Correlation between Surface Structure and Charge Ordering in Magnetite(001) Studied by Scanning Tunneling Microscopy and Spectroscopy

Agus Subagyo and Kazuhisa Sueoka
Graduate School of Information Science and Technology, Hokkaido University
Kita 14, Nishi 9, Kita-ku, Sapporo 060-0814, Japan
E-mail: agus@nano.ist.hokudai.ac.jp

Abstract. We report the observation on the charge ordering of Fe ions in a magnetite(Fe₃O₄)(001) film surface by scanning tunneling microscopy and spectroscopy (STM/STS) with a nonmagnetic W tip. The Fe₃O₄(001) film surface exhibits a B-plane termination with a (√2 × √2)R45° reconstruction. Fe cation rows running along the [110] direction show a wavelike structure. The (√2 × √2)R45° surface reconstruction is originated from the wavelike Fe rows. The current imaging tunneling spectroscopy image shows alternation of two different kinds of current peak with a separation of about 0.6 nm. Each current peak arises from the same local density of states (LDOS) of two Fe ions. The presence of Fe dimers with two different kinds of LDOS provides evidence for the charge ordering of Fe ions with different charge states. STM and STS using a nonmagnetic W tip allow us to correlate the charge ordering pattern with the surface structure.

1. Introduction
Magnetite (Fe₃O₄) (001) surface has been intensely studied for more than a decade due to interesting physical properties and because Fe₃O₄ has potential applications in spintronics. The structural properties of the Fe₃O₄(001) surface have become controversial, as variation of structures have been confirmed by scanning tunneling microscopy (STM) as well as other techniques [1, 2, 3, 4, 5, 6, 7, 8]. Surface charge ordering in the Fe₃O₄ (001) surface is an attractive phenomenon for spin-polarized STM (SP-STM) experiments [1, 2, 9, 10, 11, 12]. The first atomic scale SP-STM has been demonstrated on such a surface [1]. The difference in charge states of Fe ions could give rise to the contrast in normal STM, i.e. using a nonmagnetic tip, due to the possible difference in the local density of states (LDOS). However, the charge ordering has never been observed by STM. This leads to the suggestion of the domination of magnetic component in the contrast of the SP-STM image. Since the surface structural properties remain controversial, this fact should make it difficult to ignore the possible contribution of the chemical component in the SP-STM image by simple comparison with the STM image after replacing the tips. In this paper, we show that the charge ordering can indeed be observed by STM using a nonmagnetic W tip, allowing the direct correlation with the surface structure.
2. Experimental
The experiments were performed in an ultrahigh vacuum (UHV) system consisting of a chamber for film growth and a chamber for STM measurements. The base pressure of both chambers was \( \sim 7.0 \times 10^{-11} \) mbar. The sample was an epitaxial \( \text{Fe}_3\text{O}_4(001) \) film grown on a \( \text{MgO}(001) \) substrate. The substrate was cleaned by annealing at 1073 K for 60 min in oxygen (\( \sim 1.0 \times 10^{-6} \) mbar). The film was grown by deposition of Fe at 523 K in an oxygen pressure of \( \sim 1.0 \times 10^{-6} \) mbar. The growth rate was 1.5 ML/min and the film thickness was 20 nm. Reflection high energy electron diffraction confirmed the film to be epitaxially grown on \( \text{MgO} \) since the corresponding intensity oscillation revealing the layer by layer growth is observed. After the growth, an additional annealing in oxygen was employed for 30 min to obtain large terraces at the surface. X-ray photoelectron spectroscopy confirmed the films to be stoichiometric. STM measurements were performed at 300 K in a constant current mode. We used a W tip which was cleaned in the UHV by electron beam heating. The bias voltage was applied to the sample and the tip was set equally to the ground potential. No drift correction is applied to the STM images.

3. Results and Discussion
Bulk \( \text{Fe}_3\text{O}_4 \) has a cubic inverse spinel structure with a lattice constant of 0.8396 nm. The crystal structure is based on a fcc unit cell which is formed by \( \text{O}^{2-} \) anions and mixed valence of Fe cations occupying tetrahedrally (A-sites) and octahedrally (B-sites) coordinated interstices. Half of the ferric \( \text{Fe}^{3+} \) ions occupies the A-sites whereas the other ferric ions together with the ferrous \( \text{Fe}^{2+} \) ions occupy half of the B sites. \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) ions have an electronic configuration of \( 3d^5 \) and \( 3d^6 \), respectively. The high conductivity is due to electron hopping of the \( 3d_{\uparrow} \) electron among all the B-site \( 3d_{\uparrow} \) cores. Either of the two types of \( (001) \) planes, i.e. A-plane and B-plane, is considered to be polar, therefore reconstruction would be necessary to form a stable surface. Indeed, a \((\sqrt{2}\times\sqrt{2})R45^\circ\) reconstruction is commonly observed. By applying the autocompensation rule, the non-polar surface of a half-filled A layer \([6]\) and a B-terminated surface with oxygen vacancies \([5, 7]\) have been proposed for this reconstruction. Recently, ab initio calculations have shown that B-terminated surface has the lowest surface energy \([13]\). The relaxation can be achieved by formation of wavelike Fe rows induced by Jahn-Teller distortion. The wavelike Fe rows have been observed by STM \([7, 12, 14]\).

Figure 1. (a) STM image of the \( \text{Fe}_3\text{O}_4(001) \) film surface acquired using a W tip at tunneling parameters of a sample bias \( V_s = 2.0 \) V and a tunnel current \( I_t = 0.75 \) nA. Scan area is 50 nm \( \times \) 35 nm. (b) Low energy electron diffraction (LEED) patterns of the film indicating a \((\sqrt{2}\times\sqrt{2})R45^\circ\) surface reconstruction. (c) Cross-sectional line profile taken across several stack layers indicated by white line in the STM image.
Figure 2. High resolution STM image acquired at $V_s = 2.0\,\text{V}$ and $I_t = 0.75\,\text{nA}$. Scan area is $5\,\text{nm} \times 3\,\text{nm}$. The arrangement of the Fe ions constructed the rows is superimposed.

Our STM results revealed that the Fe$_3$O$_4$(001) film surface is terminated at a B-plane with a ($\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction as described in detail below. Figure 1(a) shows an STM image of the Fe$_3$O$_4$(001) film surface acquired using a W tip. The surface exhibits several stacked atomically flat terraces as a result of layer by layer growth. The terraces are separated by steps in height of about 0.21 nm as revealed by the cross-sectional line profile [Fig. 1(c)]. Thus, either A- or B-plane should terminate the surface. Atomic rows run in the [110] direction and their orientation turns by 90° on the neighboring terraces. The contrast in the STM image of the Fe$_3$O$_4$(001) surface should be dominated by Fe ions since the O 2p levels lie far below the Fermi level [13]. Thus, we concluded that the observed atomic rows represent Fe atom rows. This feature provides evidence for the B-plane termination.

A high resolution STM image clearly showing the atomic arrangement is shown in Fig. 2. As indicated in the image, the average row separation is about 0.6 nm and the atom separation within the rows is about 0.3 nm. These are further evidence for the B-plane termination. Another appearing feature is the wavelike structure of the Fe atom rows. This is apparently due to a subsequent alternating shift of Fe ion pairs perpendicular to the rows, as indicated by structural model superimposed on the STM image. The wavelike Fe rows induce a ($\sqrt{2} \times \sqrt{2})R45^\circ$ symmetry supporting the LEED patterns. According to the calculation result reported by Pentcheva et al. [13], such wavelike Fe rows can be modified by Jahn-Teller distortion of the surface atoms for surface relaxation. This modified B-plane termination has been found to become the most stable configuration over the entire range of accessible oxygen pressures. The atomic configuration revealed by our STM results closely matches the proposed structure.

Besides Fe atom rows with a clear single atomic resolution, Fe atom rows with less atomic resolution are also observed. Scanning tunneling spectroscopy (STS) measurement results ($I$-$V$ curves) on such Fe rows are shown in Fig. 3. Two $I$-$V$ curves marked by H and L, respectively, were taken on the same Fe row but at different atom sites. The curves exhibit a bandgap of about 1.4 eV. Considering the metallic property of the Fe$_3$O$_4$, the existence of the large bandgap in this surface suggests the transition to a semi-metallic phase probably due to freezing out of the electron hopping at the surface. Moreover, the curves exhibit a slightly different tunneling current in the positive bias voltage range. To investigate the origin of the observed different tunneling current, we have performed current imaging tunneling spectroscopy (CITS) measurements at a positive bias voltage range. A CITS image recorded at a bias voltage of 1.5 V is depicted in Fig. 4(a). Clearly, a periodic structure with two different kinds of current peak is observed. Figure 4(b) shows a cross-sectional line profile taken in the [110] direction. H (L)
Figure 4. (a) CITS image recorded at $V_s = 1.5$ V. The same kind current peaks form a $(\sqrt{2} \times \sqrt{2})R45^\circ$ symmetry, as indicated in the image. (b) Cross-sectional line profile taken along the [110] direction, i.e. parallel to the row direction, as indicated by line X. The current peak indicated by H and L represents higher and lower current peaks, respectively. (c) Model of the atomic structure and charge ordering.

peak corresponds to the H (L) curve of Fig. 3 representing the higher (lower) current peak. They alternate within the rows resulting in the modulation of H and L peaks along the rows. The distance between the same and different peaks is about 1.2 nm and 0.6 nm, respectively. A similar modulation appears in the direction perpendicular to the rows. This results in the $(\sqrt{2} \times \sqrt{2})R45^\circ$ symmetry of the similar current peak, as indicated in the unit cell.

Guiding by the CITS image and the simultaneously acquired STM image, we have been able to correlate the local current distribution with the surface structure. This can be seen in the structural model shown in Fig. 4(c). Each current peak consists of two Fe ions indicating the imaging of Fe dimers. Since the tunneling current of a STM reflects the integrated LDOS of the sample, the difference in the tunneling current, H and L peaks, should represent Fe dimers having different LDOS. The Fe dimers with different LDOS should indicate Fe dimers with different charge states, providing evidence for the presence of the charge ordering. Since the Fe ion with lower oxidation states has a larger LDOS than the Fe ion with higher oxidation states, and the STM image is taken in the empty state, therefore, the H and L peaks can be assumed as come from Fe dimer with higher oxidation states and Fe dimer with lower oxidation states, respectively. The distribution of the ordered Fe dimers with different charge states of the present work is similar to the charge ordering pattern of Fe$^{3+}$-Fe$^{3+}$ dimers and Fe$^{2+}$-Fe$^{2+}$ dimers observed by constant current SP-STM using both an antiferromagnetic MnNi tip [10, 11] and a Ni tip [12]. However, assigning integer charge to the Fe ions may not be appropriate since charge disproportionation of only 2.4 and 2.6 has been found recently at the bulk crystal below 120 K.

4. Conclusion

We have shown that the charge ordering of Fe ions having different charge states in Fe$_3$O$_4$(001) surface can be observed by STM using a nonmagnetic W tip. The Fe ions with different charge states exhibit different LDOS. These LDOS are the origin of the contrast in the CITS image. The charge ordering pattern is found to be similar to the previous SP-STM observation suggesting the contribution of the chemical component in the contrast of the SP-STM images. Still, the charge disproportionation and the influence of local stoichiometry remain to be investigated for a complete understanding of the surface charge ordering.
References

[1] Wiesendanger R, Shvets I V, Bürgler D, Tarrach G, Güntherodt H -G, Coey J M D and Graser S 1992 Science 255 583.
[2] Coey J M D, Shvets I V, Wiesendanger R, Güntherodt H -G 1993 J. Appl. Phys. 73 6742.
[3] Tarrach G, Bürgler D, Schaub T, Wiesendanger R and Güntherodt H -G 1993 Surf. Sci. 285 1.
[4] Gaines J M, Bloeman P J H, Kohlkepp J T, Bulle-Lieuwma C W T, Wolf R M, Reinders, Jungblut R M, van der Heijden P A A, van Eemeren J T W M, aan de Stegge J and de jonge W J M 1997 Surf. Sci. 373 85.
[5] Voogt F J, Fujii T, Smulders P J M, Niesen L, James M A and Hibma T 1999 Phys. Rev. B 60 11193.
[6] Chambers S A, Thevuthasan S and Joyce S A 2000 Surf. Sci. 450 L273.
[7] Stanka B, Hebenstreit W, Diebold U and Chambers S A 2000 Surf. Sci. 448 49.
[8] Mijiritskii A V and Boerma D O 2001 Surf. Sci. 486 73.
[9] Koltun R, Herrmann M, Güntherodt G and Brabers V A M 2001 Appl. Phys. A 73 49.
[10] Mariotto G, Murphy S and Shvets I V 2002 Phys. Rev. B 66 245426.
[11] Shvets I V, Mariotto G, Jordan K, Berdunov N, Kantor R and Murphy S 2004 Phys. Rev. B 70 155406.
[12] Subagyo A and Sueoka K 2006 Jpn. J. Appl. Phys. 45 2255.
[13] Zhang Z and Satpathy S 1991 Phys. Rev. B 44 13319.
[14] Pentcheva R, Wendler F, Meyerheim H L, Moritz W, Jedrecy N and Scheffler M 2005 Phys. Rev. Lett. 94 126101.
[15] Fonin M, Pentcheva R, Dedkov Yu S, Sperlich M, Vyalikh D V, Scheffler M, Rüdiger and U and Güntherodt G 2005 Phys. Rev. B 72 104436.