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Surface reconstruction of clean bcc-Fe{1 1 0}: A quasi-hexagonal top-layer with periodic height modulation

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ABSTRACT

Hexagonal-pillar shaped pure Fe single crystal whiskers with six {1 1 0} side planes were obtained by means of chemical vapor deposition. Atomically resolved scanning tunneling microscopy images obtained on the {1 1 0} surface showed a quasi-hexagonal atomic array with mesoscopic-range periodic height modulation of about 1/3 of an atomic step. This height modulation was found to be a result of an interference between the quasi-hexagonal top-layer and the sub-surface bcc-Fe{1 1 0} layer. Unit vectors of the mesoscopic-range modulation turned out to be expressed as $\begin{pmatrix} \vec{p_1} \\ \vec{p_2} \end{pmatrix} = \begin{pmatrix} 13 & 1 \\ -2 & 14 \end{pmatrix} \begin{pmatrix} \vec{u_1} \\ \vec{u_2} \end{pmatrix} = \begin{pmatrix} 12 & 1 \\ -3 & 15 \end{pmatrix} \begin{pmatrix} \vec{s_1} \\ \vec{s_2} \end{pmatrix}$, where $\begin{pmatrix} \vec{u_1} \\ \vec{u_2} \end{pmatrix}$ and $\begin{pmatrix} \vec{s_1} \\ \vec{s_2} \end{pmatrix}$ are the primitive vectors of the two-dimensional atomic array in the top-layer and those in the sub-surface layer, respectively. The two-dimensional density of atoms in the top-layer is slightly higher by 0.46% than that in the sub-surface layer.

1. Introduction

Iron is an important popular ferromagnetic metal which has been widely used since the ancient age in practical applications owing to its strength and abundance. It is a typical bcc-metal at room temperature, however, it takes fcc γ-phase 1185–1667 K and bcc δ-phase (1667–1811 K: melting point) at 1 atm [1], suggesting that the free energy depends delicately on the crystal structure [2]. In a bcc crystal each atom has 8 nearest and 6 second nearest neighbors (NN) in bulk, while an atom at the surface has reduced coordination, i.e. 4 NN and 5 second NN for {0 0 1} and 6 NN and 4 second NN for {1 1 0}. In general, a break down of the symmetry of atomic interactions generates stress, which causes surface reconstruction in the case that the stress exceeds the elastic limit. There have been found several surface reconstructions on metal surfaces ([3] and references therein). There are three types of them; (1) surface atoms move parallel to the surface to form a larger unit cell, e.g. W{0 0 1}-c(2×2) [4]. (2) A top surface atomic layer of noble metals forms a hexagonal lattice, e.g. Au{0 0 1}-(5×20), Pt{0 0 1}-(5×20), Ir{0 0 1}-(5×1) [3,5]. (3) Periodic missing atomic rows are formed on the surface, e.g. Pt{1 1 0}-(1×2) [6].

Since impurities on metal single crystal surfaces induce surface reconstruction [7,8], one must pay a lot of attention whether the surface reconstruction is of surface intrinsic origin. Absorbates of the impurities induce reconstruction on Fe surfaces [7,8]. So-called Fe single crystals which were made by a strain-anneal method include several impurities, such as C, P, and S in bulk. These segregate on the surface after every sample-annealing process and cover the Fe surface. Therefore, for a study of clean Fe surfaces, bcc α-Fe{0 0 1} single crystals made by a chemical vapor deposition (CVD) technique, which are called Fe-whisker single crystals, have been used since the whiskers consist of only Fe in bulk [9–13]. Although many investigations have been made on clean pure bcc-Fe-whisker single crystals, so far no surface reconstruction has been reported on {0 0 1} surfaces.

There have been plenty of investigations on Fe films of different modifications grown epitaxially on single crystal substrates, e.g. W, GaAs, Cu, or Au [14–18]. These Fe films suffer large stress caused by lattice mismatch between the Fe films and the substrate, and the surfaces are frequently reconstructed.

In this study, we discovered a new surface reconstruction on clean bcc-Fe{1 1 0} surfaces of three different pure hexagonal-pillar shaped α-Fe-whisker single crystals. The top surface layer is reconstructed to a quasi-hexagonal lattice with periodic height modulation in mesoscopic-range due to the interactions with the sub-surface bcc-{1 1 0} layer.

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2. Experimental

CVD has been used in order to get bcc α-phase Fe single crystals. From the gas phase, extremely high quality Fe-whiskers can be grown [9–13]. Most of the produced whiskers were rectangular pillar shape with six {001} surfaces [10]. We found, however, that a very few crystals had a hexagonal prism shape as shown in Fig. 1a. Laue X-ray diffraction patterns (Fig. 1b) and four-circle X-ray diffraction data (Fig. 1c–h) show that these whiskers grow along $\langle 111 \rangle$ direction with six side planes of bcc-{110} surfaces.

Contaminations on the Fe-whiskers were investigated by Auger spectroscopy and scanning tunneling microscopy (STM) in ultra-high vacuum (UHV). Before cleaning, the Fe-whisker was covered by oxide layers. The whisker was cleaned by Ar ion sputtering at 600 °C in a preparation chamber by following the procedure described in Ref. [12]. After these treatments, Auger spectra showed no oxygen. The clean Fe-whisker of hexagonal-pillar shape (Fig. 1a) was mounted in our STM chamber ($<1 \times 10^{-8}$ Pa). A W tip, which was cleaned by Ar ion sputtering and electron bombardment, approached the side plane of the whisker. All STM measurements were performed at room temperature (RT), and the STM images were obtained at negative bias voltages to obtain topography of sample surfaces without effects of sample local density of states [19]. Atomically resolved STM images showed an oxygen contamination below 1%.

3. Results and discussions

STM topographic images obtained on the bcc-Fe{110} surface shows several terraces with a step height of 0.21 ± 0.03 nm, which is consistent with the bcc-Fe{110} plane thickness of $\sqrt{2}a/2 \cong 0.203$ nm, where $a = 0.287$ nm is the lattice constant in the conventional bcc unit cell of α-Fe. We observed a regular array of bright patches of 4 nm in diameter on a single terrace of an Fe{110} crystallographic plane in topographic images as shown in Fig. 2a. Fourier transform of this pattern is shown in the inset of Fig. 2a, which indicates that the pattern is aligned nearly along the $[\bar{1}11]$, $[001]$ and $[\bar{1}1\bar{1}]$ directions on Fe{110}. Note that the bcc-{110} planes do not have hexagonal symmetry, but they have only two-fold symmetry.

The pattern was observed on the {110} side planes of three different hexagonal-pillar shaped Fe-whiskers. This implies that the pattern comes from a surface reconstruction intrinsic to the {110} planes of bcc-Fe. The same topographic image in higher resolution (14×14 nm^2) is shown in Fig. 2b, where not only the pattern but also atomic arrangement can be observed. The height variation along the broken arrow in Fig. 2b is shown in Fig. 2c. The height of the pattern is roughly $0.07 \sim 0.08$ nm, about 1/3 of the step height. The periodicity is about 14 atomic spacings. A two-dimensional Fourier transformed image of Fig. 2b is shown in Fig. 2d. The elements inside the solid circle in the center of the image indicate the same symmetry as the inset of Fig. 2a. White dots inside the six dotted-circles apart from the center show the symmetry of the surface atomic arrangement. Solid and dotted lines show a perfect hexagonal symmetry and a bcc-{110} symmetry, respectively. Positions of the six dotted-circles almost fit to the hexagonal symmetry (solid lines) but not to the bcc-{110} symmetry, which indicates that the surface atoms do not have a bcc-{110} symmetry, but they have almost hexagonal symmetry in spite of the fact that the X-ray measurements in Fig. 1 showed bcc-{110}. These six dotted-circles are arranged at every 61.5 ± 2.5°and the distances from the center of the image to the six dotted-circles are not exact constant (±3%). These experimental results show that the top surface layer of the bcc Fe{110}-whisker has a quasi-hexagonal two-dimensional lattice plane. This will be the essential idea for our interpretation of the experimentally observed surface reconstruction of the Fe{110} surface.

An inverse Fourier transformation with elements inside the six dotted-circles and the center circle in the Fourier transformed image (Fig. 2d) give an image shown in Fig. 2e, which shows a clear periodicity of the patterned modulation in brightness as well as the atomic array in the top-layer. From this image, we can get the unit vectors of the height modulation pattern as

$$\begin{pmatrix} \vec{p_1} \\ \vec{p_2} \end{pmatrix} = \begin{pmatrix} 13 & 1 \\ -2 & 14 \end{pmatrix} \begin{pmatrix} \vec{u_1} \\ \vec{u_2} \end{pmatrix}, \quad (1)$$

where $\vec{u_1}$ and $\vec{u_2}$ denote primitive vectors of the atomic arrangement in the top-layer. We set a whisker crystal on our STM stage as shown in Fig. 2a, i.e. the direction of one of the unit vectors of periodic modulation, $\vec{p_1}$, was set in almost [001] crystalline direction. The length of $\vec{p_1}$ was observed to be about 3.65 nm in Fig. 2e, i.e. $|\vec{p_1}|/a \approx 12.7$. Angle between $\vec{p_1}$ and another unit vector of $\vec{p_2}$ is $\phi_p \approx 63.8°$, and $k = |\vec{p_2}|/|\vec{p_1}| \approx 0.920$, i.e. $|\vec{p_2}|/a \approx 11.7$.

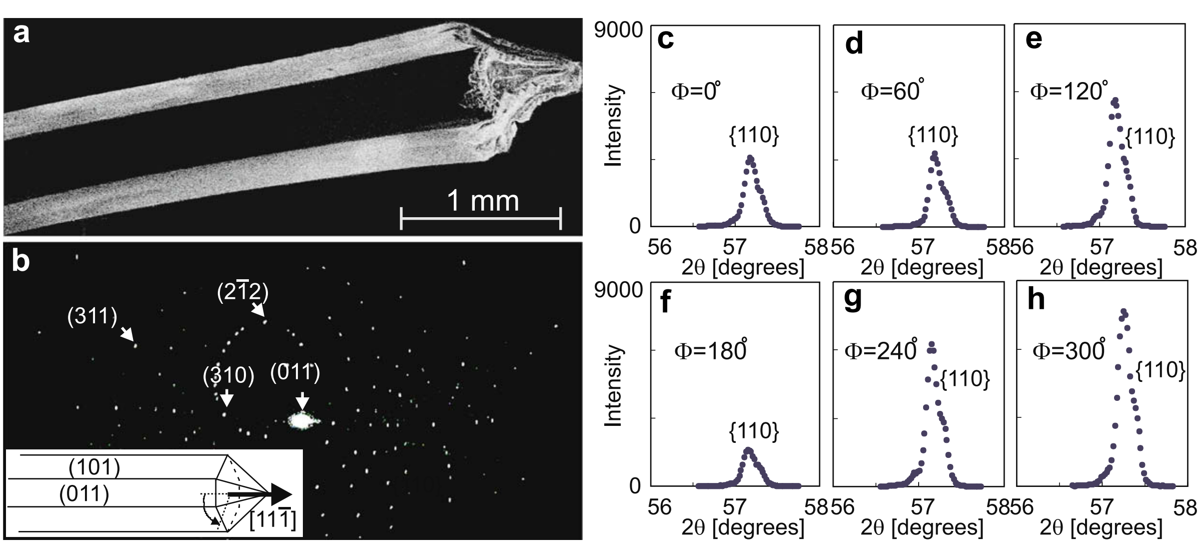

Fig. 1. (a) Scanning electron microscopy image of an Fe-whisker in hexagonal-pillar shape. (b) Laue X-ray image obtained on a side plane of the whisker in (a). An inset sketch shows the crystalline structure of the whisker. (c–h) Diffraction spectra were measured by rotating the whisker at Φ = 0° (c), 60° (d), 120° (e), 180° (f), 240° (g), and 300° (h). Six side planes of the hexagonal Fe-whisker were identified to be {110} using a four circle X-ray diffract meter.