

High quality crystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films on thin silicon substrates

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$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (001) (YBCO) films with near perfect crystallinity have been grown epitaxially on Si(100) using two intermediate buffer layers: Yttrium-stabilized zirconia (YSZ) and CeO_2 . All layers were grown by an *in situ* pulsed laser deposition process. The new films have Rutherford backscattering spectroscopy minimum yields as low as 5%, compared to 12% for YBCO films deposited directly on YSZ. The superconducting onset is above 90 K with a transition width ΔT of 1 K. After film deposition the Si substrate could be etched from the back to give a circular, 2-mm-diam, 4000 Å uniformly thick Si membrane with 300 Å YSZ, 80 Å CeO_2 , and 1500–3000 Å YBCO on top.

Several recent experiments indicate anomalies in the vibrational amplitude and momentum of Cu atoms in the high temperature superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ near the critical temperature.^{1–3} This anomalous phonon behavior may be important for the understanding of high temperature superconductivity, but the experimental results are not clear. We are therefore using another method, electron channeling radiation spectroscopy, to study YBCO.⁴ This technique is particularly well suited to measure vibration amplitudes of atoms in a crystal, but the samples used must have good crystallinity and be quite thin ($<1 \mu\text{m}$).⁵ Relativistic electrons are sent through the crystal, and the channeling radiation signal cannot be seen above the incoherent bremsstrahlung if the sample is thicker than a few thousand Angströms. As part of an electron channeling experiment on YBCO, we have therefore developed high quality YBCO films on a thin Si substrate. The technique used may be of interest for bolometer development, in which YBCO on a Si or Si_3N_4 membrane as thin as possible is preferred.⁶

In order to make a high quality YBCO film on a thin substrate we need a substrate that gives good epitaxial YBCO growth and that can be made uniformly thin. Excellent YBCO crystallinity is obtained on LaAlO_3 , SrTiO_3 , and MgO , but we know of no simple way to make a thin substrate of either material.^{7,8} Free standing microstructures of YBCO have been made from films grown on SrTiO_3 , but these are only $10 \mu\text{m} \times 50 \mu\text{m}$ in size.⁹ Si, on the other hand, can be etched by many techniques, and thin films of YBCO have been grown on Si with yttrium-stabilized zirconia (YSZ) as a buffer layer.¹⁰ However, the quality of YBCO films on YSZ/Si is not as high as on the above substrates. We therefore sought to improve the crystallinity of YBCO on YSZ/Si, and found that by growing an extra buffer layer of CeO_2 we could improve the Rutherford backscattering spectroscopy (RBS) minimum yield (χ_{min}) of the YBCO film to as low as 5% (Fig. 1). This is almost as good as the YBCO crystallinity obtained on LaAlO_3 and MgO ($\chi_{\text{min}} \approx 3\%$). Simi-

lar results were recently reported by Copetti *et al.* (but not on a system on which one can make membranes).¹¹ The reason is that CeO_2 has a very good lattice match with YBCO, resulting in excellent epitaxial growth. The first buffer layer, YSZ, ensures (001) oriented CeO_2 , and helps prevent interdiffusion of Si and YBCO. YBCO films grown on CeO_2 had a T_c 2–3 K higher than those deposited directly on YSZ (Fig. 2). After film deposition the Si substrate was etched from the back using two different chemical etches. The last etch was selective, slowing down significantly at a boron implanted layer in the Si wafer and thus leaving a uniformly thick Si membrane. Our membranes were circular with a diameter of 1–2 mm.

$16 \times 16 \text{ mm}^2$ substrates were cut from polished Si (100) wafers. To clean the surface the substrates were dipped for about 5 min in each of two boiling solutions: $\text{NH}_4\text{OH}:\text{H}_2\text{O}:\text{H}_2\text{O}_2$ (1:5:1) and $\text{HCl}:\text{H}_2\text{O}:\text{H}_2\text{O}_2$ (1:5:1). This

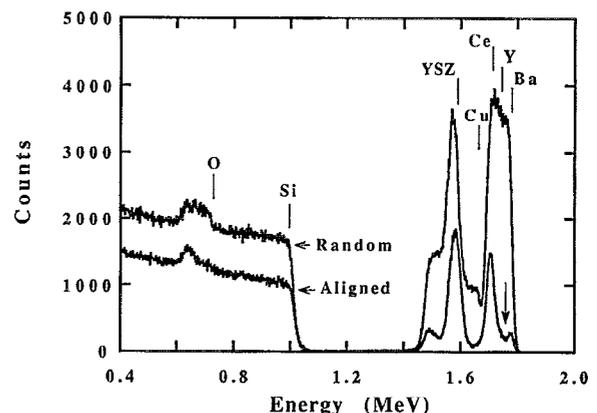


FIG. 1. Random and (001) aligned spectra of 2.0 MeV 4 He^+ ions backscattered from a 1700 Å YBCO film on $\text{CeO}_2/\text{YSZ}/\text{Si}$. χ_{min} is 5%. The steep increase in the channeled yield around 1.7 MeV is due to Ce in the buffer layer. Minimum yields were calculated at the energy indicated by an arrow in the figure.

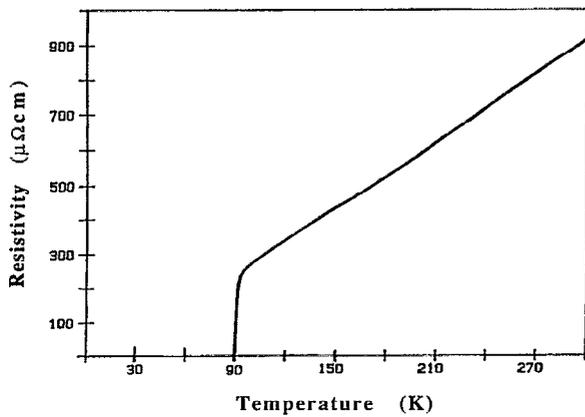


FIG. 2. Resistivity vs temperature for a 1500 Å YBCO film on CeO₂/YSZ/Si. The film has a high normal state resistivity due to fractures.

process created a thin oxide layer which embedded any organic molecules or metal atoms on the surface. A spin etch of HF:CH₃COOH:H₂O (1:10:1) removed the oxide layer and left hydrogen terminated Si.¹² The substrate was then transformed into the laser deposition chamber. Multiple laser ablation targets were mounted on a rotating polygon, and a 308 nm XeCl excimer laser generated an energy density on the targets of 1.3 J/cm² with each pulse of 17 ns. The laser firing rate was 5–6 Hz. The deposition process is described in more detail elsewhere.¹³ The base pressure was 1–2×10⁻⁷ Torr. The silicon substrates were quickly heated to 800 °C and the growth of the YSZ layer started at an O₂ pressure of 2×10⁻⁴ Torr. A deposition rate of about 0.23 Å/pulse gave the best results.

The thickness of the deposited layers varied by about 25% from the middle to the edge of the layer, and too little YSZ resulted in a reaction between the YBCO and the Si. A minimum of 300 Å YSZ was needed in order to ensure good YBCO quality over an area of 12×12 mm².

The best films were obtained with YSZ (ZrO₂ with Y₂O₃) targets with a Y₂O₃ content of 9 and 9.5 mol. %.¹⁴ The χ_{\min} of YBCO deposited directly on YSZ was typically 12%–15%. It was related to the number of YBCO in-plane orientations; x-ray ϕ scans revealed that the best crystallinity YBCO films had the [110]_{YBCO}/[100]_{YSZ} orientation only. A more detailed investigation of in-plane epitaxy of YBCO films on YSZ has been reported by Fork *et al.*¹⁵ We found that the x-ray rocking curve full width half-maximum (FWHM) did not necessarily correlate with the RBS minimum yields. A small FWHM was a necessary but not sufficient condition for a high crystallinity film. The χ_{\min} is a better measure of overall crystallinity since different phases or orientations of the material necessarily increase the channeled yield. Thus, all the films with a good χ_{\min} (<10%) had x-ray FWHM in the range 0.22° to 0.40°. In Fig. 3, a typical θ -2 θ scan shows films with the desired out-of-plane orientations YSZ(001) and YBCO(001) only.

Growing a thin layer (80 Å) of CeO₂ between the YSZ and the YBCO layers improved the YBCO χ_{\min} to 5%. The reason is that the lattice mismatch at the YBCO growth temperature is only 1% between YBCO and CeO₂ compared to

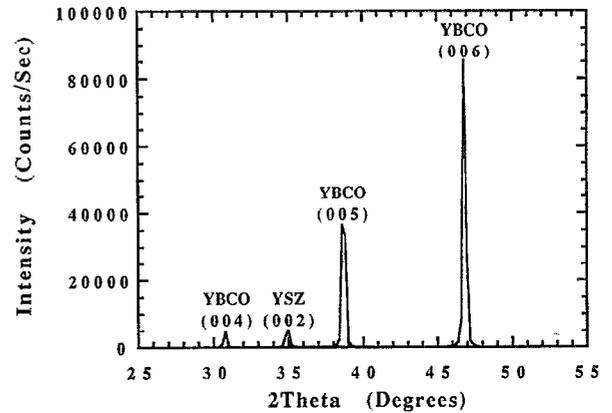


FIG. 3. X-ray θ -2 θ spectrum of a 1700 Å YBCO film on CeO₂/YSZ/Si. The YBCO (006) peak has a rocking curve FWHM of 0.23°.

6.4% between YBCO and YSZ. Both YSZ and CeO₂ have the cubic fluorite structure, and CeO₂ grew in the orientation CeO₂(001)/YSZ(001); [100]_{CeO₂}/[100]_{YSZ}. The YBCO orientation was YBCO(001)/CeO₂(001); [110]_{YBCO}/[100]_{CeO₂}. The growth parameters for the CeO₂ layer were 0.2 Torr O₂ pressure, 780 °C and a growth rate of 1 Å/pulse. The YBCO parameters were 0.2 Torr O₂ pressure, 780 °C and a growth rate of 0.25 Å/pulse. The film was then cooled to ~50 °C in 400 Torr O₂. The crystallinity of the YBCO film was extremely sensitive to the YBCO growth parameters, but did not change much with buffer layer growth parameters. Films thicker than about 500 Å developed fractures because of the stress on the film. Investigations of this effect have been described previously.¹³

In making Si membranes we took advantage of the fact that there are several etches which have much reduced etch rates in heavily B-doped Si.^{16,17} The idea was to remove the bulk of the Si from a small area on the back of the sample and then etch away the remaining few micrometers down to the B-doped layer using a selective etch. In this way we could create a uniform membrane a few mm in diameter.

Thus, prior to YSZ-CeO₂-YBCO film growth we had the substrate Si wafers B implanted to a peak concentration of 9×10¹⁹ atoms/cm³ at either 4000 or 6000 Å into the Si, which corresponded to an implantation energy of 120 or 190 keV. At such energies there is little B at the surface. We used rapid thermal annealing at 1000 °C for 10 s to regrow a high quality crystalline Si surface. Films were then deposited as described above. χ_{\min} for these YBCO films grown on B implanted Si was typically 6%–7%.

To remove the Si from the back we used two chemical etches. The first one was an isotropic acid etch that removed all but a few micrometers of the Si. The sample was mounted on a 1-in.-diam teflon disk with beeswax. The wax protected the YBCO film (facing down) and most of the Si back side (now facing up) except for a wax-free 8 mm circle centered on the middle of the teflon disk. The teflon disk was then put into a mixture of HNO₃:CH₃COOH:HF (50.0:11.5:5.5) in a tilted, rotating beaker and was allowed to roll inside this beaker for about 2 h. This process etched a U-shaped hole with a rather flat region in the middle. When the flat region

became transparent (thickness of a few micrometers) the etch was stopped by adding H₂O. The beeswax was then removed with hot trichloroethene (TCE).

A second etch was necessary to etch down to the B-doped layer and thus make a uniformly thick membrane. We used 35 wt. % KOH in H₂O, with isopropanol added so there was always a meniscus on top. The etch rate is ≈ 1 $\mu\text{m}/\text{min}$ at 50 °C and decreases by a factor of 20 at a B concentration of 10²⁰ atoms/cm³. This was sufficient for making 1–2-mm-diam membranes.

To protect the YBCO film during the last etch, a very thin layer of wax was melted onto the sample. It completely covered the YBCO film while leaving the Si edge around the film exposed. If the wax was too thick bubbles would form at the wax-YBCO interface, and any bubbles close to the membrane would cause it to break. The temperature of the KOH etch was held at around 50 °C; at lower temperatures the etch rate became extremely slow, while at temperatures higher than about 55 °C the etch rate became too fast and the membranes would break.

After etching we did x-ray scans on the membranes, and found that neither the θ -2 θ spectrum nor the rocking curve FWHM had changed. RBS measurements on the membranes gave χ_{min} of 6%–7%. Four-point probe resistance measurements on the film around the membrane showed a sharp superconducting transition, verifying that the wax had not altered the YBCO film in any way. Patterning of the membranes would be an interesting next step, and would allow for T_c measurements on the membrane only. None of the membranes broke on cooling to 50 K.

In conclusion we have made high quality crystalline YBCO films on a thin Si membrane. To make the membranes, we boron implanted Si substrates, grew YBCO films by pulsed laser deposition, and etched the Si substrates from the back using two different chemical etches. The resulting composition of the samples was 4000 or 6000 Å Si, 300 Å YSZ, 80 Å CeO₂, and 1500–3000 Å YBCO.

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¹ R. P. Sharma, L. E. Rehn, P. M. Baldo, and J. Z. Liu, *Phys. Rev. Lett.* **62**, 2869 (1989).

² T. Haga, K. Yamaya, and Y. Abe, *Phys. Rev. B* **41**, 826 (1990).

³ H. A. Mook, M. Mostoller, J. A. Harvey, N. W. Hill, B. C. Chakoumakos, and B. C. Sales, *Phys. Rev. Lett.* **65**, 2712 (1990).

⁴ L. Vestergaard Hau and J. U. Andersen, *Phys. Rev. A* **47**, 4007 (1993).

⁵ L. V. Hau, E. Laegsgaard, and J. U. Andersen, *Nucl. Instrum. Methods B* **48**, 244 (1990).

⁶ S. Verghese, P. L. Richards, K. Char, D. K. Fork, and T. H. Geballe, *J. Appl. Phys.* **71**, 2491 (1992).

⁷ M. P. Siegal, J. M. Phillips, R. B. van Dover, T. H. Tiefel, and J. H. Marshall, *J. Appl. Phys.* **68**, 6353 (1990).

⁸ R. Ramesh, D. Hwang, T. S. Ravi, A. Inam, J. B. Barner, L. Nazar, S. W. Chan, C. Y. Chen, B. Dutta, T. Venkatesan, and X. D. Wu, *Appl. Phys. Lett.* **56**, 2243 (1990).

⁹ L. P. Lee, M. J. Burns, and K. Char, *Appl. Phys. Lett.* **61**, 2706 (1992).

¹⁰ D. K. Fork, D. B. Fenner, R. W. Barton, J. M. Phillips, G. A. N. Connell, J. B. Boyce, and T. H. Geballe, *Appl. Phys. Lett.* **57**, 1161 (1990).

¹¹ C. A. Copetti, H. Soltner, J. Schubert, W. Zander, O. Hollricher, Ch. Buchal, H. Schulz, N. Tellmann, and N. Klein, *Appl. Phys. Lett.* **63**, 1429 (1993).

¹² D. B. Fenner, D. K. Biegelsen, and R. D. Bringans, *J. Appl. Phys.* **66**, 419 (1989).

¹³ D. K. Fork, D. B. Fenner, A. Barrera, J. M. Phillips, T. H. Geballe, G. A. N. Connell, and J. B. Boyce, *IEEE Trans. Appl. Supercond.* **1**, 67 (1991).

¹⁴ Most consistent results obtained with high purity homemade YSZ targets or commercial YSZ targets from Ceres Corporation.

¹⁵ D. K. Fork, S. M. Garrison, M. Hawley, and T. H. Geballe, *J. Mater. Res.* **7**, 1641 (1992).

¹⁶ K. E. Petersen, *Proc. IEEE* **70**, 420 (1982).

¹⁷ K. E. Bean, *IEEE Trans. Electron Devices* **ED-25**, 1185 (1978).