough, it is assumed that the cluster in the center has OR 2(3) from its inclined morphology and the plane spacings as indicated in the image. If that is the case the cluster should not show any crystalline image since the viewing plane is not low index one. Moreover, due to cluster deviation from the exact epitaxial angle as suggested in Fig. 1b, (121)$_{Fe}$ plane, which forms 48° angle to [121]$_{Fe}$, could appear perpendicular to the paper surface. This would exhibit (101)$_{Fe}$ lattice fringes that make 50° angle to the interface. For bcc Fe crystal, (110) spacing is 0.202 nm. As shown in the figure, the plane spacings and angle are measured to be about 0.20 nm and 50°, which is in good agreement with above assumption. Also, this agrees with the results from Fig. 1a, which shows interferences between clusters and hence bending and curvature of moiré fringes. These interferences could make clusters deviate from an exact epitaxial directions.

This cluster seems to expose about half of its body above the substrates surface, contrary to the clusters in Fig. 3a. In the Winterbottom theory, this would be written as

$$0 < (\gamma_{\text{int}} - \gamma_{\text{STO}}).$$

(3)

Thus in this case the interfacial bonding energy can roughly be estimated as $\gamma_{\text{bonding}}$ < 1.59 (J/m$^2$) from equations (1) and (3). This lower value than OR 1 case could be attributed to interfacial and/or intercluster interaction.
Based on above results, atomic models of Fe clusters with OR 1 and OR 2(3) are drawn in Fig. 4. Possible Wulff constructions are drawn in top and side views using the literature values of surface free energy $\gamma_{Fe\{110\}}/\gamma_{Fe\{100\}}$ of 0.93 [34]. Figure 4a represents the one with OR 1. Since the Wulff point, marked as a black dot, lies below the surface, the cluster itself possesses truncated pyramid shape and should appear as a square in plan-view imaging. Fig. 4b depicts the one with OR 2(3). This one is irregularly shaped and should appear as irregular octagon, or rather roundish, in plan-view. In the real case in Fig. 3b, the cluster has a slight deformation on top from the Wulff (dashed line). Along with the possibility for both OR 2 and OR 3 to appear randomly, these clusters are expected to have much wider variety of morphology than OR 1.

For the usage of these clusters in actual epitaxy, it would be preferable to have them with OR 1. They have stronger bonding with substrates, have more regular shapes, and have wetter and hence more stable morphology than OR 2(3) ones. It is expected that less deposition would result in lower density, which might improve their aligning along $<100>$ directions. Others deviate from these directions probably due to the interference between clusters as observed in a plan-view image in Fig. 2a.

There are other clusters with round shapes. Some of them are assumed to have OR 2(3), in which case they should appear as irregular octagons. They do not align to the above directions. More irregular shapes are also recognised. The numbers of squares, rounds (octagons), and ambiguous shapes are summarised in Table I. The ratio of squares and rounds are almost the same level, which confirms that there is no particular advantageous epitaxial relationship between OR 1 and OR 2(3), although it is not known what kind of epitaxial relationships the ambiguous ones have.

Even though they are densely populated and affect each other, it is indicated that square clusters are in a minority. Changing not only substrate conditions but also deposition manners would be necessary for morphology and interface control.

### IV. CONCLUSIONS

Fe clusters grown on SrTiO$_3$ {001} surfaces were studied with UHV-TEM/STM combined system. The surfaces were annealed by electron beams in UHV before deposition, and formed oxygen depleted 1x1 structures for both TEM and STM substrates.

Fe clusters grown on TEM substrates have two types of
epitaxial orientation relationships. One is a simple cube-on-cube with 45° orientation whereas the other is with a higher index interface plane. The second one grows in twins. Almost equivalent surface energies of the two interfacial planes must enable the co-existence of the two phases. It was deduced from profile observation that the clusters with the first orientation relationship have truncated pyramid shapes and stronger bonding energy. The second one seems to have near-roundish shapes with weaker bondings. The clusters influence each other so that their orientations slightly deviate. STM observation confirms the co-existence of squares and rounds (octagons). Present result show that not only surface conditions but also the cluster density affects their interface structure and morphology.