First publ. in: Applied Physics Letters 71 (1997), 26, pp. 3805-3807

Scanning probe nanostructuring of $YBa_2Cu_3O_7$: A corrosion induced abrasion

J. Boneberg,[a] M. Böhmisch, M. Ochmann, and P. Leiderer
Universität Konstanz, Fakultät Physik, D-78434 Konstanz, Germany

(Received 14 August 1997; accepted for publication 29 October 1997)

Nanostructuring experiments were performed on a $YBa_2Cu_3O_7$ thin film surface with an atomic force microscope (AFM) with a conductive tip. Measurements of the local conductivity with the AFM tip show that corrosion towards a nonconducting surface occurs on a timescale of hours under ambient conditions. The corroded surface can easily be abraded, whereas the clean $YBa_2Cu_3O_7$ surface is comparably resistive against mechanical forces. The corrosion is promoted by an electric current at positive sample bias. Thus it can be concluded that the nanostructuring process performed in former experiments with the scanning tunneling microscope consists of two steps: corrosion and succeeding abrasion. © *1997 American Institute of Physics.* [S0003-6951(97)05052-3]

The nanostructuration of high T_c superconductors is an interesting possibility for the formation of, for example, minaturized Josephson junctions or for local tuning of the superconducting properties. Different examples of such modifications with scanning tunneling microscopes under ambient conditions have been shown.[1-11] Structures as small as the coherence length have been achieved.[11] While these modifications have been reported by different groups and seem to be readily reproducible, the physical reason for the modifications is not clear. Several models for different regimes of current and voltage have been proposed, such as mechanical abrasion (sometimes also called milling), melting, electrochemistry, electromigration, and field-induced evaporation.[8-10] It seems to be accepted that at very low voltages ($U<50$ mV) abrasion takes place, whereas at very high voltages ($U>10$ V) field evaporation appears to be responsible for the modifications. In the intermediate voltage regime of around 1 V, which we address here, most of the authors discuss their results in terms of field-induced evaporation and find good agreement with the observed behavior.[6,10,11] This interpretation is not only surprising as the fields are relatively low compared to the measured evaporation field of $YBa_2Cu_3O_7$,[12] but it is also contradicted by other experimental results—where at even higher voltages and currents no surface modification was observed, when the experiments were carried out under high vacuum conditions.[13]

In addition our scanning tunneling microscope (STM) and atomic force microscope (AFM) nanostructuring studies on other layered materials (metaldichalcogenides, e.g., WSe_2) have shown a clear indication for an electrochemical reaction with water.[14,15] As there exist experimental observations which report a high corrosion reactivity of high T_c superconductors,[16-20] we wanted to test this possibility on $YBa_2Cu_3O_7$ as well. First STM experiments supported this speculation as no nanostructuring could be observed under vacuum conditions. In order to understand the ongoing processes in detail, experiments with an AFM with conducting tip were started. These allow one to distinguish between processes induced by forces or current, respectively.

For the measurements a home-built AFM was used under ambient conditions. An interferometric method is used to control the position of the tip. An additional piezo element allows one to change the load force in a controlled manner. Highly doped Si cantilevers with Pt coating[21] were used in order to apply voltage, measure current-voltage ($I-V$) spectroscopy, and local conductivity. The arrangement allows current measurements down to 2 pA at 2 kHz bandwidth. Bias voltage is applied to the sample. The superconducting $YBa_2Cu_3O_7$ thin films used here were prepared by reactive evaporation onto MgO-(100) substrates. The c-axis oriented, epitaxial films have typical onset transition temperatures of around 87 K. The thickness of the films was 200 nm.

We started with the measurement of the topography of a YBCO film at a load force of 20 nN. Astonishingly, the simultaneously measured current between tip and sample at a bias of 1 V was below the detection limit of 1 pA, however STM microscopy of the same surface has revealed stable images with monolayer resolution. We then switched off the voltage and increased the load force up to 40 nN and scanned the surface several times. This process is called cleaning further on. After this treatment the measurements with applied voltage were performed again at a load force of 20 nN. This time a current is flowing between tip and surface. The change of surface properties from a nonconducting towards a metallic behavior can be observed in $I-V$ spectroscopy (Fig. 1). Whereas on the unprepared surface no current is flowing in the range of $-2-2$ V, the cleaned surface shows a linear current behavior already at small voltages (<50 mV). Note the different magnitude of both axes in Figs. 1(a) and 1(b). It has to be added that the observed $I-V$ spectra are dependent on the force load, e.g., at higher forces a higher current is perceived.[22] With the help of such $I-V$ measurements it could be observed that the metallic behavior is not stable under ambient conditions: On a timescale of hours the measured current at a fixed voltage disappears again. A second cleaning process must be performed to reach metallic behavior once again.

In the following experiments we tested all possible combinations of force, voltage, and surface conditions. These can be summarized as follows: Applying forces <150 nN alone does not alter the topography of a cleaned YBCO surface,

---

[a] Electronic mail: johannes.boneberg@uni-konstanz.de

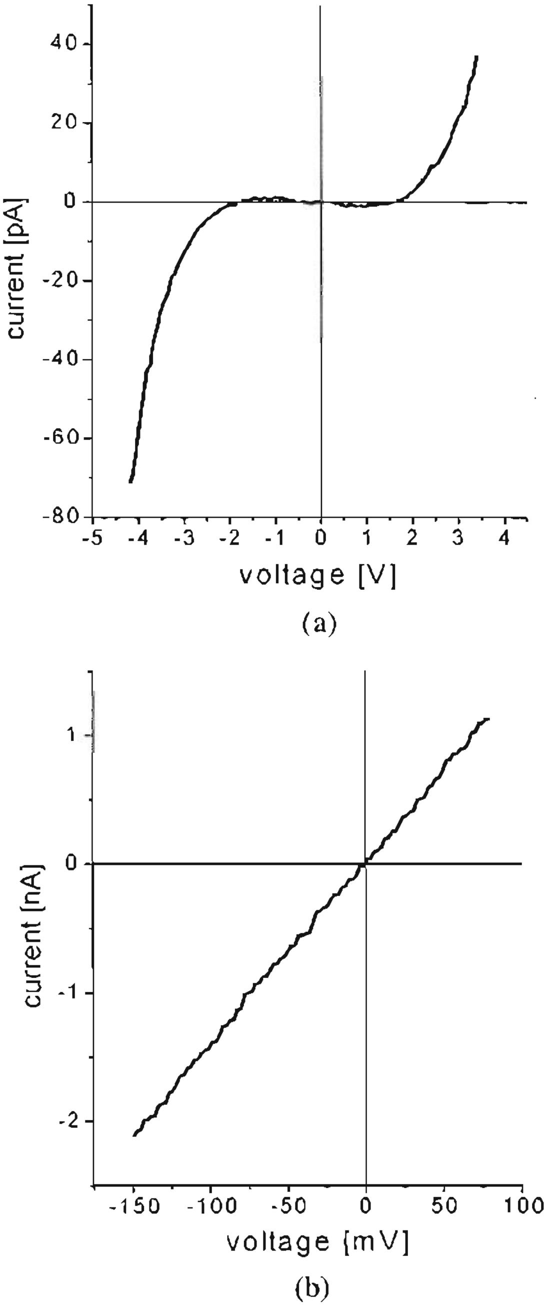

FIG. 1. Comparison of an $I-V$ spectrum of the corroded surface (a) with an $I-V$ spectrum of a cleaned surface (b) at a load of 20 nN. Note the different axes in the figures.

whereas the topography of a corroded surface is changed immediately. As long as forces < 10 nN are used the topography of both surface conditions is not altered. As soon as a positive bias voltage is additionally applied once again a marked difference can be observed. The corroded surface does not change the appearance in contrast to the cleaned surface, where a modification in conductivity can be observed. As the applied voltage is changed to the opposite sign, the surface modifications are stopped immediately. As an example, Fig. 2 (lower part) shows the appearance of the YBCO surface after a cleaning. On the left side the topography is depicted and on the right side the measured current at a bias voltage of 1.3 V. Whereas in the upper half no current can be detected in the lower half the current reaches 6 nA.

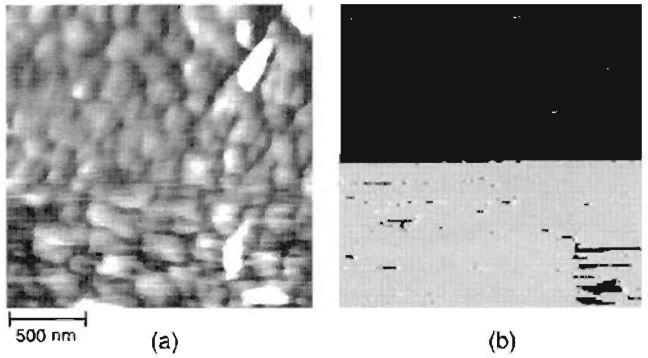

FIG. 2. Topography and simultaneously measured current at a load of 15 nN and a bias of 1.3 V. The scan size is 3.3 μm×3.3 μm, the height difference in topography is 7 nm, the current varies between 0 and 6 nA. The lower half of the scan area has been cleaned before, therefore a current of up to 6 nA can be observed. This leads in the lower part to the appearance of first surface modifications, indicated by a reduced current as nonconducting material is removed by the tip.

The applied force is 15 nN in this case, therefore the first changes of topography can already be detected in the lower part of the figure and which are always accompanied by a decrease of current. We attribute this behavior to the removal of nonconducting material. Following that the most effective way to achieve topographic modification is to scan the surface at medium forces with simultaneously applied positive voltage. Figure 3 shows a double line written in two succeeding line scans at these conditions. The lines have a diameter of around 35 nm and a length of 1 μm.

The results of the measurements imply the following model: In order to modify the clean YBCO surface current has to flow at positive voltages, which transform the material locally into a corroded state. This corroded state can then be easily abraised by mechanical forces. In the following we want to discuss this model.

The corrosion of YBCO surfaces is a well known phenomena which has been studied in different publications.[16–20] Especially the reaction with H_2O has been examined in detail. The timescale of the corrosion process depends on surface quality, e.g., the step and defect density, but also on the humidity and eventually on the CO_2 concentration as reported by Thomson *et al.*,[9] making it difficult to compare absolute numbers. However, as our measurements

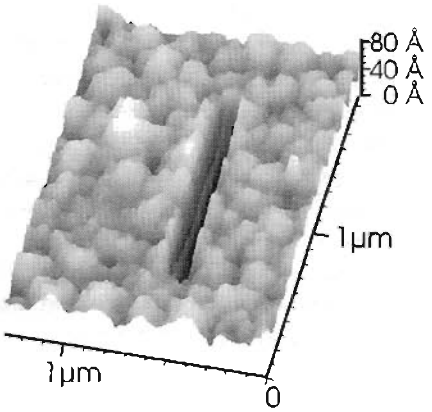

FIG. 3. Topography of a surface area where a double line was written at a force of 20 nN with applied bias of 3 V.

reveal, the corrosion process on thin films cannot be omitted as long as experiments are performed under ambient conditions.

In agreement with our results the corrosion products are known to be nonconducting, as combined STM/AFM[9] and STM/optical experiments[3] have already shown. A pronounced difference in the mechanical stability of the clean versus the corroded YBCO surface also appeared in our measurements. This is not surprising as the stability of a surface against mechanical forces depends on the chemical binding. Therefore upon altering the chemistry, the stability could change as well. Nevertheless this change could not be observed up to now, as former experiments did not combine electrical and force measurements.

A further feature is the dependence of the corrosion and thus the nanostructuring process on the polarity of the applied voltage. This behavior is known from STM/AFM measurements on other materials[14,15] as well from many other electrochemical reactions.

At this point we would like to compare our results with the results of former STM experiments, which were performed at positive bias voltage. The main features are the appearance of etching at steps, and with increasing voltage on at first smooth surfaces as well.[5] Etching is observed to increase almost linearly with current, whereas upon increasing the voltage a kind of threshold behavior appears.[10] These observations fit completely into the two-step model given above. A different threshold for the etching on step and terraces, respectively, has been observed on another surface as well.[15] For a corrosion process it would be expected that the corrosion rate is current dependent and a nonlinear behavior on bias voltage supports the existence of different redox potential in the chemical process.

In summary we have shown that AFM measurements with conducting tip reveal a new process responsible for the nanostructuring of YBCO at a bias voltage of around 1 V. First, current induced corrosion transforms the surface into a nonconducting one. Second the products are removed by mechanical abrasion. Using this new interpretation we get complete agreement with the results of former STM measurements.

The authors gratefully acknowledge helpful discussions with J. Eisenmenger, M. Hirschenberger, and T. Pfeiffer. They thank R. Semerad, W. Prusseit, H. Kinder, and P. Berberich for providing the samples. This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG), under Grant No. SFB 513.

---

[1] H. Heinzelmann, D. Anselmetti, R. Wiesendanger, and H.-J. Güntherodt, Appl. Phys. Lett. **53**, 2447 (1988).

[2] M. A. Harmer, C. R. Fincher, and B. A. Parkinson, J. Appl. Phys. **70**, 2760 (1991).

[3] J. A. Virtanen, P. Suketu, G. C. Huth, and Z. H. Cho, J. Appl. Phys. **70**, 3376 (1991).

[4] D. C. Parks, J. Wang, N. A. Clark, and A. M. Hermann, Appl. Phys. Lett. **59**, 1506 (1991).

[5] I. Heyvaert, E. Osquiguil, C. Van Haesendonck, and Y. Bruynseraede, Appl. Phys. Lett. **61**, 111 (1992).

[6] H. Olin, G. Brorsson, P. Davidsson, Z. G. Ivanov, P. Å. Nilsson, and T. Claeson, Ultramicroscopy **42–44**, 734 (1992).

[7] I. Maggio-Aprile, Ch. Renner, A. Erb, E. Walker, and Ø. Fischer, Ultramicroscopy **42–44**, 728 (1992).

[8] U. Geyer, G. von Minnigerode, and H.-U. Krebs, J. Appl. Phys. **76**, 7774 (1994).

[9] R. E. Thomson, J. Moreland, and A. Roshko, Nanotechnology **5**, 57 (1994).

[10] I. Heyvaert, E. Osquiguil, C. Van Haesendonck, and Y. Bruynseraede in *Nanolithography: A Borderland between STM, EB, IB, and X-Ray Lithography*, edited by M. Gentili, C. Giovanella, and S. Selci, NATO ASI Series (Kluwer Academic, Dordrecht, 1994), Vol. 264, p. 207.

[11] G. Bertsche, W. Clauss, and D. Kern, Appl. Phys. Lett. **68**, 3632 (1996).

[12] N. Ernst, G. Bodzech, and A. J. Melmed, J. Phys. (Paris), Colloq. **49**, C6-453 (1988).

[13] Ph. Niedermann and Ø. Fischer, J. Microsc. **152**, 93 (1988).

[14] J. Boneberg, M. Lohrmann, M. Böhmisch, F. Burmeister, M. Lux-Steiner, and P. Leiderer, Z. Phys. B **99**, 567 (1996).

[15] M. Böhmisch, F. Burmeister, J. Boneberg, and P. Leiderer, Appl. Phys. Lett. **69**, 1882 (1996).

[16] M. Yan, R. L. Barns, H. M. O'Bryan, P. K. Gallagher, R. C. Sherwood, and S. Jin, Appl. Phys. Lett. **51**, 532 (1987).

[17] R. L. Barns and R. A. Laudise, Appl. Phys. Lett. **51**, 1373 (1987).

[18] N. P. Bansal and A. L. Sandkuhl, Appl. Phys. Lett. **52**, 323 (1988).

[19] J. Zhou, D. R. Riley, A. Manthiram, M. Arendt, M. Schmerling, and J. T. McDevitt, Appl. Phys. Lett. **63**, 548 (1993).

[20] J. T. McDevitt, S. G. Haupt, and C. E. Jones, in *Electroanalytical Chemistry*, edited by A. J. Bard and I. Rubinstein (Marcel–Dekker, Inc., New York, 1996), Vol. 19.

[21] Dr. Olaf Wolter, *Nanosensors*, GmbH, D-35578 (Wetzlar-Blankenfeld, Germany).

[22] Eventually it occurs that the tip may change during a cleaning process. In this sense the observation of current is an indication of a clean surface tip combination, whereas the observation of no current is not necessarily caused by a nonconducting surface. Hence a procedure has been introduced where immediately after an experiment on YBCO the conductivity of the tip was checked on graphite.