Sample-morphology effects on x-ray photoelectron peak intensities

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The authors have used the National Institute of Standards and Technology Database for the Simulation of Electron Spectra for Surface Analysis to simulate photoelectron spectra from the four sample morphologies considered by Tougaard [J. Vac. Sci. Technol. A 14, 1415 (1996)]. These simulations were performed for two classes of materials, two instrument configurations, and two conditions, one in which elastic scattering is neglected (corresponding to the Tougaard results) and the other in which it is included. The authors considered the Cu/Au morphologies analyzed by Tougaard and similar SiO$_2$/Si morphologies since elastic-scattering effects are expected to be smaller in the latter materials than the former materials. Film thicknesses in the simulations were adjusted in each case to give essentially the same chosen Cu 2p$_{3/2}$ or O 1s peak intensity. Film thicknesses with elastic scattering switched on were systematically less than those with elastic scattering switched off by up to about 25% for the Cu/Au morphologies and up to about 14% for the SiO$_2$/Si morphologies. For the two morphologies in which the Cu 2p$_{3/2}$ or O 1s peak intensity was attenuated by an overlayer, the ratios of film thicknesses with elastic scattering switched on to those with elastic scattering switched off varied approximately linearly with the single-scattering albedo, a convenient measure of the strength of elastic scattering. This variation was similar to that of the ratio of the effective attenuation length to the inelastic mean free path for the photoelectrons in the overlayer film. For the two morphologies in which the Cu 2p$_{3/2}$ or O 1s photoelectrons originated from an overlayer film, the ratios of film thicknesses with elastic scattering switched on to those with elastic scattering switched off varied more weakly with the single-scattering albedo. This weaker variation was attributed to the weaker effects of elastic scattering for photoelectrons originating predominantly from near-surface atoms than for photoelectrons that travel through an overlayer film. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4774214]

I. INTRODUCTION

It has long been known that variations in sample morphology can have drastic effects on photoelectron intensities in x-ray photoelectron spectroscopy (XPS). Morphological parameters such as crystallinity, roughness, and island or grain dimensions can modify peak intensities and their associated inelastic tails. We will consider here photoelectron spectra and peak intensities from several sample morphologies in which the composition of an element of interest is varying with depth. For example, the intensity of a substrate photoelectron line will change considerably following deposition of an overlayer film of increasing thickness. It is, therefore, generally necessary for an analyst to deduce the morphology of the sample of interest before attempting a quantitative analysis. Alternatively, the sample morphology might be known or can reasonably be inferred from the prior history of the sample, particularly processing steps (e.g., deposition of a film), or knowledge gained from similar samples.

In a seminal 1996 paper, Tougaard showed model spectra with identical Cu 2p$_{3/2}$ photoelectron peak intensities that were obtained from four Cu/Au samples with very different morphologies: a 2.5 nm Au film on a Cu substrate, a 1 nm Cu buried film in an Au matrix, a 5 nm CuAu$_4$ alloy on an Au substrate, and a thin Cu film on an Au substrate. Although the peak Cu 2p$_{3/2}$ intensities were the same for each morphology, the samples had very different distributions of copper concentration versus depth and very different amounts of copper in the near-surface region of each sample. An XPS analysis based solely on the Cu 2p$_{3/2}$ peak intensity and the assumption of a homogeneous sample would thus yield an incorrect result for these Cu/Au morphologies. Tougaard also showed that the shapes of the inelastic spectra on the low-energy side of the 2p$_{3/2}$ peak for each morphology were very different. With use of an algorithm for photoelectron transport in the solid, analysis of the XPS peak shape (i.e., the main or no-loss peak and its accompanying inelastic region) could give information on the depth distribution of the emitting atom and the amount of that substance. Convenient software is available for this purpose. Recent reviews summarize further developments of Tougaard’s approach and algorithms for different applications.

The Tougaard algorithms and software are based on the assumption that elastic scattering of the detected photoelectrons can be neglected. Although most samples of practical
interest for XPS analyses are polycrystalline or amorphous so that diffraction and forward-focusing effects are often negligible, it is well known that elastic scattering can affect quantitative analyses and measurements of overlayer film thicknesses.\textsuperscript{1,3,5,11} We report here new calculations of XPS spectra for the morphologies considered by Tougaard. We have used the National Institute of Standards and Technology (NIST) database for the Simulation of Electron Spectra for Surface Analysis (SESSA)\textsuperscript{12,13} to simulate XPS spectra for two classes of materials, two XPS configurations, and two conditions, one in which elastic scattering is considered and the other in which it is neglected. We have considered Cu 2p\textsubscript{3/2} photoelectrons from the same (or similar) Cu/Au morphologies that were previously analyzed by Tougaard.\textsuperscript{4} Both Cu and Au are materials that are expected to show relatively strong effects of elastic scattering, as judged by their values of the single-scattering albedo, \(\omega = \lambda_i/\left(\lambda_i + \lambda_t\right)\), where \(\lambda_i\) and \(\lambda_t\) are the inelastic mean free path (IMFP) and the transport mean free path (TMFP), respectively, of photoelectrons in a solid;\textsuperscript{14} the values of \(\omega\) for Cu and Au will be shown and discussed below. We have also considered O 1s photoelectrons from similar SiO\textsubscript{2}/Si morphologies. Both Si and SiO\textsubscript{2} are materials with \(\omega\) values much less than those of Cu and Au, and thus are expected to show relatively weak effects of elastic scattering.

Figure 1 shows schematic diagrams of the four morphologies we considered with the Cu/Au compositions indicated on the left and the SiO\textsubscript{2}/Si compositions on the right. The hatched regions represent the films or phases from which the photoelectrons of interest are emitted (i.e., Cu 2p\textsubscript{3/2} or O 1s photoelectrons). The thickness of the buried layer in the morphology of Fig. 1(b) was chosen to be 1 nm for the Cu film (as in the original Tougaard work\textsuperscript{4}) or 2.5 nm for the SiO\textsubscript{2} film. For the morphologies of Figs. 1(a) and 1(b), we determined the thicknesses of the overlayer films (either Au or Si) that gave a certain Cu 2p\textsubscript{3/2} or O 1s photoelectron peak intensity. For the morphologies of Figs. 1(c) and 1(d), we determined the thicknesses of the outermost layers that gave the same photoelectron peak intensities. Peak intensities were judged to be the same as the chosen intensity if they were within 1% of that value. We discuss below the extent to which the selected thicknesses vary with elastic scattering of the photoelectrons switched on or off in the simulations for each XPS configuration.

Although Tougaard considered a CuAu\textsubscript{4} film on Au for the Fig. 1(c) morphology, we found it necessary in the present work to choose a CuAu\textsubscript{3} film on Au in order to obtain satisfactory precision in the relevant thicknesses. Thus, while the background intensity below the peak is substantially different for a 5 nm thick film and an infinite film, the peak intensity will be almost identical when the film thickness is more than three times the relevant mean escape depth for Cu 2p\textsubscript{3/2} photoelectrons.\textsuperscript{15,16} We note that the Fig. 1(c) morphology can be viewed as a representation of islands on a substrate (e.g., Cu islands on an Au substrate). For near-normal emission, possible shadowing effects from neighboring islands are negligible. Similarly, the chosen (SiO\textsubscript{2})Si\textsubscript{20} “compound” is a representation of SiO\textsubscript{2} islands on a Si substrate. The rather different stoichiometry for this compound compared to CuAu\textsubscript{3} was chosen in order to lead to similar film thicknesses for the Fig. 1(c) morphologies.

The SESSA simulations were performed for two XPS configurations in which there was a fixed angle, \(\psi\), of 55° between the direction of the incident x rays on the sample and the average direction of photoelectrons to the analyzer. For many XPS instruments, \(\psi\) is chosen to be at or close to the so-called magic angle of 54.7° at which there is no effect of anisotropy on the photoionization cross section.\textsuperscript{17} The angular-acceptance semi-angle of the analyzer was chosen to be 5°. All simulations were made with excitation by Al K\(\alpha\) x rays. In one XPS configuration, the x rays were incident on the sample at 55° with respect to the surface normal, and the average emission angle, \(\alpha\), of photoelectrons accepted by the analyzer was 0° (also with respect to the surface normal). In the other XPS configuration, \(\alpha\) was chosen to be 65° and the x-ray angle of incidence was 10°. We utilized differential elastic-scattering cross sections from the NIST electron elastic-scattering cross-section database\textsuperscript{18,19} and IMFPs from the calculations of Tanuma \textit{et al.} for Si, Cu, and Au (Refs. 15 and 20) and the TPP-2M predictive IMFP formula of Tanuma \textit{et al.}\textsuperscript{21} for SiO\textsubscript{2} and the two compounds for the Fig. 1(c) morphology discussed below, CuAu\textsubscript{3} and (SiO\textsubscript{2})Si\textsubscript{20}.

Most SESSA simulations were performed with two differential inverse inelastic mean free paths (DIIIMFPs) to represent the different probabilities of photoelectron energy loss in the outermost two materials. For the Fig. 1(c) morphologies,
however, we chose a single DIIMFP (that of Cu or SiO$_2$) to represent inelastic scattering of the photoelectrons in the assumed Cu or SiO$_2$ islands. We used the DIIMFPs of Werner$^{22}$ that are available in SESSA.

The simulations were made with intrinsic Cu 2p and O 1s spectra obtained by Tougaard from analyses of measured XPS spectra from bulk Cu (Ref. 23) and SiO$_2$ (Ref. 24) with the QUASES software.$^{7,8}$ as shown in Fig. 2. The Cu 2p spectrum in Fig. 2(a) had been measured with an unmonochromated Al K$_x$ x-ray source while the O 1s spectrum in Fig. 2(b) had been measured with a monochromated Al K$_x$ source. The intrinsic Cu 2p spectrum shows appreciable shakeup intensity at energies less than the “main” or no-loss Cu 2p peaks while there is negligible shakeup intensity in the intrinsic O 1s spectrum.

II. RESULTS

Figure 3(a) shows the Cu 2p spectra from the SESSA simulations for the Cu/Au morphologies of Fig. 1 with $\alpha = 0^\circ$ and with elastic scattering switched on. Our initial simulations were made with a 0.11 nm Cu film on an Au substrate, the same film thickness chosen by Tougaard for the Fig. 1(d) morphology. The resulting spectrum is the bottom curve of Fig. 3(a). The other spectra in Fig. 3(a) are for the other Cu/Au morphologies in Fig. 1 and were obtained by adjusting the relevant film thicknesses to give the same Cu 2p$_{3/2}$ peak intensity. Similar spectra are shown in Fig. 3(b) from the simulations with elastic scattering switched off and with film thicknesses chosen to give the same Cu 2p$_{3/2}$ peak intensities as in Fig. 3(a).

The spectra in Fig. 3 are qualitatively similar although not identical to those reported by Tougaard.$^4$ The spectra in Fig. 3(b), where elastic scattering is switched off, should be identical to those of Tougaard.$^4$ The differences observed in the film thicknesses (which were determined by the condition that they gave the same Cu 2p$_{3/2}$ peak intensity) and small differences in the shapes of the background are ascribed to differences in the chosen IMFPs as well as to differences in the DIIMFPs used here$^{22}$ and by Tougaard.$^{25}$

The spectra in Fig. 3(b) are generally similar to those in Fig. 3(a) but there are some differences. The spectrum in Fig. 3(b) for the Au film on a Cu substrate has a much higher intensity and a larger gradient at an energy of 450 eV than the corresponding spectrum in Fig. 3(a). In contrast, the inelastic tails on the two spectra for Cu and CuAu$_3$ films on an Au substrate in Fig. 3(b) are weaker than for the corresponding spectra in Fig. 3(a).

Figure 4 shows the Cu 2p spectra from the SESSA simulations for the Cu/Au morphologies of Fig. 1 with $\alpha = 65^\circ$. The shapes of the spectra are qualitatively similar to those of the corresponding spectra in Fig. 3. Although there are generally small differences in the spectra for the two emission angles, the inelastic tails on the spectra for the buried 1.0 nm Cu film in an Au matrix are much stronger for $\alpha = 65^\circ$ than for $\alpha = 0^\circ$.

The film thicknesses found from the simulations with elastic scattering switched on are given in the legends of
Figs. 3(a) and 4(a) are less than those obtained when elastic scattering is switched off [given in the legends of Figs. 3(b) and 4(b)] by about 26% for the morphologies of Figs. 1(a) and 1(b) and about 9% for the morphologies of Figs. 1(c) and 1(d). These changes will be discussed further below.

Figures 5 and 6 show the simulated O 1s photoelectron spectra from SiO$_2$ for the similar SiO$_2$/Si morphologies of Fig. 1 for $\alpha = 0^\circ$ and $\alpha = 65^\circ$, respectively. Our initial simulations were made with elastic scattering switched on and with a 0.1 nm SiO$_2$ film on an Si substrate, and the resulting spectrum is shown as the bottom curve in Fig. 5(a). Film thicknesses for the other spectra in Figs. 5 and 6 were adjusted to give the same O 1s peak intensity. The O 1s spectra in Figs. 5 and 6 are qualitatively similar to the corresponding Cu 2p spectra in Figs. 3 and 4, although an obvious difference for the O 1s spectra for Si films on an SiO$_2$ substrate or film [the morphologies of Figs. 1(a) and 1(b)] is the sharp structure associated with multiple excitations of the bulk plasmon in Si. In contrast, the DHMFP for Au consists of broad, overlapping peaks.$^{25}$ Another difference is the relatively weak inelastic tails of the O 1s spectra for (SiO$_2$)$_{20}$ and SiO$_2$ on a Si substrate [the morphologies of Figs. 1(c) and 1(d)] in Figs. 5 and 6 compared to the corresponding Cu 2p spectra for these morphologies in Figs. 3 and 4; this difference is associated with the relatively weak shakeup intensity in the intrinsic O 1s spectrum in Fig. 2(b) compared to that for the intrinsic Cu 2p spectrum in Fig. 2(a).

We point out that the spectra in Figs. 5(b) and 6(b) for the Si film on an SiO$_2$ substrate (with elastic scattering switched off) have a much higher intensity and a larger gradient at an energy of 850 eV than the corresponding spectra in Figs. 5(a) and 6(a) (with elastic scattering switched on). A similar result was found for the Au film on a Cu substrate in Figs. 3 and 4. We also note that the inelastic tails on the spectra for the buried 2.5 nm SiO$_2$ film in Si are noticeably stronger for $\alpha = 65^\circ$ in Fig. 6 than for $\alpha = 0^\circ$ in Fig. 5, particularly for the spectra with elastic scattering switched off. A similar trend was found for the spectra of the buried 1.0 nm Cu film in Au shown in Figs. 3 and 4. Finally, the film thicknesses found from the simulations with elastic scattering switched on [as shown in the legends of Figs. 5(a) and 6(a)] for the morphologies of Figs. 1(a) and 1(b) are approximately 14% less than those found with elastic scattering switched off [as shown in the legends of Figs. 5(b) and 6(b)]. The corresponding reductions for the morphologies of Figs. 1(c) and 1(d) are about 7%.

III. DISCUSSION

It is clear from Figs. 3 to 6 that inclusion of elastic scattering in a simulation changes the film thickness required to give a selected Cu 2p$_{3/2}$ or O 1s peak intensity for each of the sample morphologies of Fig. 1. Figure 7 shows plots of the ratios, $R$, of film thicknesses found with elastic scattering switched on, $t_{\text{on}}$ [as given in the legends of Figs. 3(a), 4(a), 5(a), and 6(a)], to the corresponding thicknesses found with elastic scattering switched off, $t_{\text{off}}$ [as given in the legends of Figs. 3(b), 4(b), 5(b), and 6(b)], as a function of the
single-scattering albedo, \( \omega \), defined earlier. Values of \( \omega \) were obtained from the IMFPs and TMFPs for the materials and electron energies of interest, as shown in Table I. TMFPs from the NIST Electron Effective-Attenuation-Length Database (SRD 82)\(^{26} \) were derived from calculations of differential elastic-scattering cross sections with the Dirac-Hartree-Fock potential,\(^{18,19} \) as described elsewhere.\(^{3,14} \) The single-scattering albedo is a convenient measure of the strength of elastic-scattering effects in XPS.\(^{3,14} \) The error bars for \( R \) in Fig 7 were obtained from the estimated one-standard-deviation uncertainties of the film thicknesses given in the legends of Figs. 3–6.

We show separate plots of \( R \) vs \( x \) for the morphologies (c) and (d) of Fig. 1 in Fig. 7(a) and the morphologies (a) and (b) of Fig. 1 in Fig. 7(b). Although there is some scatter, the \( R \) values in Fig. 7(b) decrease approximately linearly with increasing \( x \). This dependence can be understood from the following analysis. If elastic scattering is switched off, the Cu 2p3/2 or O 1s peak intensity from the substrate [Fig. 1(a)] or the buried Cu film [Fig. 1(b)], \( I_{\text{off}}(t_{\text{off}}) \), for an overlayer Au or Si film of thickness \( t_{\text{off}} \) will be given by

\[
I_{\text{off}}(t_{\text{off}}) = I^0_{\text{off}} \exp\left(-t_{\text{off}}/(\lambda^0 \cos \alpha)\right),
\]

where \( I^0_{\text{off}} \) is the corresponding peak intensity with no overlayer film and \( \lambda^0 \) is the IMFP of the particular photoelectrons in the film. Similarly, the peak intensity with elastic scattering switched on, \( I_{\text{on}}(t) \), for an overlayer of thickness \( t_{\text{on}} \) can be written

\[
I_{\text{on}}(t) = I^0_{\text{on}} \exp\left[-t_{\text{on}}/(L^f \cos \alpha)\right],
\]

where \( I^0_{\text{on}} \) is the peak intensity with no overlayer film and \( L^f \) is the effective attenuation length (EAL) of the Cu 2p3/2 or O 1s photoelectrons in the film. We assume initially that \( I^0_{\text{off}} = I^0_{\text{on}} \). Since the film thicknesses were adjusted to give essentially the same peak intensities in a set of simulations, \( I_{\text{off}}(t_{\text{off}}) = I_{\text{on}}(t_{\text{on}}) \), and thus

\[
R \equiv t_{\text{on}}/t_{\text{off}} = L^f/L^0.
\]

Jablonski and Powell\(^{16} \) found the following empirical relation for the ratio, \( R_{\text{EAL}} \), of the EAL to the IMFP:

\[
R_{\text{EAL}} = 1 - 0.735\omega.
\]

![Fig. 6. (Color online) Same as Fig. 5 except with \( \alpha = 65^\circ \).](image)

![Fig. 7. (Color online) Plots of the ratios, \( R \), of film thicknesses found with elastic scattering switched on [given in the legends of Figs. 3(a), 4(a), 5(a), and 6(a)] to the corresponding thicknesses found with elastic scattering switched off [given in the legends of Figs. 3(b), 4(b), 5(b), and 6(b)] as a function of the single-scattering albedo, \( \omega \), for photoelectron emission angle \( \alpha = 0^\circ \) (\( \bullet \)) and \( \alpha = 65^\circ \) (\( \square \)). The error bars for \( R \) represent one-standard-deviation uncertainties based on the uncertainties in determining the film thicknesses shown in the legends of Figs. 3–6. (a) Morphologies (c) and (d) of Fig. 1 and (b) morphologies (a) and (b) of Fig. 1. The positions of the points for \( \alpha = 65^\circ \) have been shifted horizontally to avoid overlaps with the points for \( \alpha = 0^\circ \). The dashed line in Fig. 7(b) is a plot of \( R_{\text{EAL}} \) from Eq. (4).](image)

![Table I. Values of IMFPs, TMFPs, and the single-scattering albedo, \( \omega \), for the indicated materials and electron energies.](table)

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy (eV)</th>
<th>IMFP (nm)</th>
<th>TMFP (nm)</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>553</td>
<td>1.084</td>
<td>1.772</td>
<td>0.380</td>
</tr>
<tr>
<td>Au</td>
<td>553</td>
<td>0.865</td>
<td>1.762</td>
<td>0.329</td>
</tr>
<tr>
<td>CuAu3</td>
<td>553</td>
<td>0.834</td>
<td>1.831</td>
<td>0.313</td>
</tr>
<tr>
<td>Si</td>
<td>954</td>
<td>2.356</td>
<td>13.95</td>
<td>0.145</td>
</tr>
<tr>
<td>SiO2</td>
<td>954</td>
<td>2.930</td>
<td>16.54</td>
<td>0.151</td>
</tr>
<tr>
<td>(SiO2)Si20</td>
<td>954</td>
<td>2.899</td>
<td>14.13</td>
<td>0.170</td>
</tr>
</tbody>
</table>
This relation was based on EALs calculated from an analytic solution of the kinetic Boltzmann equation within the transport approximation\textsuperscript{27,28} for 16 photoelectron lines and 9 Auger-electron lines from 5 elemental solids (Si, Cu, Ag, W, and Au) and 4 inorganic compounds (ZrO\textsubscript{2}, ZrSiO\textsubscript{4}, HfO\textsubscript{2}, and HfSiO\textsubscript{4}). The dashed line in Fig. 7(b) shows a plot of $R_{\text{EAL}}$ vs $\omega$. We see that the $R$ values in Fig. 7(b) agree reasonably with $R_{\text{EAL}}$, although the $R$ values for $\omega \approx 0.14$ lie systematically below the dashed line. These differences are due in part to the fact that EALs from the transport approximation can differ systematically from those obtained using SESSA\textsuperscript{29,30}. In addition, relation (3) is in fact an approximation since separate simulations for bulk Cu and bulk SiO\textsubscript{2} showed that $P_{\text{off}}$ for the Cu 2p\textsubscript{3/2} and O 1s peak intensities are smaller than $P_{\text{off}}$ by up to 13\% and 6.6\%, respectively. These comparisons were made for photoelectron emission angles of 0° and 65°, and larger changes were found for the more-grazing emission angle than for normal emission. Nevertheless, relation (3) together with Eq. (4) are a useful guide for indicating how film thicknesses for morphologies (a) and (b) of Fig. 1 can differ when elastic scattering is switched on or off. In particular, relation (3) and Eq. (4) can provide corrections for elastic-scattering effects to film thicknesses determined from the QUASES software. Values of $\omega$ for use in Eq. (4) can be conveniently obtained for a material of interest from IMFPs and TMFPs from SRD 82 (Ref. 26) or from SESSA (Ref. 12).

The plot of $R$ vs $\omega$ in Fig. 7(a) for morphologies (c) and (d) of Fig. 1 shows a much weaker variation than the corresponding plot in Fig. 7(b) for morphologies (a) and (b). In addition, the error bars for the $R$ values in Fig. 7(a) are generally larger than those in Fig. 7(b). Larger error bars for these ratios are considered reasonable since the thicknesses involved for morphologies (c) and (d) are smaller than those for morphologies (a) and (b). The observed $R$ values in Fig. 7(a) correspond to reductions in film thicknesses between 2\% and 14\% for morphologies (c) and (d) when elastic scattering is switched on. This result is due to photoelectrons excited in the overlayer that are backscattered by underlying atoms, particularly in the substrate, and is in agreement with the predictions of Jablonski and Tougaard\textsuperscript{31,32}. They simulated photoelectron intensities from Si, Cu, Ag, and Au matrices for a wide range of depths, photoelectron energies, and XPS configurations and found an increase in the peak intensities from thin overlayers between about 2\% and 15\% as a result of elastic scattering. These intensity increases correspond to similar decreases in our film thicknesses to maintain a constant peak intensity when elastic scattering is switched on. Jablonski and Tougaard\textsuperscript{31,32} also reported earlier on the larger effects of elastic scattering for substrate photoelectrons transmitted through an overlayer film, as shown in Fig. 7(b).

For the morphologies studied, we did not find any significant dependence of $R$ on the photoelectron emission angle $\omega$. It therefore appears that elastic-scattering effects will be of similar magnitudes for emission angles between 0° and 65°. This result can be compared with the predictions from the systematic study of Jablonski and Tougaard\textsuperscript{31,32} who found small effects of elastic scattering on peak intensities for emission angles less than about 40°. Larger effects were found for larger emission angles, with the strongest effects observed for photoelectrons originating from deep layers in materials with strong elastic-scattering effects (i.e., large values of the single-scattering albedo). Their approximate expression can be used to estimate the effects of elastic scattering on measured peak intensities\textsuperscript{31,32}. Likewise, Eqs. (3) and (4) in the present paper may be used together with values of the single-scattering albedo to estimate thickness corrections due to elastic scattering for morphology classes (a) and (b) of Fig. 1.

Our SESSA simulations do not take account of possible variations in the fraction of intrinsic or shakeup intensity accompanying photoionization in Cu or SiO\textsubscript{2} with film thickness or photoelectron emission angle and/or to possible variations in the inelastic-scattering probabilities in the vicinity of surfaces and interfaces, again as a function of film thickness or photoelectron emission angle. Pauly and Tougaard have investigated these possibilities theoretically and found that the combined effects for bulk solids can reduce peak intensities for metals and semiconductors by between 35\% and 45\% and for oxides by between 42\% and 53\% for typical XPS energies and emission angles\textsuperscript{34}. It is likely that these effects could modify the film thicknesses required to give a particular photoelectron intensity although ratios of film thicknesses with elastic scattering switched on and off (such as those given in Fig. 7) should be less affected.

**IV. SUMMARY**

We report an analysis of simulated photoelectron peak intensities for the Tougaard morphologies of Fig. 1. Elastic scattering of photoelectrons was neglected in the original simulations\textsuperscript{4}, and we have investigated this effect on film thicknesses needed to give a particular peak intensity. We utilized the NIST SESSA database to determine Cu 2p and O 1s spectra from Cu/Au morphologies and SiO\textsubscript{2}/Si morphologies in separate simulations in which elastic scattering was switched on or off. Film thicknesses were varied for each morphology and for each elastic-scattering condition to obtain a selected Cu 2p\textsubscript{3/2} or O 1s peak intensity. Two XPS configurations were considered, one in which the average photoelectron emission angle was 0° and the other in which the average emission angle was 65°.

We found that film thicknesses with elastic scattering switched on were systematically less than those with elastic scattering switched off by up to about 25\% for the Cu/Au morphologies and up to about 14\% for the SiO\textsubscript{2}/Si morphologies. For morphologies (a) and (b) of Fig. 1, the ratios of film thicknesses with elastic scattering switched on to those with elastic scattering switched off varied approximately linearly with the single-scattering albedo, a convenient measure of the strength of elastic scattering. This variation was similar to that of the ratio of the effective attenuation length to the inelastic mean free path for the photoelectrons in the overlayer film. The empirical relation found by Jablonski and Powell\textsuperscript{16} for the latter variation should thus provide a useful but approximate guide to the magnitude of...
elastic-scattering effects on film thicknesses estimated from the QUASES software for morphology classes (a) and (b).

The ratios of film thicknesses with elastic scattering switched on to those with elastic scattering switched off for morphologies (c) and (d) of Fig. 1 varied more weakly with the single-scattering albedo than for morphologies (a) and (b). This weaker variation was associated with the fact that photoelectrons from the outermost layer arise mostly from near-surface atoms (because of inelastic scattering), in contrast to the photoelectrons for morphologies (a) and (b) that travel through an overlayer film. Elastic-scattering effects are therefore expected to be weaker for morphologies (c) and (d) than for morphologies (a) and (b).

8Certain commercial software products are identified to specify particular procedures. This identification does not imply that the products are endorsed or recommended by the National Institute of Standards and Technology or that they are necessarily the most suitable for the purposes described.