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LOW CONCENTRATION OXYGEN DEPTH PROFILING BY THE $^{16}O(d,\alpha)^{14}N$ REACTION*

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ABSTRACT

The $^{16}O(d,\alpha)^{14}N$ nuclear reaction is used for depth profiling low levels of ^{16}O by means of energy analysis of the emitted α-particles. The analytic method for converting the emitted α-spectra to concentration vs depth profiles is presented and the technique is applied to a variety of thin film structures. Experimental methods for enhancing the depth resolution and sensitivity are discussed, and depth resolutions of 130 Å and sensitivities of 0.3 at.% are demonstrated.

I. INTRODUCTION

Ion backscattering has been used extensively in recent years to study the kinetics of reactions between films. While direct observation of the concentration profiles has been extremely valuable in understanding film interaction mechanisms, little consideration has been given to the presence and possible influence of oxygen. This ubiquitous contaminant in thin films can give rise to effects which may completely dominante the kinetics of reactions between films, for example, if present as a thin interface oxide layer.

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Energy analysis of emitted nuclear reaction products has recently become increasingly used an an ion beam technique for depth profiling light elements. Detection of the emitted α's from the $^{16}O(d,\alpha)^{14}N$ reaction has been demonstrated with SiO_2 targets to be a useful method to profile oxygen at high concentrations.[1] This method provides high resolution ($\lesssim$ 200 Å) with probing depths useful for thin films (~ 1 μm). However little work has been carried out at substantially reduced oxygen concentration levels.[2] For thick films an alternative reaction, $^{16}O(d,p)^{17}O$, provides a greater probing depth by a factor of ~ 10, but with a corresponding decrease in depth resolution.[3] Alternative ion beam techniques for natural oxygen detection include proton elastic scattering enhancement, elastic resonances and self-supporting films. These methods all suffer from sensitivity-limiting high backgrounds arising from matrix scattering, since there is no increase in detected particle energy as in positive Q reactions.

The present work demonstrates the use of $^{16}O(d,\alpha)^{14}N$ reaction for low level ^{16}O profiling in films and discusses aspects which limit depth resolution and sensitivity.

II. - THEORY

The energy analysis technique for depth profiling by means of nuclear reactions consists of measuring the emitted particle yield vs energy. Determination of the impurity concentration vs depth requires the same general equations as for backscattering profiling[4] and a knowledge of the matrix composition (e.g., by ion backscattering). The impurity atomic fraction is given by

$$\frac{n_I}{n_T} = \frac{\cos\theta_1}{n_T dx(dE_3)} \frac{dY(E_3)}{\frac{d\sigma(E_1)}{d\Omega_{Lab}} d\Omega_{Lab}} , \qquad (1)$$

where the geometry is defined in Fig. 1, n_I and n_T are the impurity and total target atomic density, respectively, ϕ the incident ion fluence, $d\sigma/d\Omega$ the differential cross section and $d\Omega_{Lab}$ the detector solid angle. The energies are E_0 for the incident beqm, E_1 just before the nuclear reaction event at depth x, E_2 for the emitted product at depth x and E_3 for the emitted product after traveling back out of the sample, and $dY(E_3)$ corresponds to the observed yield per energy increment dE_3. The depth increment per energy increment in atoms/cm^2 is

$$n_T dx(dE_3) = \frac{dE_3}{\left[\frac{\partial f(E_1)}{\partial E_1} \frac{\varepsilon_a(E_1)}{\cos\theta_1} + \frac{\varepsilon_b(E_2)}{\cos\theta_2}\right]} \cdot \frac{\varepsilon_b(E_2)}{\varepsilon_b(E_3)} \qquad (2)$$

where ε_a and ε_b represent the stopping powers for the incident and emitted particle, respectively, at the indicated energies. The relation for the reaction kinetics $E_2 = f(E_1)$ is given in any standard nuclear text.

At higher concentrations, Bragg's rule is used to include the influence of the impurity stopping power according to the calculated atomic fraction n_I/n_T in an iterative procedure. The only approximation involved is $\frac{\partial E_2}{\partial E_3} \approx \frac{\varepsilon_b(E_2)}{\varepsilon_b(E_3)}$ in Eq. (2) and deviations will occur here only when concentrations are both high and change appreciably with depth. The above formalism can quite easily be programmed for on-line solution of the concentration profiles in computer-based analyzed systems.

Increasing the depth resolution enhances the sensitivity for oxygen at the surface and interfaces. Following the formalism of Ref. 1

$$\delta E_3 \approx \left[\delta E_{\text{beam}}^2 + \delta E_{\text{target}}^2 + \delta E_{\text{det.}}^2\right]^{1/2} \quad , \qquad (3)$$

which together with Eq. (2) gives the resolution δx at a given depth x. The energy spread of the beam is usually negligible and that due to detector resolution (det.) is often fixed in a given experiment. However the target term is subject to more experimental control. It consists of straggling and geometry contributions ($\delta E_{\text{target}}^2 = \delta E_s^2 + \delta E_g^2$ where the emitted particle contribution dominates the δE_s term, and by standard Bohr theory

$$\delta E_3 \approx 2.355\ (4\pi e^4 Z_1{}^2 Z_2 n_T x/\cos\theta_2)^{1/2} \qquad (4)$$

with Z_1 and Z_2 the emitted particle and target atomic numbers, respectively. For flat surfaces

$$\delta E_g \approx \left[\frac{\partial f(E_1)}{\partial\theta} + \frac{x\sin\theta_2}{\cos^2\theta_2}\,\frac{\left[S_b(E_3) + S_b(E_2)\right]}{2}\right]\delta\theta_g \quad , \qquad (5)$$

due to the finite size of the beam and the detector defining slit which gives rise to $\delta\theta_g$ as shown in Fig. 1. Figure 2 shows the depth resolution for $^{16}O(d,\alpha)$ profiling as a function of target tilting for 900 keV d incident on Si at depths of 300 and 3000 Å assuming $\delta E_{\text{det.}}$ = 15 keV. Optimum depth resolution is seen to depend on both the tilt angle and the depth of analysis.

III. EXPERIMENTAL TECHNIQUE

The present experimental approach assumes that the measurement of ^{16}O depth profiles is primarily of value in conjunction with ion backscattering measurements. Thus, we fix the detection angle $\theta_{Lab} = 160°$ and use a conventional surface barrier detector The surface normal, beam and detector direction are coplanar. To control the angular spread in the detected particles we use a 2 mm wide vertical slit in front of the detector, for our 1 mm diameter beam $\delta\theta_g = 2.9°$ and $d\Omega_{Lab} = 0.00313$ sr.

A second important modification is to reduce the detector bias so that the depletion depth or active region of the detector is $d \approx 40$ m. The importance of this can be seen by comparing the energy spectra in Fig. 3 for 100 V($d \approx 100$ μm) and 10 V($d \approx 40$ μm) bias for 900 keV d incident on a 600 Å silicon nitride layer on a Si substrate. For the reduced depletion depth, protons of energy > 2 MeV deposit only ≈ 2 MeV of energy into the detector, thus reducing background due to interfering (d,p) reactions in the energy region of the 2.57 MeV emitted α particles. For the lower spectrum the sample was also tilted ($\theta_2 = 70°$) and this results in a depth resolution ≈ 150 Å at the surface (see inset for the $^{16}O(d,\alpha)$ part of the spectrum). One disadvantage of using low biases (≤ 10 V) in conventional detectors is that appreciable degradation of the detector energy resolution occurs. This effect appears to be reduced by utilizing relatively low resistivity detectors; the Au barrier silicon detectors used in these measurements had a nominal resistivity ≈ 500 Ω-cm.

The incident beam energy is important in optimizing detection sensitivity in nuclear reaction experiments. The differential cross section vs d energy for the $^{16}O(d,\alpha)^{14}N$ reaction as measured with a 210 Å SiO_2 film is shown in Fig. 4, where the absolute cross section was obtained by normalizing the $^{16}O(d,p_1)$ signal to Amsel's value[5] for the (d,p_1) reaction at 900 keV. Most analyses were carried out at 900 keV because of the relatively flat energy dependence of the cross section at energies immediately below 900 keV. Enhanced ^{16}O sensitivity can sometimes be obtained by increasing the d energy to ≈ 1050 keV, where the cross section is twice as large, however in some cases (e.g., the relatively dirty CVD silicon nitride film of Fig. 3) the back ground due to competing reactions increases even more rapidly, decreasing the effective sensitivity.

No foils are placed over the detector in these experiments. Thus the measurement time for a given ^{16}O concentration is set primarily by the intense backscattered d signal, since electronic summing of close pulses (pulse pile-up) increases the background for the emitted α particles from the $^{16}O(d,\alpha)$ reaction. In these studies total count rates were typically ≈ 5000 counts/sec and pile-up rejection electronics were used to reduce this background. Typical incident deuterium fluences required to detect a few at.% of oxygen contamination were 100-300 μC requiring 1-3 hours of analysis time.

IV. RESULTS AND DISCUSSION

In the analysis of low levels of oxygen in the near-surface region of solids and in thin films, the two quantities of primary concern are the depth resolution and the detection sensitivity. In this section, we demonstrate these two features for the

$^{16}O(d,\alpha)^{14}N$ energy analysis method and then give an example of ^{16}O profiling applied to thin film reaction studies.

As seen in Fig. 2 the primary way in which the depth resolution can be improved in the $^{16}O(d,\alpha)$ energy analysis method is by tilting the target so as to increase the path length and thus energy loss of the α particle emitted at a given depth x. Depth resolutions of the order of 100-200 Å can be readily obtained in this way in a system with a conventional backscattering geometry. An additional increase in the depth resolution can be achieved by reducing the beam area and the slit width, which reduces $\delta\theta_g$ and therefore decreases the spread in the path length and scattering angle.

An example of the improvement in depth resolution with tilting can be seen in Fig. 5 for a ≈ 2200 Å Al film on Ag. Here a dramatic sharpening in the concentration vs depth profile is observed upon tilting from normal incidence to 50° such that the emitted α particles leave the target at $\theta_2 = 70°$ from the surface normal. An example of the near-surface resolution achievable is given by the surface oxide peak on the Al film which is reduced from ≈ 500 Å for analysis at normal incidence to ≈ 130 Å for glancing incidence. Maximizing the depth resolution provides for the most sensitive detection for ^{16}O at surfaces, interfaces and in very thin oxide layers.

In contrast, the maximum detection sensitivity for thicker regions is achieved for normal incidence, where the depth resolution is reduced. This is because the background count rate is relatively unaffected by tilt angle, whereas for a given bulk

^{16}O concentration the greatest ^{16}O signal per energy increment, dE_3, is obtained for the maximum corresponding depth increment, $dx(dE_3)$. The lowest oxygen concentration which we have measured to date is shown in Fig. 6 for a thin polycrystalline Si layer with a thin SiO_2 underlay on Si for use in silicon gate microelectronic applications. The data have been analyzed without background subtraction or smoothing to better exhibit the sensitivity of the technique. A total fluence of 300 μC of d^+ was used with the analysis time ≈ 2 hours. After appropriate background subtraction the oxygen concentration in the poly-Si film is estimated to be ≈ 0.3 ± 0.1 at.%

Competing (d,α) reaction backgrounds can limit the ultimate sensitivity and are often a problem if other low-Z elements are present. When competing reactions are not a problem, the background levels arise primarily from pulse pile-up effects at high counting rates. Thus at sufficiently low analyzing beam currents, the sensitivity is limited largely by the available analysis time and acceptable total fluence on the sample. For structures with high concentrations of oxygen below the region of interest the primary limitation on sensitivity is pile-up of the elastically scattered deuteron pulses with the emitted α-particle pulses in the high oxygen concentration region, which gives a pile-up tail immediately adjacent to the region of interest.

As an example of the application of ^{16}O profiling to thin film reaction studies we consider a previously reported study[6] of the Al-Ag thin films for which we have now determined the ^{16}O contamination depth profiles in the same samples. For Al-on-Ag films a well-defined Ag_2Al intermetallic layer formed upon annealing, the kinetics of which is shown in Fig. 7. The 2 MeV He backscattering analysis demonstrated that the Ag_2Al layer growth was proportional to the square root of reaction time at a given temperature, indicating a diffusion-limited growth process. In contrast to this well-defined behavior, films sequentially evaporated in the same system but in reverse order (Ag-on-Al) exhibited completely different behavior with no apparent layer formation (e.g., 140°C point in Fig. 7). Backscattering spectra and optical observations suggested the presence of local regions where the reaction had punched through to form pipes of reacted material.

It was postulated that this drastically different behavior was due to the strong proclivity for oxygen pickup by Al films even in the $\lesssim 10^{-6}$ Torr pressures of the vapor deposition system, together with the probability that an Al underlying film for the Ag-on-Al case would grow a much thicker oxide film in the short time available between depositions than would the Ag film in the Al-on-Ag case. The oxide barrier would inhibit formation of the intermetallic phase until the barrier could be locally penetrated. This previously postulated explanation is demonstrated directly by the ^{16}O depth profiles shown in Fig. 8, where the Ag-on-Al film exhibits a buried oxygen peak indicating the presence of a thin oxide layer at the Ag-Al interface whereas the Al-on-Ag film does not. It is also interesting to note the extremely high concentration ($\simeq$ 7 at.%) of ^{16}O in the Al films with little or no ^{16}O present in the Ag films.

In summary, we have demonstrated how the $^{16}O(d,\alpha)^{14}N$ nuclear reaction can be used in the energy analysis technique to obtain high resolution, high sensitivity depth profiles of ^{16}O at contaminate-level concentrations in a standard ion backscattering geometry. Near-surface depth resolutions of ≈ 130 Å and sensitivities of ≈ 0.3 at.% have been demonstrated. Such a technique in conjunction with ion backscattering studies could contribute importantly to our understanding of thin film reactions and the influence of oxygen on thin film behavior.

Acknowledgements

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FIGURE CAPTIONS

Figure 1	Schematic of experimental geometry.
Figure 2	Calculated depth resolution vs detection angle for $^{16}O(d,\alpha)^{14}N$ as a function of $\delta\theta_g$ at a) 3000 Å and b) 300 Å depths in Si using 900 keV d, 15 keV detector resolution and θ_{Lab} = 160°.
Figure 3	Energy spectra for 900 keV d onto Si_3N_4 on Si for a) 100 V and b) 10 V detector bias.
Figure 4	Differential cross section vs incident deuterium energy in laboratory coordinates at θ_{Lab} = 160° for the $^{16}O(d,\alpha)^{14}N$ nuclear reaction. The dashed line gives results of Ref. 1 for θ_{Lab} = 145°.
Figure 5	Oxygen concentration vs depth by $^{16}O(d,\alpha)$ energy analysis for a 2200 Å Al film for a) normal incidence and b) glancing incidence (θ_2 = 70°) of the 900 keV d beam.
Figure 6	Oxygen concentration vs depth by ^{16}O (d,α) energy analysis for a polycrystalline Si layer on (100) Si with SiO_2 underlay.
Figure 7	Ag_2Al layer width vs $t^{\frac{1}{2}}$ at the indicated temperatures for Ag-on-Al and Al-on-Ag films as measured by 2 MeV He backscattering.
Figure 8	Oxygen concentration vs depth by $^{16}O(d,\alpha)$ energy analysis for the same Ag-on-Al and Al-on-Ag films used in the film kinetics measurements of Fig. 7.

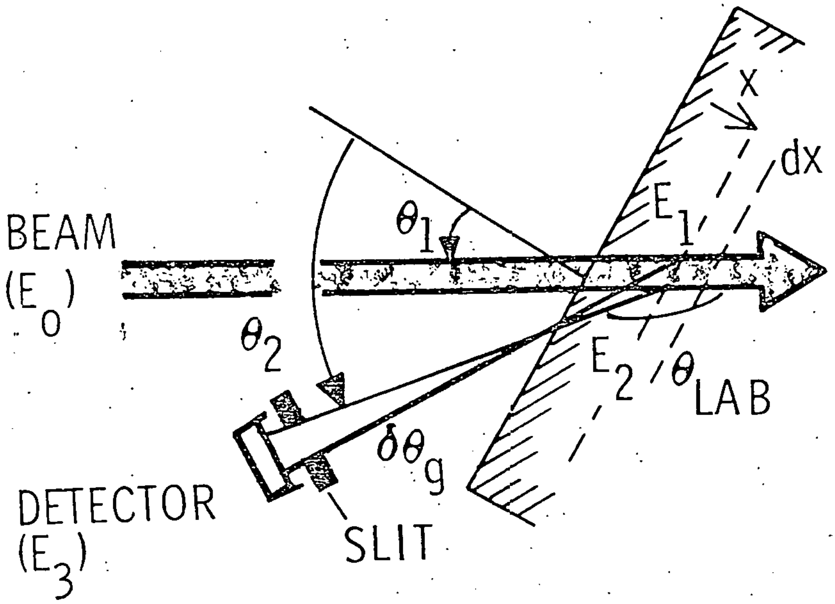

BEAM
(E_0)
θ_1
θ_2
x
dx
E_1
E_2
θ_{LAB}
$\delta\theta_g$
DETECTOR
(E_3)
SLIT

figure 7

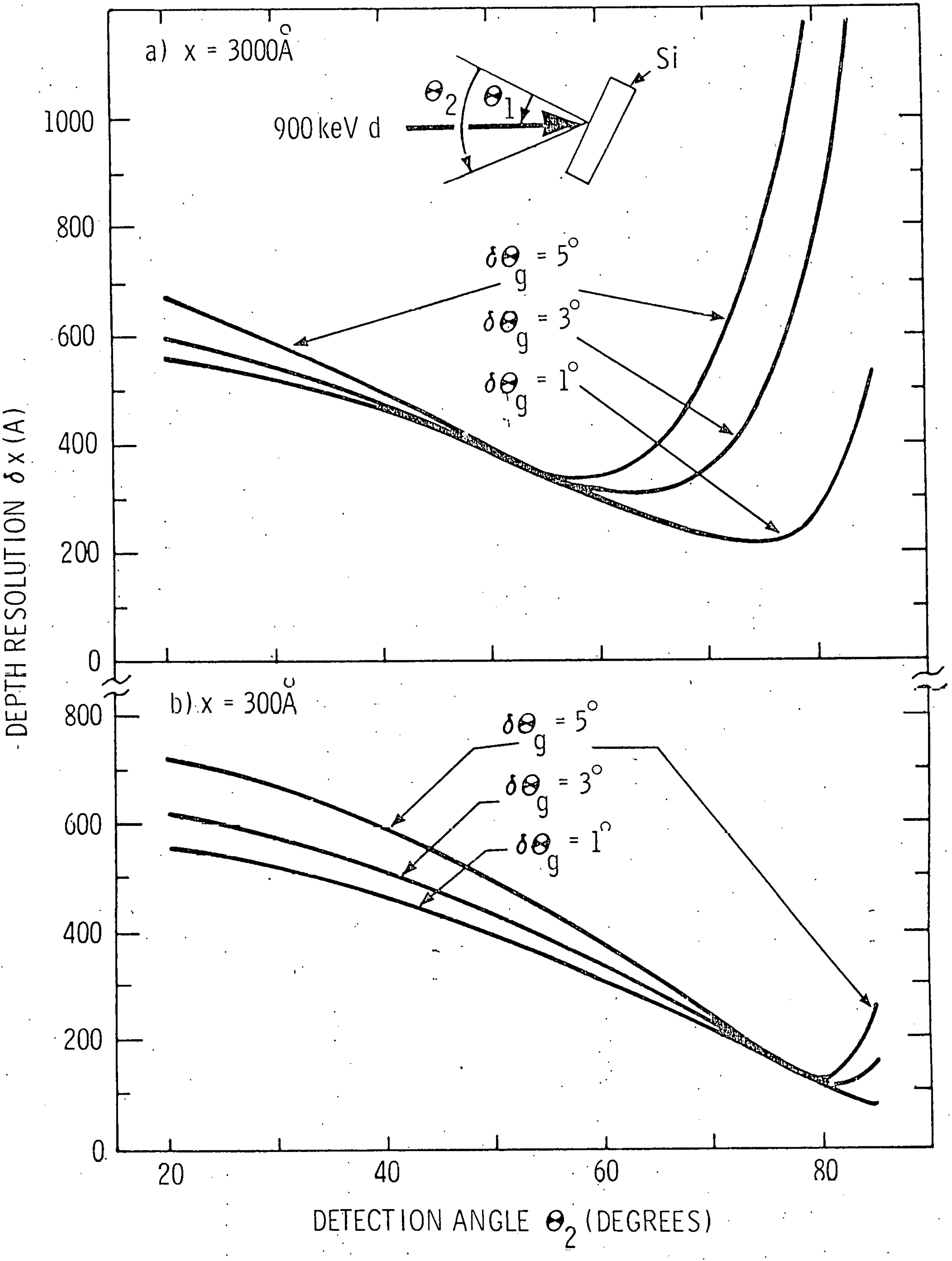
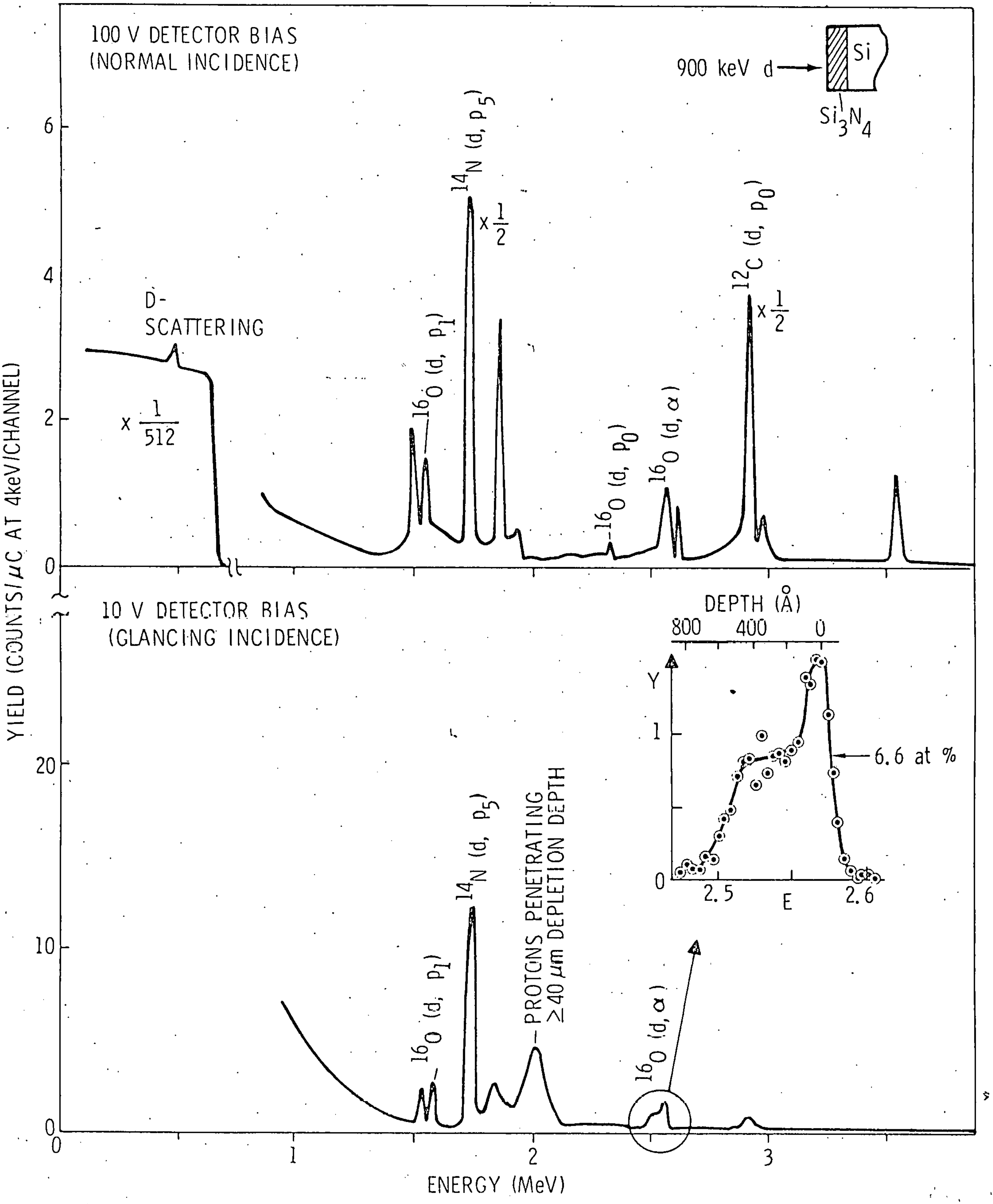
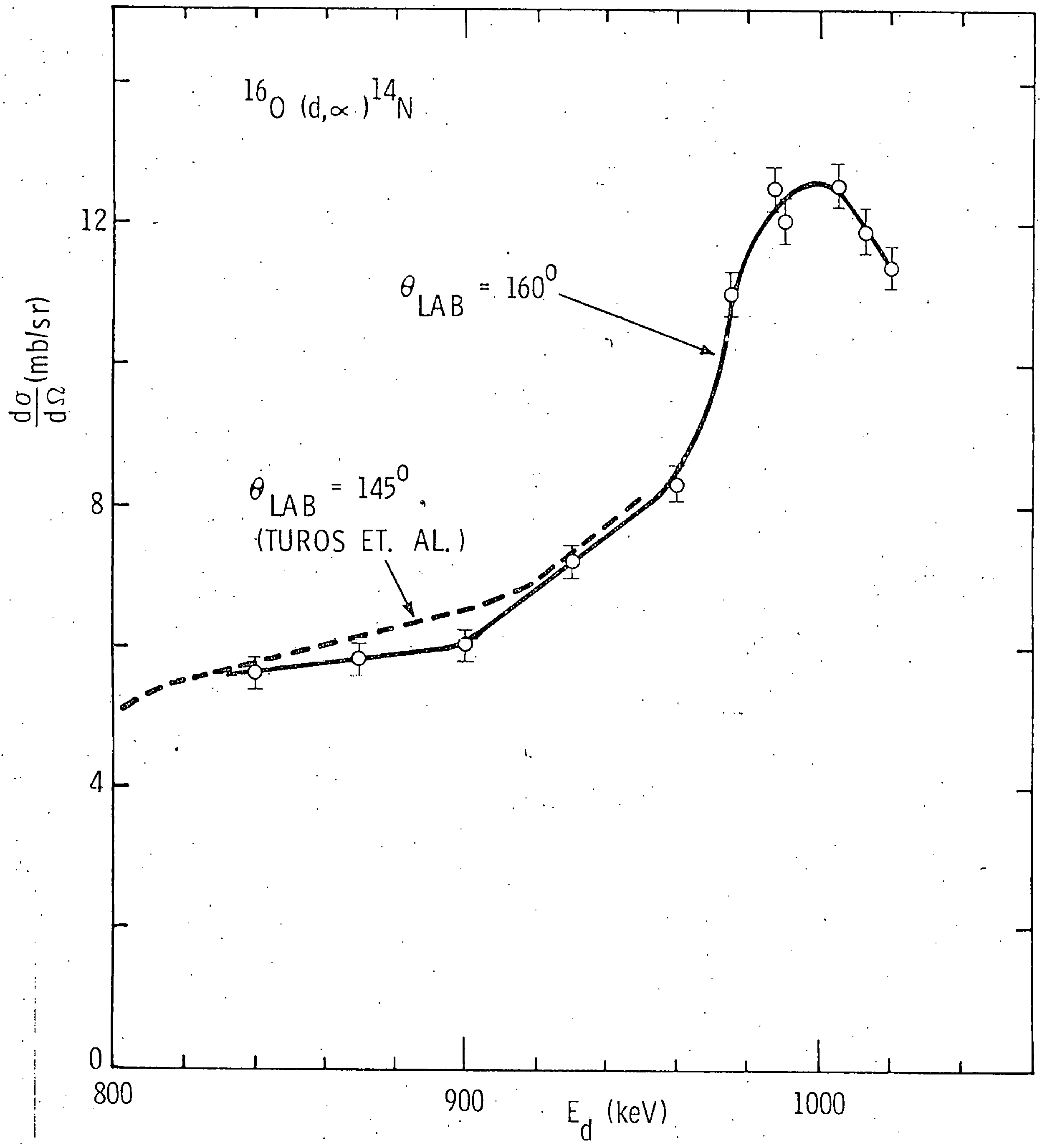

a) x = 3000Å
Si
θ_2
θ_1
900 keV d
$\delta\theta_g$ = 5°
$\delta\theta_g$ = 3°
$\delta\theta_g$ = 1°
b) x = 300Å
$\delta\theta_g$ = 5°
$\delta\theta_g$ = 3°
$\delta\theta_g$ = 1°
DEPTH RESOLUTION δx (Å)
1000
800
600
400
200
0
800
600
400
200
0
20
40
60
80
DETECTION ANGLE θ_2 (DEGREES)

figure 2

figure3

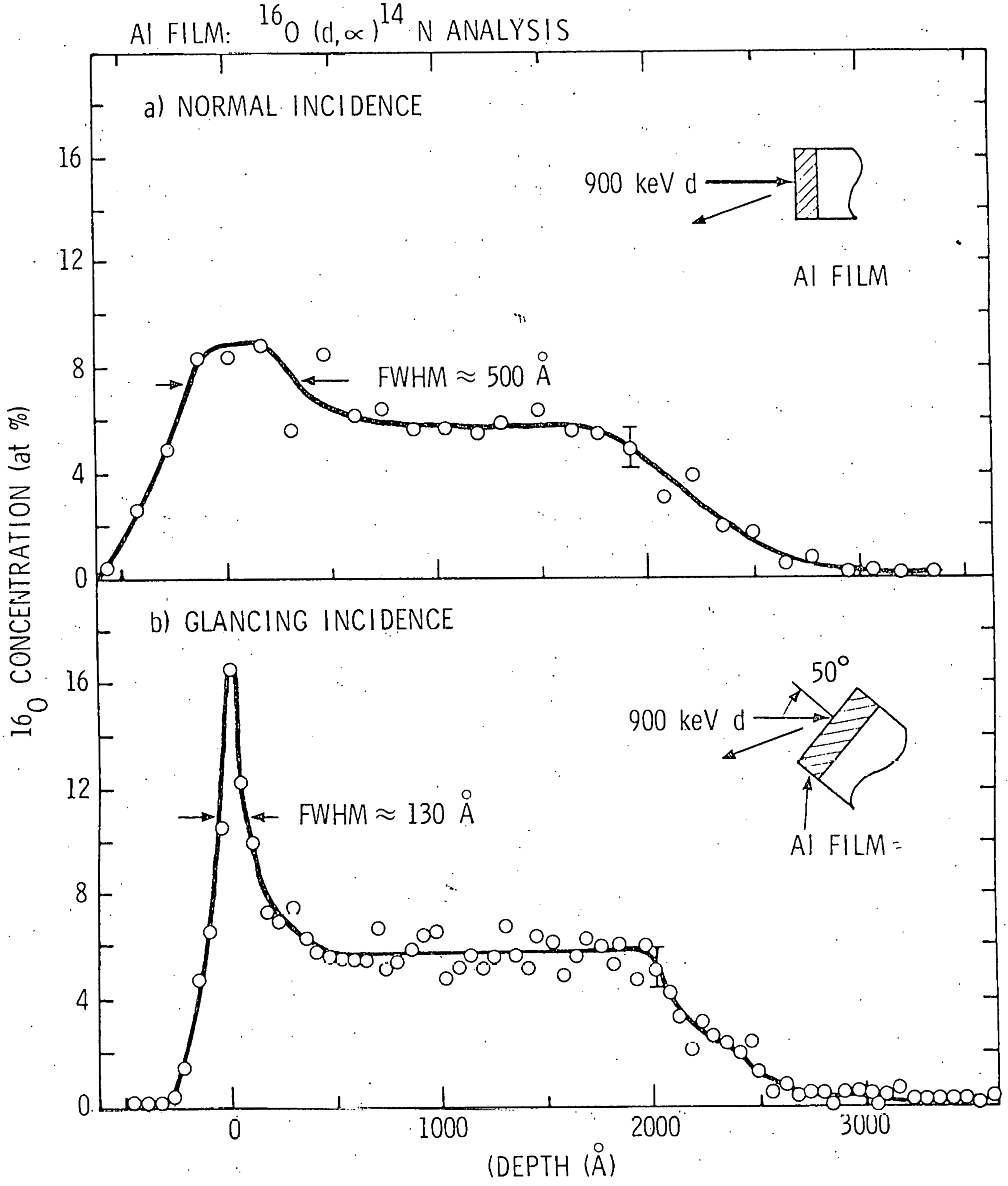

100 V DETECTOR BIAS
(NORMAL INCIDENCE)
900 keV d
Si
Si_3N_4
D-SCATTERING
x 1/512
^{16}O (d, p_1)
^{14}N (d, p_5)
x 1/2
^{16}O (d, p_0)
^{16}O (d, α)
^{12}C (d, p_0)
x 1/2
10 V DETECTOR BIAS
(GLANCING INCIDENCE)
DEPTH (Å)
800
400
0
Y
1
0
2.5
E
2.6
6.6 at %
^{16}O (d, p_1)
^{14}N (d, p_5)
PROTONS PENETRATING
≥40 μm DEPLETION DEPTH
^{16}O (d, α)
YIELD (COUNTS/μC AT 4keV/CHANNEL)
6
4
2
0
20
10
0
0
1
2
3
ENERGY (MeV)



$^{16}O\,(d,\alpha)^{14}N$
θ_{LAB} = 160°
θ_{LAB} = 145°
(TUROS ET. AL.)
$\frac{d\sigma}{d\Omega}$(mb/sr)
12
8
4
0
800
900
1000
E_d (keV)

figure 4

figure 5


Al FILM: 16O (d,α)14 N ANALYSIS
a) NORMAL INCIDENCE
900 keV d
Al FILM
FWHM ≈ 500 Å
b) GLANCING INCIDENCE
50°
900 keV d
Al FILM
FWHM ≈ 130 Å
16O CONCENTRATION (at %)
0
4
8
12
16
0
1000
2000
3000
(DEPTH (Å)

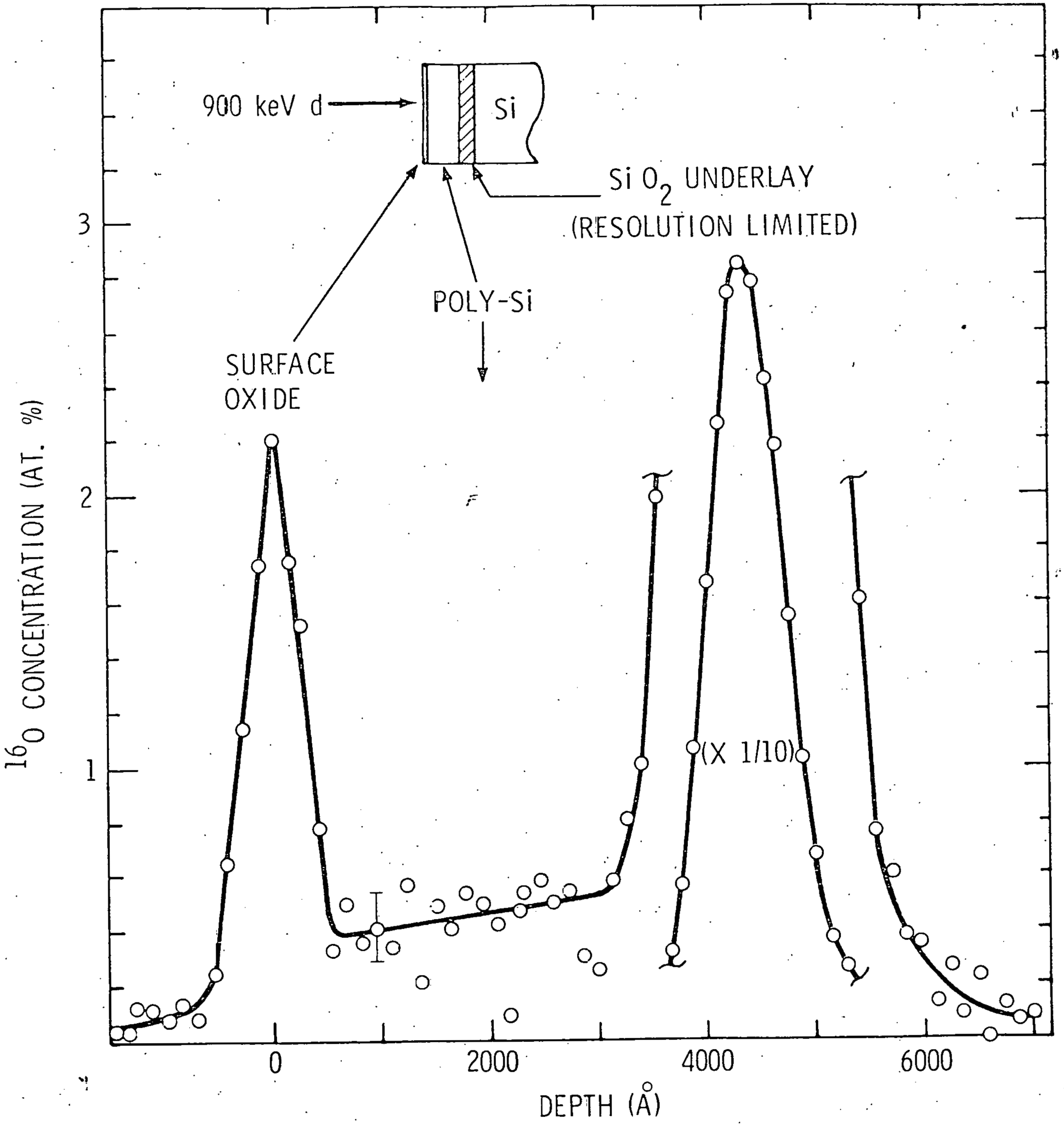
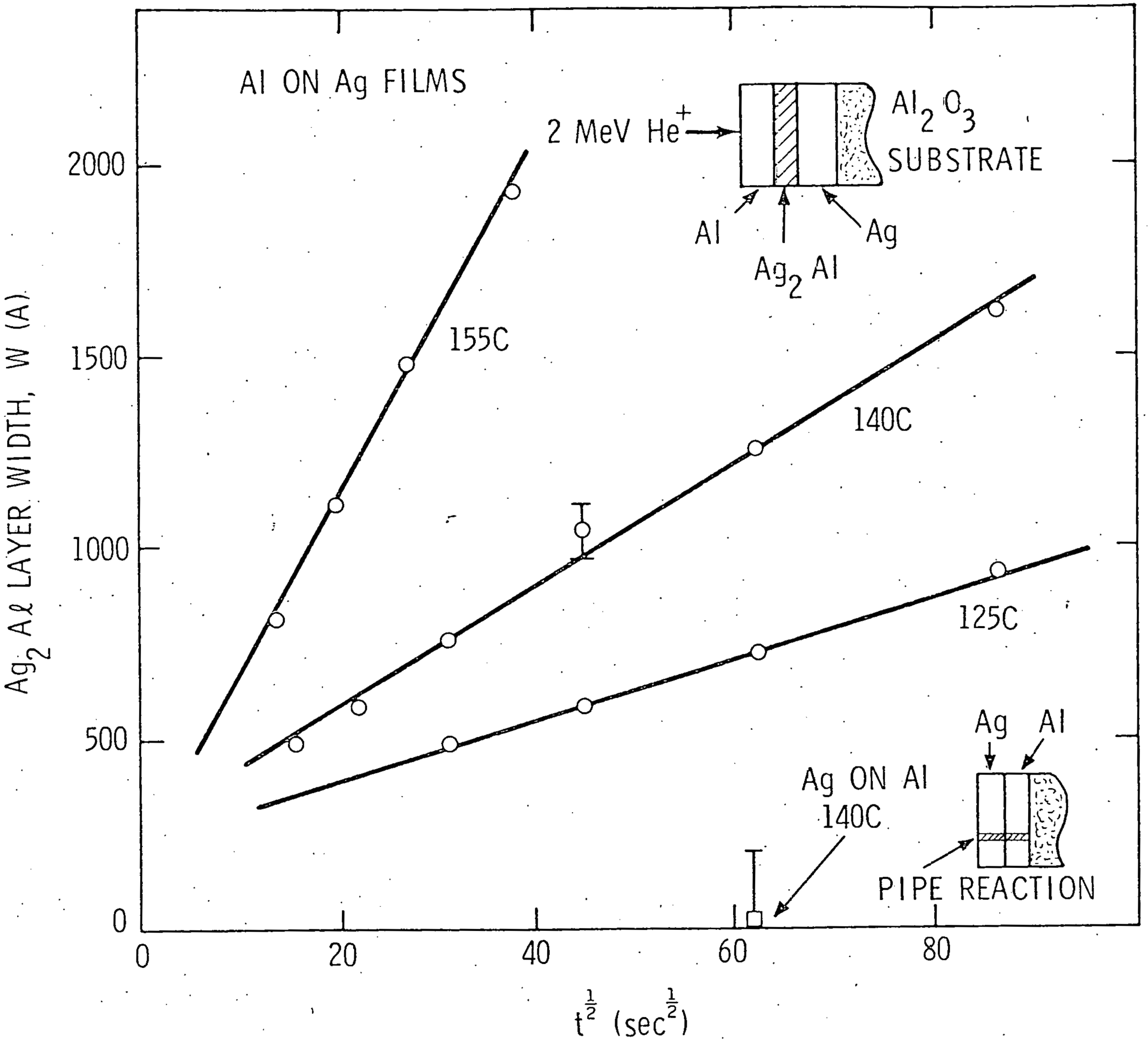

900 keV d
Si
Si O$_2$ UNDERLAY
(RESOLUTION LIMITED)
POLY-Si
SURFACE OXIDE
(X 1/10)
^{16}O CONCENTRATION (AT. %)
1
2
3
0
2000
4000
6000
DEPTH (Å)

figure 6



Al ON Ag FILMS
2 MeV He+
Al2 O3 SUBSTRATE
Al
Ag2 Al
Ag
155C
140C
125C
Ag ON Al 140C
Ag
Al
PIPE REACTION
Ag2 Aℓ LAYER WIDTH, W (A)
2000
1500
1000
500
0
0
20
40
60
80
t½ (sec½)

Figure 7

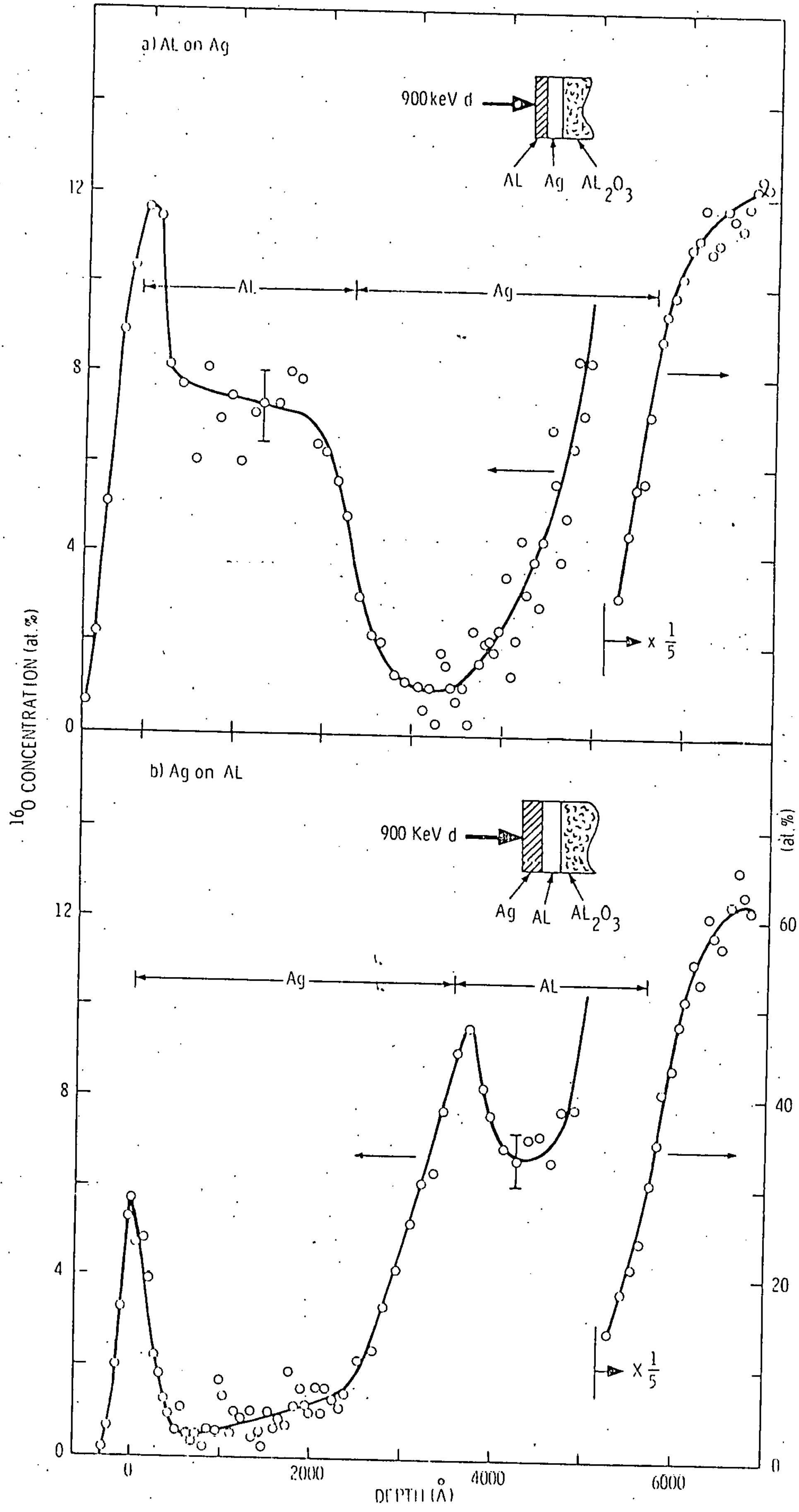

a) AL on Ag
900keV d
AL
Ag
AL_2O_3
AL
Ag
x 1/5
b) Ag on AL
900 KeV d
Ag
AL
AL_2O_3
Ag
AL
x 1/5
^{16}O CONCENTRATION (at.%)
(at.%)
0
4
8
12
0
4
8
12
0
20
40
60
0
2000
4000
6000
DEPTH (Å)

Figure 8