Atomic Surface Structures on Multi-Layered Cuprate Superconductor $Ba_2Ca_4Cu_5O_{10}(O_{1-x}F_x)_2$ Observed by STM.

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Abstract

We investigate the scanning tunneling microscopy (STM) on the multi-layered cuprate superconductor $Ba_2Ca_4Cu_5O_{10}(O_{1-x}F_x)_2$ (F0245, T_c =79 K, x = 0.72).

The STM images show clear atomic lattice structures and large random spot structures. Among the regular square-lattice atomic corrugation with the period of the lattice constant a ~0.38 nm, another kind of atomic spots arranged into the four-fold cross shaped clusters is clearly observed along the diagonal direction with the period of 0.26 nm. These clusters are being distributed inhomogeneously, which are due to the charge imbalance associated with the apical O/F rate. The apical O and F sites are also identified from the positions of such clusters in the STM topographic images.

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1. Introduction

The multi-layered cuprate superconductors $Ba_2Ca_{n-1}Cu_nO_{2n}(O_{1-x}F_x)_2$ (F02(n-1)n) [1,2] have two novel characteristic structures; the multiple stacking layers of CuO_2, and the apical fluorine (F) atom which is substituted for apical oxygen (O). Because of such characteristic structures, the superconducting critical temperature (T_c) of these materials excesses 100 K, hence, they are very attractive materials from both practical and scientific points of view.

These multi-layered cuprates have been intensively investigated by various methods, such as nuclear magnetic resonance (NMR) [3,4], angle-resolved photoemission spectroscopy (ARPES) [5], by point-contact tunneling spectroscopy [6] and scanning tunneling microscopy/spectroscopy (STM/STS) [7]. These results suggest the coexistence of antiferromagnetism and superconductivity, and the existence of the multiple Fermi surfaces and the multiple gap structures, both of which are believed to be due to the properties of "multi-layers". In typical cuprate superconductors, the apical-O layer supplies carriers to the CuO_2 layer, so called as "charge reservoir layer", but the disorder of the apical O layer is considered to directly affect the superconductivity of the CuO_2 layer [8]. On the other hand, in the case of the multi-layered cuprates, the disorder induced by the substitution of the apical O to F (anion replacement) is expected to be smaller than that by the cation replacement, such as Bi-based cuprate or La-based cuprates. For this reason, it is important to clarify the effects of apical F and O atoms on the high-T_c superconductivity. In addition, in the multi-layered cuprate superconductors, the layers including the apical sites are directly observable by STM/STS because the BaO/F layers are easily exposed to vacuum (Fig. 1(a)). This is different from the widely-investigated Bi-based cuprate superconductors.

In this paper, we present the fine structures of surface atomic arrangements of the multi-layered superconductor $Ba_2Ca_4Cu_5O_{10}(O_{1-x}F_x)_2$ (F0245) by STM technique, from which the positions of the apical O and F are able to be identified.

2. Experimental

The F0245 superconducting single crystals were fabricated by a high-pressure synthesis technique [2]. The crystal structure is shown in Fig. 1(a). Typical size of the single crystal is about 0.5 mm x 0.5 mm x 0.1 mm. The T_c ~79 K was confirmed by the temperature dependence of the magnetic susceptibility, as shown in Fig. 1(b). The composition of this compound was determined by an electron probe micro analyzer (EPMA), from which the average Ba:Ca:Cu:F ratio was obtained to be 2.00:4.01:4.94:1.44. This ratio is in good agreement with the ideal stoichiometric ratio for this compound.

The STM equipment used in this experiment is commercially based system (Omicron LT-UHV-STM) with some modifications [9, 10]. The single crystals were cleaved at 77 K under the ultra-high vacuum (UHV) atmosphere of ~10^{-8} Pa. The exposed surface is considered to be the BaF/O layers of the *ab*-plane, as indicated by the squared frames in Fig. 1(a). The Pt/Ir tip was cleaned by high-voltage field emission process with Au single crystal target just prior to the STM observations. The STM observations were carried out at the temperature of 4.9 K with the UHV condition of ~10^{-8} Pa. The STM topographies were measured by constant current-mode.

3. Results and discussion

Fig. 2(a) shows the STM topography on cleaved surface of the F0245 single crystal

with the sample bias voltage of -0.8 V. Clear atomic structures are observed but they are not simple lattice structures. There are mainly two types of periodic structures; the one is the square lattice as a background, the other is the randomly distributed bright-spot structures along the diagonal direction. Furthermore, almost all bright spots form four-fold cross shaped cluster and/or its connected pattern. The coexistence of these two kinds of structures can be observed under the relatively higher tunnel current (>0.4 nA) conditions. On the contrary, under the lower current (lower conductance) conditions, the randomly-distributed large spot structures tend to be observed without the four-fold cross shaped clusters and the square lattice structures. These features are similar to the previously reported STM images on F0256 [7]. In addition, most four-fold cross shaped clusters are arranged on the square lattice structures, which are indicated by dashed circles at the left bottom of Fig. 2(a). The first Fourier transformation (FFT) power spectrum image is shown in Fig. 2(b), giving additional information of the period of the atomic structures. We can recognize two characteristic distances d_1 = 0.38 nm and d_2 = 0.26 nm from FFT analysis indicated by arrows. The period d_1 corresponds to the lattice constant, a = 0.381 nm, that is derived from the square lattice structures in Fig. 2(a). On the other hand, the period of d_2 =0.260 nm is obtained from the bright spots along the diagonal direction, which is also recognized from the topography (Fig. 2(a)). From the crystal structure (Fig. 1 (a)), it is obvious that the O atoms at CuO_2 layers have the sequence period of $a/\sqrt{2}$ (~ 0.272 nm), and other atoms of Ba, Ca, apical F/O and Cu have the sequence period of the lattice constant, a (~ 0.381 nm). Therefore, it is natural to attribute that the period of d_2 corresponds to the separation of O atoms at CuO_2 layer.

By counting the number of these four-fold cross shaped clusters (4 spots form 1 cluster), the central sites surrounded by four bright spots occupy ~22% of whole the

central sites of the square-lattice structures within the observed area. The averaged F rate at apical F/O atomic site is estimated as x = 1.44 (72%) by EPMA analysis, *i.e.*, the rate of non-replaced oxygen (O) sites is about 28%. Additionally, by taking into account the fact that the substitution occurs only between O and F, it is very reasonable to consider that the four-fold cross shaped clusters mainly indicate the (non-replaced) apical O position. The occupied ratio of the four-fold cross shaped clusters (~22%) is slightly fewer than the total non-replaced O (~28%). This may due to the fact that some apical O transfer to other layer, such as CuO_2 sites and/or other irregular sites. In our previous work, we have already observed the large (~0.8 nm diameter) bright-spot structures in the F0256 compounds [7]. It was suggested at that time that the large spots were due to the non-replaced apical oxygen by estimating the spot density from the STM topography. If we assume that the four spots combine into such a large spot, the size of the large spots previously observed is consistent with that of the present four-fold cross shaped clusters ($2a$ ~ 0.77 nm).

It should be also interesting to clarify why and how the four-fold cross shaped clusters are formed. By replacing the apical O to F, the excess charge (hole) is generated at non-replaced apical O^{2-}, resulting in the charge imbalance. It works as a point defect of charge at topmost BaO/F layers. The excess charge is localized in the vicinity of the O site (not F site) because of the large negative charge of O. Then, the excess charge migrates and being bound to the anion atom O at the second topmost CuO_2 layer. As a consequence, the local density of states in the second topmost CuO_2 layer is being modified, which perhaps causes the cross-shaped clusters in the STM images. It is noted that, depending on the observed area, the tunnel conductance spectra show the clear double-gap structure with the size of Δ~ 45 meV and ~100 meV. This can be explained

by the coexistence of the superconductivity and the pseudogap. This may be also consistent with the observed atomic-size localization of the charge on the CuO_2 layer. One may consider the four-fold cross shaped clusters as the magnetic impurity images due to the *d*-wave symmetry, such as previously reported conductance maps on Zn doped $Bi_2Sr_2CaCu_2O_y$ [11]. However, it is difficult to consider such an impurity origin because there are too many four-fold cross shaped clusters (22% of surface sites) although the sample has few impurity (< 0.1%) conformed by the EPMA analysis.

Fig. 3(a) shows the magnified STM topography, demonstrating the fine structures of the surface, especially focusing on the four-fold cross shaped clusters. The schematic lattice lines are additionally superposed on the square lattice structures. On the basis of above discussion, Fig. 3(b) shows the suggested schematic drawing of the arrangement of the several kinds of atoms (mainly anions) at topmost surface of BaO/F layer and the second topmost CuO_2 layer (only the brighten O spots). The non-replaced apical O atoms are indicated by the thick solid circles on the crossings of the square lattice pattern surrounded by the bright spots, *i.e.*, the four-fold cross shaped clusters. The apical F atoms are indicated by the capital F letters. As the consequence, the apical F and O atoms are clearly distinguished by the characteristic four-fold bright spots. As mentioned above, it is very significant to visualize and identify the positions of apical F and O because apical F/O substitutions play an important role for the superconductivity of cuprates. For example, the (inhomogeneous) pseudo-gap phenomena widely observed by STS experiments are mainly considered to be induced by the excess oxygen and/or defects out of CuO_2 apical oxygen layer [12,13]. It is needed to clarify the relationship between the electronic states including the gap structures and the distributions of apical O and F.

4. Summary

The STM measurements on the multi-layered cuprate superconductor $Ba_2Ca_4Cu_5O_{10}(O_{1-x}F_x)_2$ have been presented. The STM images show two types of the atomic structures; the background of square lattice, and the randomly distributed four-fold cross shaped clusters along the diagonal direction. From the positions of the four-fold cross shaped clusters and the ratio of F and O obtained by EPMA analysis, the worthwhile results of distinguishing the positions of the apical O and F atoms are obtained. These results would lead to the further understandings of the effects of the apical O/F substitution properties of the high-T_c superconductivity.

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References

[1] A. Iyo, Y. Aizawa, K Y. Tanaka, M. Tokumoto, K. Tokiwa, T. Watanabe, H. Ihara, Physica C 357-360 (2001) 324.

[2] A. Iyo, M. Hirai, K. Tokiwa, T. Watanabe, Y. Tanaka, Physica C 392-396 (2003) 140.

[3] S. Shimizu, T. Sakaguchi, H. Mukuda, Y. Kitaoka, P.M. Shirage, Y. Kodama, A. Iyo, Phys. Rev. B 79 (2009) 064505.

[4] S. Shimizu, H. Mukuda, Y. Kitaoka, H. Kito, Y. Kodama, P.M. Shirage, A. Iyo, J.

Phys. Soc. Jpn. 78 (2009) 064705.

[5] Y. Chen, A. Iyo, W. Yang, X. Zhou, D. Lu, H. Eisaki, T. P. Devereaux, Z. Hussain, Z.-X. Shen, Phys. Rev. Lett. 97 (2006) 236401.

[6] N. Miyakawa, H. Haya, A. Iyo, Y. Tanaka, K. Tokiwa, T. Watanabe, T. Kaneko, Int. J. Mod. Phys. B 21 (2007) 3233.

[7] A. Sugimoto, K. Shohara, T. Ekino, Y. Watanabe, Y. Harada, S. Mikusu, K. Tokiwa, T. Watanabe, Physica C 469 (2009) 1020.

[8] H. Eisaki, N. Kaneko, D.L. Feng, A. Damascelli, P.K. Mang, K.M. Shen, Z.-X. Shen, M. Greven, Phys. Rev. B 69 (2004) 064512.

[9] T. Ekino, T. Taksaki, R.A. Ribeiro, T. Muranaka, J. Akimitsu, J.Phys.: Conf. Ser. 61 (2007) 278.

[10] A. Sugimoto, T. Ekino, H. Eisaki, J. Phys. Soc. Jpn. 77 (2008) 043705.

[11] S. H. Pan, E. W. Hudson, K. M. Lang, H. Eisaki, S. Uchida, J.C. Davis, Nature (London) 403 (2000) 746.

[12] K. McElroy, Jinho Lee, J.A. Slezak, D.-H. Lee, H. Eisaki, S. Uchida, J.C. Davis, Science 309 (2005) 1048.

[13] A. Sugimoto, S. Kashiwaya, H. Eisaki, H. Kashiwaya, H. Tsuchiura, Y. Tanaka, K. Fujita, S. Uchida, Phys. Rev. B 74 (2006) 094503.

Figure captions

Fig. 1 (color online) (a) The schematic crystal structure of $Ba_2Ca_4Cu_5O_{10}$ $(O_{1-x}F_x)_2$ (F0245) (b) Temperature dependence of the magnetic susceptibility for the F0245 single crystal.

Fig. 2 (color online) (a) The typical STM topography on F0245 (T = 4.9 K, V_{bias}= -0.8 V, I_t=0.5 nA). The four-fold cross shaped bright spots are indicated by the broken circles. (b) FFT image of the STM topography of Fig. 2(a).

Fig. 3 (color online) (a) The magnified STM topography on F0245. The schematic line lattice lines are superposed on the square-lattice structures. The schematic crystal structure of *ab*-plane is also superposed. (b) The schematic of the atomic positions on the same area of Fig. 3(a). The four-fold bright spots are indicated by the (pink-colored) broken circles, which form the four-fold cross shaped clusters. The (black-colored) thick sold circles show the non-replaced apical O atoms. The (yellow) capital F letter sites show the apical F atoms. The Cu position is just below the apical O/F.

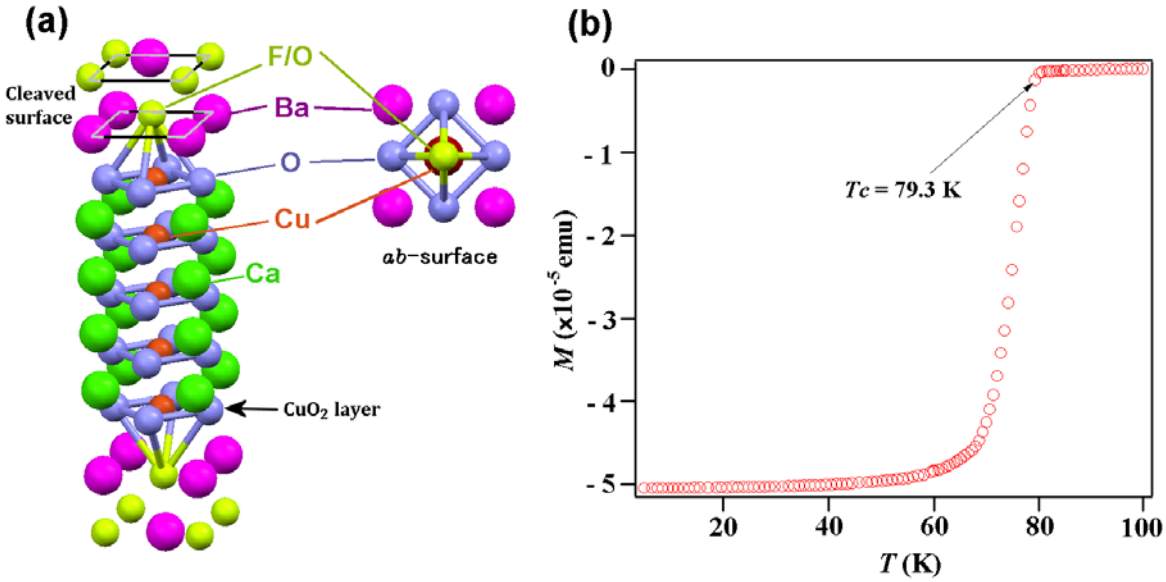

Fig. 1 Sugimoto

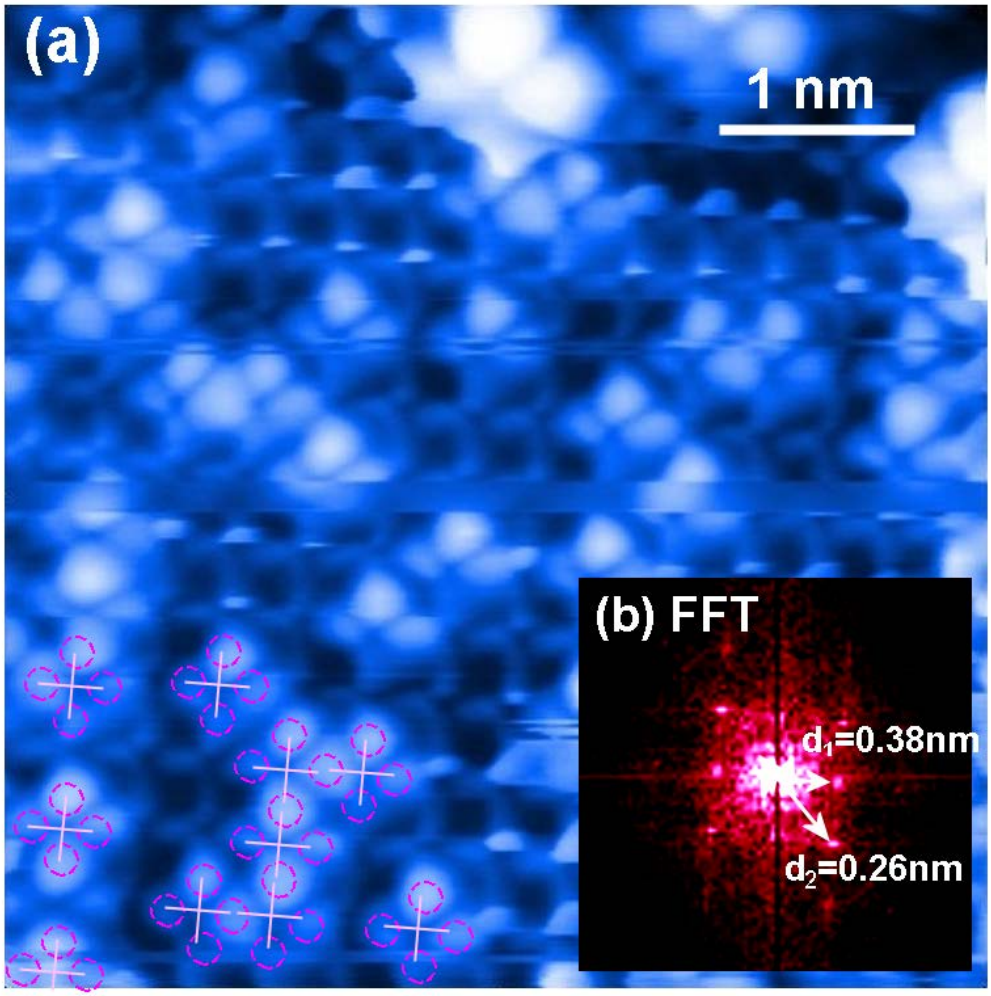

Fig. 2 Sugimoto

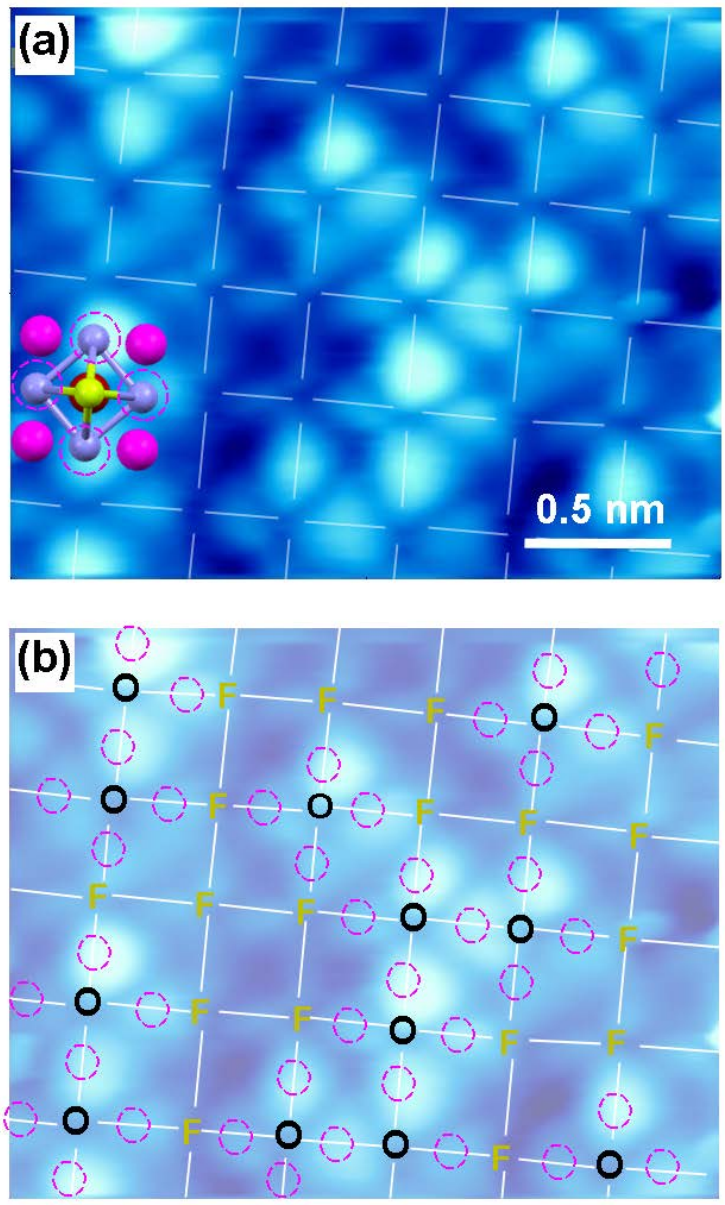

Fig. 3 Sugimoto