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Material Analysis Using Combined Elastic Recoil Detection and Rutherford / Enhanced Rutherford Backscattering Spectrometry.

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Three complimentary ion beam techniques will be combined in the analysis of oxide and nitride based materials, in particular BN/SiC and $La_{0.85}Sr_{0.15}CoO_3$. These materials can be synthesized over composition ranges which vary the physical and electrical properties, and therefore an accurate measure of the composition profiles is critical for controlling these properties. Elastic Recoil Detection (ERD) revealed the composition of light elements from H to O, and Rutherford Backscattering Spectrometry (RBS) gave the composition of heavier elements (e.g., Si, Sr, Co and La). Enhanced Rutherford Backscattering Spectrometry (ERBS) complimented these techniques by utilizing enhanced cross-sections, greater than Rutherford, to increase the signal-to-noise ratio for analysis of mid-range elements O, C, and N. ERD with 24 MeV Si ions gave profiles for H, B, and N in thin films, and 30 MeV Si was able to profile O in the top portion of heavier samples. Although 2.8 MeV He RBS worked well for heavier elements, ERBS utilized He ions at 3.5 MeV for N analysis and 8.7 MeV for O analysis, because at these energies the cross sections are 2 and 22 times Rutherford, respectively. Also, the depth of analysis was greater with ERBS because of the increased incident energy.

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DISCLAIMER

1. Introduction

Recently, new materials containing elements with Z from 5 to 8 have received increased attention in the field of material science. These new materials require new approaches for their compositional analysis. Enhanced Rutherford backscattering spectrometery (ERBS) and elastic recoil detection (ERD) have been used to study materials including: BC for use in the walls of fusion reactors and also for use as hard coatings on cutting tools and as a low dielectric constant material in VLSI circuit manufacturing; C_3N_4 , diamond-like carbon (DLC), N-doped DLC, and SiC, for use as hard coatings and for use as high temperature semiconductors; and perovskite-type metal oxides (e.g. , $La_xSr_{1-x}CoO_3$) for use as conductors, superconductors, and ferroelectrics. Thin films containing one or more of these materials are often processed in conjunction with the more conventional materials SiO_2 and Si_3N_4 . Each one of these new materials can pose its' own set of difficulties for ion-beam analysis.

Ion beam analysis techniques provide a means for quick, nondestructive composition depth profiling. The most widely available, Rutherford backscattering spectrometery (RBS), provides good depth resolution and sensitivity. However for elements that are lighter than the substrate material, other methods are sometimes more affective. For instance, under certain conditions, enhanced Rutherford backscttering spectrometry (ERBS) is a better choice. ERBS utilizes the enhanced cross section often encountered with a ^4He beam, where energies are above ~2.2 MeV, to profile mid-range elements such as O, and N. Like RBS, ERBS also provides good depth resolution and sensitivity, but is able to reach greater depth due to the increased beam energy. In those cases where RBS and ERBS prove to be ineffective, depth profiling of light elements may still be possible via elastic recoil detection (ERD). This technique differs from the previous two in that it relies on the forward recoil of the light elements that are to be profiled. ERD is well known for H profiling, but it may also be used for profiling mid-range elements such as O and N, and this paper will compare and contrast the use of ERD with ERBS for these types of elements.

Although this paper discusses three different ion beam techniques, all three are governed by the same basic physical principles. In all three cases one must consider: 1) the likelihood that a

scattering event will occur, 2) the energy transferred between incident and recoiled particles, and 3) the energy loss of both the incident particle on its' way into the target material and that of the recoiled particle as it exits the target. Many excellent quantitative discussions are already available, for example references [1] and [2], so none shall be given here.

2. Rutherford and Enhanced Rutherford, Backscttering Spectrometry

Perhaps the best known and most widely used ion beam technique is Rutherford backscattering spectrometery (RBS). RBS is best suited for the analysis of elements which are heavier than the substrate. This is due to the dependence on Z of the cross section, and because the signal from lighter elements lie on top of that from the substrate and possibly heavier surface elements in thicker samples. Figure 1 is an example of a RBS spectra in which a 2.2 MeV ^{4}He beam is scattered off of a 1240 nm thick silicon dioxide target. The scattering angle is 164°, the perpendicular to the sample surface is tilted 7° with respect to the incident beam and the total charge collected is 10μC. The sharp front edges of both the silicon and the oxygen signals are indicative of the excellent resolution obtainable with RBS, in this case 30 nm. In general RBS provides good depth profiles, however it is sometimes impossible or impractical to run long enough to get good counting statistics, and at other times a poor signal to background ratio diminishes the quality of the depth profile. Fig. 1 shows how large quantities of oxygen in a sample, such as SiO_2 , can be measured using RBS, but many new materials contain either smaller quantities of O or elements heavier than Si. Both of these conditions make RBS less effective for quantitative analysis because of a poorer O signal to substrate background ratio. Therefore, in these cases ERBS may be used to allow analysis of the mid-range elements.

Above ~2.2 MeV the cross section of mid-range elements (O, N, B, C) tend to deviates from that predicted by the Rutherford formula. This deviation often results in an increased yield from these elements. The energy dependence of the scattering cross section for ^{4}He incident on oxygen [3] is inlaid in fig.1. According to the differential scattering cross section

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{2E\sin^2\theta}\right)^2 \left\{\cos\theta + \left[1 - \left(\frac{M_1}{M_2}\sin\theta\right)^2\right]^{\frac{1}{2}}\right\}^2 \Bigg/ \left[1 - \left(\frac{M_1}{M_2}\sin\theta\right)^2\right]^{\frac{1}{2}} \qquad (1)$$

the yield from heavier elements is decreasing, as $1/E^2$, in the same energy range where the yield from oxygen is increasing. This is true of all the mid-range elements. The net result is an increased signal to noise ratio for these elements. Taking advantage of this affect may make it possible to do a quantitative analysis of mid-range elements in samples where their signal would otherwise be obscured or at least severely reduced. In order to do this, it is highly desirable to choose a region where the energy dependence of the cross section remains flat or varies slowly as a function of energy.

The analysis of $(La_x Sr_{1-x})CoO_3$ is an excellent example of this type of situation and is shown in figure 2. This is a 190 nm thick sample of $(La_{.88} Sr_{.15})CoO_3$. The spectrum was collected at a scattering angle of 164°, and once again the sample was tilted such that there was 7° between a line perpendicular to the surface and the incident beam. The total charge collected was 20 μC. With a 2.2 MeV beam of ^{4}He the O signal is almost completely overwhelmed by those of the heavier constituents. If, on the other hand, one uses 8.7 MeV ^{4}He the yield from oxygen is 22 times that predicted by the Rutherford formula [4]. At this energy the cross section is flat across a 600 KeV range which corresponds to an analysis depth that is a little less than 1 μm.

Another example of ERBS is shown in figures 3. Here the spectrum, obtained from 3.5 MeV ^{4}He beam incident on 105nm of BN atop 1140nm of SiC on a silicon substrate, is shown. The scattering angle was 164°, and the perpendicular was tilted 45° with respect to the beam, and the total charge collected was 30 μC. The depth resolution was about 15 nm. At this energy the nitrogen signal is 2x Rutherford and the carbon signal is ~6x Rutherford. Unfortunately the cross section for both ^{10}B and ^{11}B, the two main isotopes of natural B, are slightly below Rutherford and therefore another energy or method will be needed to analyze the boron. However, at 164° scattering angle and energies above ~3.7 MeV the cross section for Si has many sharp spikes and dips and no significant regions where σ is constant, any

spectra atop this background would be difficult to analyze. Because of this, another method must be employed to obtain a B profile.

5. Elastic Recoil Detection

A third ion beam analysis technique, elastic recoil detection (ERD), is useful for light element analysis ($1 \leq Z \leq 9$). The basic physical principles are the same as for both RBS and ERBS. The geometry however, is not. In ERD the incident beam is heavier than the element to be profiled and it is incident on the target at a shallow angle. Light elements in the target will be recoiled in the forward direction, some of which will be detected. ERD also makes use of a range foil that is placed in front of the detector to filter out any of the heavier incident particles scattered toward the detector. An ERD spectra of the same BN/SiC sample shown in fig. 3 is shown in Fig. 4. This time a 24 MeV Si^{5+} ion beam was used to elastically recoil H, B, and N atoms from the sample. The cross sections for 24 MeV Si on H, B, and N are Rutherford. The scattering angle was 30° and the beam was incident at a 15° angle to the sample surface. It was shown earlier that neither RBS nor ERBS was particularly well suited to produce a B profile in this case, fortunately the B signal in fig. 4 is almost completely free of any background counts and is more than large enough to give excellent signal/background counting statistics. Inlaid in fig. 4 is the B concentration profile obtained after data analysis [5]. In this case the resolution of the B profile is about 25 nm, moreover the depth of analysis was greater than the ~115 nm BN layer thickness indicated by the ERD analysis. This compares favorably to the ERBS analysis which indicated a BN layer thickness of 105 nm, and a resolution of 16 nm.

Previously 8.7 MeV ERBS was used to profile O in a $(La_{.88}Sr_{.12})CoO_3$ sample, however as an alternative 30 MeV Si ERD could be used. Fig. 5 shows a spectra and corresponding O profile. The total charge collected was 4 μC, and the geometry used is inlaid. In this case only the top ~80 nm can be profiled, approximately half of the film, but if one can assume a constant O concentration then the total O

content can be inferred from this information. On the positive side sharper resolution is obtained with ERD than with ERBS, 22nm versus 54 nm, in this case.

6. Conclusion

Due to the presence of elements heavier than Si and the decrease in content of mid-range elements, such as B, C, N and O, many of the newer materials being investigated by material scientists requires a new approach for their analysis. Through the appropriate combination of ion beam techniques, such as RBS, ERBS and ERD, most sample configurations can still be analyzed. A number of other techniques which might be used are discussed elsewhere [1][2][6]. Although the examples in the preceding discussion are but a few of the possible combinations one might encounter, they demonstrate how two or more techniques can be used in the analysis of a single sample.

[1] W.-K. Chu, J.W. Mayer, M.-A. Nicolet, Backscattering Spectrometry (Academic, New York, 1978) p. 61

[2]] J.R. Bird and J.S. Williams, Ion Beams for Material Analysis, (Academic, New York, 1989)

[3] T. Lauritsen and F. Ajzenberg-Selove, Nuclear Data Sheets for ^{20}Ne, Sets 5and 6 (National Academy of Sciences, National Research Council, 1962) p. 307.

[4] J.C. Barbour, B.L. Doyle, S.M. Myers, Phys. Rev. B. 38 (1988) 7005

[5] J.A. Leavitt and L.C. McIntyre,Jr., Nucl. Instrum. Meth. B 56/57 (1991) 734

[6] J.A. Knapp, J.C. Barbour, and B.L. Doyle, J. Vac. Sci. Technol. A 10

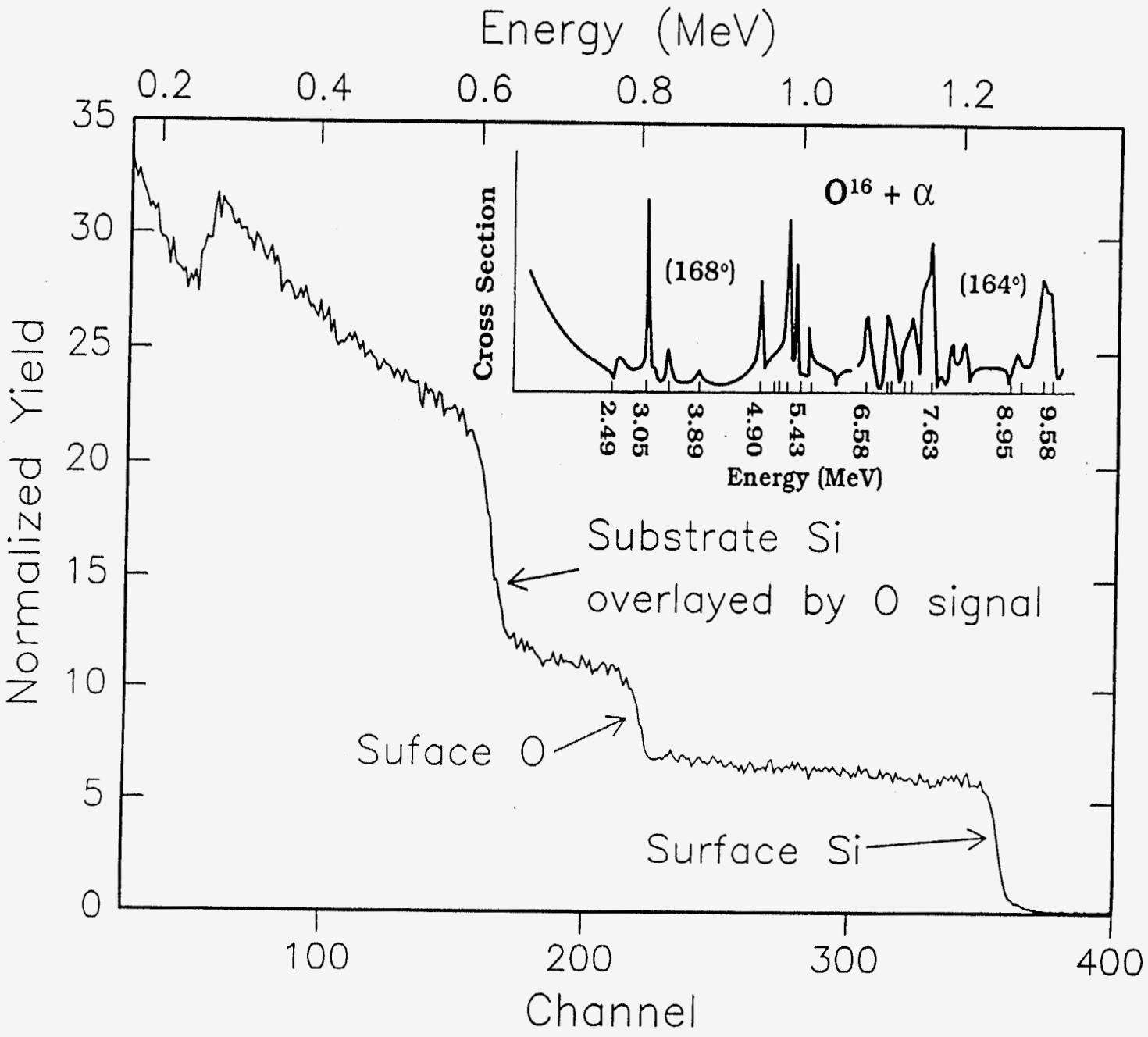
Fig. 1. For samples that contain large amounts of O, such as this 1240 nm thick SiO_2 sample, traditional 2.2 MeV ^4He RBS works quite well. The inlay shows the variation of the O cross section with energy.

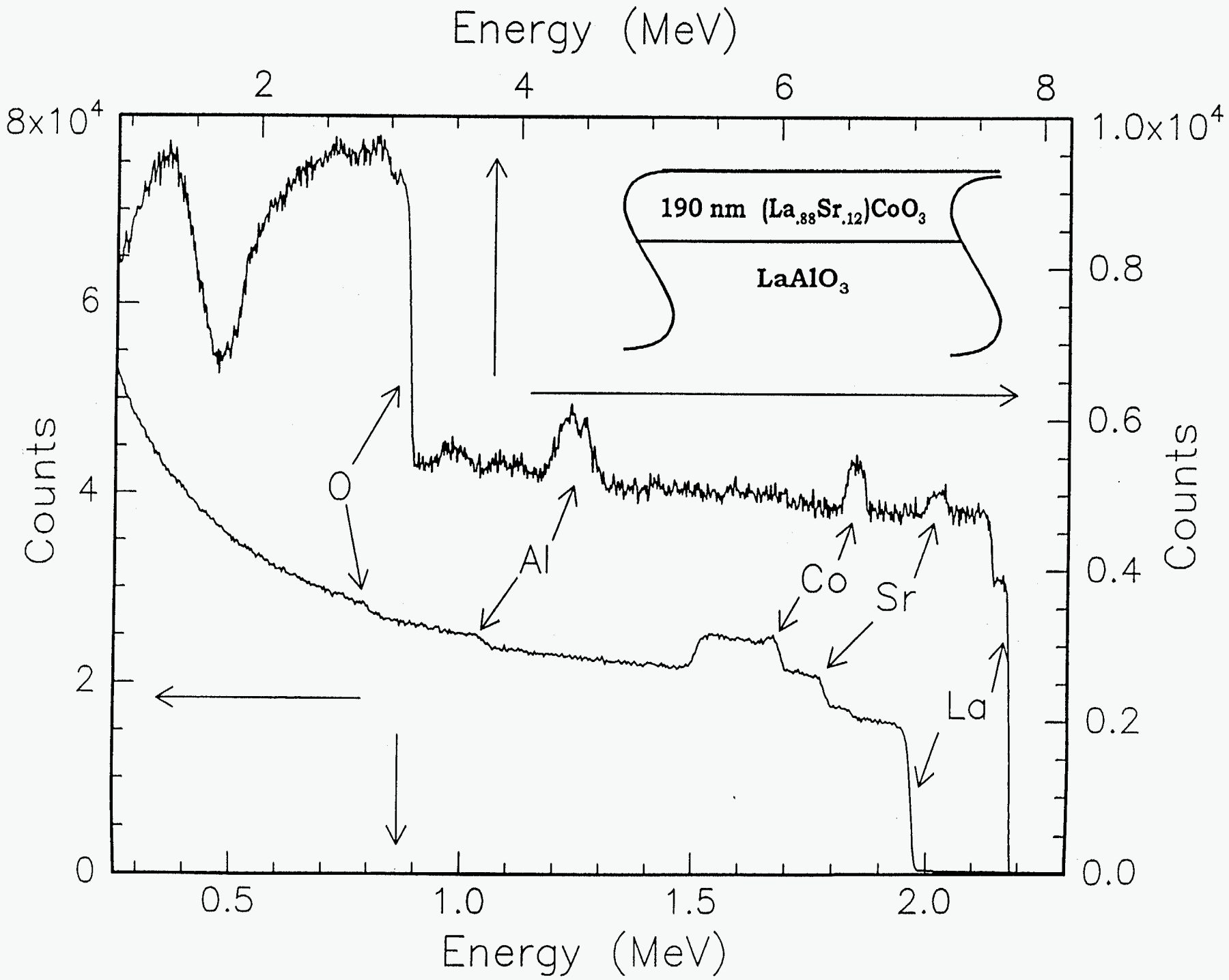
Fig. 2. Normal 2.2 MeV ^4He RBS (bottom) shows almost no O signal where as in the 8.7 MeV ^4He ERBS spectrum (top) the O signal is enhanced by a factor of 22x Rutherford. The arrows indicate the correct axis for each spectra.

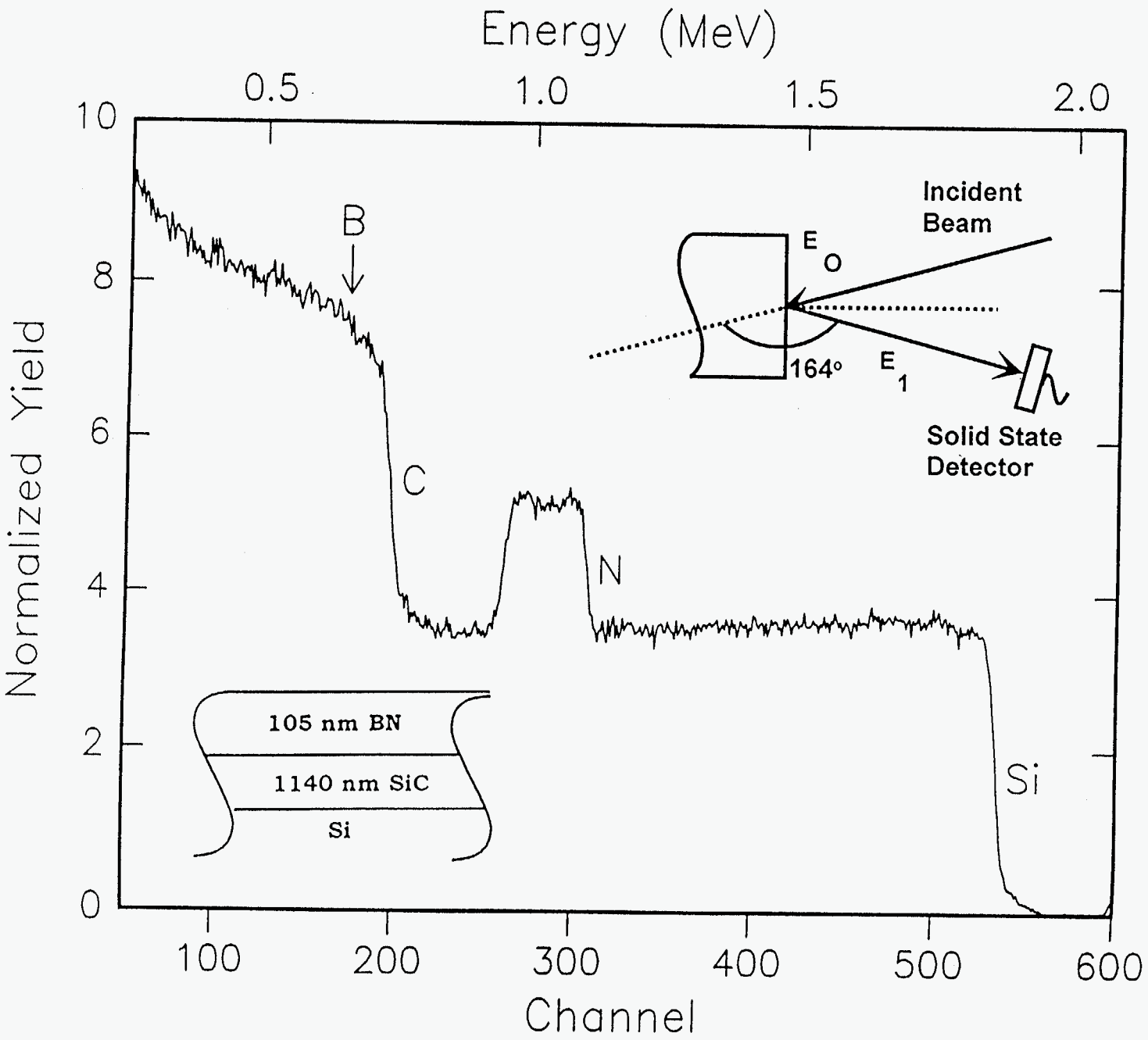
Fig. 3. The cross section for 3.5 MeV ^4He ERBS on N and C are 2x and ~6x Rutherford, respectively. Unfortunately, for this beam/energy combination the B signal is practically nonexistent.

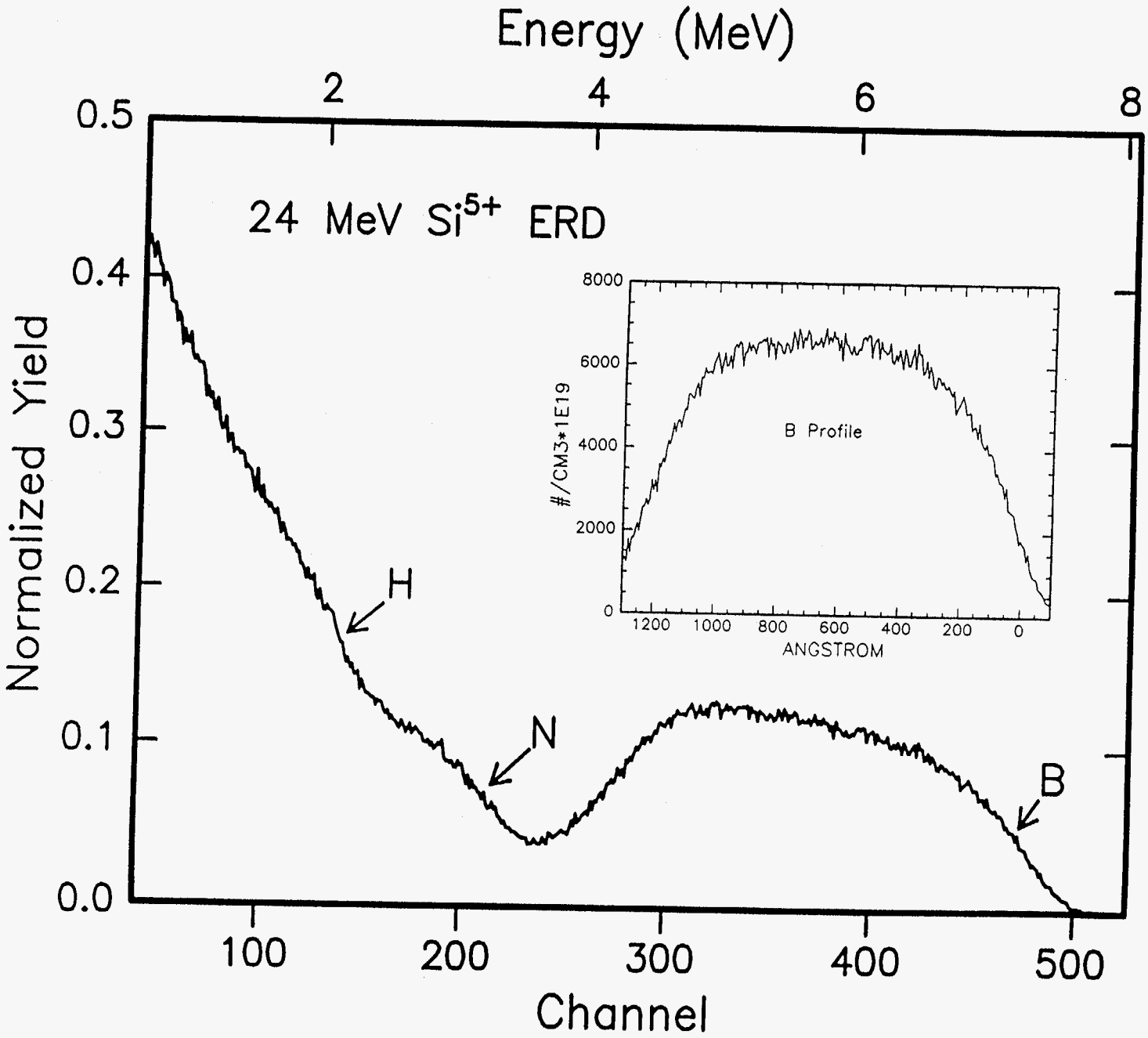
Fig. 4. 24 MeV Si ERD on the same BN/SiC sample of fig. 3 shows a B signal that has almost no background counts beneath it. The inlay shows the B profile obtained after analysis.

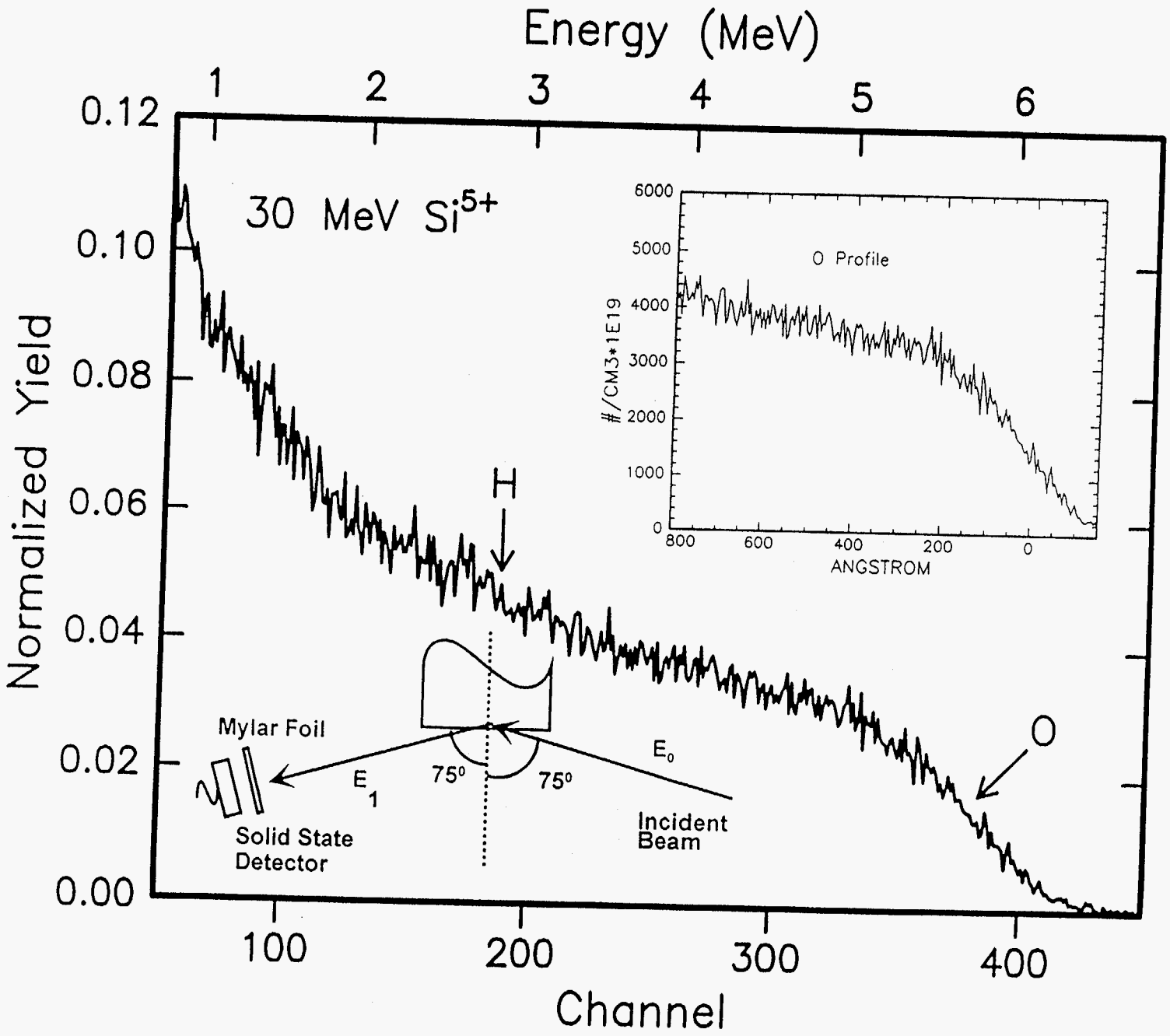
Fig. 5. As an alternative to 8.7 MeV He ERBS, 30 MeV Si ERD was able to profile the O in the top 80 nm of this $(La_{.88}Sr_{.12})CoO_3$ sample.


Energy (MeV)
0.2
0.4
0.6
0.8
1.0
1.2
Normalized Yield
35
30
25
20
15
10
5
0
100
200
300
400
Channel
Cross Section
O16 + α
(168°)
(164°)
2.49
3.05
3.89
4.90
5.43
6.58
7.63
8.95
9.58
Energy (MeV)
Substrate Si
overlayed by O signal
Suface O
Surface Si


Energy (MeV)
2
4
6
8
8x10^4
1.0x10^4
190 nm (La.88Sr.12)CoO3
LaAlO3
O
Al
Co
Sr
La
Counts
Counts
0
2
4
6
0.0
0.2
0.4
0.6
0.8
0.5
1.0
1.5
2.0
Energy (MeV)


Energy (MeV)
0.5
1.0
1.5
2.0
10
8
6
4
2
0
Normalized Yield
B
C
N
Si
Incident
Beam
E
O
164°
E
1
Solid State
Detector
105 nm BN
1140 nm SiC
Si
100
200
300
400
500
600
Channel


Energy (MeV)
2
4
6
8
0.5
0.4
0.3
0.2
0.1
0.0
Normalized Yield
24 MeV Si5+ ERD
H
N
B
100
200
300
400
500
Channel
8000
6000
4000
2000
0
#/CM3*1E19
B Profile
1200
1000
800
600
400
200
0
ANGSTROM


Energy (MeV)
1
2
3
4
5
6
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Normalized Yield
30 MeV Si5+
H
O
O Profile
#/CM3*1E19
6000
5000
4000
3000
2000
1000
0
800
600
400
200
0
ANGSTROM
Mylar Foil
E1
75°
75°
E0
Incident Beam
Solid State Detector
100
200
300
400
Channel