Ellipsometry Measurements on Refractive Index Profiles of Thin Films

JAU HWANG HO, CHUNG LEN LEE, AND TAN FU LEI

Abstract—An ellipsometry technique to measure the arbitrary refractive index profile of composite thin films is presented. The refractive index profile is obtained through a successive partitioning and computation process on measured data points with the aid of a $\Delta \varphi/T$ plot, which reduces errors. Analyses on the required number of data points in the partitioned sections, on the errors caused by the inappropriate partitioning, and on the cumulative errors have been performed. A $\Delta \varphi/T$ plot is used to monitor the overall cumulative errors of the computation. Experimental examples by applying this technique to measure the refractive index profile of $O-N-O$ and $O-N$ composite thin films are included, and results are compared with those obtained by the Auger electron spectroscopy (AES) technique. It is shown that this method is sensitive enough to determine the refractive index profile to a resolution of 20 Å.

I. INTRODUCTION

I N PRESENT VLSI MOS devices, compound thin films such as nitridized-SiO$_2$ or SiO$_2$/Si$_3$N$_4$/SiO$_2$ dielectrics have been used as the gate materials [1]-[5]. Much research work has been carried on the preparation, characterization and analysis of these dielectric films [6]-[10]. One of the techniques to characterize thin films is ellipsometry which can determine the refractive index and the thickness of films. It is very simple to apply, and its sensitivity and precision are rather high [11]-[17]. To measure the refractive index profile of thin films by using ellipsometry, a chemical thinning process is usually employed. The sample is repeatedly measured with ellipsometry and then chemically thinned to obtain successively changing ellipsometric data ($\Delta$, $\varphi$). These are then substituted into the set of ellipsometry equations

$$f(\Delta, \varphi, \phi_0, N_s, K_s, N_2, T_2, N_1, N_0, \lambda) = T_1$$

$$g(\Delta, \varphi, \phi_0, N_s, K_s, N_2, T_2, N_1, N_0, \lambda) = 0$$

(1) (2)

to solve for $N_1$, the refractive index, and $T_1$, the thickness of the etched layer of the sample, assuming a double-layer model [18]. In (1) and (2), $\phi_0$ and $\lambda$ are the incident angle and the wavelength of the monochromatic light, respectively, $N_s-iK_s$, $N_2$, $N_1$ and $N_0$ are the refractive indexes of the substrate, the bottom surface layer, the top surface layer and the ambient medium, respectively.

Errors in this procedure are usually introduced during computation due to the inherent measurement errors in parameters such as $\Delta$, $\varphi$, and $\phi_0$. As a result, the $N$-$T$ profile obtained is not accurate. In 1983, Charmet et al. [19] derived ellipsometric formulas for an arbitrary refractive index profile by using Fourier transformations, and multiple-angle ellipsometry was used to determine the refractive index profile. However, the accuracy issue was not addressed and no experimental data were taken. We have studied the effect on accuracy caused by errors in the ellipsometric parameters and have proposed a scheme to improve the accuracy [20], [21]. This is based on a double-layer model to compute the index of refraction and the thickness of the surface thin film.

In this paper, the scheme is modified and applied to measure compound thin films of arbitrary refractive index profiles. The errors are reduced by taking a large number of data points on the sample. The required number of data points to achieve the error bound goal is also investigated. The refractive index profile is obtained through a procedure of data point partitioning. The error introduced during computation of the refractive index profile due to inappropriate partitioning of data points is also studied. Experimental examples of applying this method are included and the results obtained are compared with those obtained by the AES technique. The new method is especially sensitive in determining the index of refraction of the surface layer (within 20 Å) of thin films.

II. DESCRIPTION OF THE TECHNIQUE

It has been shown [20], [21] that, in an ellipsometry measurement, two types of errors, namely the systematic errors and random errors, affect the accuracy of measurement. In order to minimize the effect of these errors, more than one measurement data are required for computing the refractive index. In particular, to minimize the effect of random errors, which are due to the instrumental resolution limitation in $\Delta$ and $\varphi$ readings of the ellipsometer, it is desired to have as many as possible measurement data on one measured thickness. An averaging technique by plotting a $\phi_0/T$ plot of these data could remove the random errors. In order to acquire a large number of measurement data, a sample area larger than 2 cm$^2$ is required. The thin film is uniformly deposited (or grown) on the surface of the sample. The sample is then gradually immersed into an etching solution (e.g., buffered HF so-

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Fig. 1(a) The $\phi_0/T$ plot of ($\Delta$, $\varphi$) data measured on a composite SiO$_2$/Si$_3$N$_4$/SiO$_2$ film. For all three layers, the estimated $N_i$ is 1.463.
(b) The $\phi_0/T$ plot for the sample of (a), but for the SiO$_2$ layer, the estimated refractive index is 1.463, and for the Si$_3$N$_4$ and the outer SiO$_2$ layers, the estimated refractive index is 1.946. (c) The same $\phi_0/T$ plot as in (b), but for the outer SiO$_2$ layer, the estimated refractive index is 1.491. (d) The same $\phi_0/T$ plot as in (c), but with thirteen partitioned sections.

After the ellipsometric measurement, the obtained ($\Delta$, $\varphi$) data corresponding to various thicknesses of the film are thus obtained. This procedure can be repeated (usually 3 times for a 100 Å film) to increase the number of data points. In this way, it is easy to acquire as many as 200 data points for a 100 Å thin film.

After the ellipsometric measurement, the obtained ($\Delta$, $\varphi$) data are fed into (1) and (2) to compute for the incident angle, $\phi_0$, and the film thickness, $T_i$, according to the technique in [21]. A $\phi_0/T_i$ graph can be plotted. The $\phi_0/T_i$ plot is computed by estimating a value for the index of refraction $N_i$ of the measured film. If the estimated $N_i$ value is correct, the plotted $\phi_0/T_i$ diagram will be a horizontal line. It is obvious that, for a nonhomogeneous film, this $\phi_0/T_i$ diagram will not be a horizontal line. However, a step-by-step estimating procedure can eventually achieve a horizontal $\phi_0/T_i$ plot. This is demonstrated by using the following experimental example.

Fig. 1(a) is a $\phi_0/T_i$ plot for a sample which has a compound Si(sub.)/SiO$_2$/Si$_3$N$_4$/SiO$_2$ structure. The sample was prepared by first growing an oxide(SiO$_2$) of approximately 250 Å, and then depositing a chemical vapor deposition (CVD) Si$_3$N$_4$ of approximately 400 Å on a Si substrate. The sample was then reoxidized at 1000°C for 40 min in a H$_2$O ambient to obtain an oxidized nitride layer. The $\phi_0/T_i$ plot of Fig. 1(a) was obtained by estimating an $N_i = 1.463$ which is the refractive index of the inner SiO$_2$ layer. It is seen that this estimated $\phi_0/T_i$ plot could be roughly divided into three parts, i.e., the inner SiO$_2$ layer, for which the $\phi_0/T_i$ plot shows a horizontal line, the Si$_3$N$_4$ layer and the outer oxidized nitride layer, which each have tilted $\phi_0/T$ curves. The Si$_3$N$_4$ layer and the oxidized nitride layer have tilted $\phi_0/T$ curves because their refractive indexes deviate from the estimated $N_i$ value of 1.463. It can also be observed that, there is a boundary between the Si$_3$N$_4$ layer and the oxidized nitride layer since the slopes of these two regions are different. From this $\phi_0/T_i$ plot, it can be seen that, the estimating
on $N_1$ can be divided into three steps. First, the refractive index of the inner $\text{SiO}_2$ is estimated and the $\phi_0/T$ plot is computed. From the obtained $\phi_0/T$ plot, the boundary between the $\text{SiO}_2$ and the $\text{Si}_3\text{N}_4$ layers can be identified. In Fig. 1(a), it is $T_1 = 240$ Å for $N_1 = 1.463$. These obtained $N_1$ and $T_1$ values can be used to compute the next estimated $N$ value and the $\phi_0/T$ plot for the outer successive layers based on the double-layer model [21]. Fig. 1(b) is the obtained $\phi_0/T$ plot for this step of computation by estimating the refractive index for the $\text{Si}_3\text{N}_4$ layer to be 1.946. The boundary between this $\text{Si}_3\text{N}_4$ layer and the oxidized nitride layer is at $T = 572$ Å, where the slope of the $\phi_0/T$ plot shows tilting downward. Finally, the same computation process is applied to the third layer again by estimating $N = 1.491$ and the $\phi_0/T$ curve is plotted in Fig. 1(c). It is seen that the $\phi_0/T$ plot shows a nearly horizontal curve. The computed refractive index profile is shown in Fig. 2(a).

In the preceding computation process, the computation can be divided into more steps. Fig. 1(d) is the $\phi_0/T$ plot on the same set of measured $(\Delta, \varphi)$ data as that for Fig. 1(c) but with thirteen computation steps. A much more linear $\phi_0/T$ plot is obtained. The corresponding computed detail refractive index profile is shown in Fig. 2(b). This shows that the boundaries between the $\text{SiO}_2$ layer and the CVD $\text{Si}_3\text{N}_4$ layer, and between the CVD $\text{Si}_3\text{N}_4$ layer and the outer oxidized nitride layer are rather vague.

### III. DISCUSSION ON ERRORS

In this technique, errors may be introduced due to inappropriate partitioning of measurement data. These errors are discussed in this section.

#### A. Random Errors Versus the Number of Measurement Data Points

In the previous section, it has been shown that more partitionings of the measured data can enhance the resolution of the refractive index profile and a truer refractive index profile can be obtained. However, the number of partitionings cannot be arbitrarily increased. This number is limited by the required number of data points within one partitioned section for the guaranteed error reduction on random errors in $(\Delta, \varphi)$ readings. In this section we study how many data points are required to achieve the required accuracy.

The study is based on a statistical treatment to estimate the random errors on the refractive index. The physical model used is the double-layer model [21]. In the model, $T_1$ is the partitioned section whose refractive index and thickness are to be computed and $T_2$ is the effective lumped layer whose effective refractive index and thickness have been determined. For the partitioned section $T_1$, there are $m$ data points which are measured for thin films of different thickness within the $T_1$ range.

For the type of the ellipsometer used in this study, the instrumental scale resolution for $\Delta$ and $\varphi$ are $1^\circ/12$ and $1^\circ/24$, respectively. Hence, during one reading, $(\Delta, \varphi)$ could be one of the following nine combinations: $(\Delta + 1^\circ/12, \varphi)$, $(\Delta + 1^\circ/12, \varphi + 1^\circ/24)$, $(\Delta + 1^\circ/12, \varphi - 1^\circ/24)$, $(\Delta - 1^\circ/12, \varphi + 1^\circ/24)$, $(\Delta - 1^\circ/12, \varphi - 1^\circ/24)$, $(\Delta - 1^\circ/12, \varphi)$, $(\Delta - 1^\circ/12, \varphi + 1^\circ/24)$, $(\Delta - 1^\circ/12, \varphi - 1^\circ/24)$. For $m$ measurements on different film thickness, the total number of possible combinations of $(\Delta, \varphi)$ readings is $9^m$. The average error on this refractive index for the $m$ data points can be defined as

$$
\delta N_{\text{avg}} = \left[ \sum_{i=1}^{9^m} \delta N_{i}\right]^{1/2}
$$

where $\delta N_{i}$ is the $i$th error corresponding to the $i$th possible $(\Delta, \varphi)$ values. This $\delta N_{\text{avg}}$ can be computed in the following way.

If, in this partitioned section, these $m$ data are distributed uniformly throughout the film thickness, $T_1$, $\delta N_{\text{avg}}$ in
(3) can be evaluated to be [22]
\[
\Delta N_{\text{avg}} = \left( \frac{2m}{9} \left( \delta n_{1,1}\delta n_{m,1} + \delta n_{1,2}\delta n_{m,2} + \delta n_{1,3}\delta n_{m,3} + \delta n_{1,4}\delta n_{m,4} \right) + \frac{m(2m-1)}{27(m-1)} \left( \delta n_{1,1} - \delta n_{m,1} \right)^2 + \left( \delta n_{1,3} - \delta n_{m,3} \right)^2 + \left( \delta n_{1,4} - \delta n_{m,4} \right)^2 \right)^{1/2}.
\]

In (4), the denotations \(\delta n_{1,i}, \delta n_{2,i}, \delta n_{3,i}, \ldots, \delta n_{9,i}\) represent the errors of refractive index for errors occurring only in the \(i\)th data due to the nine possible data caused by the effects of the resolution. For example, \(\delta n_{m,4}\) represents the refractive index error \(\delta n\) which occurs when the \(\phi\) value has a \(1^\circ/24\) deviation in the \(m\)th data point. This simple formula can be used to estimate the errors caused by inadequacy of data points within \(T\).

Equation (4) is computed and plotted in Fig. 3 in terms of the density of data for various \(T\) values assuming \(N_2 = 1.46, T_2 = 400\ \text{Å},\) and \(N_1 = 2.00\). (These values of data give the worst case estimation). It is seen that \(\Delta N_{\text{avg}}\) decreases if the density of data increases. For \(T_1 = 20\ \text{Å},\) the density of data needed to obtain an error less than 0.03 for its refractive index of 2.00 (this corresponds to a 1.5% error) is approximately 2 data points/Å. In practice, this is the density which can be achieved without too much difficulty. In the figure, in addition, the \(\Delta N_{\text{avg}}\) is smaller for thicker \(T\). For example, the errors for \(T_1 = 40\ \text{Å}\) are almost two times lower than those for \(T_1 = 20\ \text{Å}\). Hence, if the density of data is fixed and high accuracy is demanded, a thicker subsection can be chosen. The ultimate data density which can be obtained for the type of ellipsometer which has \(1^\circ/12\) and \(1^\circ/24\) instrumental resolutions for \(\Delta\) and \(\phi\) readings, respectively, is approximately 19 data points/Å.

**B. Errors Due to the Inaccurate Partitioning**

To compute the refractive index profile, it is very possible that the partitioning of data points is not at the true boundaries of the composite thin film. This inaccurate partitioning also leads to errors discussed in the following.

Fig. 4(a) shows a composite thin film with 3 layers of different refractive indexes. It is assumed that \(N_2\) and \(T_2\) of the inner layer are known, and the \(\phi_0/T\) plot of this layer is the horizontal band shown in Fig. 4(b). For the intermediate layer, the \(N_i\) and \(T_i\) are to be computed by partitioning the \((\Delta, \phi)\) data. Suppose that this partitioning is not at the boundary of \(N_i\) and \(N_{i+1}\), which is the outer layer that has another refractive index value, and instead, it is at some position \(T_i\) within the outer layer. The \((\Delta, \phi)\) data which belong to the \(N_i\) layer are grouped into those of the \(N_i\) layer (the shaded regions of Fig. 4(a)).

The computed values for \(N_i\) and \(T_i\) will then deviate from the true values of \(N_i\) and \(T_i\).

Fig. 5 shows the computed errors caused by this bad partitioning for \(N_2 = 1.46, T_2 = 300\ \text{Å}, N_i = 1.60, T_i = 50\ \text{Å}\) in terms of \(T_i\) for various \(N_i\). It is seen that the error is proportional to the difference between \(N_i\) and \(N_{i+1}\). For all \(N_i\) values, the error increases rapidly with \(T_i\) until \(T_i = 10\ \text{Å}\) and then decreases. For \(T_i = 50\ \text{Å}\), the error becomes insignificant (< 0.003).

In practice, \(T_i\) can be kept to within 10 Å by manually selecting the boundary of \(T_i\) from the \(\phi_0/T\) plot. The error introduced is negligible. For example, in Fig. 4(b), the fitted line of the zero slope for the first section, \(T_i\) intersects the band edge of the tilted band at \(T_i\). If \(N_i = 1.60\), and \(T_i = 50\ \text{Å}\), the error in \(\Delta N_i\) caused by includ-
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Fig. 5. The plot of errors produced in the computed refractive index in terms of the partitioning \( T_i \) error for various \( N_i \) values. For this computation, \( N_1 = 1.46, T_2 = 300 \text{ Å}, N_i = 1.60, \) and \( T_1 = 50 \text{ Å}. \) The dotted line is the error in the refractive index caused by including the \( (\Delta, \varphi) \) data in \( T_i \) to compute \( N_i \) for various \( N_i \) values.

ing the \( (\Delta, \varphi) \) data in \( T_i \) to compute for \( N_i \) is shown in Fig. 5 in the dotted line for various \( N_i \) values. The error is smaller than 0.02. In this example, for \( N_i = 1.70, T_1 \) is approximately 10 Å. This means that, for a refractive index profile, if there is a 0.10 \((N, 0.10)\) refractive index difference between two adjacent sections within 10 Å, this method is able to differentiate the refractive indices of these two sections. Hence, this method can offer a resolution of 20 Å in measuring the refractive index of the surface of a thin film. In Section IV on experiments, an example is to be shown to demonstrate this capability.

C. Cumulative Errors and Error Monitoring

In this section, a method is presented to monitor the cumulative errors for a computed refractive index profile after having gone through the above successive partitioning and computing process.

It has been mentioned [20] that the variations in \( \Delta, \varphi, N_i, K_i, \) etc., can be lumped into an effective deviation in \( \phi_0, \) i.e., \( \Delta \phi_0, \) and the errors introduced due to the above parameters are equivalent to the error introduced in \( \Delta \phi_0. \) The effective \( \Delta \phi_0 \) caused by each deviation in \( \Delta, \varphi, N_i, K_i, N_2, \) and \( T_2 \) for a double-layer model are computed, respectively. They are shown in Fig. 6 in terms of the film thickness of \( T_2. \) To compute the curves in Fig. 6, \( N_2, N_1, \) and \( T_2 \) are chosen to be 1.46, 2.00, and 20 Å, respectively, and the deviations: \( \delta \Delta, \delta \varphi, \delta \phi_0, \delta N_2, \delta K_2, \delta N_1, \) and \( \delta T_2 \) are assumed to be \( 0.05/12, 1^\circ/24, 0.02^\circ, 0.008, 0.008, 0.02, \) and \( 2\%, \) respectively. The true incident angle, \( \phi_0 \) is 70.00°. It is seen that, among the parameters, \( N_2 \) and \( T_2 \) cause the most deviation in \( \phi_0, \) especially when \( T_2 > 300 \text{ Å}. \) \( \Delta \phi_0 \) caused by other parameters are generally smaller than 0.05° for all \( T_2 \) regions \(< 800 \text{ Å}. \) \( N_2 \) and \( T_2 \) in this method, are the computed effective refractive index and thickness of the inner sections during the previous computation. It is thus concluded that the errors in the previously computed \( N_2 \) and \( T_2 \) have the largest affect on the computed incident angle for the next partitioned section. Hence, it is possible to gain information on the accuracy of the computation by observing the \( \Delta \phi_0 \) caused by the previously computed \( N_2 \) and \( T_2. \)

In the \( \phi_0/T \) graph, for each partitioned section, a value for \( \phi_0 \) is obtained for the corresponding computed \( N_i \) and \( T_i. \) This value of \( \phi_0 \) generally deviates from the exact value of \( \phi_0, \) which is 70.00°, due to the errors in the previously computed \( N_2 \) and \( T_2 \). The difference between these two values is \( \Delta \phi_0 \) for this computed section. This \( \Delta \phi_0 \) can be plotted in terms of \( T \) along with the \( \phi_0/T \) graph. By observing the \( \Delta \phi_0/T \) plot, we can tell the accuracy of the computation.

Fig. 2(b) is the example of the refractive index profile of the Si(sub./)/SiO\(_2\)/Si\(_3\)N\(_4\)/SiO\(_2\) compound thin film, where the corresponding \( \Delta \phi_0/T \) plot is also shown as the dotted line. For this computed profile, it is seen that \( \Delta \phi_0 \) never exceeds 0.04°. This means that the errors in the final computed refractive index profile never exceeds 0.005 (from Fig. 6). In Fig. 2(a), the refractive index profile and its corresponding \( \Delta \phi_0/T \) plot of the same sample are also included. These are computed based on the same \( (\Delta, \varphi) \) data but with three partitionings. It is seen that this \( \Delta \phi_0/T \) plot varies in much larger magnitude for each section. The average \( \Delta \phi_0 \) is \(-0.1^\circ, \) which corresponds to an 0.015 average error in the final refractive index profile computation. In practice, \( \Delta \phi_0 \) can be chosen to be within \( \pm0.1^\circ. \) The error for the computed refractive index profile can be guaranteed to be less than 0.02.

IV. Experimental Results

This technique has been used to study the refractive index profile of nitridized silicon dioxide and poly-silicon dioxide [23]. In this section, two experimental examples of applying this technique are demonstrated. They are: (1) the \( O-N-O \) structure of Fig. 1, and (2) a nitridized silicon dioxide. For both cases, the composition depth profiles obtained separately by the AES technique are included for comparison.
A. The O–N–O Structure

The detailed refractive index profile and the $\phi_0/T$ have been shown in Fig. 2(b). The corresponding AES composition profiles are shown in Fig. 7. The peak-to-peak heights of Si(LVV), N(KLL) and O(KLL) transitions are shown in terms of the sputter time. It is seen that these profiles have a good similarity with that of Fig. 2(b). However, Fig. 2(b) gives a much clearer depiction of the profile.

B. The Nitridized SiO$_2$ Structure

It had been reported that the thermal nitridation of silicon dioxide results in a compositional profile that varies with the depth [1]-[5]. Here, the refractive index profile of nitridized silicon dioxide films are measured by this ellipsometric method.

Fig. 8(a) shows the measured refractive index profile of a SiO$_2$ film nitridated at 1100°C for 5 h. It is seen that the refractive index was nearly constant throughout the film except that near the surface a thin layer of a 21 Å thickness with $N = 1.82$ existed. In the figure, the $\Delta\phi_0/T$ plot is also included. The cumulative error is seen to be very small. Fig. 8(b) is the $\phi_0/T$ plot for the profile of Fig. 8(a) near the surface region after the bulk refractive index had been computed. From this figure, the refractive index at this region is observed to be significantly higher than that of the bulk region. Hence, from this example, it is seen that this technique can detect the refractive index variation of a layer even as thin as 20 Å. The AES data for this sample are shown in Fig. 8(c). It is observed that there were nitrogen and silicon pile-ups near the surface, which might make the refractive index higher. Comparing the AES profiles of Fig. 8(c) with the refractive index profile of Fig. 8(a), both figures show the same trend. However, the refractive index profile obtained by this method reveals a much clearer picture on this nitridized SiO$_2$ film.

Fig. 9 shows another measured refractive index profile by this method for a SiO$_2$ sample which was nitridized in pure ammonia gas at 1100°C for 3 min. It is seen that for this sample, a thin (approximately 20 Å) nitrogen-rich layer of a refractive index of 1.70 also existed. There was also a nitrogen-rich interface of silicon substrate and the nitridized film. This phenomenon had also been observed.
in [1]–[5]. In the figure, the $\Delta \phi_0/T$ plot is also included and the maximum deviation in $\Delta \phi_0$ was within 0.05° which was very small.

V. CONCLUSIONS

An ellipsometry measurement technique to measure the refractive index profile of composite thin films has been proposed and demonstrated. This technique employs the error reduction scheme of [20], [21] to reduce the systematic and random errors. The profile is obtained through a procedure of partitioning the $(\Delta, \varphi)$ data. The errors introduced due to inappropriate partitionings are discussed and studied. It is found that for a partitioned section of a 20 Å thickness, 40 data points are enough to obtain an error less than 0.03 for a refractive index of 2.0. In practice, this is a datum density easily achieved by scanning the laser beam of the ellipsometer over the etched bevelled surface of the sample for three times. The errors caused by bad partitionings are usually negligible. For two adjacent sections with 0.10 refractive index difference, the thickness differentiable from the $\phi_0/T$ plot can be as thin as 10 Å. From experiments, this method has been shown to be able to offer a resolution of 20 Å in measuring the refractive index of the surface of a thin film. A $\Delta \phi_0/T$ plot has also been proposed to monitor the cumulative errors through the partitioning and computation process. This helps to minimizing the errors caused by inaccurate partitioning.

In this paper, all the computations were done on SiO$_2$ or Si$_3$N$_4$ films in the thickness range of 100–800 Å. However, this method can be applied to other composite films with other thickness ranges.

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