Designation: E 1636 – 94 (Reapproved 1999)

Standard Practice for Analytically Describing Sputter-Depth-Profile Interface Data by an Extended Logistic Function[1]

This standard is issued under the fixed designation E 1636; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers a systematic method for analyzing sputter-depth-profile interface data and for accurately characterizing the shape of the interface region. Interface profile data are described with an appropriate analytic function; the parameters of this function define the interface width, its asymmetry, and its depth from the original surface. The use of this practice is recommended in order that the shapes of composition profiles of interfaces acquired with different instruments and techniques on different materials can be unambiguously compared and interpreted.

1.2 This practice is intended to be used to describe the shape of depth profile data obtained at an interface between two dissimilar materials for that case in which the measured concentration of the outer material goes from 100 to 0 % and the inner material goes from 0 to 100 %.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 673 Terminology Relating to Surface Analysis[2]

E 1127 Guide for Depth Profiling in Auger Electron Spectroscopy[2]

E 1162 Practice for Reporting Sputter Depth Profile Data in Secondary Ion Mass Spectrometry (SIMS)[2]

E 1438 Guide for Measuring Widths of Interfaces in Sputter Depth Profiling Using SIMS[2]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, see Terminology E 673.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 Throughout this practice, the regions of the *sigmoidal profile* will be referred to as the *pre-interface*, *interface*, and *post-interface* regions. These terms are not dependent on whether a particular interface profile is a growth or a decay curve. The terms *pre-* and *post-* are taken in the sense of increasing values of the independent variable *X*, the sputtered depth.

4. Summary of Practice

4.1 Sputter depth profile interface data (composition versus depth) is fitted to an analytic function, an extended form of the logistic function, in order to describe the shape of such interface profiles.[3] Least-squares fitting techniques are employed to determine the values of the parameters of this extended logistic function which characterize the shape of the interface. Interface width, depth, and asymmetry are determined by these parameters.

5. Significance and Use

5.1 Information on interface composition is frequently obtained by measuring surface composition while the specimen material is gradually removed by ion bombardment (see Guide E 1127 and Practice E 1162). In this way, interfaces are revealed and characterized by the measurement of composition versus depth to obtain a sputter-depth profile. The shape of such interface profiles contains information about the physical and chemical properties of the interface region. In order to accurately and unambiguously describe this interface region and to determine its width (see Guide E 1438), it is necessary to define the shape of the entire interface profile with a single analytic function.

5.2 Although no general physical model currently exists for describing the shape of interface sputter-depth profiles, interface profiles do have a sigmoidal shape characteristic of the cumulative logistic distribution. Use of such a logistic function is physically plausible and is superior to other functions (for example, polynomials) that have heretofore been used for interface profile analysis in that it contains the minimum number of parameters for describing interface shapes.

5.3 Many attempts have been made to characterize interface profiles with general functions (such as polynomials or error functions) but these have suffered from instabilities and an inability to handle poorly structured data. Choice of the logistic

[1] This practice is under the jurisdiction of ASTM Committee E-42 on Surface Analysis and is the direct responsibility of Subcommittee E42.08 on Ion Beam Sputtering.

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[2] *Annual Book of ASTM Standards*, Vol 03.06.

[3] Kirchhoff, W. H., Chambers, G. P., and Fine, J., "An Analytical Expression for Describing Auger Sputter Depth Profile Shapes of Interfaces," *Journal of Vacuum Science and Technology*, , p. 1666, 1986.

function along with a specifically written least-squares procedure (described in Appendix X1) can provide statistically evaluated parameters that describe the width, asymmetry, and depth of interface profiles in a reproducible and unambiguous way.

6. Description of the Analysis

6.1 *Logistic Function Data Analysis*—In its simplest form, the logistic function may be written as:

$$Y = \frac{1}{1 + e^{-x}} \tag{1}$$

in which Y progresses from 0 to 1 as X varies from $-\infty$ to $+\infty$. The differential equation generating this function is:

$$dY/dX = Y(1 - Y) \tag{2}$$

and in this form describes a situation where a measurable quantity Y grows in proportion to Y and in proportion to finite resources required by Y. The logistic function was first named and applied to population growth in the last century by Verhulst.[4] The logistic function as a distribution function and growth curve has been extensively reviewed by Johnson and Kotz.[5] Interface profile data is fitted to an extended form of the logistic function:

$$Y = [A + A_s(X - X_o)]/(1 + e^z) + [B + B_s(X - X_o)]/(1 + e^{-z}) \tag{3}$$

where:

$$z = (X - X_o)/D \tag{4}$$

and:

$$D = 2\,D_o/[1 + e^{Q(X - X_o)}] \tag{5}$$

6.1.1 Y is a measure of the elemental surface concentration of one of the components and X, the independent variable, is a measure of the sputtered depth, usually expressed as a sputtering time. Pre-interface and post-interface elemental surface concentrations are described by the parameters A and B, respectively, the parameters A_s and B_s are introduced to account for time dependent instrumental effects. X_o is the midpoint of the interface region (interface depth or time). The scaling factor D_o is the characteristic depth for sputtering through the interface region; Q, an asymmetry parameter, is a measure of the difference in curvature in the pre- and post-interface ends of the interface region. All measures of the interface width can be determined from D_o and Q.

6.2 Fitting of interface profile data to the above functions, Eq 3 , can be accomplished by using least-squares techniques. Because these equations are non-linear functions of the three transition-region parameters, X_o, D_o, and Q, the least-squares fit requires an iterative solution. Consequently, Y, as expressed by Eq 3 , can be expanded in a Taylor series about the current values of the parameters and the Taylor series terminated after the first (that is, linear) term for each parameter. Y (obs) − Y (calc) is fit to this linear expression and the least-squares routine returns the corrections to the parameters. The parameters are updated and the procedure is repeated until the corrections to the parameters are deemed to be insignificant compared to their standard deviations. Values for interface width, depth, and asymmetry can be calculated from the parameters of the fitted logistic function.

6.3 Implementation of this procedure can be readily accomplished by making use of a specialized computer algorithm and supporting software (LOGIT) developed specifically for this application and described in Appendix X1.

7. Interpretation of Results

7.1 The seven parameters necessary to characterize the interface profile shape are determined by a least-squares fit of the interface data to the extended logistic function. These parameters are related to the three distinct regions of the interface profile. Two parameters, an intercept A and a slope $A_s$are necessary to define the pre-interface asymptote while two more, B and B_s, define the post-interface asymptote. For the analysis of typical interface profiles, it is usual to assume that both of these slopes are zero. Two more parameters, $D_o$and X_o, define the slope and position of the transition region. In addition, an asymmetry parameter Q that causes the width parameter to vary logistically from O to $2D_o$, is introduced as a measure of the difference in curvature in the pre- and post-transition ends of the transition region. If Q < O, the pre-transition region has the greatest (sharpest) curvature. If Q > O, the post-transition region has the greatest curvature. If Q = O, $D = D_o$ and the transition profile is symmetric. The parameter Q has the dimensions of $1/X$ whereas D_o has the dimensions of X. The product QD_o is dimensionless and is a measure of the asymmetry of the profile independent of its width. If the absolute magnitude of $QD_o$is less than 0.1, the asymmetry in the transition profile should be barely discernible.

7.2 The final results should include the calculated values of Y and associated statistics, the values of the determined parameters and their uncertainties, and statistics related to the overall quality of the least-squares fit.

7.3 The width of the interface region, I_f, is the depth (time) required for the decay or growth curve to progress from a fraction f of completion to $(1 - f)$ of completion. For the case where Q = O, I_f is proportional to D_o and is given by the simple formula:

$$I_f = 2\,D_o\,1n\,[(1 - f)/f] \tag{6}$$

so that, for example, the traditional 16 to 84 % interface width is 3.32 D_o.

7.4 Introduction of the asymmetry parameter Q into the extended logistic function makes the calculation of the 16 to 84 % points of the interface more complicated. In particular, for fractions f and $(1 - f)$ of completion of the interface transition:

$$X_f = X_o + 2\,D_o\,1n\,[f/(1 - f)]/[1 + e^{Q(X_f - X_o)}] \tag{7}$$

and:

$$X_{(1-f)} = X_o + 2\,D_o\,1n\,[(1 - f)/f]/[1 + e^{Q(X_{1-f} - X_o)}] \tag{8}$$

X_f and $X_{(1-f)}$ can be evaluated most readily by Newton's method of successive approximations.

[4] Verhulst, P. F., *Acad. Brux.* Vol 18, p. 1, 1845.

[5] Johnson, N. L. and Kotz, S., "Distributions in Statistics: Continuous Univariate Distributions," Houghton Mifflin Co., Boston, *2*, Chapter 22, 1970.

8. Reporting of Results

8.1 Interface profile shapes can be accurately characterized by the extended logistic function and its parameters. Results of such interface analysis should report these parameters (X_o, D_o, Q) together with their uncertainties, the standard deviation of the fit, and an interface width obtained from D_o and Q that is based on some accepted definition (for example, 16 to 84 % concentration change).

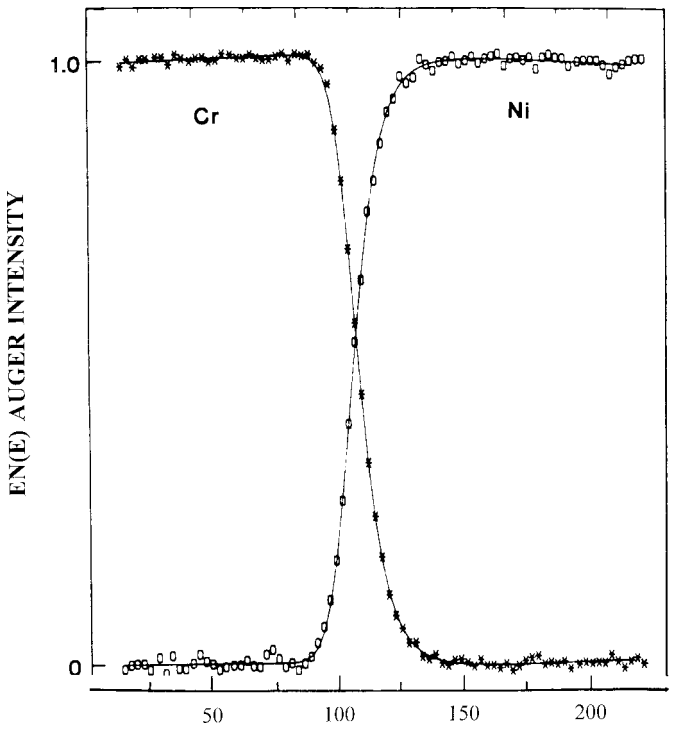
8.2 Sputtered depth, X, is often difficult to determine experimentally so that depth profile data are normally acquired with time as the independent variable. This sputtered time can be referenced with respect to a removal time obtained with a calibrated sputtering standard under the same sputtering conditions of ion energy, beam angle, current density, etc. as the interface measurement itself. In this way, time can be transformed into an equivalent depth derived from a standard material and this equivalent depth should be used in reporting the interface parameters and analysis results. Sputtering standards are available from the National Institute of Standards and Technology (SRM 2136)[6] and from the UK National Physical Laboratory (No. S7B83).[7]

9. Example of Interface Profile Data Analysis Using the Method Suggested

9.1 Sputter-depth-profile data obtained at an interface between Cr and Ni has been analyzed by fitting the extended logistic function to this data using least-squares techniques. The results of this analysis are presented in Fig. 1; the solid lines are calculated values from Eq 3 . A separate analysis was done for each constituent to determine the parameters of the fit; these are listed in Table 1. Comparison of the chromium and nickel parameters indicates the high precision attainable in describing the profile shape and in determining sputtered depth (and, therefore, interface width) with this analysis method.

10. Keywords

10.1 logistic function; sputter-depth-profile interface data



NOTE 1—The solid lines are the calculated values from Eq 3 . Parameters of the fit are given in Table 1.

FIG. 1 Typical Depth Profile of Chromium Through a Chromium (x) and Nickel (o) Interface

[6] Available from National Institute of Standards and Technology, (NIST) Gaithersburg, MD 20899.

[7] Available from UK National Physical Laboratory, Teddington, Middlesex, UK TW 10LW.

TABLE 1 Profile Parameters for a Typical Chromium/Nickel Interface

Chromium (Disappearance Profile)	Nickel (Appearance Profile)
$A = 14893 \pm 43$	$A = -88 \pm 47$
$A_s = 4.59 \pm 1.32$	$A_s = 1.65 \pm 1.46$
$B = -168 \pm 69$	$B = 10656 \pm 73$
$B_s = 4.43 \pm 1.81$	$B_s = -2.19 \pm 1.90$
$X_o = 108.2 \pm 0.1$ min	$X_o = 107.3 \pm 0.1$ min
$D_o = 2.86 \pm 0.03$ min	$D_o = 2.80 \pm 0.05$ min
$Q = -0.045 \pm 0.006$ min^{-1}	$Q = -0.047 \pm 0.008$ min^{-1}
72 data points, 20 in the interval	73 data points, 18 in the interval
Standard Deviation in $Y = 79.1$	Standard Deviation in $Y = 89.9$

APPENDIX

(Nonmandatory Information)

X1. FITTING OF DEPTH PROFILE INTERFACE DATA TO THE LOGISTIC FUNCTION BY MEANS OF A SPECIALIZED COMPUTER ALGORITHM, LOGIT[7]

X1.1 Scope

X1.1.1 This appendix describes a specialized computer algorithm and supporting software (LOGIT) developed for the fitting of depth profile interface data to the extended logistic function in order to determine the parameters of this fitted function. These parameters characterize the shape of the interface region and so define the interface width, its asymmetry, and its depth from the original surface.

X1.2 Significance and Use

X1.2.1 LOGIT has been developed to fit interface profile data to the extended logistic function. The specifically written least-squares procedure used in LOGIT results in a rapid and reliable analysis. An important feature of LOGIT is that it does not require initial estimates to be made of the parameters; it is, therefore, simple and easy to use and can run without operator intervention. LOGIT is robust in handling a wide variety of data of sigmoidal character and can deal effectively with extremely sharp profiles, noisy data, and pronounced outliers.

X1.2.2 LOGIT has been extensively tested on a variety of interface profile data; it has been found able to fit such data to the extended logistic function to within the measurement uncertainty.

X1.2.3 LOGIT is a suitable implementation procedure for use with this practice.

X1.3 Description of the Procedure, LOGIT

X1.3.1 LOGIT consists of a main program and 14 subroutines written in Fortran 77. The version available will run on IBM XT, AT, and compatible personal computers possessing a mathematics coprocessor (Intel 8087 and 80287). Typically, 250K of memory should be available for the program and its data requirements. This version is user friendly and contains various graphics subroutines for displaying the data, plotting the results of the analysis, and for graphical editing of data.

X1.3.2 It is available on diskette together with accompanying documentation and instructions for use from NIST (NISTIR88-3803).[8]

X1.3.3 LOGIT operates on ASCII text files created by the user. The data is in the form of X, Y pairs where X is the independent variable and Y is the dependent variable. The data must be in order of increasing X and should also contain at least five points within each of the pre- and post-interface limits.

X1.3.4 LOGIT provides statistical uncertainties on the parameters of the logistic function allowing assessment and comparison of data quality from different laboratories.

X1.4 Description of the Fitting Procedure Used in LOGIT

X1.4.1 Data in the form of X, Y pairs and saved in a file are fit by the method of least-squares to the following equation:

$$Y = [A + A_s(X - X_o)]/(1 + e^z) + [B + B_s(X - X_o)]/(1 + e^{-z}) \quad \text{(X1.1)}$$

where:

$$z = (X - X_o)/D, \text{ and } D = 2D_o/[1 + e^{Q(X - X_o)}] \quad \text{(X1.2)}$$

X1.4.1.1 Because these equations are non-linear functions of the three transition region parameters, X_o, D_o, and Q, the least-squares fit requires an iterative solution. Consequently, Y, as expressed above is expanded in a Taylor series about the current values of the parameters and the Taylor series is terminated after the first (that is, linear) term for each parameter. Y (obs) − Y (calc) is fit to this linear expression and the least-squares routine returns the corrections to the parameters. The parameters are updated and the procedure is repeated until the corrections to the parameters are deemed to be insignificant compared to their standard deviations.

X1.4.2 Initial estimates of the values of the parameters are calculated in LOGIT automatically by one of three methods. These methods were selected because they are least prone to false starts in situations of poorly structured data. Choice of method is determined in LOGIT if the preceding method fails to converge in the requisite number of iterations.

X1.4.3 *The Least-Square Analysis*—A cycle of up to p iterations is executed in which, at the end of each iteration, the parameters are updated before the next iteration is performed. The number of iterations p is chosen on the basis of experience with particular classes of data. If p is selected to be a prime number, oscillations between two or three local minima can be identified by performing repeated multiples of p iterations. Generally, if convergence takes longer than eleven iterations, the solution is unstable in the sense that all of the parameters cannot be determined from the data. In most cases, instability of the fit can be interpreted by the program and the source of the instability removed by varying one fewer parameter in the least-squares fit. Messages keep the user informed of these situations. The confidence limits for the logistic curve calculated from the parameters of the least-squares fit are directly determined in LOGIT.

X1.4.4 Situations with few data in the transition region can be accommodated by LOGIT but with some loss in accuracy.

X1.4.5 *Post-Fitting Tests*—Following the cycle of p iterations, four tests are performed to judge the quality of the fit, to test the assumption of the determinability of X_o, D_o, and Q, and to test the determinability of the asymptotic parameters A_s and B_s. If a test is failed, the analysis is repeated holding certain parameters constant. The user has control, however, over whether the analysis is repeated or not.

[8] Kirchhoff, W. H., "Logistic Function Data Analysis Program LOGIT," *NISTIR88-3803*, National Institute of Standards and Technology, 1988.

X1.4.5.1 The philosophy underlying the performance of the post-fitting tests is that the parameters A_s, B_s, and Q are less critical in the analysis of the logistic profile than the parameters D_o and X_o. In general (but not always), the former are of a heuristic nature and have little basis in the theory underlying the use of the logistic function in a particular application.

X1.4.6 *Outlier Identification and Rejection*—If directed to do so, LOGIT will, following completion of analysis, identify outliers using criteria provided by the user. If any are identified and if LOGIT is directed to do so, the data will be refit with the outliers dropped from the data being fit. The standardized residuals are used for the identification of the outliers. A standardized residual is the number of standard deviations by which $Y_{obs} - Y_{calc}$ differs from its expected value of zero, that is, the value of $Y_{obs} - Y_{calc}$ divided by the standard deviation of $Y_{obs} = Y_{calc}$. For extensive data sets, a value of standardized residual greater in absolute magnitude than 3.0 is generally an outlier.

X1.5 Analysis Procedure Using LOGIT

X1.5.1 LOGIT is used in an interactive configuration for the analysis of interface profile data. Options are selected by the user in response to a series of questions. Use of graphical editing as well as of graphical display is readily available. The user can select the following:

X1.5.1.1 Which data files are to be analyzed,

X1.5.1.2 Where the results of the analysis are to be stored or displayed,

X1.5.1.3 Which parameters are to be varied,

X1.5.1.4 Which data are to be included in the analysis,

X1.5.1.5 Whether or not outliers are to be excluded from the fit and if so, using what criteria,

X1.5.1.6 Which post-fitting tests are to be applied, and

X1.5.1.7 Whether or not data for a plotting program are to be saved.

X1.5.2 A complete description, in tutorial form, is given for the use of LOGIT together with responses from the program and comments on the interpretation of the responses.

X1.5.3 Six data files of test data accompany the program and may be used to evaluate program performance as well as for familiarization in the use of LOGIT.

X1.6 Results of the Analysis

X1.6.1 The final results of the interface profile analysis obtained with LOGIT include the original data, the calculated values of Y and associated statistics, the values of the determined parameters and their uncertainties, and statistics related to the overall quality of the least-squares fit.

X1.6.2 Use of these parameters to characterize the interface profile has been described in the accompanying Practice E 1636.

X1.7 Summary Demonstration of LOGIT

X1.7.1 The accompanying two figures demonstrate the features of LOGIT. They depict a depth profile analysis of an interface between chromium and nickel. The vertical axis is a measure of the chromium concentration through the interface and the horizontal axis is a measure of the depth into the interface. These data accompany the documentation of the program as one of the test data sets.

X1.7.2 Fig. X1.1 presents the analysis of the data in which outliers were not to be identified. The data are represented with open circles and the vertical bars are two standard deviations as determined by the least-squares fit and should be a measure of the overall measurement precision. The smooth curve represents the best fit of the data to:

$$Y = \frac{A}{1 + e^{z}} + \frac{B}{1 + e^{-z}} \tag{X1.3}$$

where:

$$z = (X - X_o)/D, \tag{X1.4}$$

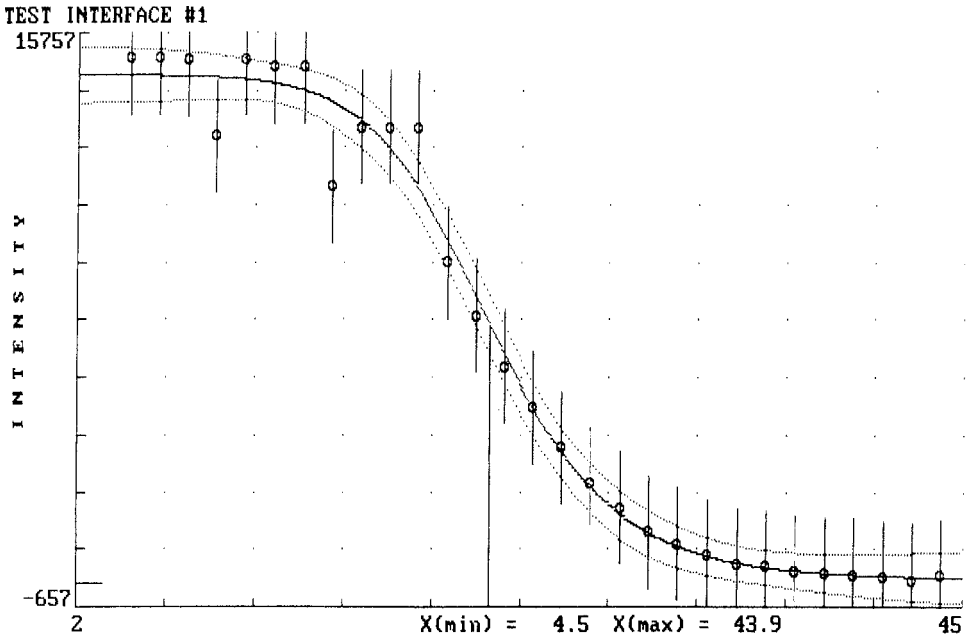
and:

$$D = 2D_o/[1 + e^{Q(X-X_o)}] \tag{X1.5}$$

The dotted curve on either side of the curve of calculated values represents two standard deviations in the calculated values. The values of the parameters and their standard deviations are given. *A* is a measure of the pre-interface concentration of chromium and *B* is a measure of the post-interface concentration. *XO* is the midpoint of the interface, *DO* is the width parameter of the interface and *Q* is an asymmetry parameter, which in this case indicates that the interface is sharper on the pre-interface side.

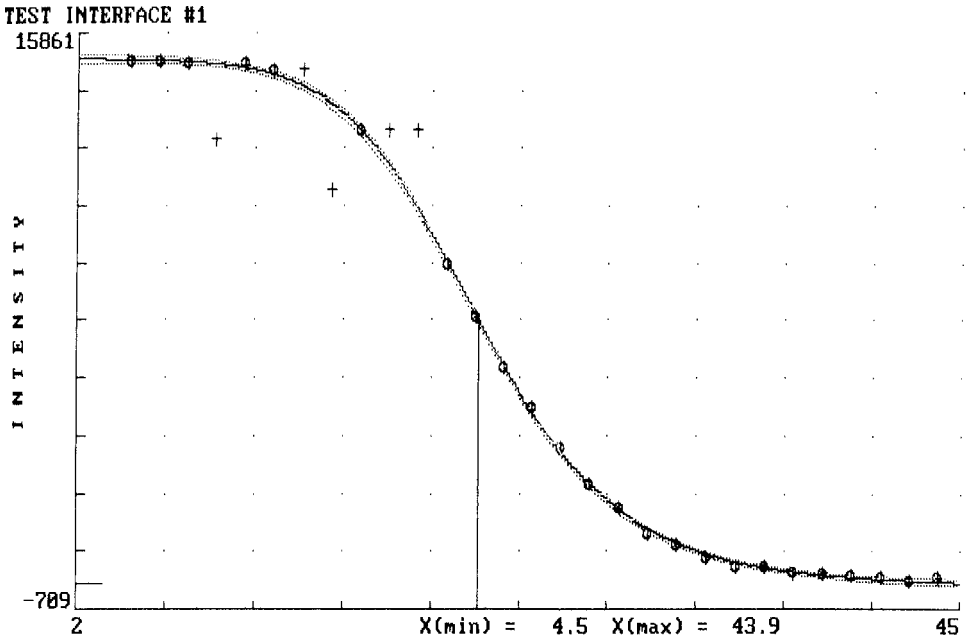
X1.7.3 Fig. X1.2 presents the same data except that LOGIT has been instructed to locate and delete from the fit all outliers lying more than three standard deviations from their calculated values. These five outliers are shown as crosses. The standard deviation of the fit has improved by nearly an order of magnitude as have the uncertainties on the derived parameters. The vertical error bars are still depicted but, because of their low size, can only be easily seen as the vertical bars associated with the outliers. Similarly the plus and minus two standard deviation curves are present but resolvable only at the extremes of the profile.

X1.7.4 The only operator involvement in conducting the analysis was in instructing LOGIT which parameters were to be varied, whether or not outliers were to be identified and eliminated from the analysis, what criteria were to be used in the identification of outliers, and which analyses were to be plotted.



Standard Deviation = 788.0
A = 14558.0 ± 392.0
B = 120.0 ± 437.0
X0 = 22.04 ± 0.37
D0 = 3.03 ± 0.34
Q = −0.027 ± 0.050

FIG. X1.1 Depth-Profile Data Analysis With Outliers Not Identified



Standard Deviation = 98.5
A = 15113.0 ± 62.0
B = −53.0 ± 69.0
X0 = 21.498 ± 0.059
D0 = 3.448 ± 0.057
Q = −0.0315 ± 0.0066

FIG. X1.2 Depth-Profile Data Analysis With Outliers Deleted