A Method for Obtaining Stress-Depth Profiles by Absorption Constrained Profile Fitting of Diffraction Peaks

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Abstract

A new absorption constrained profile fitting method has been developed for use in depth profile analysis of residual stress using x-ray diffraction data at a series of fixed incidence angles. By explicitly accounting for absorption of x-rays during the peak fitting process this method establishes a direct association between a chosen layer depth and resulting fit data. While peak positions are still converted to stress values via conventional methods the method yields plots of average values of stress for layers whose thickness and depth can be independently chosen, rather than plots of stress as a function of 1/e penetration depth. An example of the application of the method to the determination of the residual stress versus depth profile in a 600 nm sputtered W film is presented.

Introduction

Historically, various methods for extracting depth profiles of residual stress from x-ray diffraction peaks have been reported in the literature (1-7). The earliest method (which is still used in some applications) involved collecting a series of diffraction peaks with a layer of material being removed after each pattern was collected (1-2). More recently developed depth profiling methods used a series of fixed incidence diffraction profiles to investigate residual stress as a function of depth. In each case, the peak positions obtained from the diffraction data were associated with the 1/e penetration depth, $\tau$. Subsequently, $\tau$-profiles of residual stress were converted to z-profiles using either a LaPlace transformation technique or numerical methods. Although these more recent depth profiling methods have the advantage over the layer removal method in that they are non-destructive, they are not ideal. In particular, these depth profiling methods are subject to the following limitations:

1. It is difficult to establish the uniqueness of the solution.
2. The LaPlace transformation method can only be used in cases where the profiling depth is much less than the film thickness (5).
3. Since the conventional definition of an expression for $\tau$ assumes a semi-infinite diffracting medium (8), $\tau$ characterization of diffraction data from thin films does not represent a consistent fraction of the diffracted intensity (the fraction of intensity associated with each $\tau$ value depends upon the film thickness, incidence angle and hkl considered).
4. There is insufficient constraint for unique profile fits to be obtained when peaks from different layers are close together in 20.
5. If the structure or the stress state is layered, absorption of the beam with depth is not properly accounted for in the subsurface layers.
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Conventional Peak Fitting

Standard fitting functions usually take the form indicated\(^{(2,9)}\):

\[
I_{2\theta} = I_{\text{Peak}} \left[ \text{Shape Function} \right] + \left[ \text{background} \right] \quad (1)
\]

Here \(I_{2\theta}\) is the intensity at a specified measurement angle \(2\theta\), \(I_{\text{Peak}}\) is a scale parameter, the \textit{background} term is generally a linear function of \(2\theta\) and the \textit{Shape Function} can be one of several standard functions (Gaussian, pseudo Voigt, Pearson 7, etc.). Typically, the shape function is defined so that it varies in magnitude between 0 and 1 hence, the need for the scale parameter \(I_{\text{Peak}}\) to adjust the fitting function to the same vertical scale as that of the data. In the case where diffraction peaks overlap (e.g., diffraction data generated by reflections in different phases) each peak is fitted separately so as to minimize the least-squares error:

\[
\text{Least Squares Error} = C_o \left( \sum \left( I_{2\theta_{\text{Fit}}} - I_{2\theta_{\text{Data}}} \right)^2 \right)^{0.5} \quad (2),
\]

as illustrated in figure 1. Here \(I_{2\theta_{\text{Fit}}}\) is given by,

\[
I_{2\theta_{\text{Fit}}} = I_{\text{Peak} 1} \ast \left( \text{Shape Funct. 1} \right) + I_{\text{Peak} 2} \ast \left( \text{Shape Funct. 2} \right) + \left[ \text{background} \right] \quad (3)
\]

and \(C_o\) is a weighting factor, e.g. the reciprocal of the number of data points in the pattern.

![Figure 1. Conventional peak fitting of diffraction data.](image)

Ordinarily, the peak intensities are independent, however, if they are related the results of this fitting process may no longer be physically meaningful. For example, if the two peaks in figure 1 result from two layers of a single phase in different stress states occurring at different depths, the intensities of the two peaks would be related by the absorption of x-rays as illustrated in figure 2.
Figure 2. Representation of diffracted intensity from a single-phase film exhibiting different stress states as a function of depth.

**Absorption Factor**

To account for this absorption, we start with the expression for the fraction of the total integrated intensity, $G_z$, coming from a surface layer of thickness, $z$, in an infinitely thick diffracting medium (8):

$$G_z = \frac{\int_{z=0}^{z=z} dI_D}{\int_{z=0}^{z=\infty} dI_D}$$  \hspace{1cm} (4),

where $dI_D$ is given by,

$$dI_D = \left( \frac{I_0 a b}{\sin \alpha} \right) e^{-\mu z \left( \frac{1}{\sin \alpha} + \frac{1}{\sin \beta} \right)} dz$$  \hspace{1cm} (5),

with $dI_D$ = an increment of diffracted intensity from a layer of thickness $dz$, $I_0$ = incident beam intensity, $a$ = the volume fraction of crystallites correctly oriented for diffraction, $b$ = the fraction of incident energy diffracted per unit volume, $\mu$ = the linear absorption coefficient and $\alpha$, $\beta$ and $z$ are as defined in figure 3. Expressing $\alpha$ and $\beta$ in terms of $\theta$ and $\psi$ (defined in figure 3) $dI_D$ becomes:

Figure 3. Fixed incidence angle diffraction geometry.
\[ dI_D = \left( \frac{I_o a b}{\text{Sin} \alpha} \right) e^{-\mu z} \left( \frac{2 \text{Sin} \theta \text{Cos} \psi}{\text{Sin}^2 \theta - \text{Sin}^2 \psi} \right) \, dz \]  \hspace{1cm} (6),

and using the Wolfsteig\(^{(10)}\) expression for the \( \Omega \) goniometer, \( \tau = (\text{Sin}^2 \theta - \text{Sin}^2 \psi)/(2\mu \text{Sin} \theta \text{Cos} \psi) \) yields:

\[ dI_D = \left( \frac{I_o a b}{\text{Sin} \alpha} \right) e^{-\frac{\text{Sin} \alpha}{\tau}} \]  \hspace{1cm} (7).

Upon substitution of (7) in (4) the \( I_o, b \) and \( \text{Sin} \alpha \) terms cancel out but if the texture varies with depth the \( a \) terms should be retained. Considering an arbitrary layer defined by depths \( z_{\text{Upper}} \) and \( z_{\text{Lower}} \) in a film of total thickness \( T \), after integration equation (4) becomes:

\[ G_z = \left( \frac{a^*}{a} \right) \left( e^{-\frac{x_{\text{Upper}}}{\tau}} - e^{-\frac{x_{\text{Lower}}}{\tau}} \right) \frac{1 - e^{-\frac{T}{\tau}}}{1 - e^{-\frac{T_{\text{Upper}}}{\tau}}} \]  \hspace{1cm} (8),

where \( a^* = \) the volume averaged texture of the layer defined by depths \( z_{\text{Upper}} \) and \( z_{\text{Lower}} \) and \( a = \) the volume averaged texture for the entire film thickness. The ratio \( (a^*/a) \) can be considered a relative texture coefficient (RTC) and the second term in equation (8) is the factor which expresses the absorption dependence. Thus, we define the terms RTC and (absorption) as follows:

\[ \text{(RTC)} = \frac{a^*}{a} \]  \hspace{1cm} (9),

\[ \text{(absorption)} = \frac{e^{-\frac{x_{\text{Upper}}}{\tau}} - e^{-\frac{x_{\text{Lower}}}{\tau}}}{1 - e^{-\frac{T}{\tau}}} \]  \hspace{1cm} (10).

**Absorption Corrected Fitting Function**

The primary reason for incorporating the absorption term (equation 10) into the fitting function is that it allows for the partitioning of diffraction data based upon specified depth boundaries in addition to accounting for some of the sources of asymmetry inherent in the data. Thus for a given layer:

\[ \text{Fit Function} = \text{(RTC)} \times \text{(absorption)} \times \text{(Shape Function)} \]  \hspace{1cm} (11),

and for the whole film \( I_{2\theta \text{Fit}} \) (i.e., the value which is compared to the data during the least-squares minimization process) is given by,

\[ I_{2\theta \text{Fit}} = I_{\text{Global}} \times \left( \sum_i \text{Fit Functions} \right) + \left[ \text{background} \right] \]  \hspace{1cm} (12).
where \( I_{\text{Global}} \) is a scale factor similar to the \( I_{\text{Peak}} \) term in equation (1), and \( \Sigma \) (Fit Functions) is the sum of the fit functions at each \( 2\theta \) value from each of the i layers in the film. Since a lab Cu K\( \alpha \) x-ray source was used, the shape function in equation (11) is redefined as:

\[
\left( \text{Shape Function} \right)_{\text{Doublet}} = \left( \text{Shape Function} \right)_{K\alpha_1} + \left( \text{Shape Function} \right)_{K\alpha_2} \quad (13).
\]

**Profile Fitting**

The method described above was applied to diffraction data obtained from a 600 nm W film sputtered on a glass substrate, using Cu K\( \alpha \) radiation, the 321 reflection at \( 2\theta \approx 131^\circ \) with fixed incidence angles \( \alpha \) from \( \alpha = 0.6^\circ \) to \( \alpha = 65^\circ \) on a Siemens D500 diffractometer. The number of layers chosen for modeling was either 2 or 3 (2 or 3 layer model) with the boundaries of the layers adjustable within certain limits. The RTC values for each layer were initially fixed at unity while the shape parameters were refined. If the fit was not sufficiently good the RTC values were subsequently refined. The shape function term in equation (13) was chosen to be the pseudo-Voigt function:

\[
I_{\text{Shape Function}} = \frac{\eta}{1 + \left( \frac{2\theta - 2\theta_{\text{Peak}}}{0.5 \times \text{FWHM}} \right)^2} + \frac{1 - \eta}{2} \left( \frac{2\theta - 2\theta_{\text{Peak}}}{0.5 \times \text{FWHM}} \right)^2 \quad (14).
\]

where \( \eta \) = a scalar weight coefficient, \( 2\theta_{\text{Peak}} \) = the maximum intensity position, and FWHM = the full width of the peak at half the maximum intensity. This function was chosen for two reasons.

1. Lorentzian, Gaussian and pseudo Voigt functions were all used to fit LaB\(_6\) (SRM 660) diffraction data collected on the diffractometer used for the film measurements. The pseudo-Voigt results provided the best agreement with published NIST 2\( \theta_{\text{Peak}} \) values.

2. Peak broadening due to small crystallite size is better described by a Lorentzian function while that due to strain is better described by a Gaussian shaped function\(^{12}\). Both crystallite size and residual strain were expected to contribute to the breadth of the W peaks.

During peak fitting the following constraints were imposed on the variables:

- \( \left( 2\theta_{\text{Peak}} \right)_i \): \( 2\theta_{\text{Low}} \leq \left( 2\theta_{\text{Peak}} \right)_i \leq 2\theta_{\text{High}} \), where the Low and High subscripts refer to the first and last measurement angles monitored,
- \( \left( 2\theta_{\text{Peak}} \right)_i \): \( \left( 2\theta_{\text{Peak}} \right)_i \leq \left( 2\theta_{\text{Peak}} \right)_{i+1} \),
- \( \left( \text{FWHM} \right)_i \): \( 0.15^\circ \geq \left( \text{FWHM} \right)_i \) (0.15\(^\circ\) was the instrumental broadening),
- \( \eta_i \): \( 0 \leq \eta_i \leq 1 \),
- \( I_{\text{Global}} \): \( I_{\text{Global}} > 0 \)

\( I_{\text{Background}} \) was obtained from a linear fit to the background intensity on either side of the peaks and was not refined. The K\( \alpha_1 \) - K\( \alpha_2 \) doublet effect is addressed in the fitting process by using independent fit variables to represent the K\( \alpha_1 \) contribution and dependent fit variables to represent the K\( \alpha_2 \) as follows:
2\theta_{K\alpha_2} = 2\ast \text{ArcSin} \left( \frac{\lambda_{K\alpha_2} \ast \sin \theta_{K\alpha_1}}{\lambda_{K\alpha_1}} \right), \text{FWHM}_{K\alpha_2} = \text{FWHM}_{K\alpha_1}, \ \eta_{K\alpha_2} = \eta_{K\alpha_1}, \ \text{and} \ I_{2\theta K\alpha_2} = 0.497 \ast I_{2\theta K\alpha_1}.

The layer boundaries were selected as follows: for the 2-layer model, the limits were \((0,z_1)\) for the first layer and \((z_1,T)\) for the second. A series of fits was performed on each diffraction pattern using a series of different \(z_1\) values, as a means of extracting depth characteristics in the data. Thus, the first \(z_1\) value was arbitrarily chosen to have the smallest value for which the intensity (evaluated at \(2\theta=122^\circ\)), was greater than or equal to 20% of the total intensity. This original \(z_1\) value was increased by a fixed increment whose value depended upon the depth range being surveyed (e.g., \(\Delta z = 10\ \text{nm}\) for \(z_1\) values less than 200 nm, \(\Delta z = 20\ \text{nm}\) for \(z_1\) values less than 300 nm and \(\Delta z = 30\ \text{nm}\) for \(z_1\) less than 470 nm). For each diffraction pattern the total number of fits in the series was determined by the largest value of \(z_1\) such that layer 2 still accounted for 20% of the total intensity.

The second fit in the series (using an incremented value of \(z_1\)), used the results of the first fit as starting values. Similarly, all subsequent fits used the previous solution as the starting values. An example illustrating this process is given in table 1.

Table 1. Initial and refined values of variables for a series of fits performed on the 321 reflection of W with \(\alpha = 1.5^\circ\).

<table>
<thead>
<tr>
<th>Initial Values</th>
<th>Fit Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20 nm 20-600 nm</td>
<td>0-20 nm 20-600 nm</td>
</tr>
<tr>
<td>(K\alpha_1 - 1)</td>
<td>(K\alpha_1 - 2)</td>
</tr>
<tr>
<td>(I_{\text{Global}})</td>
<td>(I_{\text{Global}})</td>
</tr>
<tr>
<td>(2\theta_{\text{Peak}})</td>
<td>(2\theta_{\text{Peak}})</td>
</tr>
<tr>
<td>FWHM</td>
<td>FWHM</td>
</tr>
<tr>
<td>(\eta)</td>
<td>(\eta)</td>
</tr>
<tr>
<td>RTC</td>
<td>RTC</td>
</tr>
<tr>
<td>0.6000</td>
<td>0.5691</td>
</tr>
<tr>
<td>131.0000</td>
<td>132.0000</td>
</tr>
<tr>
<td>2.5000</td>
<td>2.8000</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.5000</td>
</tr>
<tr>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>0.6089</td>
<td>0.5680</td>
</tr>
<tr>
<td>131.6039</td>
<td>131.8979</td>
</tr>
<tr>
<td>1.8658</td>
<td>4.0959</td>
</tr>
<tr>
<td>0.0000</td>
<td>0.1945</td>
</tr>
<tr>
<td>1.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

For the three layer model, the limits were \((0, z_1), (z_1, z_2)\) and \((z_2, T)\) respectively, and two series of fits were performed. In the first series \(z_1\) and \(z_2\) values were selected and all three sets of shape parameters were refined. However, to investigate one effect at a time, \(z_2\) and its corresponding fit parameters were held constant for each of the \(z_1\) incremented fits performed thereafter. Similarly, in the second series of fits, a three peak fit was initially performed but this time \(z_1\) and its corresponding shape parameters were held constant for each ensuing \(z_2\) incremented fits. An example of this process is given in table 2.
Table 2. Initial and refined values of variables for a series of constant $z_2$ fits performed on the 321 reflection of W with $\alpha = 65^\circ$.

<table>
<thead>
<tr>
<th>Initial Values</th>
<th>Fit Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-110 nm</td>
<td>110-440 nm</td>
</tr>
<tr>
<td>$K\alpha_1 - 1$</td>
<td>$K\alpha_1 - 2$</td>
</tr>
<tr>
<td>$I_{Global}$</td>
<td>0.7200</td>
</tr>
<tr>
<td>$2\theta_{Peak}$</td>
<td>128.0000</td>
</tr>
<tr>
<td>FWHM</td>
<td>2.5000</td>
</tr>
<tr>
<td>$\eta$</td>
<td>0.5000</td>
</tr>
<tr>
<td>RTC</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

It was found that 2-layer fits were sufficiently accurate for the data obtained at $\alpha$ values $\leq 10^\circ$. Above these values, 2-layer fits required RTC values $\neq 1$ whereas 3-layer fits were satisfactory with RTC = 1. Examples of 2-layer and 3 layer fits are given in figures 4 and 5 respectively.

Figure 4. Two layer fit (0-70 nm and 70 - 600 nm) for 321 data from a 600 nm W film.
To check the accuracy of the new fitting process, the fit results obtained with the new method were compared with those obtained using conventional peak fitting software\(^9\). In particular, the (1,3,10) and (4,1,6) reflections from SRM 1976 collected (using \(\alpha = 5^\circ\)), were fit using each method. For sake of consistency, both methods employed the same shape function (pseudo-Voigt), considered the same ranges of 2\(\theta\) values and the fits were initiated using the same starting set of fit parameters. Since the new fitting function is designed to partition diffraction data based upon depth and there were no distinct depth features in the diffraction peaks a two peak fit was performed on each diffraction peak using a large \(z_1\) value so as to effectively zero out the influence of the second fit function. In table 3, the fit values are presented along with % difference values using the conventional peak fit values as a reference. For both reflections, the agreement between the two fitting functions is excellent. The difference in \(\eta\) parameter values may be due to a difference in the convergence criteria used by each method or it may be related to the absorption induced asymmetry in the data which is accounted for in the new profile fitting method.

**Depth Profiles of Residual Stress**

As an example of the application of the new method, the results of the refinements on the 600 nm thick W film specimen were used to calculate depth profiles of residual stresses in the film. The procedure used is described elsewhere\((12,13)\). Briefly, the stress state in the film was found to be equi-biaxial hence, the stress-free lattice spacing \(d_0\) could be obtained as a function of depth using Hauk’s expression for the tilt angle \(\psi^*\) at which the lattice spacing is stress free\(^2\). For tungsten, this angle was given by the expression:
Table 3. Fit data from two reflections of Al₂O₃ (SRM 1976) with α = 5

<table>
<thead>
<tr>
<th>Method</th>
<th>I</th>
<th>2θ</th>
<th>FWHM</th>
<th>η</th>
<th>(h,k,l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>2401.44</td>
<td>127.6349°</td>
<td>0.2080°</td>
<td>0.3790</td>
<td>(1,3,10)</td>
</tr>
<tr>
<td>New</td>
<td>2394.24</td>
<td>127.6349°</td>
<td>0.2076°</td>
<td>0.3203</td>
<td>(1,3,10)</td>
</tr>
<tr>
<td>Percent Difference</td>
<td>1</td>
<td>-0.30</td>
<td>2θ</td>
<td>0.00</td>
<td>FWHM</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>I</th>
<th>2θ</th>
<th>FWHM</th>
<th>η</th>
<th>(h,k,l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>4484.04</td>
<td>136.0246°</td>
<td>0.2100°</td>
<td>0.4850</td>
<td>(4,1,6)</td>
</tr>
<tr>
<td>New</td>
<td>4473.11</td>
<td>136.0247°</td>
<td>0.2098°</td>
<td>0.4318</td>
<td>(4,1,6)</td>
</tr>
<tr>
<td>Percent Difference</td>
<td>1</td>
<td>-0.24</td>
<td>2θ</td>
<td>0.00</td>
<td>FWHM</td>
</tr>
</tbody>
</table>

\[
\sin^2 \psi^* = \frac{2v}{1 + v} = 0.4375 \quad (15).
\]

Using these \(d_o\) values and linear \(d\) vs. \(\sin^2 \psi\) plots constructed for layers of a given thicknesses from refined peak positions of diffraction data obtained at different incidence angles, the in-plane stress in each layer was calculated using:

\[
a_{\phi \psi} = a_0 \left( \frac{1 + v}{E} \sigma_{11} \sin^2 \psi \right) + a_{\phi \psi=0} \quad (16),
\]

with \(E = 384.6\) GPa and \(v = 0.28^{(14)}\). Stresses were plotted versus layer midpoint depth as shown in figure 6.

Figure 6. Depth profile of residual stresses in a 600 nm W film using a three layer model and stress-free lattice parameter values.
Conclusions

The new profile fitting method is more appropriate for the analysis of depth profiles of residual stress in single phase films than conventional profile fitting in that it partitions the fit to the x-ray data in proportion to the absorption of x-rays incident on and diffracted from a given layer. In addition, the method allows the user to systematically partition and analyze x-ray data based upon user selected layer boundaries. Finally, the method does not use 1/e penetration depth to characterize x-ray data, rather it generates an exponentially weighted average of the measured quantity for layers whose thickness and depth can be independently chosen subject to having sufficient diffracted intensity for fitting purposes.

References