Precise determination of moiré pattern in monolayer FeO(111) films on Au(111) by scanning tunneling microscopy

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Monolayer iron-oxide films are attractive for both spintronic application and surface chemical catalysis. However, the detailed atomic structure of the FeO monolayer which is crucial for understanding the physical and chemical properties of the films is not well understood. In this work, we fabricate high-quality monolayer FeO films on the Au(111) substrate by molecular-beam epitaxy. High-resolution scanning tunneling microscopy measurements simultaneously reveal the close-packed atomic arrangement and hexagonal moiré pattern of the monolayer FeO and were combined with hexagonal commensurate mode calculations to establish the atomic structure of the monolayer FeO(111) with respect to the Au(111) substrate. The identification of this stable commensurate arrangement of FeO(111) monolayer on Au(111) paves the way for the exploration of its fundamental science and its applications in industry.

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I. INTRODUCTION

Oxide materials have been widely used in fundamental scientific research and modern technology. They can exist in a vast array of compositions and thereby exhibit significant varieties in terms of physical and chemical properties. These properties can be further manipulated by doping or slight alteration to the stoichiometry. Furthermore, a reduction in the oxide dimensionality can introduce unique two-dimensional (2D) phases with distinct physical and chemical properties, and therefore ultrathin oxides films have been actively investigated in various research fields in the last several decades [1] for applications such as advanced nanomaterials [2], components of electronic devices [3], and heterogeneous catalysts [4].

Recently, topological quantum properties such as the quantum anomalous Hall effect have been predicted to exist in several ultrathin oxide materials such as V$_2$O$_3$ [5], Nb$_2$O$_3$ [6], and Fe$_2$O$_3$ [7], suggesting that these materials are promising for novel applications. However, unlike the typical two-dimensional materials derived from bulk materials that are stabilized by the van der Waals interlayer interactions, the ultrathin oxide films grown on a substrate are affected by the strong interactions between the oxide overlayers and the substrate. As a result, the properties and the atomic structures of ultrathin oxide films are strongly influenced by the interface interactions [8–11], and as such, it is highly desirable to elucidate the relationship between the atomic structure of ultrathin oxide films and the interface interactions.

Iron oxides hold an important position amongst all oxide materials because of their ability to act as catalysts within industrial processes such as the Fischer-Tropsch reaction, the synthesis of styrene, and gas-sensing applications [12–17]. Previous investigations have revealed that the monolayer iron-oxide film is a single layer of FeO(111), and this monolayer film has been grown on various metal substrates such as Pt(111) [18], Pt(100) [19], Mo(100) [20], Cu(001) [21], Cu(110) [22], Ru(0001) [23], Au(111) [24], Pd(111) [25], Pd(100) [26], Ag(001) [27], and Ag(100) [28]. The monolayer FeO(111) films exhibit significant differences in the lattice constant and coincidence pattern due to various interface interactions, which tend to bring about an impact on their physical and chemical properties. In particular, the FeO(111)/Au(111) system is more promising for use in applications because of the inertness of the Au(111) substrate. However, due to the complex geometry of the FeO(111)/Au(111) interface, the exact structure and atomic model for FeO(111)/Au(111) system is not established as yet, and requires detailed investigation and clarification.

In this work, we grew a monolayer FeO(111) film on Au(111) substrate by molecular-beam epitaxy (MBE), and then characterized it by scanning tunneling microscopy (STM). It was found that due to the interface interactions, the lattice of the monolayer FeO(111) is slightly stretched compared to that of the bulk. Furthermore, a hexagonal moiré pattern resulting from the coincidence between the FeO(111) lattice and the Au(111) lattice was observed. By analyzing the atomic arrangements and the commensuration mode of the moiré pattern observed in high-resolution STM images, we established the atomic structure model of the monolayer FeO(111) films with respect to the Au(111) lattice.

II. PROCEDURES

Our experiments were carried out in a home-built low-temperature STM apparatus combined with an MBE chamber.
FIG. 1. STM images of the iron-oxide overlayer on Au(111) for a submonolayer coverage after annealing at the temperature of (a) 300 °C (100 nm × 100 nm, bias = −1.5 V, I = 0.03 nA), (b) 350 °C (100 nm × 100 nm, bias = −2.0 V, I = 0.01 nA), and (c) 400 °C (100 nm × 100 nm, bias = 1.3 V, I = 0.02 nA). Insert in panel (a) shows the atomic structure of an individual triangular island and illustrates the rhombic structure of α-Fe2O3(0001) (1 nm × 1 nm, bias = 0.1 V, I = 0.05 nA). FeO terraces and substrate Au are highlighted by corresponding letters. (d)–(f) Line profiles of La, Lb, and Lc indicated by red line in (a)–(c). La and Lb show the height of triangular islands is about 5 Å and the height of irregular hexagonal islands is 2 Å. Lc shows the periodicity of the hexagonal superstructure is 3.17 nm.

with a base pressure of 1 × 10⁻¹⁰ mbar. The monolayer FeO(111) film was epitaxially grown on Au(111) substrate by the two-step oxidation method in the MBE chamber. First, a single-crystal Au(111) substrate was cleaned by several cycles of argon-ion sputtering (1.5 keV, 2 × 10⁻⁵ mbar) followed by annealing at 600 °C. Subsequently, iron atoms were thermally evaporated onto Au(111) surface held at room temperature. The sample was then exposed in molecular O₂ atmosphere at a pressure of 10⁻⁷ mbar for 5 min and was further annealed to 300–400 °C. After the preparation, the sample was in situ transferred to the STM chamber for characterization. The STM images were recorded in the constant current mode at the liquid helium temperature by an electrochemically etched W tip. The bias voltages are given with respect to the sample.

III. RESULTS AND DISCUSSION

The STM images presented in Fig. 1 show the morphology of the iron-oxide overlayer on Au(111) with a submonolayer coverage after annealing at the substrate temperatures of 300, 350, and 400 °C, respectively. For the substrate temperature of 300 °C, the islands of iron oxide on Au(111) show two different morphologies [Fig. 1(a)], with triangular, trapezoidal, and parallelogramlike islands belonging to the first morphology type and irregularly hexagonal islands belonging to the second morphology type. The line profile across the two kinds of islands [Fig. 1(d)] reveals that the height of the triangular islands is approximately 5 Å, and that of the irregular hexagonal island is nearly 2 Å. The former is consistent with the previously reported height of the α-Fe₂O₃ nanoparticles [29], while the latter is ascribed to a single layer of oxygen-terminated FeO based on the previous reports [30–32]. A close examination of the STM image [inset of Fig. 1(a)] shows the rhombic structure on the triangular island and the surface lattice parameter of 3.16 Å for the irregular hexagonal island, providing further support for our conclusions. With the annealing temperature increased to 350 °C, as shown in Fig. 1(b), most of the α-Fe₂O₃(0001) islands disappear while the coverage of the FeO islands increased significantly, indicating a phase transition from α-Fe₂O₃(0001) to FeO(111). When the sample is annealed at 400 °C, the α-Fe₂O₃(0001) islands disappear completely, and a continuous monolayer FeO(111) film is formed on Au(111) [Fig. 1(c)] with a hexagonal moiré pattern observed on the FeO(111) film surface. The line profile for the FeO(111) film [Fig. 1(c)] reveals that the periodicity of the moiré pattern is approximately 3.17 nm, which is comparable with the reported value (3.4 ± 0.4 nm) in a previous experimental study [24].

To elucidate the atomic structure model of the monolayer FeO(111) on Au(111), we performed high-resolution STM measurements on the surface of the FeO(111) film with various tip-bias values. The results of the measurements are
Domains are characterized by Fe atop Pd atoms and O at local stacking orders of FeO(111) on the substrate. The top of Pd(111) substrate [25]. Analysis of the STM images of the FeO lattice and the underlying Au(111) substrate. Similar moiré pattern arising from the coincidence of the structures of the FeO(111)/Pd(111) surface interaction and charge transfer between the metallic Au substrate and polarized FeO film, which removes the surface Au(111) reconstruction beneath the FeO(111) film and the Au(111) surface simultaneously, and the profiles across the FeO(111) surface presented in Fig. 3(b) indicate that the lattice parameter of FeO(111) is approximately 0.316 nm. In comparison to the calculated parameters in the phase diagram of Fig. 3(c), it is observable that the experimentally measured parameters coincide with the combination of the parameters represented by the red dot in Fig. 3(c). The Wood notation of this red dot and two black dots nearest to the red dot were also presented in Fig. 3(c) to clarify the FeO superstructure with respect to the Au(111) lattice. The calculated periodicity of the moiré pattern represented by A is 3.2 nm, which is very close to the experimental value (3.17 nm) obtained from Fig. 1. The rotation angle between the moiré pattern and the FeO(111) lattice obtained by subtracting $\theta$ from $\phi$ is 8.92°, which is also in good agreement with the measured angle of 9°. We were thus able to establish the atomic model of monolayer FeO(111) on Au(111) surface, as shown in Fig. 3(d). This model can explain the observed superstructure very well. The identification of this stable commensurate arrangement of FeO(111) on Au(111) is highly relevant for the exploration of its fundamental physical and chemical properties and of its use in technological applications.

The growth of ultrathin FeO films on various metal substrates has been investigated in previous studies [18–28]. According to previous reports, the FeO films possess either hexagonal or square lattice symmetries depending on the surface structures of the underlying substrates. Table I presents the experimental results obtained for the FeO(111) monolayers grown on several substrates reported in the literature. On most substrates, the FeO(111) films are not continuous. Only on Ru(0001), Pd(111), and Pt(111) can large-area monolayer FeO(111) films with good continuity be formed. This is most likely due to the weak interactions between the FeO(111) overlayers and these relatively inert substrates. Figure 4 shows a plot of the lattice parameter of the FeO(111) films versus the lattice constant of the substrate.
FIG. 3. (a) High-resolution STM image (6 nm × 6 nm) of the atomic structure of the FeO(111) film and Au(111) surface. Above the yellow dashed line, the scanning parameters are sample bias = −200 mV, I = 0.1 nA; below the yellow dashed line, the scanning parameters are sample bias = −20 mV, I = 1.0 nA. The FeO terrace, substrate Au, and a visible herringbone structure are highlighted by corresponding letters. (b) The profiles cross the FeO(111) and Au(111) surface indicated by the red and black arrows in (a). (c) The phase diagram of parameters calculated by a systematic approach of commensurate mode, where $b$ is the lattice parameter of FeO(111), $A$ is the coincidence structure periodicity, $\theta$ is the rotation angle between FeO and Au(111), and $\phi$ is the angle between moiré pattern and Au(111). The black dots and one red dot represent a series of calculated combinations of the parameters $[b, A, \theta, \phi]$. The red dot represents the combination of the parameters which coincide with the experimentally measured parameters. The values of two black dots nearest to the red dot are also presented. The Wood notation of this red dot and two black dots are presented below the $[b, A, \theta, \phi]$ to clarify the FeO superstructure with respect to the Au(111) lattice. (d) Model of atomic structure of the 1-ML FeO(111) film on Au(111) surface. The moiré-type superstructure unit cell is indicated by the black dotted rhombic mark. The three different high-symmetry domains of the moiré structure are indicated, along with the definitions used in this work.

The lattice parameter of the FeO(111) films tends to be larger as the lattice parameter of the substrate increases, which suggests that the FeO(111) monolayer on the substrates undergoes an expansion of the lattice parameter compared to the bulk value (3.07 Å) due to the interface strain effect. As a result, the polarized Fe–O bonds in the FeO monolayer become less buckled. Since the surface polarization/chemical potential of FeO/Au(111) is highly correlated to surface buckling (surface

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Cu(001) [21]</th>
<th>Ru(0001) [23]</th>
<th>Pd(111) [25]</th>
<th>Pd(100) [26]</th>
<th>Pt(111) [18]</th>
<th>Pt(100) [19]</th>
<th>Ag(001) [27]</th>
<th>Ag(100) [28]</th>
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<tr>
<td>Lattice parameter (Å)</td>
<td>2.56</td>
<td>2.7</td>
<td>2.75</td>
<td>2.75</td>
<td>2.77</td>
<td>2.77</td>
<td>2.88</td>
<td>2.88</td>
</tr>
<tr>
<td>FeO(111) monolayer</td>
<td>Lattice parameter (Å)</td>
<td>3.04</td>
<td>3.08</td>
<td>3.1</td>
<td>3.09</td>
<td>3.08</td>
<td>3.05</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>Superstructure type</td>
<td>$p(8 \times 8)$</td>
<td>$p(8 \times 8)$</td>
<td>$c(8 \times 2)$</td>
<td>$(\sqrt{91} \times \sqrt{91})R5.2^\circ$</td>
<td>$p(2 \times 9)$</td>
<td>$c(2 \times 10)$</td>
<td>$p(2 \times 11)$</td>
</tr>
<tr>
<td></td>
<td>Superstructure periodicity (Å)</td>
<td>20.5</td>
<td>21.6</td>
<td>22</td>
<td>26.4</td>
<td>5.5 × 24.9</td>
<td>5.5 × 27.7</td>
<td>5.8 × 31.8</td>
</tr>
</tbody>
</table>

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films can be formed. A number of important findings came to light. The continuous monolayer FeO(111) film with its large area is fabricated by the MBE method and two-step oxidation process in ultrahigh vacuum. High-resolution STM images reveal the close-packed atomic arrangement and hexagonal moiré pattern of the monolayer FeO(111) film. Using these STM images together with hexagonal commensurate mode calculations, the atomic commensuration of the FeO(111) lattice in respect to Au(111) was established. The realization of a large continuous monolayer FeO(111) film provides an ideal system for the investigation of quantum effects in low-dimensional oxide materials. In addition, compared to previously reported results for the monolayer FeO(111) on metal substrates, we conclude that the lattice of the FeO(111) monolayer on Au(111) is more expanded due to the larger lattice parameter of Au(111). The variable atomic structure and superstructure are predicted to provide an approach for the modulation of the physical and chemical properties of the film. To understand the unique properties of ultrathin FeO(111) films, further measurements, such as the measurements of the magnetic structure, adsorption behavior, catalytic activity, and influence of the metallic substrate ought to be carried out in future research.

IV. SUMMARY

In summary, upon systematic investigation of the growth and characterization of an FeO(111) monolayer on the Au(111) substrate, a number of important findings came to light. The continuous monolayer FeO(111) film with its large area is fabricated by the MBE method and two-step oxidation process in ultrahigh vacuum. High-resolution STM images reveal the close-packed atomic arrangement and hexagonal moiré pattern of the monolayer FeO(111) film. Using these STM images together with hexagonal commensurate mode calculations, the atomic commensuration of the FeO(111) lattice in respect to Au(111) was established. The realization of a large continuous monolayer FeO(111) film provides an ideal system for the investigation of quantum effects in low-dimensional oxide materials. In addition, compared to previously reported results for the monolayer FeO(111) on metal substrates, we conclude that the lattice of the FeO(111) monolayer on Au(111) is more expanded due to the larger lattice parameter of Au(111). The variable atomic structure and superstructure are predicted to provide an approach for the modulation of the physical and chemical properties of the film. To understand the unique properties of ultrathin FeO(111) films, further measurements, such as the measurements of the magnetic structure, adsorption behavior, catalytic activity, and influence of the metallic substrate ought to be carried out in future research.

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