Scanning Tunneling Microscopy / Spectroscopy on Multi-Layered Cuprate Superconductor $Ba_2Ca_5Cu_6O_{12}(O_{1-x}F_x)_2$

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Abstract

Scanning tunneling microscopy/spectroscopy (STM/STS) measurements on multi-layered cuprate superconductor $Ba_2Ca_5Cu_6O_{12}(O_{1-x}F_x)_2$ are carried out. STM topographies show randomly distributed bright spot structures with a typical spot size of ~ 0.8 nm. These bright spots are occupied about 28% per one unit cell of *c*-plane, which is comparable to the regular amount of apical oxygen of 20% obtained from element analysis. Tunneling spectra simultaneously show both the small and the large gap structures. These gap sizes at 4.9 K are about Δ ~ 15 meV and ~ 90 meV, respectively. The small gap structure disappears at the temperature close to T_C, while the large gap persists up to ~200 K. Therefore, these features correspond to the superconducting gap and pseudogap, respectively. These facts give evidence for some ordered state with large energy scale even in the superconducting state. For the superconducting gap, the ratio of $2\Delta_S / K_B T_C$ = 4.9 is obtained with T_C = 70 K, which is determined from temperature dependence of the tunneling spectra.

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1. Introduction

The multi-layered cuprate superconductors are unique kind of superconducting materials whose critical temperature (T_C) excesses 100 K. The T_C does not monotonically increase with increasing the number of copper oxygen (CuO_2) layer (n) but there is the upper limit of T_C at n =3 or 4 [1]. This fact indicates that doping rate at each CuO_2 layer is inhomogeneous and not uniform.

Recently, a series of multi-layered cuprate superconductors $Ba_2Ca_{n-1}Cu_nO_{2n}(O_{1-x},F_x)_2$ (F02(n-1)n) with apical fluorine atoms (F) has been successfully synthesized including large-scale single crystals [2, 3]. These material properties can be controlled by changing the number of CuO_2 layers (n) and/or by changing the anion ratio of O^{2-} and F^- at apical atomic sites. Recent NMR and angle-resolved photoemission spectroscopy (ARPES)[5] experiments confirmed that the F0234 is a self-doped superconductor having doped electrons and holes simultaneously [4], thus consisting of both kinds of the Fermi-surface sheets [5]. For this reason, the direct observation of gap structure and local density of state (LDOS) with those temperature dependences is particularly important for the basic understanding of superconductivity. In fact, the tunneling spectra measured by point contact technique have revealed the coexistence of pseudo-gap and small gap [6].

In this paper, we present the first direct observation of atomic resolved surface structure and temperature-dependent tunneling spectroscopy of the multi-layered superconductor $Ba_2Ca_5Cu_6O_{12}(O_{1-y}, F_y)_2$ (F0256) by STM/STS technique.

2. Experimental

The F0256 superconducting single crystals were fabricated by a high-pressure synthesis technique [2]. The T_C ~70 K was conformed by the temperature dependence of the resistance measured by a standard four-electrode method (measurement of *RT*) as shown in Fig. 1(b). This compound system strongly prefers an under-doped state [2]. The typical size of the single crystal is about 1 mm x 0.6 mm x 0.1 mm, as shown in Fig. 1(c). The 6-layered CuO_2 phase was determined by an X-ray diffraction (XRD) and electron probe micro analyzer (EPMA). The EPMA analysis revealed that the average Ba:Ca:Cu:F ratio was 2.00:5.13:5.78:1.59, which is in good agreement with the ideal stoichiometric ratio for this compound. The large-size single crystal of this phase is relatively easier to obtain than that of other phase. Furthermore it is easy to cleave like $Bi_2Sr_2CaCu_2O_y$ (Bi2212) superconducting single crystals. Therefore, it is very suitable for STM/STS measurement. The exposed surface is considered to be the Ba-F/O layer of c-plane, as indicated by squared frames in the schematic model of Fig. 1(a).

The STM equipment used in this experiment is commercially based system (Omicron LT-STM) with some modifications [7, 8]. The single crystals were cleaved at 77 K under the ultra-high vacuum atmosphere of ~10^{-8} Pa. The Pt/Ir tip was cleaned by high-voltage field emission process with Au single crystal target just prior to the STM and STS observations. The STM observations were carried out at the temperature range from 4.9 K to 70 K by the heating system with the ultra-high vacuum condition of ~10^{-8} Pa.

3. Results and discussion

Figure 2 shows the STM topographic images on cleaved surface of the F0256 single crystal. In Fig. 2(a), the random distribution of bright spots with several angstrom-size

is clearly observed. These random structures were observed not only in this sample bias voltage *Vs*=0.8 V but also in almost all of the observed bias voltages (from *Vs* = –1.0 V to +1.0 V). On the other hand, the faint periodic corrugations of the surface structure were additionally observed at 45 K, as shown by the white circles in Fig. 2(b). This periodic length (~ 0.4 nm) was comparable with the *a*-axis lattice constant obtained by XRD measurement (*a* ~ 0.385 nm). Therefore, these faint periodic images were due to the atomic structure of *c*-plane. On the other hand, the length scale of the random-bright spots looks larger than that of the atomic corrugation scale. The density of the random spots n_{spot}, which is obtained by counting the number of the random white spots is n_{spot} ~ 1.86 nm^{-2} within the STM measurement area, while the F/O (or Ba) atomic site density is estimated n_{atom} ~ 6.57 nm^{-2} from the lattice constant (*a* ~ 0.385 nm). Therefore, the random spots were occupied about 28% of the F/O (or Ba) atomic site. From the element analysis by EPMA, the averaged fluorine (F) ratio at apical F/O atomic site is estimated as *x* = 1.6 (80%), *i.e.*, the ratio of non-replaced oxygen (O) site is about 20%. If we assume that the cleaved surface is Ba-F/O layer, we consider that the random bright spots are mainly due to the (non- replaced) apical O atoms. However, there is the discrepancy between the spot density n_{spot} and the ratio of apical O atoms, about 71%. It is considered that the STM topography is sensitive to the fine charge valance of the surface and there may be some over-counting sites or other origins such as the impurity sites. Further precise experiments including the atomic-site-dependent dI/dV measurements will reveal these issues. Such investigations will be presented elsewhere.

Next, to clarify the properties of the gap structures on F0256, the measurements of temperature-dependent tunneling spectra were carried out. In order to obtain the systematic data, the spectra were averaged over whole observed area because it is

difficult to identify exactly the same position by the thermal fluctuations. Fig. 3(a) shows the averaged tunneling spectra on F0256 single crystal at 4.9 K, 70 K and 205 K with the wide bias range from -0.2V to 0.2V. At 4.9 K, the spectrum shows two kinds of gap edges, one is around ±20mV (indicated by arrows) and the other is around +90mV. The two kinds of gap edge structures observed by STS look very similar to the previously observed tunnel spectrum of F0234 by point contact method [6]. The simultaneous two gap structures were commonly observed in electron-doped cuprates, $Nd_{2-x}Ce_xCuO_4$ [9] and $Sm_{1.85}Ce_xCuO_4$ [10]. Together with the fact that the similar shapes of conductance spectrum on electron-doped cuprates and the gap ratio of $2\Delta/K_BT_C$ discussed later, the surface observed by STM/STS seems to correspond to the electron-doped CuO_2 layer, which is nearest from the apical (O/F) site. This result is consistent with the NMR experiment, which shows that the outer layer is the electron-doped CuO_2 layer in F0234[4]. The larger gap structure persists up to 205 K, while this structure disappears at 238 K, as shown in Fig. 3(a). This energy and temperature scale (T^*~ 200 K) are comparable with the widely observed pseudogap. It is consistent that the *RT* curve along the *c*-axis shows the minimum point at *T*~ 220 K in F0256, which indicates that some ordered state with large energy scale, such as anti-ferromagnetic order [10], etc, stand below T^*~ 200 K.

Figs 3(b) shows the tunneling spectra including the details of the small gap structures at various temperatures with the narrow bias voltage range from -40mV to +40mV. The small gap structures were observed with faint peaks or the shoulders. It may due to that this compound is in the under doped regime because it is well known that the gap peaks are suppressed in under doped cuprates. To clarify the gap amplitude from these faint gap structures, the fitting curves are calculated on the basis of the Dynes's function modified with a gap of $d_{x^2-y^2}$-wave symmetry and with an additional liner function,

$$\frac{dI}{dV}(V) \propto \int_{-\pi/2}^{\pi/2} \mathrm{Re}\left[\frac{eV - i\Gamma}{\sqrt{(eV - i\Gamma)^2 - \Delta^2 \cos^2 2\theta}}\right] d\theta + kV\,, \qquad (1)$$

where Γ and k are the Dynes broadening parameter and a constant, respectively. The fitting curves are presented as the solid lines in Fig. 3(b). The fitting results show, for example, Δ = 14.7 (meV), Γ = 4.4 (meV) and k = 5.15 x 10^{-3} (V^{-1}) at 4.9 K. The gap parameters Δ at various temperatures are plotted in Fig. 3(c) together with Δ_{BCS} (T) obtained from the BCS theory by the broken lines. The observed $\Delta(T)$ data basically follows the Δ_{BCS} (T) line. The ratio of $2\Delta/K_BT_C$ ~ 4.9 lies within the strong-coupling BCS theory, ~ 4.2.This ratio is smaller than Bi2212 (= 7~10) or $La_{2-x}Sr_xCuO_4$ (= 5~10), but is comparable to $YBa_2Cu_3O_y$ (= 4~6) and electron-doped $Ln_{2-x}Ce_xCuO_4$ (= 4~7, Ln= lanthanides) [9-13]. It can be interpreted that the smaller ratio $2\Delta/K_BT_C$ for F0256 is due to the inner superconducting gap well separated from the outer pseudogap, while for a Bi2212, the gap feature one looks like mixtures of superconducting gap and pseudogap.

4. Summary

The STM/STS measurements on the multi-layered cuprate superconductor $Ba_2Ca_5Cu_6O_{12}(O_{1-x}F_x)_2$ have been performed. The STM topography shows the random spot structures with the typical size of 0.8 nm. These spots occupy about 28% of one unit cell of *c*-plane, which is considered to be mainly due to the non-replaced apical O atoms or some impurities. The temperature dependence of averaged tunnel spectra shows two kinds of gap features, one is the superconducting gap Δ~15 meV disappearing around T_C, the other is large (pseudo) gap of ~ 90 meV, which persists up

to 200 K. The temperature dependence amplitude of the Δ basically follows the BCS dependence, which thereby gives the small ratio of $2\Delta/K_BT_C = 4.9$ as compared with the other cuprate superconductors. This smallness could be connected with the well separated inner superconducting gap and the outer pseudogap.

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Figure captions

Fig. 1 (a) The schematic crystal structure of $Ba_2Ca_5Cu_6O_{12}(O_{1-x}F_x)_2$ (F0256) (b) The temperature dependence of resistance of F0256. (c) Optical-microscope photograph of the cleaved single crystal. The white line corresponds to 500μm .

Fig. 2 (a) The typical STM topography on F0256 (T= 4.9 K, V_{bias}= 0.8 V, I_t=0.25 nA). (b) The STM topography with atomic corrugation (T= 45 K, V_{bias}= 0.4 V, I_t =0.2 nA.) The position of the sample is different from (a). The length scale is the same for two figures.

Fig. 3 (a) The averaged tunnel spectra with the bias range from -0.2 V to +0.2 V at 5, 70, and 205 K. The large gap structure survived up to ~220 K. The each curve is shifted by 0.4 for the clarity. (b) Temperature evolution of the averaged tunnel spectra on F0256, together with the fitting curves in each spectrum. The each curve is shifted by 0.4. (c) The temperature dependence of small gap Δ obtained from the fitting parameter of Fig. 3 (b).

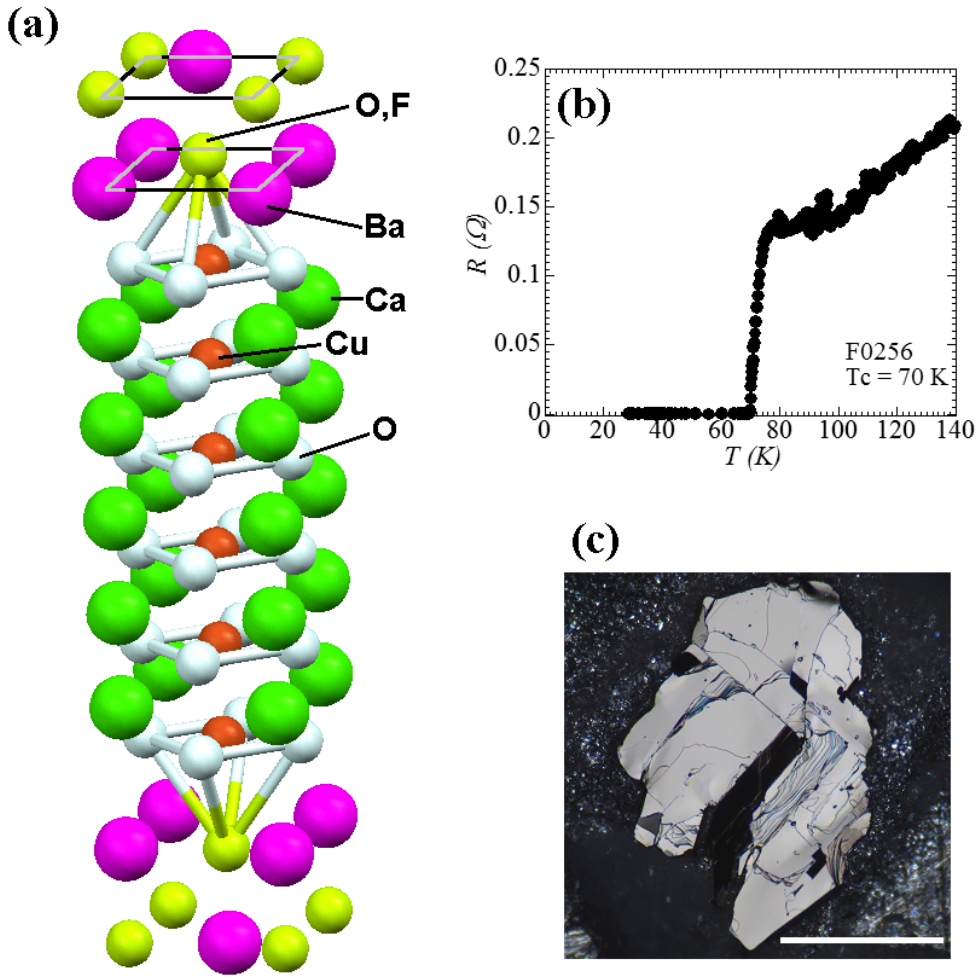
(a)
O,F
Ba
Ca
Cu
O
(b)
R (Ω)
T (K)
F0256
Tc = 70 K
0.25
0.2
0.15
0.1
0.05
0
0
20
40
60
80
100
120
140
(c)

Fig. 1

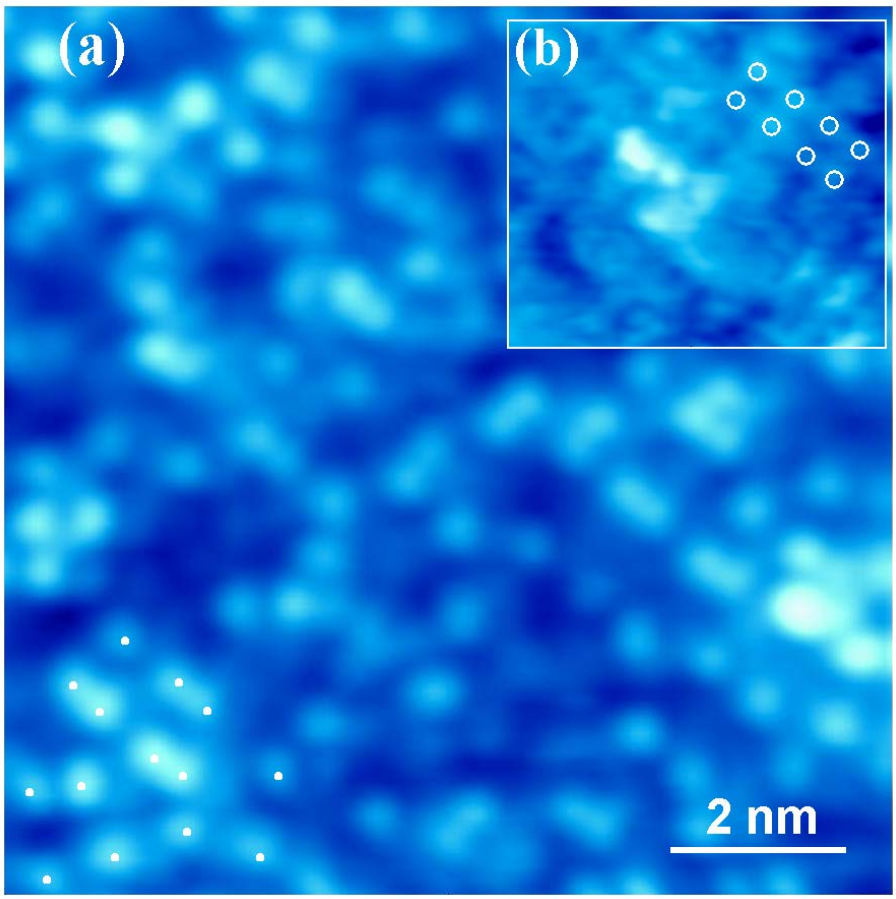

Fig. 2

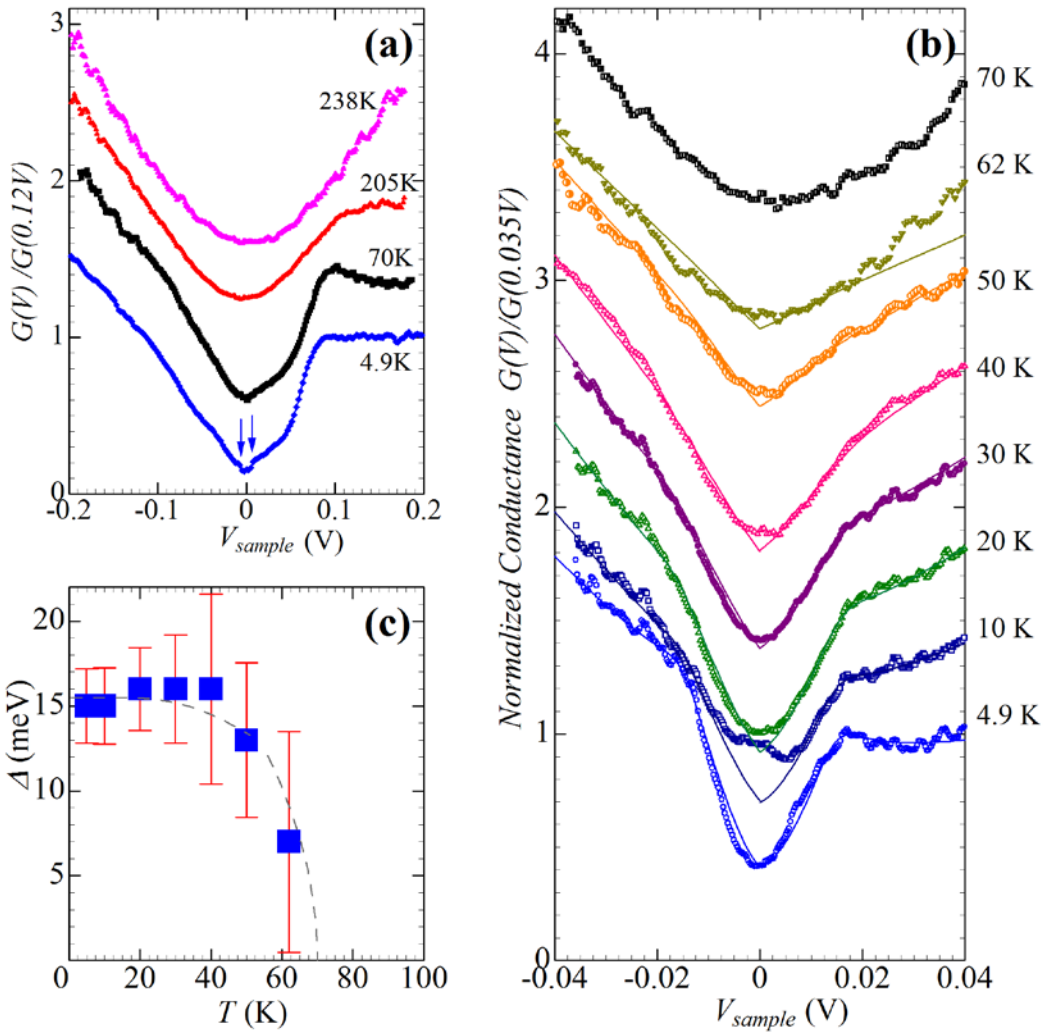
(a)
238K
205K
70K
4.9K
G(V) /G(0.12V)
V_sample (V)
(b)
70 K
62 K
50 K
40 K
30 K
20 K
10 K
4.9 K
Normalized Conductance G(V)/G(0.035V)
V_sample (V)
(c)
Δ (meV)
T (K)

Fig. 3