Modification of a $YBa_2Cu_3O_{7-\delta}$ Thin Film Using an Atomic Force Microscope *

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A $YBa_2Cu_3O_{7-\delta}$ thin film is modified by a probe electric field of an atomic force microscope to form a ridge with the width of only a grain cell. The modification varies with the operation parameters of the bias voltage, the moving velocity of the probe and the ambient humidity. Energy dispersive spectroscopy analysis shows only oxygen deficiency in the modified YBCO thin film. As a result, the suppressed superconductivity was found in the junction crossing the ridge.

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Since the invention of the scanning tunnelling microscope (STM) and atomic force microscope (AFM), much interest has been concentrated on their applications as a nanometre-scale patterning tool for a series of materials.[1] A nanometre-scale structure fabricated by STMs or AFMs on metals and semiconductors has been reported.[2-7] Many efforts have also been made on high-temperature superconductors (HTS), including single crystals and thin films.[8-17] It provides a promising method for fabricating weak links in HTS. A few attempts have been carried out in this way.[18-20] Song *et al.*[21] reported on the successful fabrication a Josephson junction using an AFM. The mechanism of patterning on metals and semiconductors by STMs and AFMs has proven to be tip-induced anodic surface oxidation except mechanical material removal. However, due to the complex ingredients of HTS compared with conventional metals and semiconductors, the mechanism of patterning on HTS by STMs and AFMs is still unclear. Several possible mechanisms have been proposed, for example, mechanical material removal, field evaporation, thermal evaporation, and electrochemical etching, etc.

In this Letter, a $YBa_2Cu_3O_{7-\delta}$ (YBCO) HTS thin film is modified by an AFM with a voltage biased conducting tip as a probe. The topography of the modification was measured *in situ* by the AFM. We discuss the modification dependences on working conditions, including the ambient humidity, bias voltage and scanning velocity of the probe. Significant degradation of superconductivity can be measured and the mechanism of the degradation is discussed in accordance with the energy dispersive spectroscopy (EDS) of modified YBCO thin films using a scanning electron microscope (SEM).

For our study, a *c*-axis oriented epitaxial thin film of YBCO was deposited on a MgO substrate by pulsed laser ablation, which has typical critical temperatures of around 87 K. The thickness of the film was about 150 nm. The experiments described herein utilized an improved system based on a commercial AFM (Nanoscope Ⅲ a of Digital Instruments). The samples were mounted on the sample holder of the AFM working in the contact mode. Because the MgO substrate is an insulator, one electrode was fixed on to the film by silver paste to bias the thin film. The other was connected to the ground and also had good electrical contact with the probe. The constant voltage with a typical value of 5 − 10 V was biased between the thin film and the probe of the AFM.

Ordinarily the tip of the AFM probe is very sharp with dimensions of less than 10 nm. When the thin film is biased, it may be modified under the strong electric field formed between the tip and thin film. The topography of the thin film can be figured out *in situ* by the AFM. Figure 1(a) shows the topography of an original YBCO thin film. Grain cells with the dimensions of 100 − 200 nm are observed clearly. The bright parts greater than grain cells are the outgrowth formed often in the film deposited by pulsed laser ablation. While biasing the thin film with +10 V, the probe scans along a straight line with a velocity of 0.25 μm/s for 20 s. The ambient humidity is about 35%. Figure 1(b) shows the typical topography of the modified YBCO thin film, after powering off the bias voltage. A ridge line with the length of 5 μm is observed at the position where the probe scanned, which is consistent with the scanned distance. This suggests that the YBCO thin film was modified under the strong electric field formed between the scanning probe and the thin film. An AFM image of the ridge is shown in Fig. 2. A row of grain cells expanded and formed the ridge under the strong electric field. The height of the ridge is about 150 nm, similar to the thickness of the thin film. This shows that the modification of the YBCO thin film can be controlled on

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one row of grain cells, which reaches the one dimension limit on the thin film.

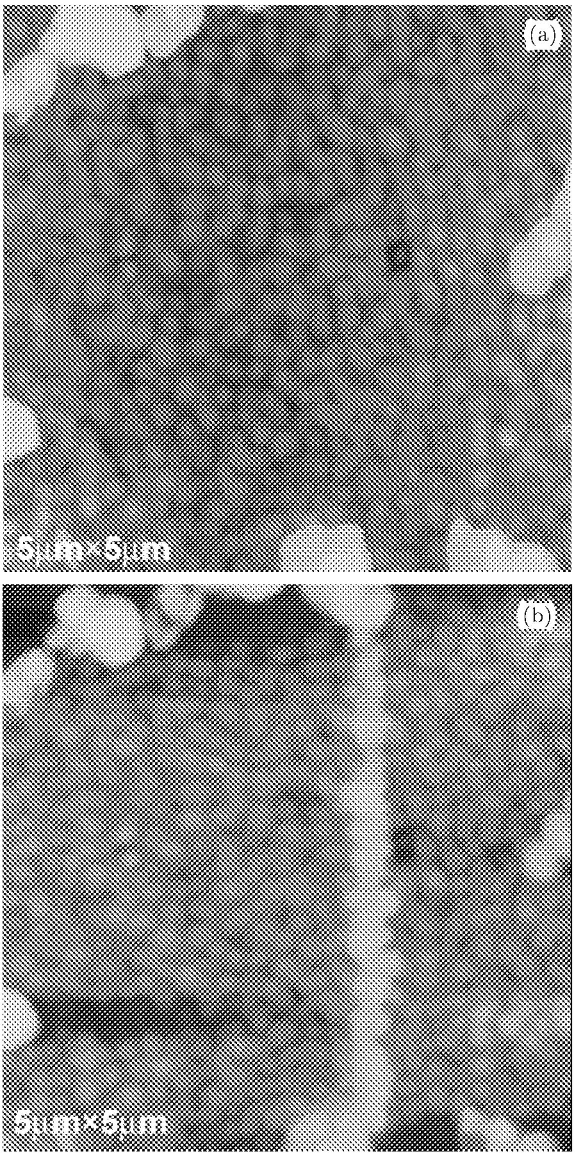

Fig. 1. (a) Topography of an original YBCO thin film. (b) Topography of YBCO thin films modified by the AFM probe electronic field. The voltage of the probe is +10 V, the scanning velocity of the probe is 0.25 μm/s, and the ambient humidity is 35%.

To obtain further information about the modification induced by the probe electric field, the parameters related to the modification were studied systematically. The bias voltage and rate of scanning velocity decided the degree of modification. With the higher bias voltage and lower rate of scanning velocity, the ridge formed was wider and higher, and vice versa. Figure 3 shows the width of the ridge varying with the applied bias voltage. Moreover, a threshold of bias voltage is found in the measurements, which is about −4 V in Fig. 3. No obvious modification was observed when the bias voltage was less than the threshold. The ambient humidity is also an important factor to the

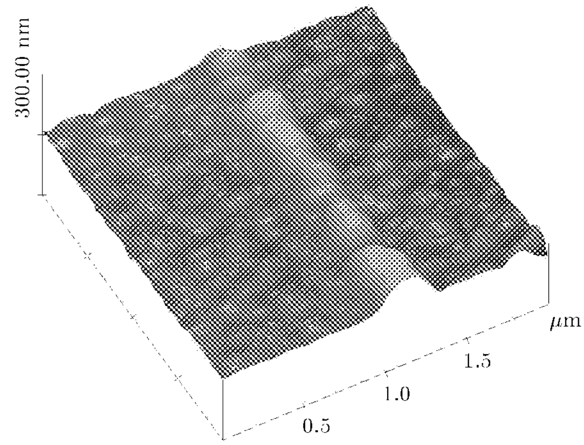

Fig. 2. Topography of the ridge.

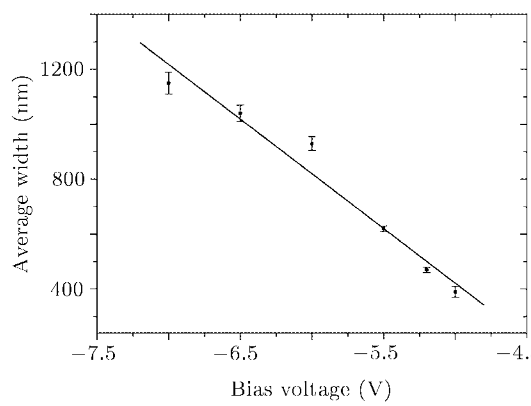

Fig. 3. Average width of ridge versus bias voltage. The scanning velocity of the probe is 0.20 μm/s, and the ambient humidity is 50%.

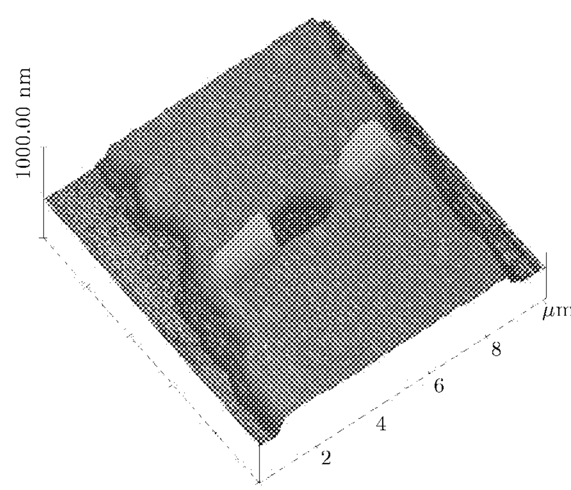

Fig. 4. Unusual topography in the groove region for operation parameters: relative humidity 70%, probe voltage −8 V, and scanning velocity 0.2 μm/s.

the modification. When humidity is very low (below 25%), there are no changes on the thin film even with the maximum bias voltage allowed by the system (12 V). Under higher humidity, the modification becomes easier. Figure 4 shows the topography of modification under high bias voltage and high humidity. The ridge is not uniform. Part of it was replaced by the groove, where no YBCO materials existed. The sample shown in Fig. 4 is YBCO micro-strips formed on the MgO substrate by chemical etching.

According to the results described above, there must be physical and chemical reactions occurring in the YBCO thin film under a strong probe electric field. The ingredient of the ridge might be different from conventional YBCO thin films. Previous propositions, such as mechanical material removal, field evaporation and thermal evaporation, could not explain why the ridge always formed instead of the groove in a few reports.[9,16] The modification independence of voltage polarity excludes the possibility of tip-induced anodic oxidation. To measure the possible ingredient change in the ridge, a square with a size of $5 \times 5\,\mu\mathrm{m}^2$ was modified by the probe electric field on the YBCO thin film. The EDS spectra of Y, Ba, Cu and O were measured separately. The decrease of O content was registered in the modified square in comparison with the unmodified areas on the same thin film. However, no evident changes of Y, Ba or Cu were found. Under a strong probe electric field, some O atoms in the thin film obtain extra energy and escape from the thin film, which causes a decrease of oxygen content. When the electric field is less than a specific value, the oxygen cannot escape from YBCO, so the threshold exists. The oxygen deficiency may result in changes of structure and ingredient in the modified thin film. The diversified resultant replacing YBCO was a possible reason for formation of the ridge. On the other hand, the vapour in the air plays an important role in the modification. However, the mechanism is unclear yet. Huh *et al.*[22] suggested that water could remove oxygen from the surface of YBCO thin films. The vapour near the surface of the thin film should be an important carrier for oxygen to escape from YBCO, so the modification is sensitive to the humidity. The loose resultant in the ridge may be evaporated under the high electric field and humidity and the groove formed instead, which is similar to the results observed by Bertsche *et al.*[17] Furthermore, a resistance increases by nearly ten times at room temperature and a decrease of critical temperature from 85 K to 43 K were measured in the junction crossing the ridge. The decrease of oxygen in YBCO can lead to an increase in the resistivity as well as to a decrease of the critical current.[23] Furthermore, the disorder of the structure in the ridge may also cause suppressed superconductivity in the ridge.

In summary, a YBCO thin film has been modified under the probe electric field of an AFM and the resolution of the modification reached the sub-micrometre scale. The results depended strongly on the operation parameters: the bias voltage, the moving velocity of the probe and ambient humidity. The electric field induced oxygen deficiency of the modified thin film was measured by EDS analysis. The superconductivity was suppressed in the modified area. Further analysis of the changes of the ingredients is still ongoing. To improve the stability and consistency of the modification, the degradation of superconductivity in the ridge provides the possibility of directly fabricating Josephson junctions in HTS using this technique.

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