1-16-1990

Composition Depth Profiles of High Temperature Superconducting Materials by Energetic Elastic Backscattering

C. R. Gossett
SFA, Inc.

Utah State University
MERRILL-CAZIER LIBRARY

COMPOSITION DEPTH PROFILES OF HIGH TEMPERATURE SUPERCONDUCTING MATERIALS BY ENERGETIC ELASTIC BACKSCATTERING

C.R. Gossett*

SFA, Inc, Landover, MD
and
Naval Research Laboratory, Washington, D.C.

Abstract

A review is given of the application of high energy elastic backscattering spectrometry techniques for profiling high-temperature superconducting (HTSC) materials in thin film form. The use of higher bombarding ion energies provides most of the advantages of the more common lower energy or Rutherford backscattering (RBS) but additionally allows profiling to a greater thickness and, by a much larger sensitivity for light elements, permits profiling carbon and oxygen in the presence of heavier substrates. Examples for HTSC materials are given.

* Address for correspondence:

Surface Modification Branch
Condensed Matter and Radiation Sciences Division
Code 4670
U.S. Naval Research Laboratory
4555 Overlook Ave, S.W.
Washington, D.C. 20375-5000

Introduction

An area of application of the new high-temperature superconducting (HTSC) materials which many experts feel will be first to be exploited is that of thin films, principally with electronic technological uses. However, the development of such thin-film devices of HTSC materials has proved to be difficult; and much effort has been expended in developing appropriate deposition methods, noninteracting substrates, and annealing techniques. The key to superconducting behavior lies in the appropriate structure, but this is achieved only when the necessary stoichiometry (or relative composition) of the constituents is present.

This paper describes the use of higher bombarding ion energies for elastic backscattering, which has proved to be very successful in determining not only the average composition of the elements making up the film, but also the profile of the composition as a function of depth in the film. The later measurements have proved invaluable in developing HTSC films because the composition depth profile exposes many of the difficulties which arise due to the interfacial reactions, diffusion of the constituents, or tendency to aggregate. These problems may typically occur, especially in connection with the high-temperature annealing usually necessary to achieve the desired structure.

The use of elastic backscattering (2,4) in the 1-3 MeV range of bombarding energies, commonly called Rutherford backscattering spectrometry (RBS) in the literature, has proved itself preeminent in the nondestructive profiling of thin films over the last decade. This technique has also been widely applied to HTSC thin films and there are many examples in the current and recent literature, which are not reviewed here.

Although the use of higher bombarding energies to gain greater mass separation as well as provide certain narrow resonances in non- Rutherford cross sections for profiling has been reported, the potential for profiling the common light elements C, N, and O by elastic backscattering in the presence of heavier elements, due to the enhanced non-Rutherford cross sections at higher energies, has only recently been recognized or applied. This report reviews the application of such high energy elastic backscattering methods to the burgeoning research field of thin film HTSC materials. A comparison of spectra from the

present high energy elastic backscattering technique and low energy (RBS) is presented in ref. 6.

The use of higher energy for such applications has required the selection of particular bombarding energies for which the common light element cross sections (primarily oxygen for HTSC) are relatively smoothly varying. This development effort occurred independently at the Naval Research Laboratory (6) and at the Sandia National Laboratory (1). Further valuable development occurred at the Los Alamos National Laboratory (7), as a result of the enhancement found in the Sandia work.

Method

One of the major limitations of low energy elastic backscattering, where typically cross sections for all but the very lightest elements (Li, Be and B) remain Rutherford (or electrostatic), is the squared dependence on the atomic number of the Rutherford cross section. As a consequence of this, the common light elements C, N and O may be detected with considerably less sensitivity than heavier elements. This problem is exacerbated by the kinematic relationships of elastic backscattering which provide that the distributions arising by scattering from these light elements appear in a backscattering spectrum at lower energies than those for heavier elements. Thus, the light element distributions may typically be superimposed upon the distributions from heavier elements, particularly from thick samples or substrates. By decreasing the signal to noise this effect often further reduces the sensitivity for detecting and profiling the common light elements.

An additional consideration in profiling thin films is the importance of the separation of the distributions for each element in the backscattering spectrum. These distributions, positioned according to the kinematics of the backscattering, arise from energy loss in the material; and their extent in terms of the energy of the observed scattered ion depends upon the thickness of the film and the stopping powers of the elements. Overlap of distributions is inherently ambiguous, as an individual event cannot be distinguished as the scattering by a given element near the surface from that by a somewhat heavier element deeper within the sample. Obviously complete separation of the distributions for elements in the films is desirable, for in such cases the measurement of the relative composition of the elements in the film may depend only upon the integration of the distributions and the Rutherford cross sections, which are themselves calculable with good precision.

Low energy elastic backscattering has been extensively used to profile thin-film HTSC materials, because the constituents of the some of the most promising ceramic materials, the yttrium-barium-copper-oxides (YBCO) and bismuth-strontium-calcium-copper-oxide (BSCCO) materials, fortuitously have combinations of masses which produce more or less uniform energy separation between their high energy (surface) edges, thus reducing the opportunity for overlap of the distributions. However, at ordinary RBS energy (2 MeV) the films may not be thicker than about 100 nm (1000 Å) without producing overlap (see ref. 6).

At least in the earlier stages of development, it was difficult to obtain films this thin which were super-conducting; thus, there was an impetus for measuring thicker films. At NRL we chose the method of going to higher energies to achieve this. The energy separation between two different elements in the spectrum is a direct function of the bombarding ion energy. Therefore, if the bombarding energy is raised, a comparable increase in resolvable thickness will be achieved. In addition, because the stopping powers are a monotonically decreasing function of energy in this region, the effective thickness will be further increased at higher energies. Thus, by increasing the bombarding energy from 2.0 to 6.2 MeV we obtain an improvement in resolvable thickness of a factor of about 5, allowing unambiguous profiling of thin films of HTSC materials to about 0.5 μ thickness.

At the higher energies an additional benefit was found, which has since proved to be the dominant reason for using the method: the advantage that the cross sections for the light elements C, N, and O proved to be considerably enhanced over Rutherford cross sections, depending upon the choice of bombarding energy and scattering angle. This effect arises because at the higher energies, at least for light elements, the distance of closest approach has come into the range of the nuclear forces, and the mechanism is no longer an electrostatic interaction but is a nuclear interaction.

Unlike the Rutherford (electrostatic) interaction with its smooth and predictable behavior, nuclear interactions depend upon the parameters of the specific nuclear energy levels involved in complicated ways. Thus, the cross section is no longer readily calculable as in the Rutherford case, but must be calibrated under the particular conditions of the profiling experiment. The loss of this simplicity is overcome by the enhanced yields for the light elements (a factor of 10 for oxygen at 6.2 MeV) which makes it possible to profile these elements with greater precision, even when superimposed on a heavier substrate, such as a preferable material for HTSC thin films, $SrTiO_3$.

Because the nuclear cross sections may vary strongly with energy in some regions, it is necessary to find bombarding energy regions where the cross section is nearly constant, or at least smoothly varying over an energy range appropriate to the thickness of the thin film, in order to take advantage of the enhancement for profiling. It is here that the choices made in different laboratories have varied. The approach at Sandia (1) and Los Alamos (7) has been to utilize a fairly extensive, relatively flat region of cross section just below about 8.9 MeV. This results in a high enhancement of a factor of 22-25 for oxygen over the Rutherford cross sections.

We have chosen a lower bombarding energy of 6.2 MeV which produces a smoothly varying region above a dip in the yield at about 6.0 MeV and below a rise above 6.2 MeV (as shown in ref. 6). This region is sufficiently broad to more than cover the thickness which can be depth resolved for the metallic members of the common HTSC Materials. The enhancement by a factor of about 10 is less than that reported for 8.8 MeV, but the 6.2 MeV bombard-

ing energy also produces a smoothly varying cross section and considerable enhancement (factor of 50) for carbon (example in ref. 6). The Sandia and Los Alamos groups do not report on carbon enhancement at their energy. Although we do not commonly observe carbon in HTSC films except as a surface contaminant, we find this enhancement of sensitivity very useful to assure researchers of the absence of carbon with the film, because it is well known that small amounts of carbon have deleterious effects in HTSC materials.

The principal reason for restricting to the lower energy, however, is to keep the cross sections for the metallic elements of the HTSC film in the range of Rutherford interaction. The Los Alamos group reports (7) that deviations from Rutherford are observed for copper above about 7 MeV and for yttrium above about 8 MeV with the barium expected to be Rutherford to 9 MeV or greater. In the determination of profiles by computer analysis of the spectra (see, for instance, ref. 3) from our HTSC samples, we find it a considerable advantage to assure that these metallic elements remain Rutherford, obviating a less certain correction for the experimentally observed ratio to Rutherford. However, it should be noted that at a bombarding energy of 6.2 MeV calcium and lighter elements are non-Rutherford.

In summary, the advantages of bombarding at higher than normal energies for low energy backscattering are greater depth of coverage with full resolution for most HTSC materials and the considerable enhancement of the cross sections for light elements while (in the case of 6.2 MeV bombardment) maintaining Rutherford cross sections for the metallic elements. Although it is not of particular interest to HTSC materials, we have also reported (5) energies at which the cross section for nitrogen is also reasonably smoothly varying and for which an enhancement of nearly a factor of ten is shown. That article also provides a parameterization of the ratios to Rutherford for the cross sections for C, N and O at the bombarding energies we suggest. These ratios may be used in calculations or simulation programs, for instance RUMP (3), to evaluate profiles. However, we recommend the measurement of those ratios using stoichiometric standards in the individual researchers' experimental configuration, since they are angle dependent.

The disadvantages of using the higher energy elastic scattering include the above mentioned necessity of measuring the ratio to Rutherford for the light elements under the experimental conditions used in the HTSC profiling. Additionally, at high energies there is a problem of using substrates containing elements in the region between oxygen and titanium, where the cross sections are not only non-Rutherford, but are generally strongly varying with energy. Thus, the common substrate components Mg, Si and Al are so strongly varying as to make the determination of the oxygen concentration in the HTSC film difficult or impossible except at the high energy edge. When the oxygen profile for the whole film thickness is required, we prefer to use substrates for which all the elements other

than oxygen remain Rutherford, such as $SrTiO_3$ or yttrium-stabilized zirconia.

The difficulty in profiling the common light elements in the presence of heavier elements inherent in low energy backscattering may be overcome by other methods than those reported here. Much effort has been devoted over the years to the development of nuclear reaction analysis (NRA) as an alternative, particularly for light elements. Because of the typically lower cross sections for nuclear reactions at lower energies, these methods are usually more difficult and time consuming to apply than elastic backscattering; and, because NRA is specific to one isotope only, it additionally requires obtaining a backscattering spectrum for the remaining elements of the sample. In addition, if one or both of the participating particles is a hydrogen isotope, the profiling generally lacks depth resolution due to lower stopping powers.

More recently, elastic recoil detection (ERD) employing heavier incident ions has been utilized for profiling light elements. Where the compositions are such that the recoiling element may be identified without ambiguity, this can be a fast, useful method, although the use of absorber foils leads to some degradation in depth resolution, and the depth of analysis is severely limited by the high stopping power of the incident ions. That method also requires separate elastic backscattering for profiles of other elements in the sample.

Some of the surface sensitive spectroscopies are also applicable for profiling, although they require a surface removal technique (commonly sputtering); and it has become increasingly evident that preferential sputtering and other inherent artifacts may present difficulties. In this laboratory, where a large number of HTSC thin-film samples have been studied in support of an extensive development program, we have found the high energy elastic backscattering the most satisfactory method in dealing with thin films of these materials.

Examples

The efficacy of the high energy elastic scattering technique is best demonstrated by examples. Those shown in Fig. 1 are taken from the large number of samples analyzed at NRL.

Figure 1a shows the spectrum of a thin-film YBCO on a $SrTiO_3$ substrate. The separation of the oxygen distribution from the smoothly varying distribution of the Sr and Ti in the substrate is indicated. This distribution may be compared with a similar determination from a single crystal $SrTiO_3$ standard defining the ratio to Rutherford for the oxygen and thus the oxygen profile of the film (see ref. 6 for details). The solid line for the metallic elements is for the computer simulation (3) fit to the data (dots) and determines the composition depth profile.

Figure 1b shows the spectrum for a nearly perfect as-deposited YBCO film on a MgO substrate. The film is very uniform, resulting in the almost flat-topped distributions, and is very nearly stoichiometric as determined from
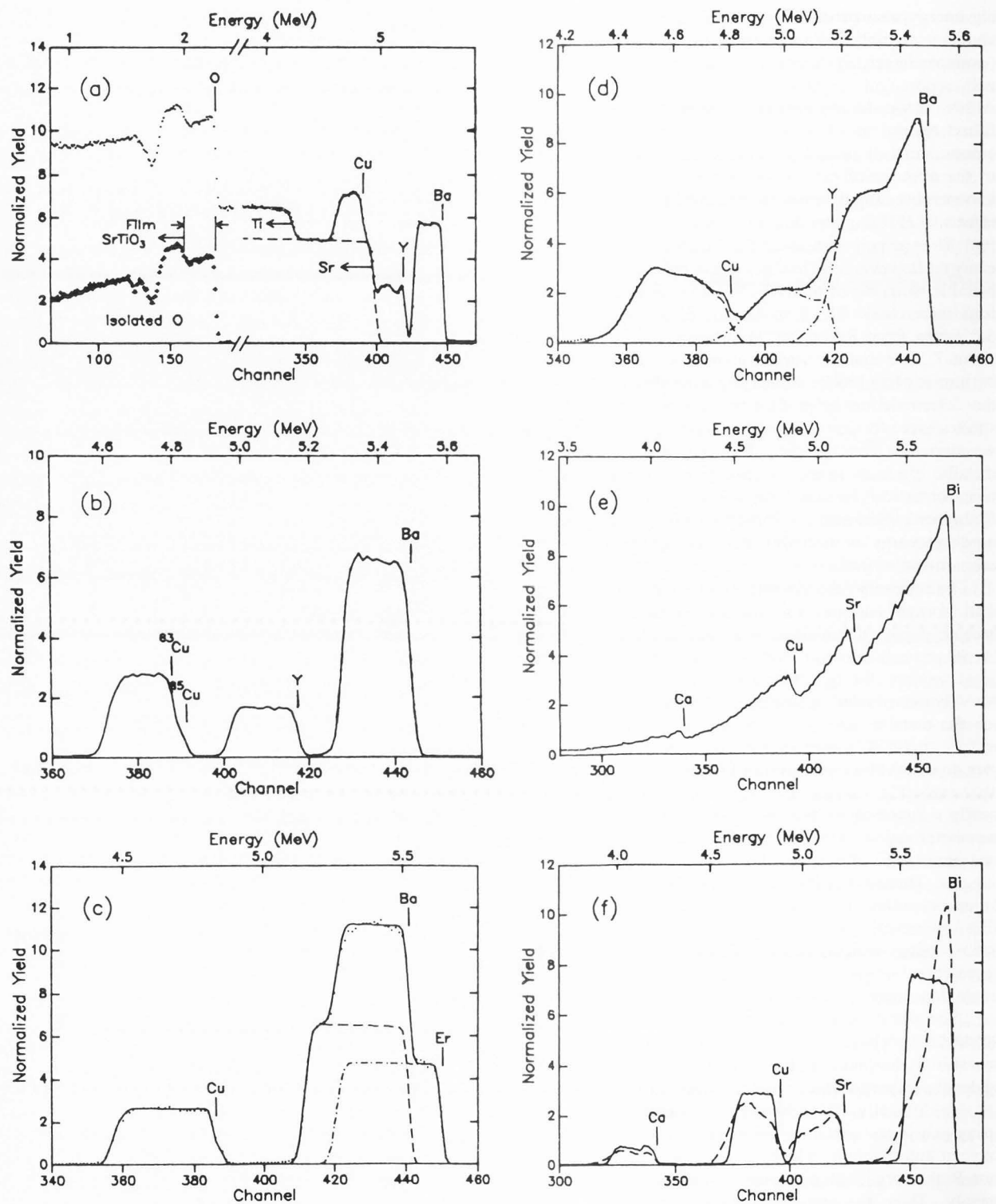
Fig. 1 — (a) through (f) examples of elastic backscattering spectra for various thin-film HTSC samples (see text "Examples" for discussion of individual spectra).

integrating the distributions. The enhanced mass separation at higher energies is demonstrated by the ^{63}Cu-^{65}Cu separation indicated, which is not observed at lower energies.

Figure 1c shows a spectrum from an erbium-barium-copper-oxide (EBCO) film, where the erbium and barium distributions overlap considerably. It is seen that, at least when the samples are reasonably uniform, the computer simulation can successfully profile the sample and separate the constituent components with little ambiguity. In this case direct integration is impossible and the stoichiometry is available only from the computer fit, which depends on the somewhat less accurately known stopping powers as well as the elastic scattering cross sections.

Figure 1d shows a more typical example of an unsuccessfully annealed sample where the considerably non-uniform and somewhat overlapping distributions are profiled using the computer simulation. The composition vs depth profile which was adjusted to provide the computer simulation fit shown in the solid line may be used to identify the problems leading to the nonuniformity in the deposition and anneal of such samples. Note that a uniform distribution would produce relatively flat-topped distributions as in fig. 1b, and the deviations from this in the observed distributions suggest diffusion of Ba toward the surface (high-energy edge). The fit is not unique in regions of overlap, and this ambiguity could be avoided by higher bombarding energies. However, this figure indicates the power of the simulation routine (3) in fitting very complex spectra, even with some overlap.

Figure 1e shows a spectrum of a type frequently seen for annealed BSCCO samples where the almost exponential dropoff from the surface for all metallic elements is characteristic of the considerable aggregation, or forming into non-planar structures, which produce very nonuniform thickness, and which may occur at the phase transition to the polycrystalline structure. This effect is readily observed by scanning electron microscopy (SEM).

Figure 1f shows for a BSCCO film the as-deposited (solid line) film and the effect of a high-temperature anneal (dashed line), which in this instance has resulted in diffusion of some of the elements without loss and a tendency toward aggregation. The structure apparent in the lowest energy (calcium) distribution is due to the non-Rutherford cross section at 6.2 MeV. The other metallic elements remain Rutherford.

Similar results have been obtained at the other laboratories where high energy elastic backscattering is used (see ref. 1 and 7, where the oxygen cross section enhancement is more prominent than shown here, as described above).

Conclusions

The examples above show that the methods of high energy elastic backscattering can be very productively applied to determining the composition depth profiles of thin films of HTSC materials, and that the resulting information may be of considerable assistance in the development of production techniques by calibrating the stoichiometry of the films and helping to diagnose the problems which plague efforts to produce thin-film superconductors of good uniformity and reproductibility.

Acknowledgements

References

1. Barbour JC, Doyle BL, Myers SM (1988). Measurement of the Oxygen Content in High-T_c Superconductors: Enhanced Resonant Ion-scattering Analysis. Phys. Rev. B38, 7005-7008.

2. Chu WK, Mayer JW, Nicolet M-A (1978). Backscattering Spectrometry. Academic Press, New York, NY, 1-384.

3. Doolittle LR (1985). Algorithms for The Rapid Simulation of Rutherford Backscattering Spectra. Nucl. Instr. and Meth. in Phys. Res. B9, 344-351.

4. Feldman LC, Mayer JW (1986). Fundamentals of Surface and Thin Film Analysis. North-Holland, Amsterdam, Neth., 13-68.

5. Gossett CR (1989). Non-Rutherford Elastic Backscattering for Light Element Cross Section Enhancement. In: Applications of Accelerators in Research and Industry, '88. J.L. Duggan and I.L. Morgan (eds), Nucl. Instr. and Meth. in Phys. Res. B40−41, 813-816.

6. Gossett CR, Grabowski KS, Van Vechten D (1988). Depth Profiling High T_c Materials with 6.2 MeV He Ion Elastic Backscattering. In: Thin Film Processing and Characterization of High-Temperature Superconductors. J.M.E. Harper, R.J. Colton, L.C. Feldman (eds), AIP Proceedings No. 165, 443-450.

7. Martin JA, Nastasi M., Tesmer JR, Maggiore CJ (1988). High-Energy Backscattering of Helium Ions for Compositional Analysis of High-Temperature Superconducting Thin Films. Appl. Phys. Lett. 52 (25), 2177-2179.