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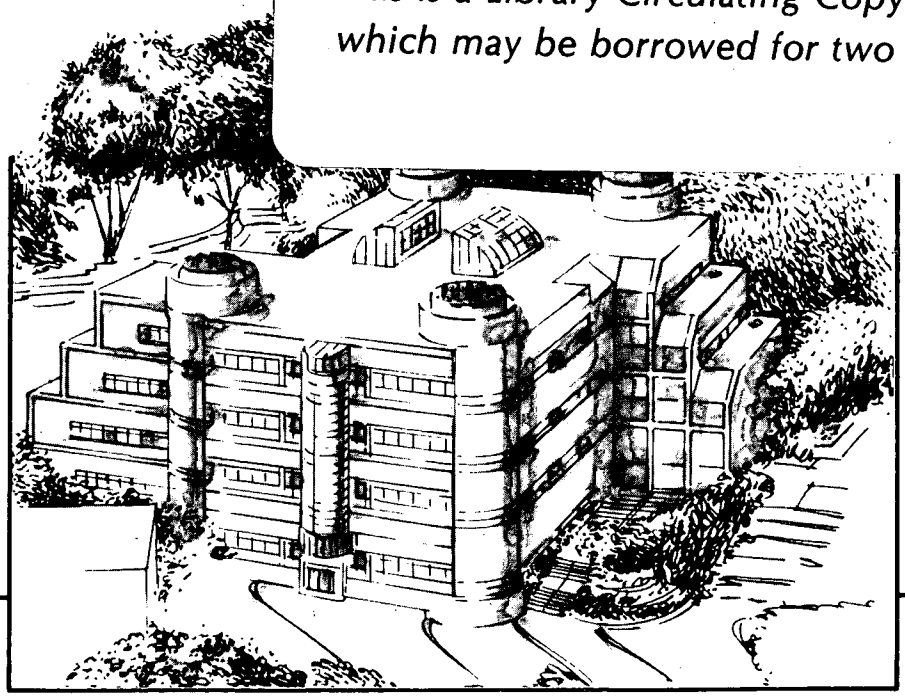

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INVESTIGATIONS OF THIN FILMS ON GaAs USING THE PROTON RESONANT SCATTERING TECHNIQUE

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ABSTRACT

We have characterized a number of thermally stable thin film/GaAs systems including thin films of refractory metal silicides and nitrides as well as dielectric films on GaAs substrates using MeV proton scattering technique. Thin films of tungsten silicides, zirconium nitride and silicon dioxide on GaAs subtrates are investigated. The enhanced proton scattering cross sections of nitrogen, silicon and oxygen at their corresponding resonant energies enable us to accurately measure the compositions of these films. The advantages and disadvantages of this technique regarding depth resolution, accessible depth, and mass resolution compared to the conventional Rutherford backscattering spectrometry for thin film analysis are discussed.

I. INTRODUCTION

Recently the interests in high-speed and high density GaAs metal-semiconductor field effect transistor (MESFET) integrated circuits have stimulated the development of new device processing concepts which are simple and compatible with future GaAs IC scaling. The self aligned gate (SAG) technique [1] is one of these new concepts. In the SAG process, the Schottky barrier gate of a MESFET is also used as an implantation mask for the formation of the source and drain regions of the device. Implantation is followed by a high temperature annealing step (>850°C). This requires thermally stable and electrically reproducible GaAs Schottky contacts. Another approach of the SAG process is to use a dielectric substitutional gate [2], e.g. SiO_2 as the implantation mask. The metal gate is then deposited after the high temperature post-implantation annealing. Consequently, high temperature stability of the Schottky gate is not essential in this process. This approach is sometime referred to as the low temperature SAG process, and the former as the high temperature SAG process [3].

In the last five years, many investigators have explored the thermal stability of refractory metals [4, 5] as well as the alloys [6], silicides [7-12] and nitrides [13-18] of refractory metals as gate materials for the high temperature SAG GaAS MESFET fabrications. Among these materials, refractory silicides and nitrides are the most promising ones because of their high temperature stability (>850°C) and low resistivity.

In most of these studies, the compositions and structures of the contacts were investigated with conventional Rutherford backscattering spectrometry (RBS) using 1-2 MeV helium ions and/or sputtering Auger electron spectroscopy

(AES) techniques. In addition to being destructive, sputtering AES also requires standards for quantitative analysis which makes the technique not very attractive for thin film analysis. Conventional RBS, on the other hand is ideal for fast, quantitative and non-destructive depth profiling of thin films. However, for most of the gate materials of interest, a low atomic number (Z) component is involved (for example, N in NbN, ZrN and WN, and Si in WSi). Since the backscattering yield in a RBS experiment depends on the square of Z, RBS is not sensitive in the detection of a low Z element on a high Z substrate. Consequently, the compositions of thermally stable contact systems such as tungsten silicides, tungsten nitrides, niobium nitrides, zirconium nitrides, titanium nitrides, etc. on GaAs substrates cannot be studied effectively with RBS.

It is known that in MeV proton backscattering, the scattering cross sections for the light elements boron, carbon, nitrogen, oxygen and silicon are significantly enhanced due to nuclear elastic resonance [19,20]. Limited applications of this technique, proton resonant scattering (PRS), have been carried out for the analysis of implanted helium, carbon and oxygen ions in metals [21], the composition of semi-insulating polysilicon films [22], and ion implanted polymers [23]. In this paper, we present results on the applications of PRS to the study of thermally stable GaAs contacts relevant to the SAG fabrication process. Important parameters of PRS, such as depth resolution, mass resolution, and depth of analysis are discussed. The strengths and weaknesses of this technique for the study of thin films as compared to RBS are also reviewed.

II. EXPERIMENT

Samples analysed in this work include thin films (≈500-3000 Å) of tungsten silicide with two different compositions, zirconium nitride, and silicon dioxide on GaAs substrates. A sample of thick silicon carbide film (≈2μm thick) on silicon substrate is also analysed to illustrate the improved accessible depth of the PRS technique. All the samples are prepared by reactive sputtering deposition on chemically cleaned substrates.

Proton beams with energy in the range of 1 to 2 MeV generated by the 2 MeV Van de Graaff accelerator at the Lawrence Berkeley Laboratory were used for PRS experiments. The backscattered protons were collected by a silicon surface barrier detector located at an angle of 165° with respect to the incident beam. 2 MeV He- RBS experiments were also performed on these samples with identical scattering geometry for direct comparison with the PRS measurements.

The PRS spectra were analysed by using the known scattering cross sections of protons at $^{12}C(p,p)^{12}C$, $^{14}N(p,p)^{14}N$, $^{16}O(p,p)^{16}O$ and $^{28}Si(p,p)^{28}Si$ resonances tabulated in recently published reports [20, 24, 25]. Energy loss data of protons in solids were taken from the energy loss table of Northcliffe and Schilling [26].

III. RESULTS

Figure 1(a) shows a 2.0 MeV He-RBS spectrum of a 3000-Å tungsten silicide film on GaAs. The silicon signal height H_{Si} in the RBS spectrum is about 10% of the signal height of the GaAs substrate H_{GaAs}. Since H_{Si} is comparable to the statistical fluctuation of H_{GaAs}, the composition of the film deduced

from this spectrum is subject to a large error (≈22%). Figure 1(b) shows the PRS spectrum of the same sample at the $^{28}Si(p,p)^{28}Si$ resonance. The H_{Si} in this spectrum is about 30% of H_{GaAs}. The composition of the film is estimated from the PRS spectrum to be [W]:[Si] ≈ 1:1.1 to within a 6% error. The first row in Table I shows a summary of the results of the RBS and PRS analyses of this sample.

A sample of a tungsten silicide contact on GaAs substrate with a lower silicon content than the previous sample is also investigated with RBS and PRS with their corresponding backscattering spectra shown in Figure 2(a) and (b). From Figure 2(a), it is obvious that composition analysis of this sample using the RBS technique is difficult if not impossible. In fact, the silicon signal in Figure 2(a) is almost invisible. PRS spectrum of the sample shown in Figure 2(b) indicates a significant enhancement of the silicon signal height. Using the scattering cross section data in references 20, 24 and 25, the composition of the film is estimated to be [W]:[Si] ≈ 1:0.5 to within 15% accuracy. These results are summarized in row II in Table I.

The dramatic difference in the energy loss characteristics between helium ions and protons in solids is illustrated in Figures 1 and 2. Note that the energy loss ΔE of a helium ion through the WSi layer is ~7 times that of a proton. This is also true for other target materials [27]. The significance of this difference in the analytical power of RBS and PRS to thin films will be discussed in the next section.

Zirconium nitride is another thermally stable GaAs Schottky contact which is compatible with the SAG process. The diode characteristics of ZrN/GaAs were found to be close to ideal after annealing at ≈850°C with rapid thermal processing (~10 seconds) [18]. Results of the backscattering experiments on this contact system with 2.0 MeV $^{4}He^{+}$ and protons at $^{14}N(p,p)^{14}N$ resonant

energy are shown in Figure 3. Note that the nitrogen signal in the RBS spectrum (3(a)) is totally masked by the GaAs background. In the PRS spectrum (3(b)), the presence of nitrogen in the film is detected. Moreover, the composition of this film is measured from the PRS spectrum and is [Zr]:[N] ≈ 1:2 with 13% uncertainty (row III in Table I).

Dielectric films such as SiO_2 and Si_3N_4 can also serve as substitutional gates for the SAG GaAs MESFET process [2] as mentioned previously. In addition, these films have also been used as encapsulating layers on GaAs (and other III-V compounds) to prevent the evaporation of As (group V constituents) during high temperature annealing [28]. Figure 4 shows the RBS and PRS spectra of a sample of 1500-Å SiO_2 film deposited on GaAs substrate. Composition analysis of this film by RBS is subject to a large error (>25%) since both of the constituents in the film are of lower mass than GaAs. The PRS spectrum (4(b)) shows that both the silicon and oxygen signals are substantially enhanced with respect to the GaAs background. The oxygen to silicon ratio measured by PRS is ≈2:1 with a 9% error. Because of the small energy loss of protons in the film, the sample was tilted by 55° with respect to the beam in the PRS experiment so as to increase the effective thickness of the film by a factor of ≈2.5.

IV. DISCUSSIONS

We have demonstrated with our experiments that PRS is a much more sensitive tool than RBS in the composition analysis of thin film samples with low Z elements (N, O, and Si) on a high Z substrate (GaAs). However, since the energy loss of protons in solids is much less than that of He ions, depth sensitivity of PRS is rather poor. Depth resolution in a backscattering

experiment is defined as $\delta x = \delta E/[S_0]$ where δE is the system energy resolution and $[S_0]$ is the effective energy loss of the projectile ion in the target. δE for both RBS and PRS is about the same ($\simeq$15-20 keV), while $[S_0]$ for protons is about seven times less than that of He ions. Therefore the depth resolution of RBS is about seven times better than PRS for our range of parameters.

While the smaller energy loss of proton degrades the depth sensitivity of PRS, it increases the accessible depth of the technique. Figure 5 shows the RBS and PRS spectra of a sample with a 2μm thick SiC film on Si. Aside from the improvement in the determination of the composition of the film by PRS (row V in Table I), the increased accessible depth of proton also reveals the thickness of the film in the PRS spectrum. Hence, proton backscattering is useful in the analysis of films with thickness larger than ~1μm.

We also observe in Figures 1 to 4 that in the PRS spectra, the GaAs substrate background is relatively flat in comparison to that in the RBS spectra. This is due to the $(Z_1 Z_2/E)^2$ dependence of the backscattering cross section where Z_1, Z_2 are the atomic numbers of the projectile and target, respectively and E is the energy of the projectile. As a result the increase in slope of the GaAs substrate background in the proton backscattering spectrum is four times less rapid than that in the α backscattering spectrum. This further improves the sensitivity of PRS in analyzing low Z elements on high Z substrates.

Another important parameter in backscattering experiments of multi-component targets is mass resolution, δM. δM is defined as follows:

$$\delta M = \frac{\delta E}{E_0 (dK/dM_2)}$$

where δE is the system energy resolution, E_0 the incident energy of the projectile and dK/dM_2 is the change of the kinematic scattering factor K with respect to the target mass M_2. Since δE and E_0 are similar for RBS and PRS, dK/dM_2 is the only factor effecting a difference in mass resolutions of the two techniques. It is well known that dK/dM_2 increases as the projectile mass increases [19]. Therefore better mass resolution is expected for RBS than PRS. Figure 6 shows the calculated mass resolutions of He ion and proton scattering as a function of the target mass M_2 assuming typical values of δE=15 keV, E_0=1.5 MeV and θ=180° for both curves. For a target mass larger than 20 AMU, mass resolution of RBS is many times better than PRS. The improved mass resolution of RBS is very obvious in Figure 3 where the Zr signal is well resolved from the GaAs signal in RBS while in PRS, it is only partially resolved. However, for most thermally stable GaAs contact systems of interest, the mass differences in the components are large enough that mass resolution of the analyzing technique is not a critical issue.

Aside from mass resolution and depth resolution, there are two parameters which determine the applicability of the PRS technique to thin film analysis, namely the scattering cross section at resonance and the energy widths of the resonant peaks. Since the scattering cross sections $d\sigma/d\Omega$ for protons by low Z elements are very sensitive to the scattering angle θ [20], it is desirable to experimentally determine $d\sigma/d\Omega$ as a function of incident proton energy E for different scattering angles for C, N, O and Si. This has been carried out for the $^{16}O(p,p)^{16}O$ scattering [24]. The sensitivity of $d\sigma/d$ to E at resonances is another important consideration for PRS analyses of thin films. A systematic study has been carried out by Rauhala [25] measuring the scattering cross section of C, N and Si as a function of E at θ=170°. Results of Rauhala's work indicate that the ΔE (full width at half maximum) at the

resonances are rather sharp: $\Delta E(C) \simeq 45$ keV, $\Delta E(N) \simeq 15$ keV and $\Delta E(Si) \simeq 70$ keV. However, since energy loss of protons in matter is small, the sharpness of the resonance peaks do not limit the applicability of PRS on thin film samples.

V. CONCLUSIONS

Several thermally stable contacts on GaAs compatible with the SAG GaAs MESFET fabrication process have been analyzed with both RBS and PRS. The enhanced scattering cross sections of N, O and Si in PRS facilitate accurate determination of the compositions of the contact films. The depth resolution of PRS is poor due to the small energy loss of protons in solids. However, this also enables us to analyze films which are too thick for RBS analysis (~1-5μm). The degraded mass resolution of PRS does not affect its applicability to the characterizations of multi-component films with components of very different masses. Our results also show that in combination the RBS and PRS techniques are very powerful for the investigations of multi-component films (with at least one of the components having a low Z: C, N, O or Si) on high Z substrates. While PRS is used for accurate composition analysis, RBS can be used for depth profiling. An additional advantage of using these two techniques is that the same equipment, namely a small accelerator and a scattering chamber pumped down to a vacuum of $\sim 10^{-6}$ Torr, can be used for both.

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REFERENCES

1. N. Yokoyama, T. Minura, M. Fukuta, and H. Ishikawa, 1981 International Solid State Circuits Conference Dig. Tech. Papers, p.218 (1981).
2. T. Terada, Y. Kitaura, T. Mizoguchi, M. Mochizuki, N. Toyoda, and A. Hojo, IEEE GaAs IC Symp. Tech. Dig. p. 138 (1983).
3. S. P. Kwok, J. Vac. Sci. Technol. B4, 1383 (1986).
4. K. Matsumoto, N. Hashizume, H. Tanone, and T. Kanayama, Jpn. J. Appl. Phys. 21, L393 (1982).
5. K. M. Yu, S. K. Cheung, T. Sands, J. M. Jaklevic, N. W. Cheung, and E. E. Haller, J. Appl. Phys. 60, 3235 (1986).
6. N. Yokoyama, T. Ohnishi, K. Odami, and M. Abe, IEEE International Electronic Devices Meeting Tech. Dig., p. 80 (1981).
7. W. F. Tseng and A. Christou, IEEE International Electronic Devices Meeting Tech. Dig., p. 174 (1982).
8. J. K. Truman and P. H. Holloway, J. Vac. Sci. Technol. A3, 992 (1985).
9. N. Yokoyama, T. Ohnishi, T. Nukamura, and H. Nishi, Mater. Res. Soc. Symp. Proc. Series 54, 401 (1986).
10. T. Ohnishi, N. Yokoyama, H. Onodera, S. Suzuki, and A. Shibatomi, Appl. Phys. Lett. 43, 600 (1983).
11. Z. Zhu, N. W. Cheung, Z. V. Lemnois, M. D. Strathman, and S. B. Stimmell, J. Vac. Sci. Technol. B4, 1398 (1986).
12. A. Callegari, G. D. Spiers, J. H. Magerlein, and H. C. Guthrie, J. Appl. Phys. 61, 2054 (1987).
13. J. R. Waldrop, Appl. Phys. Lett. 43, 87 (1983).
14. H. Yamagishi, Jpn. J. Appl. Phys. 23, L895 (1984).

15. N. Uchitomi, M. Nagaoka, K. Shimada, T. Mizoguchi, and N. Toyoda, J. Vac. Sci. Technol. B4, 1392 (1986).

16. A. E. Geissberger, R. A. Sadler, F. A. Leyenaa, and M. L. Balzan, J. Vac. Sci. Technol. A4, 3091 (1986).

17. X. W. Wu, L. C. Zhang, P. Bradley, D. K. Chin, and T. Van Duzer, Appl. Phys. Lett. 50, 287 (1987).

18. L. C. Zhang, S. K. Cheung, C. L. Liang, and N. W. Cheung, Appl. Phys. Lett. 50, 445 (1987).

19. W. K. Chu, J. W. Mayer, and M.-A. Nicolet, Backscattering Spectrometry, (Academic Press, New York, 1978).

20. J. W. Mayer and E. Rimini, eds., Ion Beam Handbook for Materials Analysis (Academic Press, New York, 1977).

21. R. S. Blewer, Appl. Phys. Lett. 23, 593 (1973).

22. C. Jeynes, R. E. Miles, M. Bolt, and J. G. Simmons, Nucl. Instrum. Meth. B15, 275 (1986).

23. L. Calcagno and G. Foti, Nucl. Instrum. Meth. B15, 288 (1986).

24. M. Luomajarvi, E. Rauhala, and M. Hautala, Nucl. Instrum. Meth. B9, 255 (1985).

25. E. Rauhala, Nucl. Instrum. Meth. B12, 447 (1985).

26. L. C. Northcliffe and R. F. Schilling, Nucl. Data Tables A7, 233 (1970).

27. J. F. Ziegler, Handbook of Stopping Cross Sections for Energetic Ions in All Elements (Pergeamon Press, New York, 1980)

28. J. D. Oberstar and B. G. Streetman, Thin Solid Films 103, 17 (1983).

Table I. A summary of the composition analyses of the samples by 2.0 MeV He-RBS and PRS. The errors measured in these analyses are associated with the statistic error in the backscattering yield. The errors in the scattering cross section data are not taken into account.

Sample	RBS		PRS	
	Composition	Error (%)	Composition	Error(%)
I. WSi/GaAs	[W]:[Si]=1:1	22	[W]:[Si]=1:1.1	6
II. WSi/GaAs	not measurable		[W]:[Si]=1:0.5	15
III. ZrN/GaAs	not measurable		[Zr]:[N]=1:2	13
IV. SiO_2/GaAs	[Si]:[O]=1:2	>25	[Si]:[O]=1:2	9
V. SiC/Si	[Si]:[C]=1:1.1	16	[Si]:[C]=1:1.1	3

FIGURE CAPTIONS

Fig. 1 Backscattering spectra of 2.0 MeV He-RBS (a) and 1.60 MeV PRS (b) of a 3000 Å WSi film on a GaAs substrate. The composition shown is measured with PRS.

Fig. 2 Backscattering spectra of 2.0 MeV He-RBS (a) and 1.60 MeV PRS (b) of a 1500 Å WSi/GaAs contact. The Si content in this film is much lower than that in Fig 1.

Fig. 3 Backscattering spectra of 2.0 MeV He-RBS (a) and 1.67 MeV PRS (b) of a 700 Å ZrN/GaAs contact. Note that the nitrogen signal in the RBS spectrum is invisible while that in the PRS spectrum is much above detection limit.

Fig. 4 Backscattering spectra of 2.0 MeV He-RBS (a) and 1.60 MeV PRS (b) of a 1500 Å SiO_2 film on GaAs.

Fig. 5 Backscattering spectra with 2.0 MeV He particles (a) and 1.50 MeV protons (b) from a sample of 2μm SiC film on Si substrate.

Fig. 6 Calculated curves of mass resolution of 180° backscattering of He ions (solid curve) and protons (dashed curve) as a function of the target mass. The incident ion energy and energy resolution for both cases are assumed to be 1.5 MeV and 15 keV, respectively.

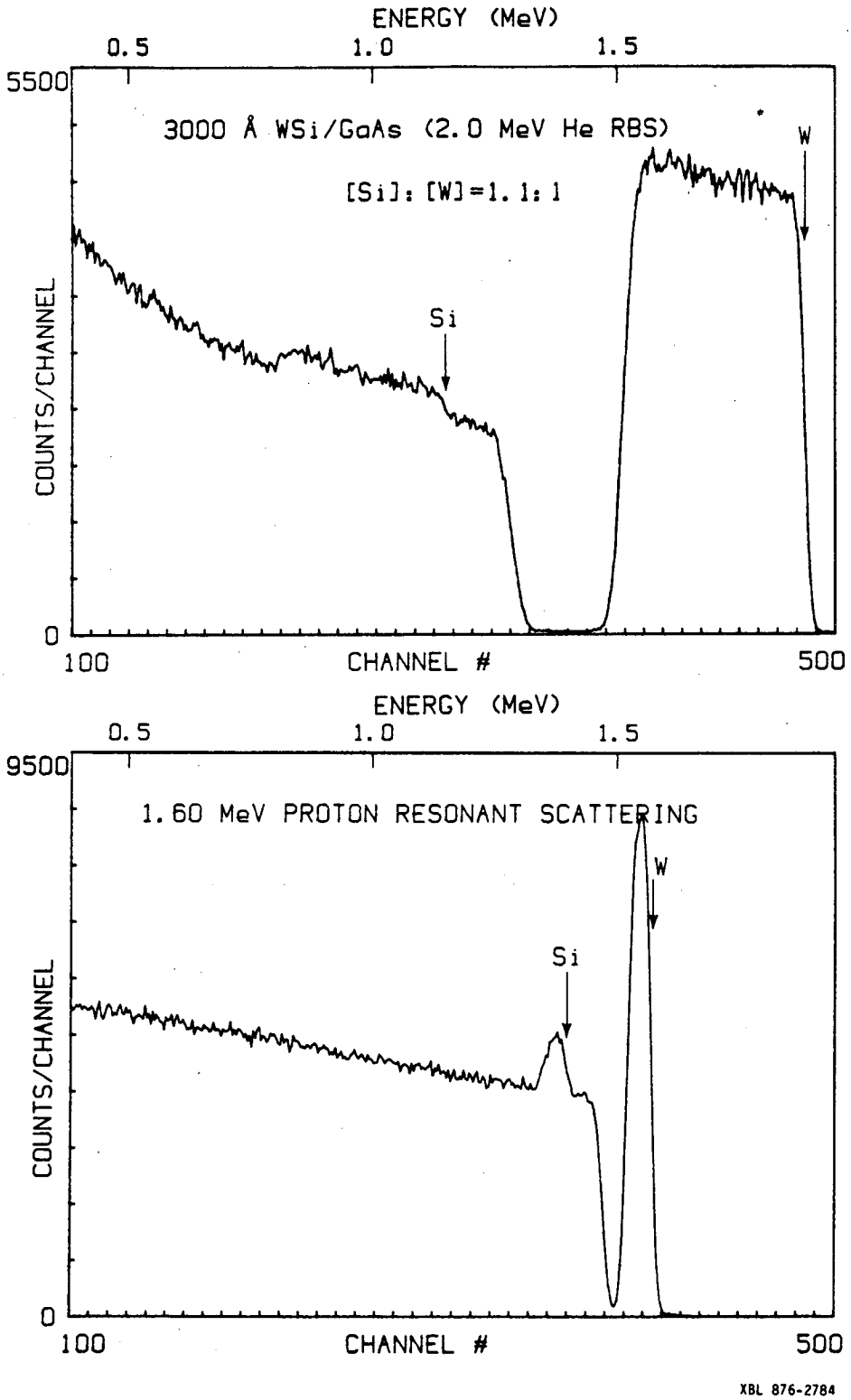
ENERGY (MeV)
0.5
1.0
1.5
5500
3000 Å WSi/GaAs (2.0 MeV He RBS)
[Si]: [W]=1.1:1
W
Si
COUNTS/CHANNEL
0
100
CHANNEL #
500
ENERGY (MeV)
0.5
1.0
1.5
9500
1.60 MeV PROTON RESONANT SCATTERING
W
Si
COUNTS/CHANNEL
0
100
CHANNEL #
500
XBL 876-2784

Figure 1

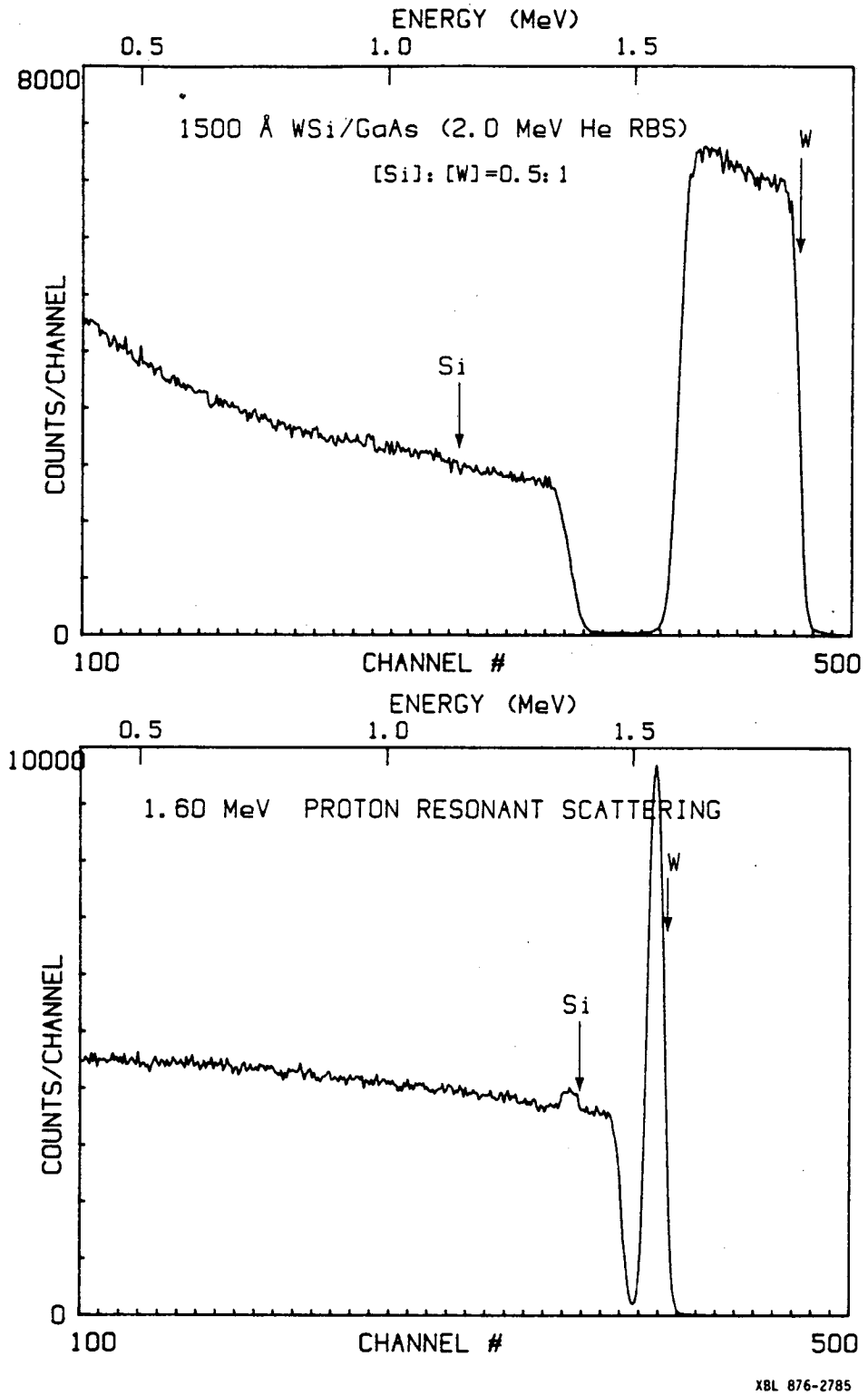
ENERGY (MeV)
0.5
1.0
1.5
8000
1500 Å WSi/GaAs (2.0 MeV He RBS)
[Si]: [W]=0.5: 1
W
Si
COUNTS/CHANNEL
0
100
CHANNEL #
500
ENERGY (MeV)
0.5
1.0
1.5
10000
1.60 MeV PROTON RESONANT SCATTERING
W
Si
COUNTS/CHANNEL
0
100
CHANNEL #
500
XBL 876-2785

Fig. 2

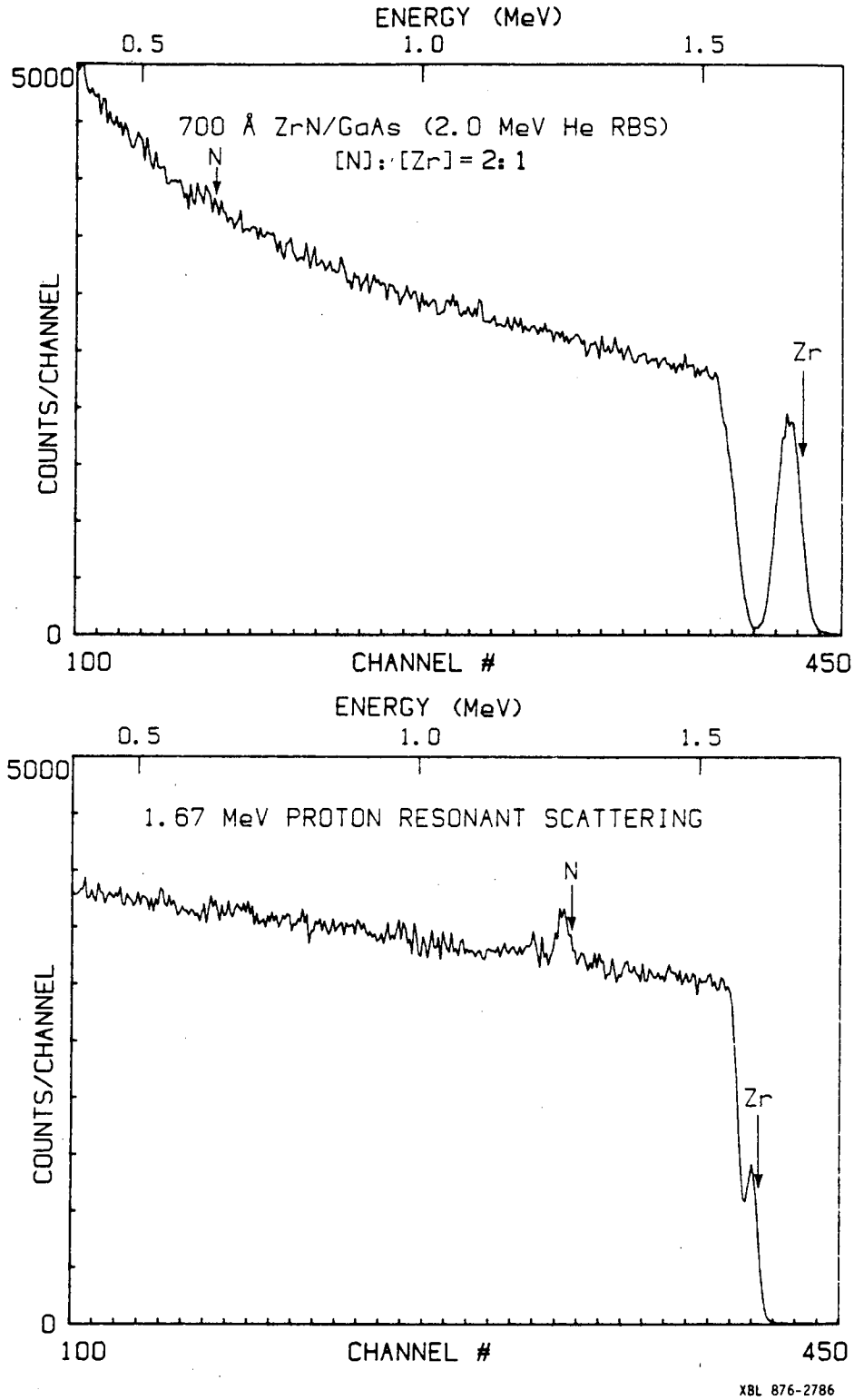
ENERGY (MeV)
0.5
1.0
1.5
5000
700 Å ZrN/GaAs (2.0 MeV He RBS)
[N]:[Zr] = 2:1
N
Zr
COUNTS/CHANNEL
0
100
CHANNEL #
450
ENERGY (MeV)
0.5
1.0
1.5
5000
1.67 MeV PROTON RESONANT SCATTERING
N
Zr
COUNTS/CHANNEL
0
100
CHANNEL #
450
XBL 876-2786

Fig. 3

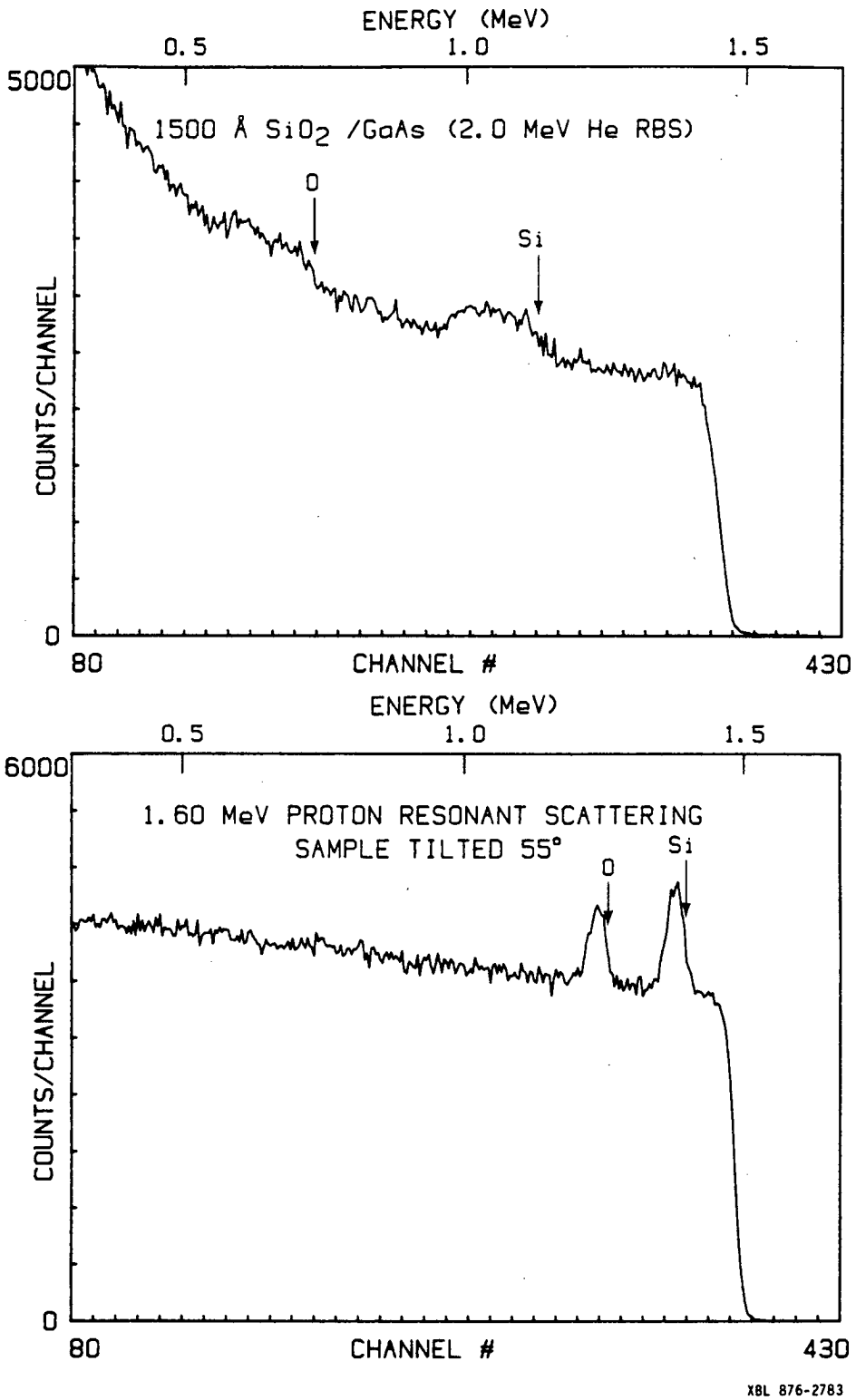
ENERGY (MeV)
0.5
1.0
1.5
5000
1500 Å SiO2 /GaAs (2.0 MeV He RBS)
O
Si
COUNTS/CHANNEL
0
80
CHANNEL #
430
ENERGY (MeV)
0.5
1.0
1.5
6000
1.60 MeV PROTON RESONANT SCATTERING
SAMPLE TILTED 55°
O
Si
COUNTS/CHANNEL
0
80
CHANNEL #
430
XBL 876-2783

Fig. 4

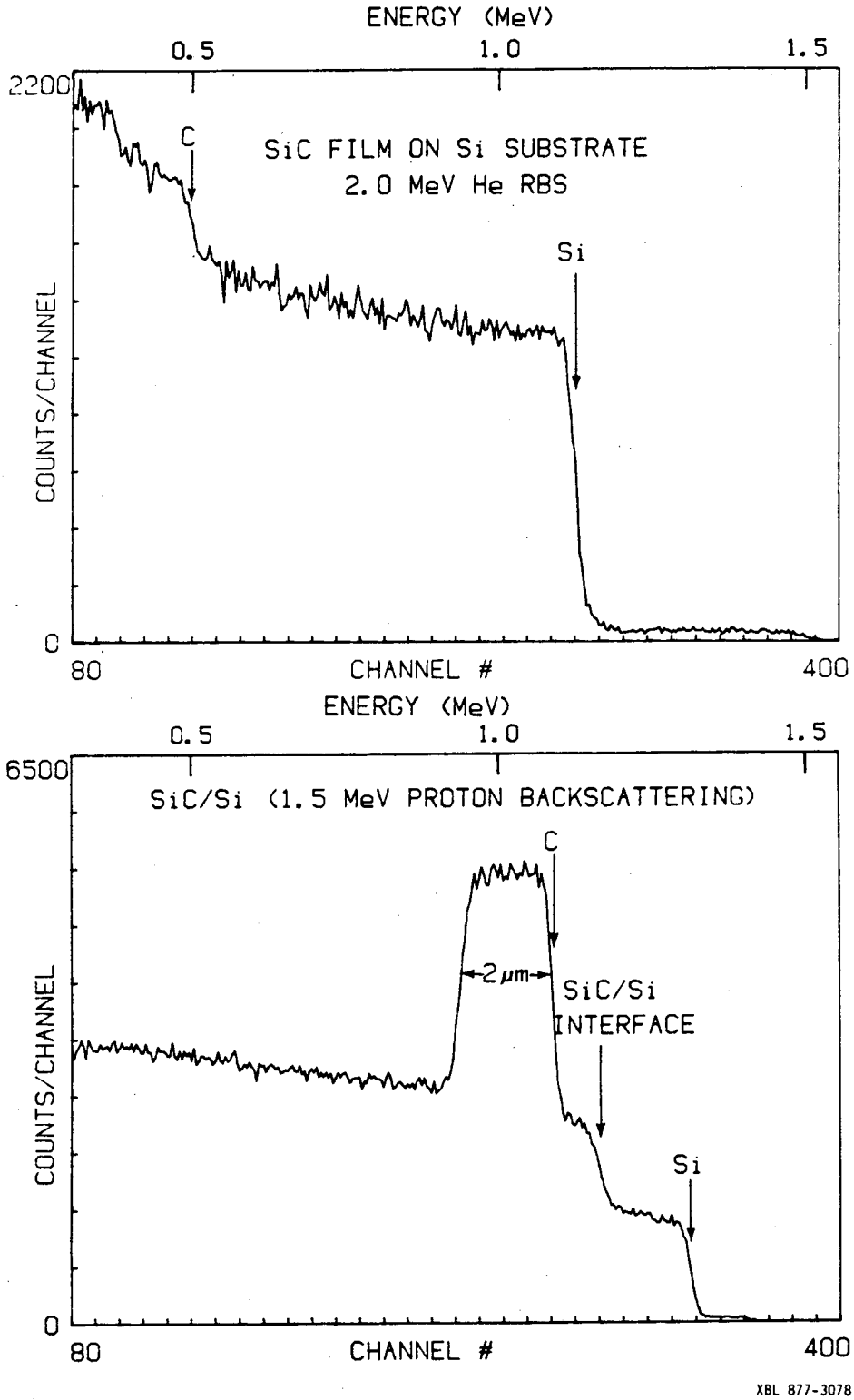
ENERGY (MeV)
0.5
1.0
1.5
2200
C
SiC FILM ON Si SUBSTRATE
2.0 MeV He RBS
Si
COUNTS/CHANNEL
0
80
CHANNEL #
400
ENERGY (MeV)
0.5
1.0
1.5
6500
SiC/Si (1.5 MeV PROTON BACKSCATTERING)
C
2 μm
SiC/Si
INTERFACE
Si
COUNTS/CHANNEL
0
80
CHANNEL #
400
XBL 877-3078

Fig. 5

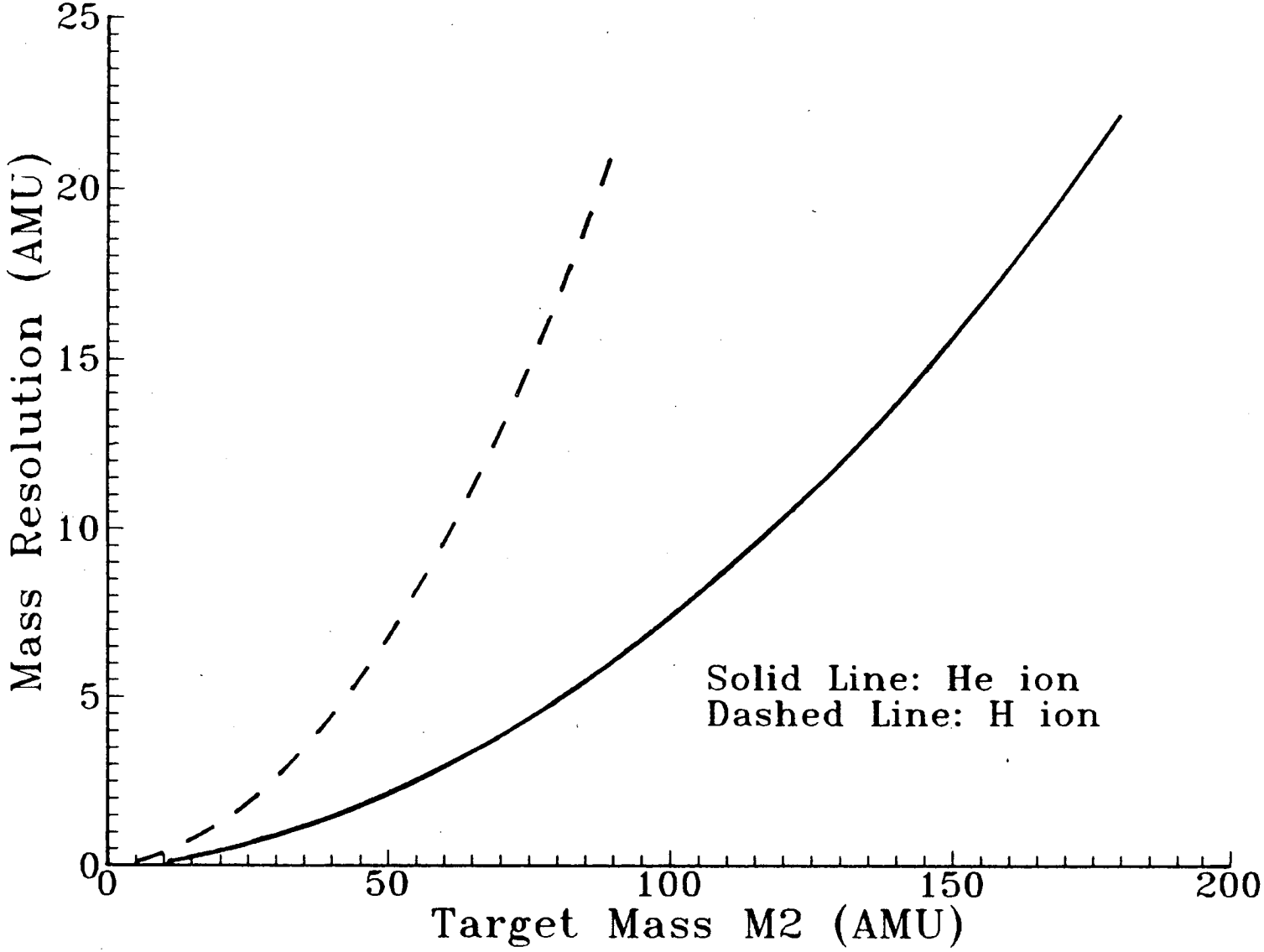

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Fig. 6