Surface structures and energy gap of $\text{YBa}_2\text{Cu}_3\text{O}_y/\text{PrBa}_2\text{Cu}_3\text{O}_y$ superlattices and $\text{YBa}_2\text{Cu}_3\text{O}_y$ thin films probed with a scanning tunneling microscope and a scanning force microscope

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Abstract

We report here the results of investigations using a scanning tunneling microscope (STM) and a scanning force microscope (SFM) on $\text{YBa}_2\text{Cu}_3\text{O}_y/\text{PrBa}_2\text{Cu}_3\text{O}_y$ (YBCO/PrBCO) superlattices and YBCO thin films. STM and SFM measurements were performed in air at 295 K while the tunneling spectroscopy was carried out in vacuum ($< 10^{-3}$ Torr) at 4.3 K. STM images were observed to exhibit the atomic structure of $[(\text{YBCO})_n/(\text{PrBCO})_m]_l$ superlattices where the subscripts n and m refer to the numbers of unit cells of the individual YBCO or PrBCO layers respectively and l is the number of repetitions of the $(\text{YBCO})_n/(\text{PrBCO})_m$ cell. The STM images of a $[(\text{YBCO})_1/(\text{PrBCO})_1]_{40}$ superlattice show atoms aligned with a lattice parameter of 3.81 Å along the crystal a -axis and 3.89 Å along the crystal b -axis. SFM images show a periodic variation on the YBCO surface. In the tunneling spectra, the current–voltage characteristics at 4.3 K show Coulomb staircases. The tunneling conductance at 4.3 K reveals conductance peaks at $2\Delta = 3.5, 17.0; 23.5$ and 41 meV and the curve dI/dV versus V has a zero bias conductance. The tunneling spectra of YBCO thin films showed semiconducting or superconducting behaviors depending on the tip–sample distance.

1. Introduction

Scanning tunneling microscopy (STM) has been successfully used in recent years to measure the basic properties, such as the energy gap, surface topography, surface adhesion and deformation [1] of high- T_c superconductors, particularly within a short coherence length and with inhomogeneity of the surface [2]. The properties of $\text{YBa}_2\text{Cu}_3\text{O}_y/$

$\text{PrBa}_2\text{Cu}_3\text{O}_y$ (YBCO/PrBCO) superlattices that are studied include the superconducting transition temperature [3] and the growth mechanisms [4]. The YBCO layer, as thin as only one unit cell, maintains a transition temperature of about 19 K, whereas the PrBCO layer is required to be 10–15 times thicker [5] maintaining a low T_c . Experimental measurements on ultrathin YBCO films with a thickness of one or two unit cells revealed no superconductivity [6]. This result is attributed to the existence of large distortions in the lattice structure of YBCO film near the free surface and at the interface between the substrate and the film. Further, the YBCO surface

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has been observed to be unstable at 300 K in ultra-high vacuum (UHV) [5]. List et al. [7] have used low-temperature photoemission experiments to show a loss of chain oxygen at the cleaved $\text{EuBa}_2\text{Cu}_3\text{O}_{7-y}$ surface when the sample is warmed above 80 K. Measurements on YBCO single crystals have indicated that the crystals must be cleaved below 40 K to retain surface oxygen. A recent report on the atomic image of a cold cleaved single crystal of YBCO indicates that CuO chains disappear when the sample is warmed to 70 K [2].

Several STM and scanning force microscopy (SFM) measurements on YBCO oxides have been reported in the literature [8–12]. However, only a few have been able to achieve reproducible atomic resolution [2] at a low temperature whereas reproducible atomic resolution has not been achieved so far at room temperature. We report here atomic images of a $[(\text{YBCO})_n/(\text{PrBCO})_m]_l$ superlattice using STM and atomic disorder in the SFM images for a YBCO thin film at $T = 300$ K. The subscripts n and m refer to the numbers of unit cells of the individual YBCO or PrBCO layers respectively and l is the number of repetitions of the $(\text{YBCO})_n/(\text{PrBCO})_m$ cell. The surface features between $[(\text{YBCO})_n/(\text{PrBCO})_m]_l$ superlattice and YBCO thin film have been observed to differ in air at room temperature. Tunneling spectra show Coulomb staircases when the distance between sample to the tip is varied. The superconducting gap 2Δ about 40 meV was obtained by analyzing the results assuming a simple BCS-like density of states of quasi-particle excitations. The conductance peaks were smaller or equal to the BCS value $3.52k_B T_c$. These peaks are important for discussing the stability of YBCO thin film with an unstable nature of CuO chains on the cleaved surface. The atomic resolution in STM and SFM images and tunneling spectra offers insight in the surface properties of high- T_c thin films.

2. Experimental

Thin films of YBCO/PrBCO superlattices were grown in an off-axis RF magnetron sputtering system [13] using YBCO and PrBCO targets which were mounted face to face in the vacuum chamber. Details of the growth of superlattices will be de-

scribed elsewhere. The YBCO thin films grown by a laser-ablation technique have $T_c = 90$ K. Except for the $(\text{YBCO}_1/\text{PrBCO}_1)_{40}$ sample which showed a weak satellite peak, the X-ray diffraction patterns of all other samples revealed a clear structure of superlattices. STM and SFM images were recorded in air at 295 K while the tunneling spectroscopic measurement was carried out in vacuum ($< 10^{-3}$ Torr) at 4.3 K. All STM images were recorded using a chemically etched W-tip operated in a constant tunneling current mode with various scan rates. A positive bias voltage was applied to the sample and was varied from 100 to 150 mV. The SFM images were recorded using a commercially available microfabricated Si-on-SiN cantilever with a constant force mode and varied scan rates. Typically forces ranged from 30 to 100 nN. Chemically etched tungsten wire was used to record the tunneling spectra (STS) in a vacuum tunneling mode at liquid-helium temperature.

3. Results and discussion

Fig. 1(a) shows an atomic image of a fresh $(\text{YBCO}_1/\text{PrBCO}_1)_{40}$ (sample a) superlattice directly grown on a SrTiO_3 (001) substrate with $T_c = 80$ K, where T_c is the critical temperature. The top layer of the superlattice is a YBCO layer. The features of the images vary neither in shape nor orientation with the scanning frequency and are reproducible on subsequent images. The depth profile along a line is shown in Fig. 1(b). Atoms 1 and 2 can be observed to align in parallel lines with a lattice parameter of 3.81 Å along the crystal a -axis and 3.89 Å along the crystal b -axis within experimental errors. The STM scanner was calibrated with graphite. This is for the first time that atomic features of a YBCO/PrBCO superlattice have been observed at 295 K. The sample “a” did not show clear satellite peaks in the powder X-ray diffraction pattern, but the sample was epitaxial and showed preferred orientation along the crystal c -axis; we believed that the said atomic images correspond to a region in which the sample retains its local crystal structure and c -axis periodicity.

For one unit cell of a c -axis oriented YBCO cell, the lattice structure consists of layers of CuO–BaO–

Fig. 1. (a) STM image of a $(\text{YBCO}_1/\text{PrBCO}_1)_{40}$ superlattice at $T = 300$ K. The image was taken in a constant-height mode with $V_t = 0.285$ V and $I_t = 7.38$ nA. The scanned area was 3×3 nm². A depth profile along the marked line is shown in (b). The arrows mark the position of atoms a and b. The distance between atoms a and b is ~ 3.81 Å. A depth profile along the marked line (b) is shown and the distance between atoms 1 and 2 is ~ 3.89 Å.

$\text{CuO}_2\text{--Y--CuO}_2\text{--BaO--CuO}$. If cleavage occurs in a YBCO single crystal, for instance, between BaO and CuO_2 , there will be regions in which CuO--BaO layer peels away to reveal the top CuO_2 plane. Similarly, if the cleavage occurs between BaO and CuO, there will be regions of CuO chain-terminated surface. It was shown by Edwards et al. [2], that atomic STM images exhibiting parallel chains in cleaved YBCO single crystal, similar to the ones presented here are likely to be due to the CuO chains which exhibit a rather pronounced metallic behavior compared to the other planes. Therefore, the observed atomic STM images are likely to be due to the CuO chains. On the other hand, Rajagopal et al. [3] have used an interlayer-coupling model to demonstrate how the interlayer or intralayer coupling strength can depend on the nature of growth of unit cells on different substrates. The results indicate that if the growth of YBCO layers initiate on the SrO layer of SrTiO_3 , one might obtain a stacking of the type $\text{SrO--CuO}_2\text{--Y--CuO}_2\text{--BaO--CuO--...}$. Their arguments also suggested that if the growth of YBCO layers initiate on the TiO_2 layer of SrTiO_3 , the arrangement is $\text{TiO}_2\text{--BaO--CuO--BaO--CuO}_2\text{--Y--...}$. Thus it implies that Y or Ba atoms may be present on the $(\text{YBCO}_1/\text{PrBCO}_1)_{40}$ surface. However, from the conduction point of view, the BaO or Y plane is less conductive compared to the CuO_2 planes and hence is less likely to appear on surface whereas the presence of CuO_2 planes on the $(\text{YBCO}_1/\text{PrBCO}_1)_{40}$ surface is possible due to the metallic and conductive nature of the CuO_2 planes. Our present observations therefore suggest that the presence of the CuO_2 planes or the CuO chains on the $(\text{YBCO}_1/\text{PrBCO}_1)_{40}$ surface are equally likely.

The fresh $[(\text{YBCO})_3/(\text{PrBCO})_5]_{16}$ surface features as shown in Fig. 2, are reproducible in overlapping scans and are independent of the scanning frequency confirming that they are real. They do not consist of a simple atomic image with atoms in the structure being under some disorder "pollution". From the image of the $[(\text{YBCO})_3/(\text{PrBCO})_5]_{16}$ superlattice, it is difficult to identify the nature of the disorder pollution. However, it is certain from the images that atomic resolution of the superlattice surface exists within a small area. This conclusion is consistent with our observation of clear atomic images as shown in Fig. 1. If the surface of the

Fig. 2. STM image of a $[(\text{PrBCO})_3/(\text{YBCO})_5]_{16}$ superlattice with $V_t = 0.263$ V and $I_t = 4.88$ A. The scanned area was 6.2×6.2 nm². The surface shows atomic images and the polluted surface.

$[(\text{YBCO})_3/(\text{PrBCO})_5]_{16}$ superlattice arises from the cleavage plane between BaO and CuO layers, then the surface of the sample reveals CuO chains. Removing or adding an oxygen atom, or shifting its coordination with the copper atom in the chain alters the electronic properties of the high- T_c superconductor [14,15]. This situation may cause disorder “pollution” as shown in Fig. 2.

Fig. 3 shows the SFM surface morphology of a YBCO thin film on SrTiO_3 (110), confirmed by successive scans and is found to be independent of the scanning frequency. Fig. 3(a) reveals a periodic image of a YBCO thin film. The image obtained by SFM at 295 K still shows the atomic corrugations. An SFM image along a cross-section line appears in Fig. 3(b). We observed defects consisting of oxygen-deficient sites along the axis. The distance between the peaks is ~ 4 to 5 Å. These SFM features of a YBCO thin film measured at 295 K in air are consistent with the previous observations and experimental results [2,16,7], viz. for instance the oxygen-deficient surface, surface disorder and the disappearance of the Cu–O chain.

Fig. 4(a) shows the tunneling spectra of YBCO film on MgO (001) substrates at $T = 4.3$ K. It is

characterized by the existence of “multi-gap” structures with gap values $2\Delta_1 = 3.5$ meV, $2\Delta_2 = 17.0$ meV, $2\Delta_3 = 23.5$ meV and $2\Delta_4 = 41$ meV. The dI/dV versus V curve was reproducible at the specified tunneling voltage and current. The largest observed gap $2\Delta_4 = 41$ meV presumably has a contribution from the CuO_2 plane, the smallest observed gap $2\Delta_1 = 3.5$ meV has a contribution from the CuO_2 chains whereas the “inner gaps” have a contribution from the anisotropy in the order parameter caused by surface roughness. The surface roughness

10 Å

10 Å

Fig. 3. SFM image of a thin YBCO film (200 nm) on SrTiO_3 (110) taken at $T = 300$ K. The image was taken with a force 30–100 nN. The scanned areas were (a) 7.1×7.1 nm² and (b) 3.9×3.9 nm². The image reveals non-periodic disorders of atomic images, a depth profile along the diagonal direction (b) appears shown in (c).

Fig. 4. Curves of dI/dV vs. V for a YBCO film at $T = 4.3$ K for (a) $V_t = 2.64$ mV, $I_t = 2.64$ nA; conductance maxima were observed at $2\Delta_1 = 3.5$, $2\Delta_2 = 17.0$, $2\Delta_3 = 23.5$ and $2\Delta_4 = 41$ meV. The arrows indicate the position at which conductance maxima occur; (b) $V_t = 1.23$ mV, $I_t = 2.88$ nA. The arrows indicate the position of conductance maxima with $2\Delta \sim 42$ meV.

projects variation in the order parameters of the sample relative to the tip on the atomic scale. The tunneling spectra depend on the ratio between the layer contribution and the chain contribution [17] since the order parameters vary along CuO_2 layers and CuO chains. "Inner gaps" have been reported in STM and STS studies on the (110) surface on YBCO single crystals [18]. Other possibilities for "inner gaps" include the anisotropic contribution with s wave or d wave symmetry [19,20], a mixture of s and d wave [21] or a tunnel tip stuck to a semiconducting top layer on the film. Fig. 4(b) shows a tunneling spectrum probed at another position. A single gap was observed with a value $2\Delta \sim 41$ meV. The gap value is determined from the conductance

peaks (shown in Fig. 4) assuming the conventional BCS theory that reflects the spherical symmetric nature of the pair wave function. Hence $2\Delta/k_B T_c = 5.27$ is in agreement with the other data measured in YBCO compounds [22].

Fig. 5 shows tunneling spectra of a YBCO film with a constant bias voltage $V = 0.122$ V at $T = 4.3$ K. The tunneling spectra alter from a semiconducting-gap structure to a superconducting-gap structure as the tunneling current is increased (thus reducing the distance between the tip and the sample). If the YBCO film is covered with a monolayer of BaO on the surface, the latter would be responsible for a semiconducting gap. When the tip approaches the surface of YBCO film, the charge carriers tunnel into

Fig. 5. dI/dV vs. V for a YBCO film on MgO (001) at a constant bias voltage $V_t = 0.122$ V and $T = 4.3$ K, (a) $I_t = 2.32$ nA, (b) $I_t = 2.63$ nA and (c) $I_t = 2.9$ nA.

Fig. 6. Curves of (a) I - V and (b) dI/dV for a YBCO film on MgO (001) at a constant bias voltage $V_t = 0.126$ V and $T = 4.3$ K for three bias currents: (a) $I_t = 2.06$ nA, (b) $I_t = 1.6$ nA and (c) $I_t = 1.25$ nA.

the CuO_2 layer and are responsible for the tunneling spectrum in quasi-two-dimensional superconductivity.

We have also observed Coulomb staircases [23,24] in the I - V curves when the distance from the tip to the sample and the grain sizes of YBCO films were varied. Fig. 6 shows the curves of I - V and dI/dV versus V at $T = 4.3$ K with a tunneling currents $I_t = 2.06$, 1.59 and 1.23 nA for a YBCO film at a fixed biased voltage $V = 0.127$ V. The voltage period in these curves was $\Delta V = 6.25$ mV. The voltage period did not change with the tip-sample distance. A voltage shift which appears in the dI/dV curves, presumably due to trapped charges in the grain, therefore affects the tunneling spectrum of the sample and results in voltage shift at zero bias voltage in dI/dV versus V . If the two-junction model [25] is applied to describe the tunneling spectrum and if the grain near the tip is considered to contribute mainly to the Coulomb staircase, then the grain has a capacitance $C = e/\Delta V \sim 2.56 \times 10^{-17}$ F.

4. Conclusion

We observed, for the first time, a clear atomic image on a $(\text{YBCO}_1/\text{PrBCO}_1)_{40}$ superlattice and a YBCO thin film in air at 295 K using an air STM or SFM system. By varying the distance from the tip to the sample, we observed Coulomb staircases that reveal the charging effects of the grain junctions in YBCO films at 4.2 K in vacuum. The characteristics of current versus voltage show “multi-gap” structures, resulting from the anisotropy of the YBCO films.

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References

- [1] R.P. Vasquez, M.C. Foote, B.D. Hunt and L. Bajuk, J. Vac. Sci. Technol. A 9 (1991) 570.
- [2] H.L. Edwards, J.T. Markert and A.L. de Lozanne, Phys. Rev. Lett. B 69 (1992) 2967.

- [3] A.K. Rajagopal and S.D. Mahanti, Phys. Rev. B 44 (1991) 10210.
- [4] S.J. Pennycook, M.F. Chisholm, D.E. Jesson, D.P. Norton, D.H. Lowndes, R. Feenstra, H.R. Kerchner and J.O. Thomson, Phys. Rev. Lett. 67 (1991) 765.
- [5] J.Z. Wu, C.S. Ting, W.K. Chu and X.X. Yao, Phys. Rev. B 44 (1991) 411.
- [6] X.X. Xi, J. Geerk, G. Linker, Q. Li and O. Meyer, Appl. Phys. Lett. 54 (1989) 2367.
- [7] R.S. List, A.J. Arko, Z. Fisk, S.-W. Cheong, S.D. Conradson, J.D. Thompson, C.B. Pierce, R.J. Bartlett, N.D. Shinn, J.E. Schirber, B.W. Veal, A.P. Paulikas and J.C. Campuzano, Phys. Rev. B 38 (1988) 11966.
- [8] D.P. Norton, D.H. Lowndes, X.Y. Zheng, S. Zhu and R.J. Warmack, Phys. Rev. B 44 (1991) 9760.
- [9] R.E. Thomson, J. Moreland, N. Missert, D.A. Rudman, S.C. Sanders and B.F. Lole, Appl. Phys. Lett. 63 (1993) 614.
- [10] H.P. Lang, H. Haefke, G. Leemann and H.J. Güntherodt, Physica C 194 (1992) 81.
- [11] H. Haefke, H.P. Lang, G. Leemann and H.-J. Güntherodt, Appl. Phys. Lett. 60 (1992) 3054.
- [12] S. Chen, L.M. Wang, W.B. Jian, S.Y. Wang, H.C. Yang and H.E. Horng, J. Appl. Phys. 76 (1994) 2535.
- [13] A.V. Narlikar et al., Appl. Phys. Lett. 60 (1992) 1896.
- [14] L.M. Wang, H.H. Sung, J.H. Chern, H.C. Yang and H.E. Horng, J. Appl. Phys. 73 (1993) 8419.
- [15] J.K. Burdett, Physica C 191 (1991) 282.
- [16] J.D. Jorgensen, S. Pei, P. Lightfoot, H. Shi, A.P. Paulikas and B.W. Veal, Physica C 167 (1990) 571.
- [17] S. Tanaka, T. Nakamura, M. Liyama, N. Yoshida, S. Takano, F. Shoji and K. Oura, Appl. Phys. Lett. 59 (1991) 3637.
- [18] J. Kane, Q. Chen, K.-W. Ng and H.-J. Tao, Phys. Rev. Lett. 72 (1994) 128.
- [19] S. Tanaka, E. Ueda and M. Sato, Physica C 224 (1994) 126.
- [20] Z.-X. Shen et al., Phys. Rev. Lett. 70 (1993) 1553.
- [21] G.D. Mahan, Phys. Rev. Lett. 71 (1993) 4277.
- [22] G. Kotliar and J. Liu, Phys. Rev. B 38 (1988) 5142.
- [23] J.S. Tsai, I. Takeuchi, S. Ishitake, J. Fujita, S. Miura, T. Terashima, Y. Bando, K. Iijima and K. Yamamoto, Physica C 157 (1989) 537.
- [24] S.T. Ruggiero and J.B. Barner, Phys. Rev. B 36 (1987) 8870.
- [25] I. Takeuchi, J.S. Tsai, T. Yoshitake and S. Satoh, Physica C 185–189 (1991) 2565.
- [26] See, for instance, M. Amman, S.B. Field and R.C. Jaklevic, Phys. Rev. B 48 (1993) 12104; R. Wilkins, E. Ben-Jacob and R.C. Jaklevic, Phys. Rev. Lett. 63 (1989) 801; Z.Y. Rong, A. Chang, L.F. Cohen and E.L. Wolf, IEEE Trans. Magn. 28 (1992) 67.