Unoccupied electronic states of the high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$ investigated by two-photon photoemission spectroscopy

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Two-photon photoemission spectroscopy (2PPES) has been applied to an optimally doped high-temperature superconductor (HTSC) $Bi_2Sr_2CaCu_2O_8$(Bi2212). 2PPES with photon energy between 4.0 and 4.9 eV revealed four structures, labeled as *A* to *D*, arising from unoccupied states at <0.5, 1.8, 2.7, and 3.7 eV above the Fermi level (E_F), respectively. Structures *A* and *B* show no strong polarization dependence, whereas structures *C* and *D* appear in *p*-polarization configuration and completely disappear in *s*-polarization. The polarization dependence indicates that the unoccupied states for structures *A* and *B* are composed of orbitals parallel to the CuO_2 plane. The unoccupied states for structures *C* and *D* are composed of atomic orbitals perpendicular to the CuO_2 plane. Unoccupied states for structures *A* and *B* are attributed to the unoccupied band of carrier and the upper Hubbard band, respectively.

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I. INTRODUCTION

The electronic structures of high-temperature superconductors (HTSCs) have been extensively studied by various spectroscopic methods. Especially, occupied states just below E_F are measured with angle-resolved photoemission spectroscopy (ARPES) of energy resolution as high as meV.[1] On the other hand, the methods to probe the unoccupied states are not comparable to ARPES in the energy resolution. Since unoccupied states play key roles in carrier transportation, optical properties, and so forth, a high-resolution spectroscopy of the unoccupied states is important. Here we have applied two-photon photoemission spectroscopy (2PPES) to probe the unoccupied electronic states. Though the energy resolution of 2PPES is limited by a bandwidth of a short-pulse laser light, it is substantially higher than those of the inverse photoemission spectroscopy (IPES)[2–7] or x-ray absorption spectroscopy (XAS).[8–11]

In 2PPES, the first photon excites an electron from an initial occupied state to an intermediate unoccupied state, and the second photon stimulates photoemission from the intermediate state.[12] In 2PPES with photon energy of $h\nu$, two processes compete giving photoemission peaks at $E_i+2\,h\nu$ (2 $h\nu$ process) and at $E_m+h\nu$ (1 $h\nu$ process), where E_i and E_m are the energies of occupied and unoccupied states, respectively. The 2 $h\nu$ process is due to direct two-photon excitation from the initial occupied state to a free electron final state above the vacuum level via virtual intermediate states, and the 1 $h\nu$ process is due to one-photon photoemission from the unoccupied state populated by dephasing or relaxation of photoexcited electrons. When the photon energy is varied, these peak energies move twice or once of the photon energy increment, giving the energies of the initial state and the intermediate state. An advantage of 2PPES over optical methods[13–19] or electron energy loss spectroscopy[8,20] is that the energies are obtained with respect to E_F. The method has been successfully applied to the image-potential states on metal surfaces,[12,21–23] semiconductors,[24–26] and adsorbed molecules.[27–31] However, few 2PPES works have been performed on HTSCs.[32,33] Here we report 2PPES for optimally doped $Bi_2Sr_2CaCu_2O_8$(Bi2212) to reveal unoccupied electronic states. Preliminary results have been reported in our previous paper.[32] We chose the optimally doped Bi2212 as the sample, because it is a typical material of HTSC and high quality single crystal is available.

II. EXPERIMENT

The apparatus consists of a titanium sapphire (Ti:Sa) laser system and an ultrahigh vacuum (UHV) photoelectron spectrometer. We used two Ti:Sa lasers, Mai-Tai (Spectra Physics) and Mira 900F (Coherent). The pulse durations were 80 and 100−120 fs for the former and the latter lasers, respectively. The output of the Ti:Sa laser was frequency tripled into a photon energy range from 4.0 to 4.9 eV. The power was typically regulated to $\leqslant 0.1$ nJ/pulse by using a neutral density filter. The light was focused with a quartz lens of 350 mm focal length on a sample surface in the UHV chamber at an angle of 60° from the surface normal. The photoelectrons emitted to the surface normal were measured with a hemispherical energy analyzer (VG, CLAM 2). Overall resolution including the bandwidth of the laser light and the resolution of the analyzer was better than 30 meV as measured from the E_F feature of a copper sample cooled to 30 K. An optimally doped single-crystal of Bi2212 ($T_c \sim 90$ K) was cleaved by Scotch tape under a vacuum of 3×10^{-8} Pa at room temperature (RT). The *c* axis of Bi2212 is parallel to the surface normal. Azimuth angle of the crystal was not specified. All the experiment was performed at RT.

III. RESULTS AND DISCUSSIONS

A. Unoccupied states and their symmetries

2PPES results for a sample (labeled as sample 1) at RT measured with *p*-polarized light of different photon energies are shown in Fig. 1. The sample was biased by −1.0 V from the chamber ground. The horizontal axis is the intermediate

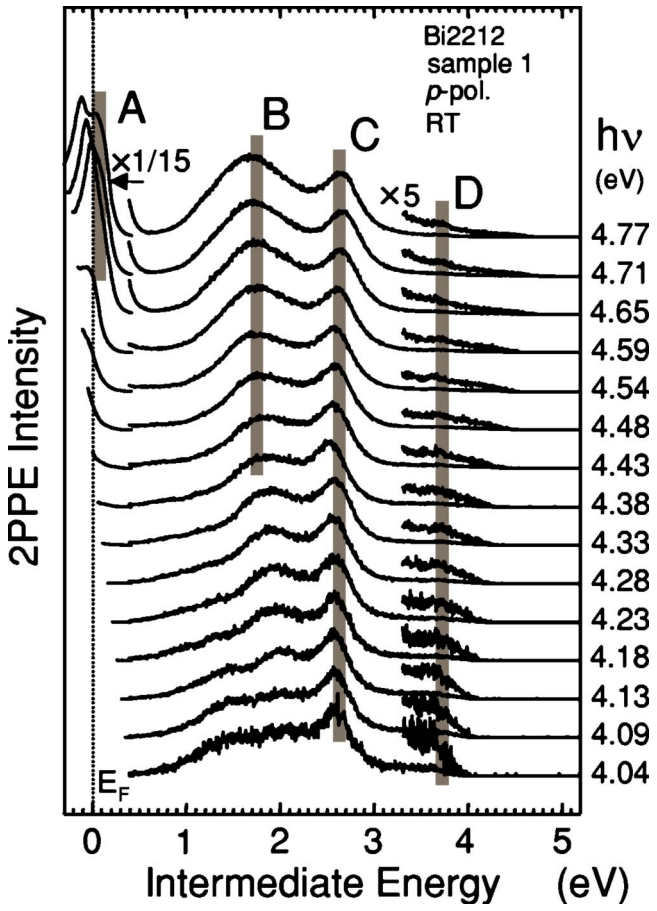

FIG. 1. Normal emission 2PPES results for Bi2212 measured at room temperature with *p*-polarized light of the photon energies shown at the right-hand side. The sample is labeled as "sample 1." Four structures denoted as *A* to *D* arise from respective unoccupied states. The intensity of each spectrum is normalized to structure *C*. Part of the spectra around structure *D* is magnified by 5 times. Spectra around structure *A* are demagnified by factor 15.

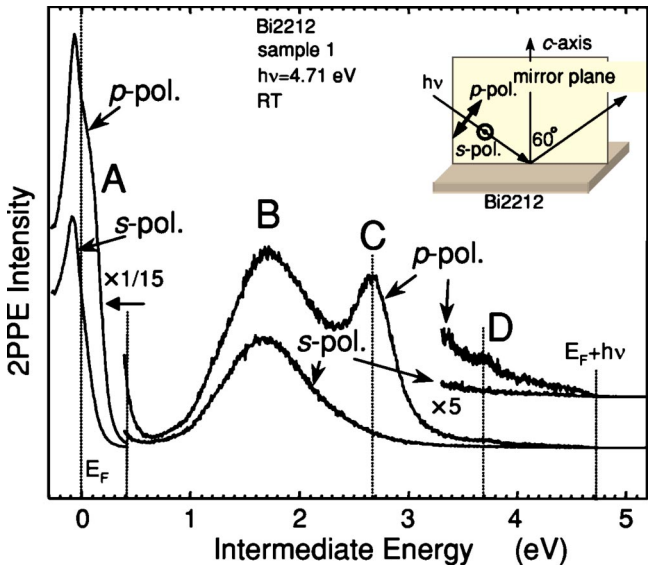

FIG. 2. Polarization dependence of 2PPES measured at the photon energy of 4.71 eV. Structures *C* and *D* disappear in *s*-polarization configuration, and structures *A* and *B* are observed both in *p*- and *s*-polarization configurations. A part of the spectrum around structure *D* is expanded by 5 times, and spectra around structure *A* are demagnified by factor 15. The inset shows the directions of the light electric vector for *p*- and *s*-polarization configurations.

energy $E_e - h\nu$, where E_e is the energy of photoelectrons with respect to E_F. Structures *A* to *D* are denoted by vertical lines. The vertical alignments of the peak positions indicate that the structures are due to the 1 $h\nu$ process. The energies of the unoccupied states are <0.5, 1.8, 2.7, and 3.7 eV for structures *A* to *D*, respectively.

The polarization dependence at photon energy of 4.71 eV is shown in Fig. 2. Structures *A* and *B* show no strong polarization dependence. Meanwhile, structures *C* and *D* are clear in *p*-polarization, and completely disappear in *s*-polarization. The polarization dependence was similar to that in Fig. 2 for all the photon energies shown in Fig. 1. The polarization dependence reveals the symmetry of the unoccupied states. Here, only photoemission processes from intermediate states are taken into account, since the intermediate states for the 1 $h\nu$ process are populated after elastic or inelastic scatterings. Assuming plane waves for photoelectrons, the final state of photoemission process has even parity under reflection with respect to the mirror plane defined by the incident light and the surface normal.[34] The disappearance of structures *C* and *D* with the odd-symmetric *s*-polarized light indicates that the unoccupied states for structures *C* and *D* are even-symmetric with respect to the mirror plane. The symmetries of unoccupied states for structures *A* and *B* are not purely even or odd. Taking account of the layered structure of Bi2212, structures *A* and *B* arise from orbitals parallel to the CuO_2 plane, and structures *C* and *D* from orbitals perpendicular to the CuO_2 plane.

B. Structures *A* and *B*

Structure *A* appeared at photon energy higher than 4.4 eV, which is close to the work function. The structure was partly overlapped with a structure at an energy region below E_F. We label as *A* only the structure above E_F. The peak below E_F is due to one-photon photoemission from occupied states. The dip at E_F in the spectrum at the photon energy of 4.77 eV shown in Fig. 1 is the indication that one-photon and two-photon photoemission components are separately observed. In order to further confirm that structure *A* is due to two-photon photoemission from an unoccupied state just above E_F, a time-resolved experiment was performed at the photon energy of 4.43 eV as shown in Fig. 3. The laser light was divided into two beams (pump and probe pulses) and introduced onto the surface with a skewed configuration.[21,31] The photoemission intensity at the intermediate energy of 0.3 eV was measured as a function of the optical delay time (Δt). The fast decay at $\Delta t < 200$ fs is close to the autocorrelation of the laser pulse, indicating that the unoccupied state is populated by a direct photoexcitation. The slowly decaying component visible at $\Delta t > 200$ fs arises from electron dynamics at the unoccupied state. The shoulder around 300 fs

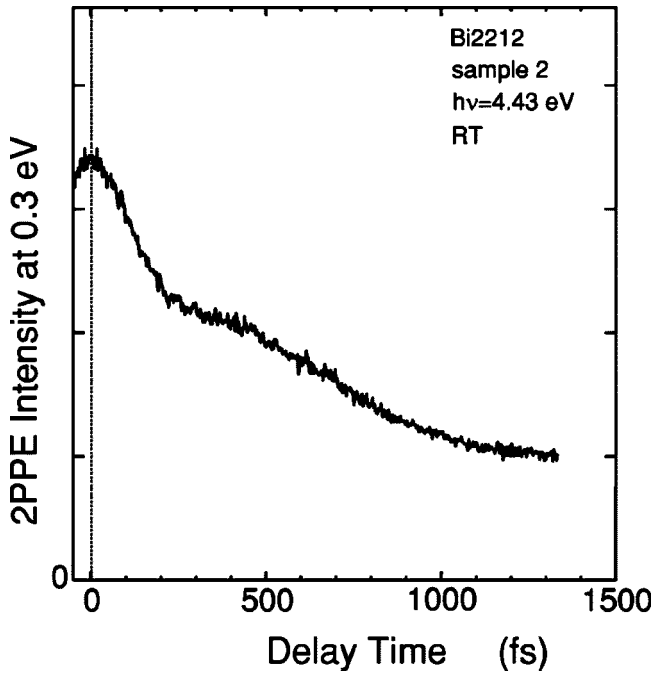

FIG. 3. Photoemission intensity at the intermediate energy of 0.3 eV is plotted against the pump-probe delay time (Δt). The fast decay at $\Delta t < 200$ fs and the slow decay with the shoulder at $\Delta t = 300$ fs indicate that the unoccupied state was populated by both direct photoexcitation and the cascade. The ratio of intensities at $\Delta t = 0$ and >1000 fs was 3.4, indicating that contribution of one-photon photoemission from occupied states is small.

indicates that the unoccupied state is also populated by cascade from upper states. The lifetime of electron decay process was several hundred fs. The ratio of intensities at $\Delta t = 0$ and >1000 fs was about 3.4, which is larger than the ideal value of 3.0.[21,31] The large ratio indicates that the contribution of one-photon photoemission from thermally excited occupied states is very small, and suggests a contribution of nonequilibrium-electron heating by the pump light.[35]

The intensities of structures *A* and *B* were found to increase as the sample bias voltage became higher negative voltage, indicating that the low-energy photoelectrons emitted at large emission angles were collected by the bias voltage. Thus the structures are due to angle-integrated photoemission. The 2PPES results can be compared with the optical conductivity spectroscopy for HTSCs and their parent insulators.[13–16] Optical conductivity below 1 eV for Bi system arises from mobile carriers and the weight at 1.5–2.5 eV arises from the charge transfer (CT) excitation.[13,14] The spectral features of the carrier and CT excitations resemble structures *A* and *B* in their peak energies and widths. Thus, the unoccupied state for structure *A*, just above E_F, is attributed to the unoccupied band of mobile carriers and structure *B* is related to the Cu 3*d* upper Hubbard band (UHB). Since the carrier band and the UHB are parallel to the CuO_2 plane,[34,36] these assignments are consistent with the polarization dependence. The UHB feature in 2PPES is clear even for the optimally doped Bi2212, while the CT excitation in optical conductivity is strongly suppressed.[13,14] The suppression of the CT excitation has been discussed to be due to the degree of the local spin order which rapidly decreases with doping.[37,38] On the other hand, 2PPES simply reflects the density of the unoccupied states. The deep valley between structures *A* and *B* is attributed to the CT gap. The gap energy larger than 1 eV is in agreement with the optical conductivity for the single crystalline Bi system.[13] The valley feature of 2PPES has not been observed in IPES in which unoccupied states due to Cu 3*d*-O 2*p* and Bi 6*p*-O 2*p* hybrids were observed at the energy region.[6] It seems as if an unresolved selectivity is working in the pumping process.

C. Structures *C* and *D*

Structures *C* and *D* were not dependent on the bias voltage. The energy of structure *C*, 2.7 eV, is close to the IPES structure at 2.9 eV.[3–5] The IPES structure was attributed to a component of the UHB or the Bi 6*p* derived state. The unoccupied state for structure *C* cannot be the UHB because of the symmetry. An out-of-plane unoccupied state involving Cu $3d_{3z^2-r^2}$ is known for $La_{2-x}Sr_xCuO_4$.[8,39,40] The width of structure *C*, which is as sharp as 0.3 eV, implies a relation with the theoretical Cu $3d_{3z^2-r^2}$+O $2p_z$ unoccupied state.[39,40] But, the energy of structure *C* is too high to be compared with the state that is at several hundred meV above E_F. Unoccupied states derived from Bi $6p_z$ (Ref. 41) or from a hybrid state between Cu $3d_{3z^2-r^2}$ and Cu 4*s* (Ref. 42) may contribute to structure *C*. In *p*-polarized Cu-L_3 XAS, a step-like structure at about 3–5 eV above the absorption edge was attributed to the unoccupied Cu $3d_{3z^2-r^2}$.[11] The relation between our structure *C* and the XAS result is not clear because the shape and width are different.

Expanded view of 2PPES results measured for "sample 2" are shown in Fig. 4. The intensity of each spectrum is normalized to structure *C*. The sample bias voltage was changed to −0.5 V to reduce the background due to structure *B*. In Fig. 4 where the spectra are plotted against the intermediate energy, the peak positions of structure *C* are not aligned on a single vertical line, but are aligned on two lines with separation of 0.2 eV; at an intermediate energy of 2.6 eV for $h\nu$ smaller than 4.23 eV and at 2.8 eV for $h\nu$ larger than 4.54 eV. The deviation from the alignment on a single vertical line is not due to dispersion of the relevant states, because strong dispersion in the normal direction is not probable for the layered material. Otherwise, the unoccupied state for structure *C* is considered to be composed of two subcomponents. Similarly, energies of structure *D* are aligned on two lines with separation of 0.2 eV.

The fine features of structures *C* and *D* were found to be slightly dependent on samples. The energies of them measured for different samples are plotted in Fig. 5 against the photon energy. The energy separations of the subcomponents are 0.2 eV for samples 2, 4, and 5. The separation was smaller for samples 1 and 3, for which the structures were weak. We assume that the clearer features for samples 2, 4, and 5 reflect the intrinsic property. Structure *C* is aligned on a line of slope 2 within the photon energy region between 4.23 and 4.54 eV. This suggests that the structure at the photon energy region is due to the 2 $h\nu$ process from an initial state of −1.6 eV, which is close to the O 2*p* state at −1.5 eV

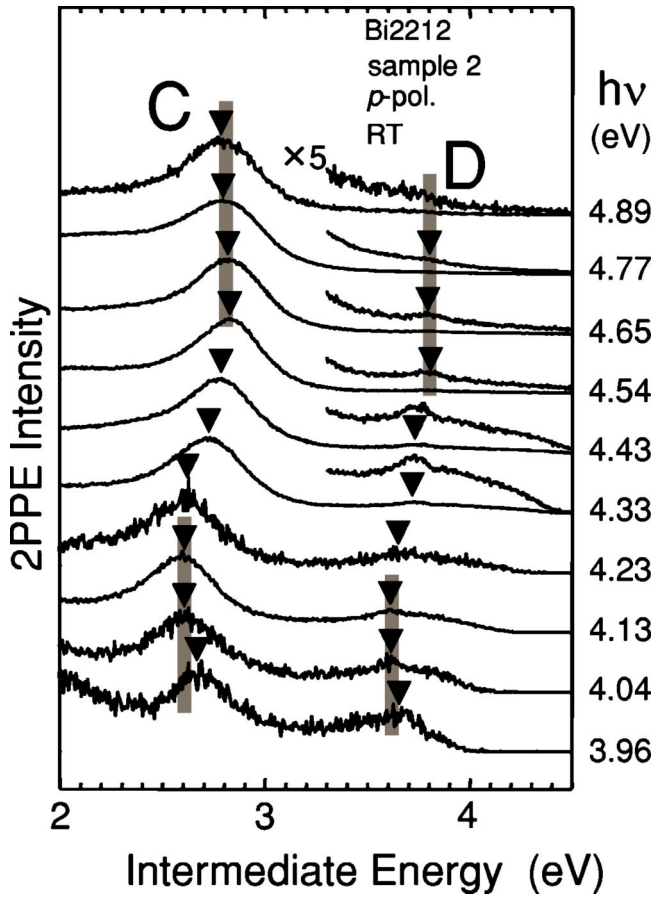

FIG. 4. Expanded 2PPES of "sample 2" measured at room temperature plotted against the intermediate energy. Structure *C* is composed of two intermediate states at 2.6 and 2.8 eV with energy separation of 0.2 eV. Spectra around structure *D* are magnified by factor 5. Structure *D* also shows two subcomponents. The different signal-to-noise ratios of the traces are due to different accumulation times.

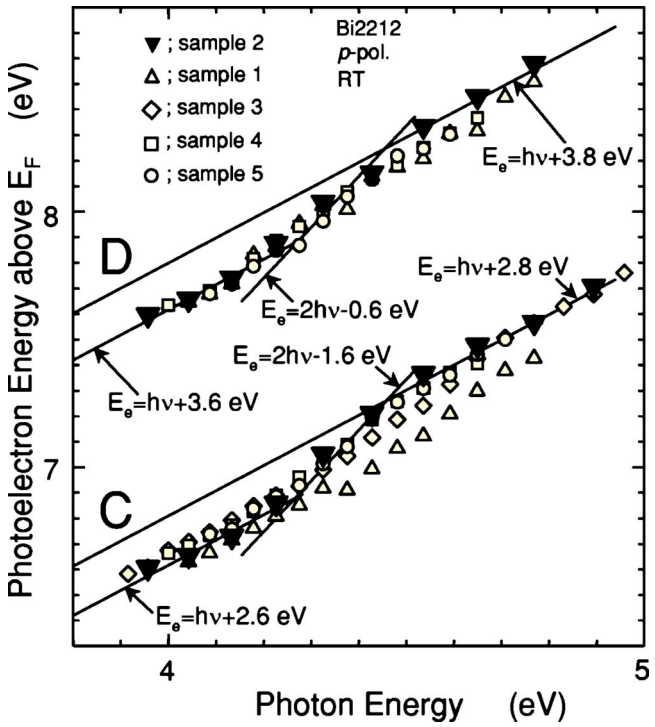

FIG. 5. Final energies of structures *C* and *D* are plotted against the photon energy. The closed triangles measured for sample 2 correspond to those in Fig. 4. Experimental points for other samples are shown with open symbols. The lines with slopes of 1 and 2 fitted to the data sets of samples 2, 4, and 5 are also shown. The slope 2 line for structure *C* indicates that the initial state is at −1.6 eV.

observed in ARPES works.[43–45] Since the unoccupied state of even-parity (structure *C*) was not excited with *s*-polarized light, the initial state is symmetric with respect to the mirror plane. Thus O $2p_z$ orbital may be relevant to the initial state of structure *C*.

Though the origin of the subcomponents for structure *C* is not clear, the energy separation is similar to the spin-flip energy of 0.2 eV observed in a resonance Raman scattering work[46] on $Sr_2CuO_2Cl_2$. No spectroscopic feature comparable to structure *D* has been reported. The similarities on subcomponents and on the polarization dependence suggest that the origin of structure *D* is strongly correlated with structure *C*.

IV. CONCLUSIONS

We have successfully observed the in-plane and the out-of-plane unoccupied states by means of 2PPES. The energy resolution that is higher than IPES or XAS is advantageous to reveal unknown unoccupied states. Though the origins of structures *C* and *D* are not clear at the present stage, the unoccupied states might be a clue to resolve the long discussed[8,47] role of apical oxygen and the out-of-plane electronic structure to the superconductivity. The present results show the importance of further experiments on temperature dependence, doped-hole dependence and on time-resolved electron dynamics.

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