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# Correlation between modulation structure and electronic inhomogeneity on Pb-doped Bi-2212 single crystals

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**Abstract**

The correlation between nanometer-size electronic states and surface structure is investigated by scanning tunneling microscopy/spectroscopy (STM/S) on Pb-doped $Bi_{2-x}Pb_xSr_2CaCu2O_{8+y}$ (Pb–Bi-2212) single crystals. The advantage of the Pb–Bi-2212 samples is that the modulation structure can be totally or locally suppressed depending on the Pb contents and annealing conditions. The superconducting gap ($\Delta$) distribution on modulated Pb–Bi-2212 samples showed the lack of correlation with modulation structure except a slight reduction of superconducting island size for the *b*-axis direction. On the other hand, the optimal doped Pb–Bi-2212 ($x = 0.6$) samples obtained by reduced-annealing showed totally non-modulated structure in topography, however, the spatial distribution of $\Delta$ still showed inhomogeneity of which features were quite similar to those of modulated samples. These results suggest that the modulation structure is not the dominant origin of inhomogeneity although it modifies the streaky $\Delta$ structure sub-dominantly. From the gap structure variation around the border of narrow gap and broad gap regions, a trend of the coexistence of two separated phases i.e., superconducting phase and pseudogap like phase, is detected.


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## 1. Introduction

It has widely been reported that $Bi_2Sr_2Ca$-$Cu_2O_{8+y}$ (Bi-2212) superconductor has a nature of nanometer-size inhomogeneous electronic states [1–7]. It is considered the existence of inhomogeneity is related to the mechanism of high-$T_c$ superconductivity. Many influential or dominant origins of inhomogeneity were considered: (1) chemical inhomogeneity such as impurities [3] or carrier doping by excess oxygen [2,4]; (2) structural distortion such as supermodulation; (3) other new electrical phase without chemical or lattice disorder, however, the origin has not been clarified yet. Although a normal Bi-2212 shows supermodulation structure along the *b*-axis direction with the period of 5*b*, these structures are known to be modified due to the Pb-doping as well as the growth conditions [8–10]. Furthermore, the surface with non-modulated structure is considered to give us useful information of more real nature of superconductivity because of free from periodic structural disorder, which may affect inhomogeneous superconductivity.

In present paper, in order to clarify the correlation between the structural lattice disorder and the electronic states, we precisely measured superconducting gap ($\Delta$) distributions by using scanning tunneling microscopy/spectroscopy (STM/S) on Pb-doped $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+y}$ (Pb–Bi-2212) single crystals with various periods of modulation and completely non-modulation structure.

## 2. Experimental

The Pb–Bi-2212 (nominally, $Bi_{2.18-x}Pb_xSr_{1.88}$-$CaCu_2O_{8+y}$, $x = 0$, 0.6, 0.8) single crystals were fabricated by traveling solvent floating zone method. As-grown samples with $x = 0.6$, 0.8 were over doped (OD) regime and critical temperature ($T_c$) was about 80 K. The Pb free optimal doped (OP) Bi-2212 samples ($x = 0$, $T_c = 93$ K) were also prepared for comparison. The optimal doped Pb–Bi-2212 ($x = 0.6$, $T_c = 96$ K) samples were obtained by reduced-annealing of 650 °C at 16 h under Ar gas atmosphere and quenching.

A home-build STM unit stored in a low temperature chamber was kept around 9 K during the measurements. The Pb–Bi-2212 single crystals were transferred to the STM unit soon after the cleavage inside the low temperature chamber under the ultra-high vacuum atmosphere. The Pt/Ir tip was cleaned by high voltage field emission process with Au film target just prior to the STM/S observations.

## 3. Results and discussion

Fig. 1 shows the topographic images ((a) $x = 0$, (b) $x = 0.6$, (c) $x = 0.8$) and spatial gap ($\Delta$) distributions ((A)–(C)) with the same area as topographies in various types of Pb–Bi-2212 single crystals obtained by STM/S observation. The values of $\Delta$ were defined as the half of peak-to-peak voltage in the conductance spectra ($dI/dV$ vs. $V$). The supermodulation structures were clearly present in each topographies along the *b*-axis direction with the periodic length of $\lambda \sim 2.7$ nm in (a), $\lambda \sim 6.5$ nm in (b) and $\lambda \sim 6.5$ nm in (c), respectively. Although normal Pb free Bi-2212 is all covered with modulated structure as seen in Fig. 1(a), highly Pb-doped Bi-2212 system has two phase structure; α-phase with modulation longer than Pb free Bi22212 and β-phase without modulation seen at the right bottom side of Fig. 1(c). The large-scale STM images of α- and β-phase structure were previously reported [6].

In Fig. 1(A), $\Delta$ map forms slightly modulated structure along the supermodulation direction embedded in the randomly inhomogeneous gap distribution. The inset of two-dimensional (2D) Fourier power spectrum in Fig. 1(A) shows the same direction and periodic length ($\lambda = 2$–$3$ nm) of topographic modulation (indicated by arrows). These streaky structures were formed as slightly enlargement of $\Delta$ the position of defects in the crest of modulation in topographic image. It is speculated that excess oxygen at BiO sheet might reduce the superconductivity, if we assume the invisible excess oxygen was in the defects. On the other hand, the distributions of $\Delta$ in Pb–Bi-2212 ($x = 0.6$, 0.8) (Fig. 1(B) and (C)) are exactly not similar to the modulation structure, but have some

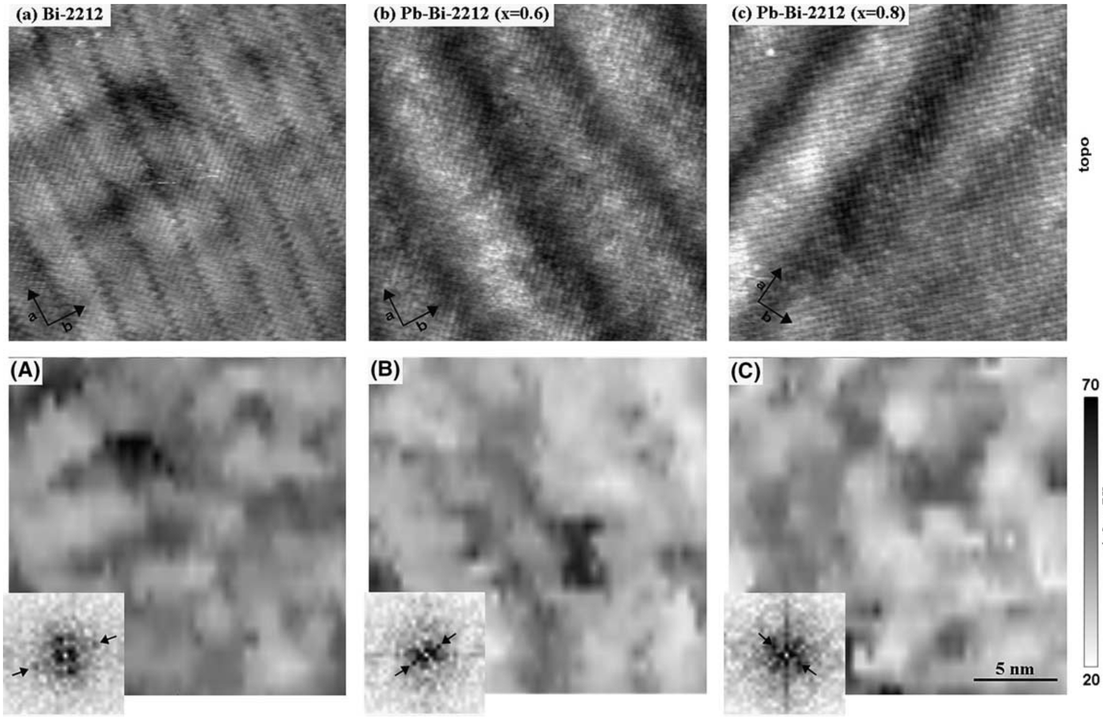


Fig. 1. STM topographies and gap ($\Delta$) maps taken at various types of Pb–Bi-2212 surface in 20 nm × 20 nm area: (a) Pb free Bi-2212 (optimum doped) STM topography and (A) $\Delta$ map with the same area as (a) (average of $\Delta_{AV} = 41.8$ meV, standard deviation $\sigma = 6.6$ meV); (b) Pb–Bi-2212 ($x = 0.6$, over doped) topography and (B) $\Delta$ map ($\Delta_{AV} = 34.3$ meV, $\sigma = 7.1$ meV); (c) Pb–Bi-2212 ($x = 0.8$, over doped) topography and (C) $\Delta$ map ($\Delta_{AV} = 34.8$ meV, $\sigma = 7.5$ meV). Insets in (A)–(C) are 2D Fourier power spectrum of each $\Delta$ maps.

effects of modulation structure from the viewpoint of direction of modulation and periodic length, as shown in the arrows in the inset of 2D Fourier power spectrums in each $\Delta$ maps. It was not exactly, however, the gap $\Delta$ tend to be narrower at halfway of the slope of the modulation. Furthermore, at β-phase (at right bottom side of Fig. 1(c)), the amplitude of $\Delta$ is slightly narrower than α-phase. This tendency is consistent with the result of enlargement of $\Delta$ at the crest of modulation in topography as mentioned above. At the position of halfway of the supermodulation, $CuO_2$ sheet might be fewer distorted as compared with the position of crest or valley of supermodulation structure, and slightly easier to form the superconducting phase. Anyway, the superconductivity was restrained by topographic supermodulation subdominantly. It is considered that there are any other dominant origins of this superconducting inhomogeneity.

We have obtained completely modulation free Pb–Bi-2212 single crystals by reduced annealing and quenching. It is considered that the modulation free structure reduces one of order and to give us a true nature of electric state of superconductivity. Fig. 2(a) shows the topographic image of modulation free Pb–Bi-2212 single crystal with atomic resolution and was conformed that there is no modulation structure within $160 \times 160\ \mathrm{nm}^2$ field of view by STM observation. Fig. 2(b) and (c) shows the diffraction patterns of transmission electron microscope (TEM) on quenched Pb–Bi-2212 ($x = 0.6$, OP) and as-grown Pb–Bi-2212 ($x = 0.6$, OD) single crystals taken along the [0 0 1] direction, respectively. The satellite spots corresponding to the modulation structure are clearly seen

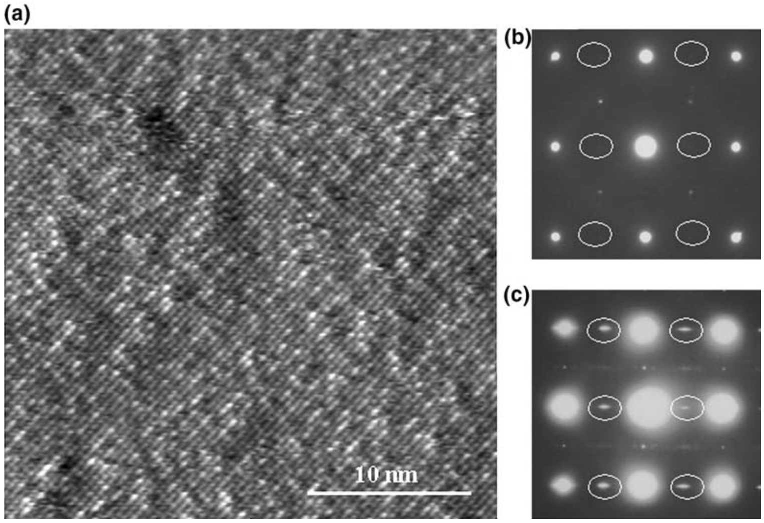


Fig. 2. (a) STM topography on modulation free Pb–Bi-2212 ($x = 0.6$). ($I_t = 0.1$ nA, $V_{bias} = 0.07$ V, 30 nm × 30 nm area). (b) Diffraction pattern of TEM on modulation free Pb–Bi-2212. (c) Diffraction pattern of TEM on as-grown Pb–Bi-2212. The satellite spot positions corresponding to the modulations are marked by circles.

in as-grown samples in Fig. 2(c), however, no satellite spot can be seen in Fig. 2(b), showing completely no modulation structure in reduced annealed and quenched Pb–Bi-2212.

Fig. 3 shows the (a) STM topographic image of modulation free Pb–Bi-2212 and (b) gap ($\Delta$) distribution in the same area. The topographic image shows no modulation structure, but has weak contrast due to electric inhomogeneity, and $\Delta$ map show the inhomogeneous structures very clearly, even though the modulation free superconductor. Although the order of the direction of Cu–O (Bi–O) bond was slightly present, the periodic structure along the *b* (*a*)-axis direction was not seen. These results show again that supermodulation is not dominant origin of inhomogeneous superconductivity.

Compared with OD samples, spatial variation of $\Delta$ in OP sample tends to change suddenly and more distinguishable between the superconducting (SC) region (with narrower $\Delta$ and high coherent peak in conductance spectrum; brighter area in Fig. 3(b)) and low temperature pseudogap (LTPG) region (with broader $\Delta$ and low peak; darker area in Fig. 3(b)). To clarify the continuity (or discontinuity) of spatial transition of LTPG to SC states, spatial changing of spectra from LTPG region to SC region was examined. Fig. 3(c) shows the conductance spectra along the point A–G in Fig. 3(b) with the interval of 0.24 nm. The spectra of A–C show typical LTPG state with large and broad peak of $\Delta$, however, the small sub-states were also exist within broad gap peak (indicated by arrows). The sub-gap like structures were also seen at outside of coherent superconducting gaps in SC region nearly beside the LTPG region (spectrum D and E, indicated by arrows). The inner energy state within LTPG gap were corresponding to superconducting gap in SC region, these gaps were overlapped around the border of two regions. This implies that LTPG gap is not connect to SC gap smoothly but discretely, and the LTPG and SC states could be exist simultaneously around the border of these two state.

On the other hand, the continuous changing from narrow $\Delta$ to large $\Delta$ was also observable in the same sample and other OD samples. It may due to spatial resolution of sampling or due to tip condition, however, from our experiment, these two gap structures in the vicinity of the border frequently tend to be seen in optimum doped samples. This tendency is consistent with the

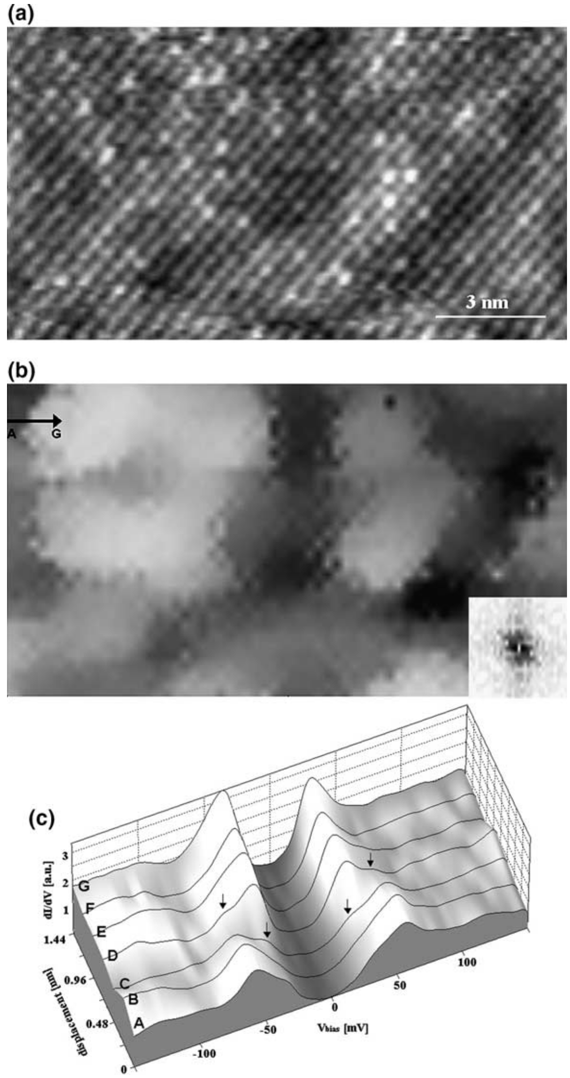


Fig. 3. (a) The STM topography and (b) $\Delta$ maps on modulation free Pb–Bi-2212 ($x = 0.6$) with 0.24 nm spatial resolution ($\Delta_{AV} = 43.9$ meV, $\sigma = 9.6$ meV). The gradation scale of $\Delta$ is same as Fig. 1. Insets in $\Delta$ map are 2D Fourier power spectrum of this $\Delta$ map. (c) The 3D view of conductance spectra from the position of A–G in (b).

"granular" superconductivity in underdoped Bi-2212 [2] and coexistence of pseudogap and superconducting gap [11]. The two types of electric phases (SC and LTPG state) become more separately not simply reduction of SC region size or broaden of $\Delta$ as decreasing the doping level, indicating that the inhomogeneous structure was not simply formed due to the local doping level, but has some other mechanism may also be happen in the nanoscale inhomogeneous superconductor.

## 4. Summary

The low temperature STM/S observation was performed on Pb–Bi-2212 including completely non-modulated single crystals to clarify the effect of the modulation structure to the electronic states of superconductivity. The $\Delta$ distributions of modulated Pb–Bi-2212 show exactly not similar to the modulation structure, but have some periodic order corresponding to modulation. The inhomogeneous $\Delta$ distribution was also observed on completely supermodulation free optimal doped Pb–Bi-2212. The conductance spectra in the vicinity of the border of SC and LTPG show two gap structures. These results suggest that the modulation structure is not the dominant origin of inhomogeneity although it modifies the patch size sub-dominantly. The spatial $\Delta$ variations tend to become more separately as decreasing the doping level.

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