Appl. Phys. A 67, 403–405 (1998)

Applied Physics A
Materials
Science & Processing

Patterning of $YBa_2Cu_3O_{7-\delta}$ films using a near-field optical configuration

J.D. Pedarnig[1,*], **H. Göttlich**[2], **R. Rössler**[1], **W.M. Heckl**[2], **D. Bäuerle**[1]

[1] Angewandte Physik, Johannes-Kepler-Universität Linz, A-4040 Linz, Austria
[2] Institut für Kristallographie und Angewandte Mineralogie, Ludwig-Maximilians-Universität München, D-80333 München, Germany

Received: 3 July 1998/Accepted: 6 July 1998

Abstract. Thin superconducting $YBa_2Cu_3O_{7-\delta}$ films have been patterned by means of an arrangement employed in scanning near-field optical microscopy (SNOM). Standard SNOM probes were modified to achieve high transmission for direct writing by oxygen depletion in N_2 atmosphere. The written lines are about 1.5 μm wide and show a semiconductor-like resistivity behavior ($\delta \geq 0.5$). The morphology of illuminated regions is about the same as that of the YBCO films.

PACS: 07.79.Fc; 74.25.Fy; 74.76.Bz

High-temperature superconducting (HTS) thin films become increasingly important for microwave applications, various types of sensors, etc. They can be prepared by various techniques including chemical vapor deposition (CVD), co-evaporation, pulsed-laser deposition (PLD), and sputtering. Because of the relatively simple synthesis and the excellent superconducting properties, $YBa_2Cu_3O_{7-\delta}$ (YBCO) has become one of the most important compounds. Film patterning can be performed by standard wet-chemical etching, ion-beam etching, laser ablation, and laser direct writing. In the latter technique, the oxygen content is locally decreased/increased by laser-induced heating in a reducing/oxidizing atmosphere [1–7]. Whereas oxygen-saturated YBCO ($\delta < 0.1$) shows a metal-like resistivity behavior and a superconducting transition at $T_c \approx 92$ K, material with $\delta > 0.5$ is semiconducting. Laser direct writing was performed by using standard focusing techniques, which yield diffraction-limited spot sizes. Scanning near-field optical microscopy (SNOM), however, has proven to be a powerful tool for sub-wavelength focusing and sample imaging with a spatial resolution down to about 40 nm [8]. SNOM has been applied for near-field lithography of photoresists [9–13], the patterning of ferroelectric [14] and a-Si:H surfaces [15], and for pulsed-laser-induced desorption of molecules [16].

In this paper we report on first experiments on the patterning of $YBa_2Cu_3O_{7-\delta}$ films using a SNOM-type setup. For generating the intensities required in direct-writing experiments, fiber probes with increased apertures and highly increased optical transmission were fabricated from standard near-field probes.

1 Experimental

YBCO films were prepared by pulsed-laser deposition (PLD) using KrF excimer-laser radiation ($\lambda = 248$ nm, $\tau_l \approx 25$ ns, $\phi = 3.25$ J/cm^2) [1, 17]. Films were grown on (001) MgO substrates and annealed in situ in O_2. The films had an optimum oxygen content ($\delta \approx 0$), they were *c*-axis oriented, and had a thickness of $h = 220$ nm. The electrical and superconducting properties of films were measured on 800-μm-long and 22.5-μm-wide bridges fabricated by wet-chemical etching. Fully oxygenated $YBa_2Cu_3O_7$ films had transition temperatures of $T_c \approx 88$ K and critical current densities $j_c(77\,K) \approx 4 \times 10^6$ A/cm^2. The $YBa_2Cu_3O_{7-\delta}$ films used in the present study were slightly oxygen depleted with $T_c \approx 85.6$ K and $j_c(77\,K) \approx 10^6$ A/cm^2 ($\delta < 0.2$) [18].

For direct writing, a modified SNOM (Topometrix Company) with fast and sensitive non-optical shear force distance control [19] was used. Experiments were performed in a closed chamber, which was flushed with N_2 gas (0.2 l/s). The radiation of a multi-line Ar^+ laser (454 nm–514 nm) was coupled into the quartz fiber of the SNOM. The laser power in the fiber was varied between 7 mW and 30 mW and was measured with a photodiode by opening a fiber-to-fiber coupler (transmission > 90%). The probe–sample distance control turned out to be sensitive to the gas flow and laser power. For either strong gas flow or high laser power, a decrease of the shear force signal was detected when the feedback loop was open. With engaged feedback and small probe–sample distances an increase in the noise of the error signal was observed. Stable distance control in the flowing gas ambient and with high laser powers was achieved for friction forces between probe and sample of ≈ 1 nN. The probe scan rate was in all of the experiments $v_s = 2.5$ μm/s.

Fiber probes for direct writing were fabricated from single-mode quartz fibers with a core diameter of 3.6 μm,

---

[*] Corresponding author

cladding diameter of 125 μm, and cut-off wavelength of 514 nm. Standard SNOM fiber probes with ≈ 60 nm apertures and ≈ 100 nW maximum transmitted power were prepared by fiber pulling and subsequent coating of the tapered region with chromium (20 nm) and aluminum (100 nm). Laser-modified probes with transmissions up to 100 μW were fabricated from standard probes by laser damaging of the metal coating applying 12 mW input power [20–22]. Mechanically modified probes with transmissions up to 5 mW (for 30 mW input power) were produced from standard probes by laser damaging and subsequent breaking by mechanical bending of the fiber tip in the tapered region. Broken fiber tips appeared smooth in SEM images and had diameters of $d \approx 4$ μm.

2 Results and discussion

Direct-writing experiments were performed on patterned $YBa_2Cu_3O_{7-\delta}$ films by scanning the fiber probe across the YBCO bridges. Figure 1a,b show optical micrographs of two bridges. The bridges appear bright due to the strong reflection of the YBCO, while the transparent MgO substrate appears dark. Particulates formed during film deposition are found on both the bridges and the substrate. By repetitive scanning, lines with reduced oxygen content and with widths of about 1.5 μm (3 scans, Fig. 1a) and 4 μm (50 scans, Fig. 1b) were obtained. AFM images (Fig. 1c,d) revealed no changes in film morphology, except for a scratch on each stripe (width ≈ 1 μm, depth < 10 nm). These scratches are due to accidental mechanical interactions between the fiber probe and the film surface.

The width of lines is determined by the optical aperture of the fiber probe, the drift of the scan line, and the intensity required for light-induced modification of YBCO films, which is about $2\,\mathrm{mW}/\mu\mathrm{m}^2$ [6]. In our experiments, direct writing succeeded with the mechanically modified fiber probes which were scanned at distances ≤ 20 nm to the film surface. The intensities achieved with standard near-field probes and laser-modified fiber probes were too low for light-induced oxygen depletion.

The electrical resistivities of bridges are compared in Fig. 2. Originally, the bridges showed a metal-like temperature dependence above the critical temperature T_c, with room temperature resistivities between 0.4 and 0.6 mΩ cm (Fig. 2a). After direct writing, the room temperature resistivities of bridges I and II increased to > 1 mΩ cm and showed a semiconductor-like temperature dependence (Fig. 2b). The small dip near T_c is due to the superconducting transition in non-exposed parts of the bridges. Bridge III was not exposed and shows identical resistivities before and after the experiments.

From the semiconductor-like resistivity behavior and the changes in optical reflectivity, we conclude that direct writing produced oxygen-deficient lines across the YBCO bridges. Since bridges were non-superconducting after laser writing, oxygen depletion of lines should extend throughout the full depth of bridges with $\delta \geq 0.5$.

With $h/d \ll 1$ and $D_{\mathrm{YBCO}}/v_S d \gg 1$ we can estimate the laser-induced temperature rise along the film surface normal, $\theta(z) = T(z) - T(\infty)$, from the one-dimensional stationary heat conduction equation $-\mathrm{d}^2\theta(z)/\mathrm{d}z^2 = (\alpha/\kappa) I_w \exp[-\alpha z]$ [1], where $T(\infty)$ is the temperature far away from the processing region. For YBCO we employ the following parameters: the thermal diffusivity $D \approx 10^{-2}\,\mathrm{cm}^2/\mathrm{s}$, the absorption coefficient $\alpha = 17\,\mu\mathrm{m}^{-1}$, and the thermal conductivity

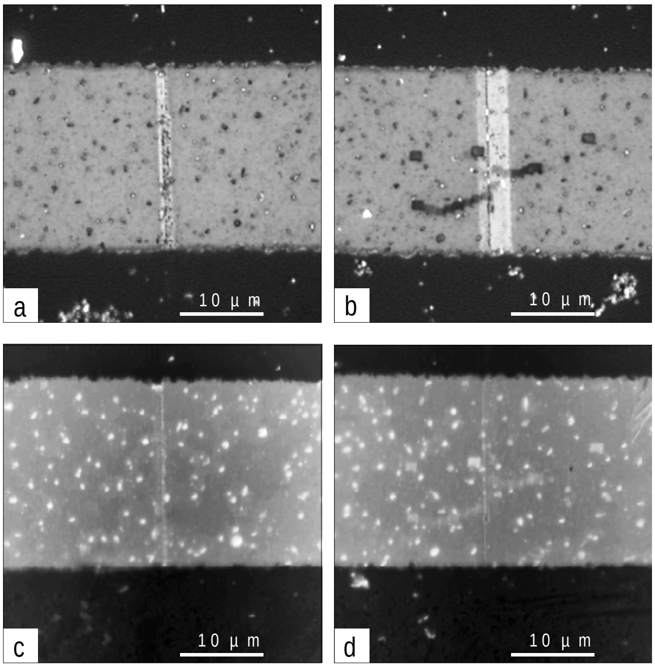

Fig. 1a–d. Optical micrographs (**a**, **b**) and AFM topographic images (**c**, **d**) of lines written across $YBa_2Cu_3O_{7-\delta}$ film bridges. The lines are 1.5 μm (**a**) and 4 μm (**b**) wide and appear bright. The morphology of films within the processed region remains essentially unchanged (**c**, **d**)

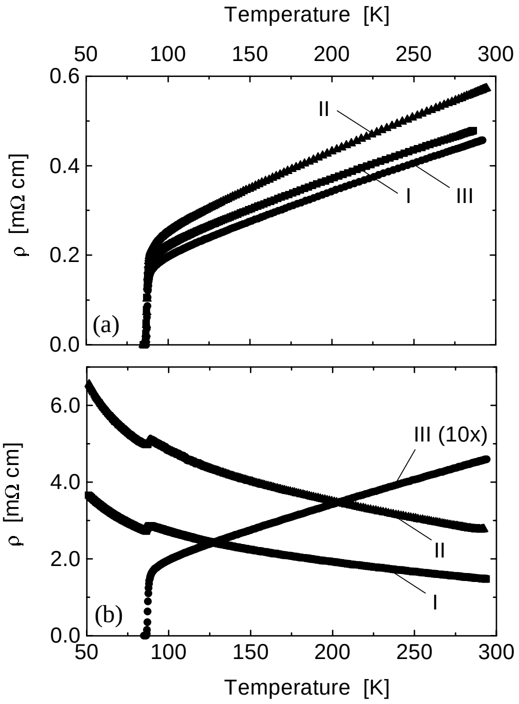

Fig. 2a,b. Resistivities of bridges before, (**a**), and after, (**b**), direct writing. **a** Metal-like temperature dependence with zero resistance at $T_c \cong 85.6$ K. **b** Semiconductor-like temperature dependence. Bridge III was not exposed and shows identical resistivities before and after the experiments

$\kappa \approx 0.02\,\mathrm{W/cm\,K}$. For a three-layer system consisting of the YBCO film, the film–substrate interface with a thermal boundary resistance $R_\mathrm{b} = 5 \times 10^{-4}\,\mathrm{cm^2K/W}$ [23] and the MgO substrate as a perfect heat sink, we obtain for a writing intensity $I_\mathrm{w} = 2\,\mathrm{mW/\mu m^2}$ a surface temperature $T(0) = 280\,°\mathrm{C}$. The temperature at the film–substrate interface is $T(h) = 120\,°\mathrm{C}$. These values are lower than the reported activation temperature for oxygen loss of $\mathrm{YBa_2Cu_3O_7}$ in reducing atmosphere. Thermogravimetric measurements on YBCO pellets yielded activation temperatures in the range $400\,°\mathrm{C}$–$500\,°\mathrm{C}$ [18, 24, 25]. The resistivities of the modified lines, $\rho_\ell(T)$, were estimated from the resistivities of bridges before and after direct writing. For oxygen-deficient YBCO one would expect $\rho_\ell(T)/\rho_\ell(300\,\mathrm{K}) = \exp[(T_0/T)^n]$ with $n = 1/3$ and $n = 1/4$ for $2D$ and $3D$ thermally-activated variable range hopping, respectively. In our experiments, the line resistivities did not show such a strong temperature dependence. This may be related to the non-uniform oxygen depletion within the film.

3 Conclusion

Direct patterning of superconducting $\mathrm{YBa_2Cu_3O_{7-\delta}}$ films using a near-field optical configuration produced a resolution of about 1.5 μm. The oxygen-depleted lines were non-superconducting, exhibited semiconductor-like resistivities, and showed a changed optical reflectivity without significant changes in surface morphology. Near-field direct writing on YBCO films with sub-wavelength spatial resolution would require improved near-field probes which withstand high light intensities. However, near-field writing of oxygen-enhanced patterns into oxygen-deficient films would require lower writing intensities due to the significantly lower activation temperature for oxygenation. Lower writing intensities would be required also for near-field writing on tilted films taking advantage of the much higher oxygen diffusivity along the a, b plane of YBCO. As a consequence, fiber probes with smaller apertures could be used to produce patterns with smaller linewidths.

Acknowledgements. We thank the German Bundesministerium für Bildung und Forschung (project 13N72056) and the Austrian Jubiläumsfonds der Österreichischen Nationalbank for financial support.

References

1. D. Bäuerle: *Laser Processing and Chemistry* (Springer, Berlin, Heidelberg 1996)
2. G. Liberts, M. Eyett, D. Bäuerle: Appl. Phys. A **45**, 313 (1988)
3. G. Liberts, M. Eyett, D. Bäuerle: Appl. Phys. A **46**, 331 (1988)
4. M. Rothschild, J.H.C. Sedlacek, J.G. Black, D.J. Ehrlich: Appl. Phys. Lett. **52**, 404 (1988)
5. Y.Q. Shen, T. Freltoft, P. Vase: Appl. Phys. Lett. **59**, 1365 (1991)
6. R. Sobolewski, W. Xiong, W. Kula: Appl. Phys. Lett. **64**, 643 (1994)
7. R.C. Dye, R.E. Muenchhausen, N.S. Nogar, A. Mukherjee, S.R.J. Brueck: Appl. Phys. Lett. **57**, 1149 (1990)
8. D.W. Pohl, D. Courjon (Eds.): *Near Field Optics* (Kluwer, Dordrecht 1993)
9. G. Krausch, S. Wegscheider, A. Kirsch, H. Bielefeldt, J.C. Meiners, J. Mlynek: Opt. Commun. **119**, 283 (1995)
10. I.I. Smolyaninov, D.L. Mazzoni, C.C. Davis: Appl. Phys. Lett. **67**, 3859 (1995)
11. A. Naber, H. Kock, H. Fuchs: Scanning **18**, 567 (1996)
12. J. Aizenberg, J.A. Rogers, K.E. Paul, G.M. Whitesides: Appl. Phys. Lett. **71**, 3773 (1997)
13. M. Hamano, M. Irie: Jpn. J. Appl. Phys. **35**, 1764 (1996)
14. J. Massanell, N. Garcia, A. Zlatkin: Opt. Lett. **21**, 12 (1996)
15. S. Madsen, M. Müllenborn, K. Birkelund, F. Grey: Appl. Phys. Lett. **69**, 544 (1996)
16. D. Zeisel, S. Nettesheim, B. Dutoit, R. Zenobi: Appl. Phys. Lett. **68**, 2491 (1996)
17. S. Proyer, E. Stangl, M. Borz, B. Hellebrand, D. Bäuerle: Physica C **257**, 1 (1996)
18. R.J. Cava, A.W. Hewat, E.A. Hewat, B. Batloog, M. Marezio, K.M. Rabe, J.J. Krajewski, W.F. Peck Jr., L.W. Rupp Jr.: Physica C **165**, 419 (1990)
19. J.D. Pedarnig, H. Göttlich, W.M. Heckl: accepted by Probe Microscopy (1998)
20. A.H. La Rosa, B.I. Yakobson, H.D. Hallen: Appl. Phys. Lett. **67**, 2597 (1995)
21. D.I. Kavaldjiev, R. Toledo-Crow, M. Vaez-Iravani: Appl. Phys. Lett. **67**, 2771 (1995)
22. M. Stähelin, M.A. Bopp, G. Tarrach, A.J. Meixner, I. Zschokke-Gränacher: Appl. Phys. Lett. **68**, 2603 (1996)
23. S. Zeuner, H. Lengfellner, W. Prettl: Phys. Rev. B **51**, 11903 (1995)
24. J.M. Tarascon, W.R. McKinnon, L.H. Greene, G.W. Hull, E.M. Vogel: Phys. Rev. B **36**, 226 (1987)
25. K. Conder, J. Karpinski, E. Kaldis, S. Rusiecki, E. Jilek: Physica C **196**, 164 (1992)