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Crystalline perfection of as-deposited high-T_c superconducting thin-film surfaces: Ion channeling and x-ray photoelectron spectroscopy study

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Axial ion channeling in as-deposited high-T_c Y-Ba-Cu oxide superconducting thin films on (100) $SrTiO_3$ and x-ray photoelectron spectroscopy (XPS) on the film surfaces were performed. The angular yield profile near the film surface for Ba and the surface peak intensity were measured using 3-MeV He ions. For channeling normal to the substrate, a minimum yield of 7%, compared to ~2–3% for single crystals, was obtained. The results of ion channeling and XPS studies indicate that the as-deposited films have good crystallinity as well as stoichiometry to within ~1 nm of the film surface.

High-T_c superconducting thin films with J_c over 1×10^6 A/cm^2 at 77 K have been prepared,[1,2] and it was recently demonstrated that films with good superconducting properties and smooth surfaces could be fabricated only by a low-temperature deposition process.[3] For electronic applications of the new high-T_c superconductors it is crucial to have films with smooth superconducting surfaces in order to delineate micron and submicron features and to fabricate junction devices consisting of superconducting layers sandwiching an insulator or a normal metal. In these junctions, the superconducting material must have a high-T_c superconducting layer right up to the interface to within the superconducting coherence length of the material, which is ~0.43 nm along the c axis and ~3.1 nm in the a-b plane.[4] By utilizing surface sensitive techniques such as x-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS) in the channeling mode, it is possible to obtain information about the film surfaces and interfaces. The channeling technique has been widely used to characterize various crystalline materials, single crystals with some disordered regions, polycrystalline films on single-crystal substrates and so on.[5] Recently, Stoffel, Morris, Bonner, and Wilkens[6] showed that single crystals of $YBa_2Cu_3O_x$ have excellent crystallinity and stoichiometry to within about 1 nm of the surfaces by using RBS in the channeling mode. XPS has also been utilized to obtain information on the chemical state of the surface layer of the superconductors.[7] In this communication, we report the results of axial ion channeling and XPS studies on as-deposited high-T_c Y-Ba-Cu oxide superconducting thin films on (100) $SrTiO_3$, and show that the crystallinity and composition of the material is good up to the surface to within 1 nm, which is comparable to the superconducting coherence length.

$YBa_2Cu_3O_x$ films were prepared using a single-target pulsed laser deposition technique.[3,8] More recently, as-deposited superconducting thin films with zero-resistance temperatures of about 90 K on $SrTiO_3$ and over 77 K on sapphire were fabricated at a substrate holder temperature of 650 °C (the quoted temperature is measured on the substrate holder rather than on the substrate surface where the measured temperature is at least 100 °C lower). The details of the new preparation process will be published elsewhere.[9] RBS and channeling measurements were made on a dual-axis goniometer using 3-MeV He^{2+} ions with a 1-mm beam size. XPS spectra were taken on as-deposited films without any cleaning steps. The spectra were recorded in a KRATOS XSAM800 instrument equipped with a multichannel detector. The resolution of the XPS system was set to yield a peak width of 0.85 eV for the Ag($3d_{5/2}$) line.

In Fig. 1. we show a random RBS spectrum, and an aligned channeling spectrum for a ~4100-Å as-deposited Y-Ba-Cu oxide superconducing thin film on (100) $SrTiO_3$. The solid line in the figure is a simulation of $Y_1Ba_2Cu_3O_x/SrTiO_3$ using the RUMP program.[10] The result shows that the film has a composition close to ideal stoichiometry through the entire thickness. The aligned channeling spectrum shows a large reduction in the backscattering yield in the film and about 50% reduction (which depends on the film thickness) in the yield from the substrate. The minimum yield for Ba, measured near the surface, is ~7% compared to 3.5% for channeling of 1.66-MeV He^+ on single crystals.[6] Although the ion energy for channeling is different from that of Ref. 6, the comparison shows that the as-deposited films have good long-range crystalline order. The minimum yield of 7% is the smallest value reported for the high-T_c superconducting thin films on any substrate. X-ray diffraction study[9]

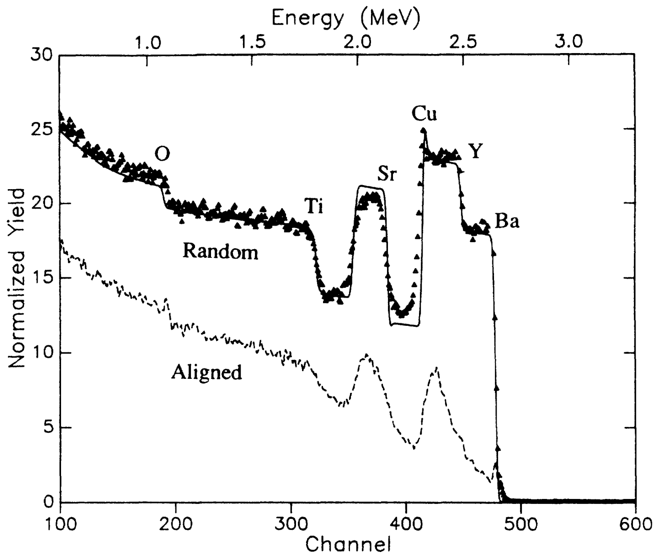

FIG. 1. Random and aligned RBS (3-MeV He^{2+})spectra for an as-deposited Y-Ba-Cu oxide superconducting thin film on $SrTiO_3$. The solid line is a simulation of 4100-Å $Y_1Ba_2Cu_3O_{7-x}/SrTiO_3$.

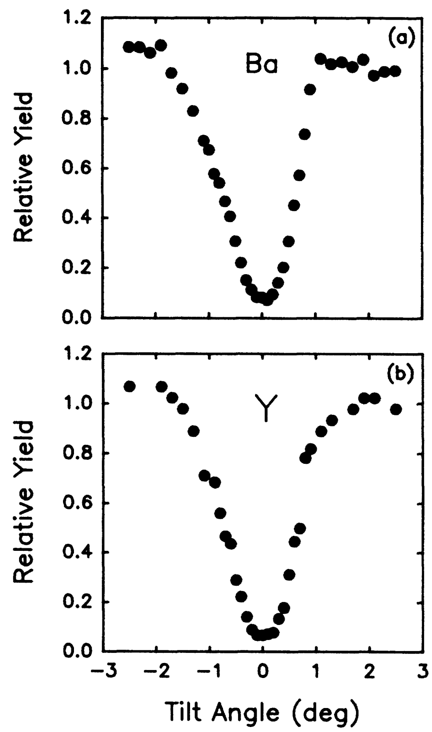

FIG. 2. Angular yield profile using 3-MeV He ions. (a) Ba and (b) Y. The full angular width is about 1.5° for both Ba and Y.

shows that the as-deposited films on (100) $SrTiO_3$ are oriented with the c axis perpendicular to the substrate surface. The 7% minimum yield suggests that at least 95% of the c axis in the film is oriented. The rapid increase in the channeling yield from the film indicates that in the film there is a large number of defects, which causes dechanneling of the He ions. Preliminary transmission electron microscopy (TEM) studies show existence of stacking faults in the films.

The angular yield of Ba was measured and the results are shown in Fig. 2(a). The angular profile is not symmetric due to ion beam damage. The angular yield was measured from positive to negative tilt angles. A full angular width ($2\Psi_{1/2}$) is $\sim 1.5°$ for a 3-MeV He^+ ion energy. The $\Psi_{1/2}$ is proportional to $(1/E)^{1/2}$, where E is the ion energy.[5] Using the full angular width of 2.3° measured on single crystals made at 1.66-MeV He^+ ions,[5] we deduce 1.7° for the full angular width at 3 MeV, which is close to the number measured. Angular yield measurements for Y and Cu were attempted. Because of a large background due to backscattering from the heavier elements Ba and the substrate Sr, only the Y angular yield could be estimated. The angular profile for Y is shown in Fig. 2(b). The full angular width at 3 MeV is about 1.5°, which is close to the results from a Monte Carlo simulation.[11] The minimum yield for Y is difficult to estimate accurately because the background correction is needed.

For a textured polycrystalline material, assuming a Gaussian distribution of crystallite orientations, it has been shown[12] that

$$\chi = 1 - \frac{1-\chi_0}{1+(\sigma/\overline{\Psi}^0_{1/2})^2 \ln 2},$$

where χ is the minimum yield for the polycrystalline material, σ is the standard deviation of the spread in the crystalline orientations (mosaicity), $\overline{\Psi}^0_{1/2}$ and χ_0 are the half width for the angular profile and minimum yield for channeling in the single crystal. It has been shown that the minimum yield is a function of ion energy.[5] We estimate the minimum yield for Y-Ba-Cu-O single crystals at 3 MeV to be $\sim 2\%$ using the data from Ref. 6. Taking $\chi = 7\%$, $\chi_0 = 2\%$, and $\Psi^0_{1/2} = 0.85°$ (deduced from the data in the Ref. 6), σ, the mosaicity, is estimated to be less than 0.24° showing that the film has grown epitaxially on the $SrTiO_3$ substrate during deposition.

The most interesting feature for us in the channeling spectrum is the Ba surface peak. The area under the surface peak is proportional to the density of atoms on the surface and is a measure of the crystalline order at the surface.[5] A disordered surface layer of ~ 1 nm was estimated at the surface based on the surface peak assuming the 1:2:3 composition.

The surface layer composition and thickness can also be determined using XPS. We found that the surface layer of as-deposited films is barium enriched. In Fig. 3(a), Mg $K\alpha$ XPS data for the Ba($3d_{5/2}$) region for the 1:2:3 compound film at two different take-off angles, 15° (curve 1) and 85° (curve 2), are given. For comparison, the Ba($3d_{5/2}$) region from an *in situ,* freshly scraped high-T_c superconducting $Y_1Ba_2Cu_3O_{7-x}$ pellet is also shown (curve 3). The Ba($3d$) region shows two peaks, one at 778 eV and the other at 780 eV. These two peaks are resolved into two Gaussian distributions of equal widths (1.7 eV), as shown in Fig. 3(b). The peak at 778 eV is due to Ba in the 1:2:3 phase.[13] At a low angle of collection when only the surface region is examined, the peak at 780 eV is the largest (curve 1) and, therefore, the 780 eV peak is due to Ba at the surface. The corresponding O($1s$)

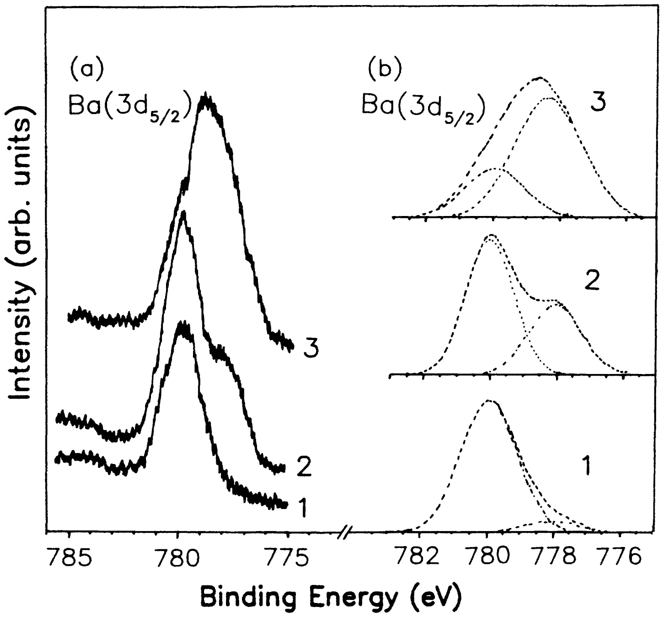

FIG. 3 XPS spectra for the Ba($3d_{5/2}$) region. (a) For an as-deposited superconducting film at two different photoelectron take-off angles: 15° (curve 1) and 85° (curve 2), and for a bulk superconductor (curve 3). (b) Two Gaussian distribution fitting for (a) with peak energies of 778 and 780 eV, and equal width of 1.7 eV.

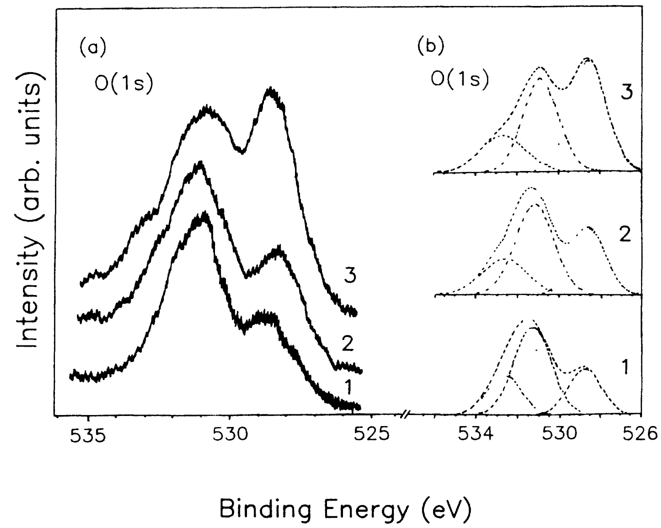

FIG. 4. O($1s$) XPS spectra (a) for an as-deposited superconducting thin film at two different photoelectron take-off angles: 15° (curve 1) and 85° (curve 2), and for a bulk superconductor (curve 3). (b) Deconvolution of the XPS spectra in (a) using three Gaussian distributions at peak energies of 528.5, 531, and 532.7 eV, respectively.

region is shown in Fig. 4. Clearly, we see three O($1s$) peaks at 528.5, 531, and 532.7 eV in the 1:2:3 pellet as well as 1:2:3 film at a collection angle of 85°. These three peaks are assigned to O^{2-}, O^{1-}, and $O_2{}^{2-}$ types of oxygen.[14] However, in the film, the intensity of the 531-eV peak is higher which correlates with the surface Ba. At 15°, the 531-eV peak intensity relatively increases (curve 1) and this further confirms its association with surface Ba ions. Even at the low collection angle, significant intensities at 528.5 and 532.7 eV are seen because the mean escape depth for the O($1s$) photoelectron is larger than that for the Ba($3d$) one. The XPS spectrum for C($1s$) shows a small peak at 288.5 eV attributable to carbonate ions. The intensity of oxygen due to $CO_3{}^{2-}$ calculated from the C($1s$) signal does not account for more than 5% of the total intensity in the 531-eV region. Further, Ba($3d_{5/2}$) peaks in the case of $BaCO_3$ and $Ba(OH)_2$ appear at 782 eV and we do not see a peak in this region. Therefore, the 780-eV Ba($3d_{5/2}$) peak is associated with the 531-eV O($1s$) peak and represents some form of Ba oxide. It is known that Cu (which is also present in the surface layer) with Ba gives O($1s$) and Ba($3d$) at 531 and 780 eV, respectively.[15] It should be noted that in films with Y:Ba:Cu in the 1:2:3 ratio but in which the 1:2:3 superconducting phase is not formed, mainly the 531- and 780-eV peaks in O($1s$) and Ba($3d_{5/2}$) are seen and the 528.5- and 778-eV peaks develop only after an oxygen anneal.[16] We therefore conclude that these two peaks are associated with the superconducting 1:2:3 phase. If we assume that the superconducting thin film has perfect 1:2:3 crystallinity, the metal elements, counting along the c axis of the film from the surface, will have the following sequences: (1) Cu-Ba-Cu-Y, (2) Y-Cu-Ba-Cu, (3) Cu-Y-Cu-Ba, and (4) Ba-Cu-Y-Cu depending upon which atomic layer terminates the surface. The film will exhibit both in channeling and XPS spectra a Cu and Ba enriched surface layer if the sequence is (1) or (4), while the surface will be Cu and Y enriched in the case of (2) or (3). Under the assumption of perfect crystallinity, our films are likely to have a surface elemental sequence of (1) or (4) based on the XPS results. Moreover, since Ba is the most reactive element of all the three metals, the film surface may be Ba enriched due to the formation of barium oxides on the surface. The surface composition of the film was estimated from the intensities of Ba($3d$), Cu($2p$), and Y($3d$) peaks. At the 85° angle the composition was $Y_{0.88}Ba_{2.05}Cu_3O_x$ while at the low collection angle of 15°, the composition was $Y_{0.48}Ba_{2.06}Cu_3O_x$.

The mean escape depth for the Ba($3d$) photoelectron is of the order of 15 Å (Ref. 17) and at this escape depth significant superconducting phase can be detected. Only at a take-off angle of 15° which corresponds to a sampling depth of 10 Å, do we lose the bulk contribution. We estimate the thickness of the barium enriched surface layer to be about 10 Å, which is consistent with the result from the ion channeling study. This experiment therefore clearly demonstrates that the as-deposited superconducting films (grown by the laser deposition technique) have 1:2:3 stoichiometry up to ~10 Å of the film surface.

In summary, using axial ion channeling and XPS techniques, it was found that as-deposited superconducting thin films made by laser deposition have good crystallinity as well as composition to within ~10 Å of the film surface. Work is being pursued to improve and characterize the surface quality even further, and to check the tunneling properties of the surfaces prepared by the laser technique.

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[1]P. M. Mankiewich, J. H. Scofield, W. J. Skocpol, R. E. Howard, A. H. Dayem, and E. Good, Appl. Phys. Lett. **51**, 1753 (1987).

[2]Y. Enomoto, T. Murakami, M. Suzuki, and K. Moriwaki, Jpn. J. Appl. Phys. **26**, L1248 (1987).

[3]X. D. Wu, A. Inam, T. Venkatesan, C. C. Chang, E. W. Chase, P. Barboux, J. M. Tarascon, and B. Wilkens, Appl. Phys. Lett. **52**, 754 (1988).

[4]W. J. Gallagher, T. K. Worthington, T. R. Dinger, F. Holtberg, D. L. Kaiser, and R. L. Sandstrom, in *Superconductivity in Highly Correlated Fermion System,* edited by M. Tachiki, Y. Muto, and S. Maekawa (North-Holland, Amsterdam, 1987), pp. 228–232.

[5]L. C. Feldman, J. W. Mayer, and S. T. Picraux, *Materials Analysis by Ion Channeling* (Academic, New York, 1982).

[6]N. G. Stoffel, P. A. Morris, W. A. Bonner, and B. J. Wilkens, Phys. Rev. B **37**, 2297 (1988).

[7]J. Halbritter, P. Walk, H.-J. Mathes, B. Haeuser, and H. Rogalla, in *Proceedings of the International Conference on High-T_c Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, 1988,* edited by J. Müller and J. L. Olsen [Physica C **153 – 155**, 127 (1988)].

[8]D. Dijkkamp, T. Venkatesan, X. D. Wu, S. A. Shaheen, N. Jisrawi, Y. H. Min-Lee, W. L. McLean, and M. Croft, Appl. Phys. Lett. **51**, 619 (1987); X. D. Wu, D. Dijkkamp, S. B. Ogale, A. Inam, E. W. Chase, P. F. Miceli, C. C. Chang, J. M. Tarascon, and T. Venkatesan, Appl. Phys. Lett. **51**, 861 (1987).

[9]A. Inam, M. S. Hegde, X. D. Wu, T. Vankatesan, P. England, P. F. Miceli, E. W. Chase, C. C. Chang, J. M. Tarascon, and J. B. Watchman, Appl. Phys. Lett. **53**, 908 (1988).

[10]L. R. Doolittle, Nucl. Instrum. Methods Phys. Res. Sect. B **9**, 344 (1985).

[11]N. G. Stoffel (private communication).

[12]H. Ishiwara and S. Furukawa, J. Appl. Phys. **47**, 1686 (1976).

[13]P. Steiner, V. Kinsinger, I. Sander, B. Siegwart, S. Hufner, and C. Politis, Z. Phys. B **67**, 19 (1987); W. K. Ford, C. T. Chen, J. Anderson, J. Kwo, S. H. Liou, M. Hong, G. V. Rubenacker, and J. E. Drumheller, Phys. Rev. B **37**, 7924 (1988).

[14]D. D. Sarma, K. Sreedhar, P. Ganguly, and C. N. R. Rao, Phys. Rev. B **36**, 2371 (1987).

[15]M. Ayyoob and M. S. Hegde, Surf. Sci. **147**, 361 (1984).

[16]M. S. Hedge (unpublished).

[17]S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Sci. **192**, L849 (1987).