J Mater Sci (2009) 44:2167–2170
DOI 10.1007/s10853-009-3365-3

LETTER

A new method to experimentally determine the thermal expansion coefficient, Poisson's ratio and Young's modulus of thin films

E. Çetinörgü

Received: 8 December 2008 / Accepted: 23 February 2009 / Published online: 12 March 2009

The objective of this letter is to present a novel procedure to determine the thermal expansion coefficient, the Poisson's ratio, and the Young's modulus of a thin film deposited only on one substrate. The internal film stress (σ_f), thermal expansion coefficient (CTE, α_f), Poisson's ratio (ν_f), and Young's modulus (E_f) of metal oxide films are very important in optical devices. These parameters are affected by the deposition method and deposition conditions, which could have a significant impact on the device applicability and reliability [1]. In addition, the mechanical properties and the internal stress of thin films differ significantly from those of bulk materials due to the effects of interfaces, microstructure, and underlying substrates. Hence, when there is a need to know α_f, ν_f, and E_f of deposited films, it is necessary to determine them directly on the film, a process generally involving the measurement of the internal film stress, which may be so high that in some cases the substrate can distort and the film can crack and peel [2]. The internal stress in a thin film deposited on a substrate consists of two components: intrinsic stress σ_i and thermal stress σ_{th}. The intrinsic stress results from the deposition processes which influence the microstructure of the material. It could generally consist of epitaxial mismatch (related to the formation of a lattice mismatch composite with a coherent and partially coherent surfaces), structural defects like macroscopic voids, gas entrapment or phase transformation. The thermal stress results from the mismatch between the CTEs of the film and that of the substrate [3].

Various experimental techniques have been developed to measure the internal stress, and the elastic and mechanical properties of thin films. Commonly used techniques include strain measurement techniques such as X-ray diffraction, atomic force acoustic microscopy (AFAM), and deflection (bending) techniques based on measuring the curvature and/or deflection of the substrate [2, 4]. The deflection methods include optical interferometry, and mechanical dilatometry. The determination of the CTE requires the concurrent measurement of displacement, and temperature, on a thin film, during an appropriate thermal cycle. In such procedure, stress determination is based on the deflection measurement of thin circular or cantilever strip substrates coated with a homogeneous film. Similarly, evaluating the Poisson's ratio (ν_f), which is the ratio of transverse contraction strain to longitudinal extension strain in the direction of stretching force, is important for applications and leads to the determination of the elastic Young's modulus.

When film stress (σ_f) is determined by measuring the sample curvature before and after the deposition, e.g., by a laser deflection system, the stress can be calculated from the Stoney formula [5]:

$$\sigma_f = \frac{1}{6R}\frac{E_s d_s^2}{(1-\nu_s)d_f} \qquad (1)$$

where d_s and d_f are the thickness of the substrate and the film, respectively, and E_s and ν_s are the Young's modulus and the Poisson's ratio of the substrate, respectively and R is the net change in the substrate radius of curvature before and after the deposition.

The two-substrate method for the derivation of the CTE requires the determination of $d\sigma_f/dT$ on two different substrates with known CTEs. Generally, the dependence of the internal stress of a film on temperature T is given by the expression [6]:

E. Çetinörgü (✉)
Department of Engineering Physics, Ecole Polytechnique
of Montreal, Montreal, QC H3C 3A7, Canada
e-mail: eda@eng.tau.ac.il

$$\sigma_f(T) = \sigma_i + (\alpha_s - \alpha_f)\frac{E_f}{1 - \nu_f}(T - T_d) \tag{2}$$

where σ_i is the intrinsic stress produced during film deposition, α_s is the substrate's CTE, α_f is the film's CTE, E_f is the film's Young's modulus, and T_d is the deposition temperature. The ratio $E_f/(1-\nu_f)$ is the biaxial elastic modulus of the film. The second term on the right in Eq. (2) is the thermal stress that results from the CTE mismatch. Generally, the derivative $d\sigma_f/dT$, which is obtained by measuring σ_f as a function of T, can be a function of T. However, when all of the parameters in Eq. (2) are constant, i.e., do not depend on T, the derivative $d\sigma_f/dT$ is also constant, and is expressed by:

$$\frac{d\sigma_f}{dT} = \frac{E_f}{1 - \nu_f}(\alpha_s - \alpha_f) \tag{3}$$

As under these conditions the plot of σ_f against T will be a straight line, $d\sigma_f/dT$ can be determined from the line slope. Equation (3) depends on three unknown film parameters: α_f, E_f, and ν_f, of which E_f and ν_f are lumped together. Hence, the calculation of α_f requires an additional determination of the value of $d\sigma_f/dT$ for the same film, but deposited on a different substrate material. This is the procedure on which the two-substrate method is based, and then α_f is obtained from the following relation [7]:

$$\alpha_f = \frac{\alpha_{s2}\frac{d\sigma_f}{dT}\Big]_{s1} - \alpha_{s1}\frac{d\sigma_f}{dT}\Big]_{s2}}{\frac{d\sigma_f}{dT}\Big]_{s1} - \frac{d\sigma_f}{dT}\Big]_{s2}} \tag{4}$$

where indices "1" and "2" correspond to substrates "1" and "2", and the α_S's are the substrate CTEs.

E_f and ν_f can be determined following an additional measurement of the E_r of the film by nanoindentation. E_r is a function of Young's modulus (E_i) and the Poisson's ratio (ν_i) of the indenter, and of the film's biaxial modulus, as expressed by [8]:

$$\frac{1}{E_r} = \frac{1 - \nu_f^2}{E_f} + \frac{1 - \nu_i^2}{E_i} \tag{5}$$

The Poisson's ratio of the film, ν_f, can be expressed by the following relation derived from Eqs. (2)–(5):

$$\nu_f = \left(\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}\right)\frac{d\sigma_f}{dT}\frac{1}{\alpha_s - \alpha_f} - 1 \tag{6.1}$$

or,

$$(\nu_f + 1)(\alpha_s - \alpha_f) = \left(\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}\right)\frac{d\sigma_f}{dT} \tag{6.2}$$

The application of Eq. (6.1) is sensitive to the error in the experimental values of ($d\sigma_f/dT$), and significantly depends on accurate values of the CTEs. ν_f of the deposited film can be obtained only if the CTE of the substrate materials are suitable and accurately known [7]. It should be noted that when α_f is determined by the two-substrate method, two values of ν_f and E_f can be calculated by Eq. (6.1), depending on which α_s is used. The agreement between these two values of ν_f and E_f is an indicator of the data consistency.

Heretofore, all previous methods of determining the CTE of films by measuring coated substrate bending and temperature depended stress required performing the measurements on at least two coated substrates. Moreover, no method for the determination of the mechanical parameters of thin films by measuring the stress–temperature dependence with only one substrate has been reported. However, as mentioned above, the objective of this letter is to present a single substrate procedure to determine α_f, ν_f, and E_f of films by measuring the σ–T dependence and the E_r of the film only using one substrate coated with the investigated film. The proposed new procedure is labeled "one-substrate method".

The one-substrate method is based on a formal derivation of Eq. (6.2) by α_f noting that the parameters on the right term of this equation are assumed to be constant. The result of the derivation is the following relation:

$$(\alpha_s - \alpha_f)\frac{d\nu_f}{d\alpha_f} = (1 + \nu_f) \tag{7}$$

Algebraically manipulating Eq. (7) produces the following relation between α_f and ν_f:

$$\nu_f = \left[\left(\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}\right)\frac{d\sigma_f d\nu_f}{dT\, d\alpha_f}\right]^{1/2} - 1 \tag{8}$$

The derivative $d\nu_f/d\alpha_f$ can be obtained by applying the following steps:

1. Calculate ν_f as a function of α_f using Eq. (6.1). In this case, ν_f is a dependent variable and α_f is an independent one. The range of α_f over which ν_f was calculated was limited by the condition $0 < \nu_f < 0.5$ [9], which is true for almost all materials, except for some microstructures that show negative Poisson's ratio.
2. The average value of $d\nu_f/d\alpha_f$ was determined by fitting a straight line to the plot of ν_f as a function of α_f, requiring $R^2 \geq 0.96$, where R is the regression coefficient.
3. The value of $d\nu_f/d\alpha_f$ was the slope of the fitted line and was applied in Eq. (8) to calculate ν_f.
4. The coefficients α_f and E_f were calculated using the derived value of ν_f inserted in Eqs. (5, 6.1, 6.2).

Utilizing the above mentioned procedure to the studied oxides, it was found that the numerically calculated value of $d\nu_f/d\alpha_f$ by the five point approximation was practically constant over the relevant range of α_f, justifying the application of Eq. (8) to calculate ν_f. In fact, the ratio $\Delta\alpha_f/\alpha_f \sim 0.04$ is resulting in the approximate constancy of $d\nu_f/d\alpha_f$.

The one-substrate method was tested by determining ν_f, α_f, and E_f of niobium oxide, tantalum oxide, and silicon dioxide films. These films are widely used in optical filters as high and low index of refraction materials. Various deposition techniques and deposition conditions have been used to deposit these layers. The CTEs for the oxides of niobium, tantalum, and silicon are reported to vary from -2.0×10^{-6} to 5.8×10^{-6} (°C^{-1}) [10, 11], 2.3×10^{-6} to 6.72×10^{-6} (°C^{-1}) [12–14], 0.38×10^{-6} to 3.1×10^{-6} (°C^{-1}) [2, 3], respectively, indicating a significant data spread. Similarly, the ν_f of the oxides of niobium, and silicon is reported to be 0.23 [15], 0.17 [11, 15], respectively.

In the present study, thin films of niobium oxide, tantalum oxide, and silicon oxide were deposited using dual ion beam sputtering on one side polished Si (100) and GaAs (100) substrates at room temperature. Film σ was evaluated by measuring sample curvature (R) in a Flexus FLX-2900 (Tencor) laser deflection system before and after the deposition. The film temperature was in the range 30–240 °C, cycled in N_2 atmosphere, using the same heating rate (0.75 °C/min) for all oxides. The Si and GaAs substrates biaxial modulus and thermal expansion coefficient were 180 GPa and 2.60×10^{-6} °C^{-1}, and 124 GPa and 5.12×10^{-6} °C^{-1}, respectively. E_r of the deposited films was obtained using a triboindenter, where E_i and ν_i were 1140 GPa and 0.07, respectively. The niobium oxide, silicon dioxide, and tantalum oxide film thickness was ~0.92, 0.95, and 1.2 µm, respectively, determined by spectroscopic ellipsometry.

In Fig. 1a and b, plots of film stress as a function of temperature for tantalum oxide and silicon dioxide, films are presented as an example. It may be seen that σ_f varied approximately linear with T, indicating that $d\sigma_f/dT$ is ~constant. The values of $d\sigma_f/dT$ of niobium oxide, tantalum oxide, and silicon dioxide films on Si substrate were -4.0×10^5, -3.6×10^5, and 5.2×10^4 [Pa/°C], respectively. On the other hand, the values of $d\sigma_f/dT$ of these oxide films deposited on GaAs substrates were 4.8×10^4, 1.4×10^5, and 3.2×10^5 [Pa/°C], respectively. In Fig. 2a and b, plots of ν_f as a function of α_f, where ν_f was kept in the range 0.2–0.47, are presented for tantalum oxide films deposited on two substrates. The linearity of the plots indicates the constancy of $d\nu_f/d\alpha_f$.

In Table 1, we list the values of ν_f, α_f, and E_f of deposited films determined using the one-substrate method, whereas the values of these parameters obtained by the two-substrate method are listed in Table 2. Each coefficient in Table 1 has two values, depending on the substrate. In Table 2, ν_f and E_f also have two values, depending on the substrate parameters used in the calculation. The CTEs of all oxides obtained by applying the two-substrate method or the one-substrate method are consistent and agree well—the spread is less than 1%. The value of ν_f derived by the one-substrate method depended on the substrate on which the film was deposited, and the deviation in its values was less than 12%. The values of E_f for silicon dioxide and niobium oxide derived by the one-substrate effectively did not depend on the substrate; however, the values of E_f for niobium oxide in Table 1 depended on the substrate, deviating between substrates by ~30%. A similar situation was observed with the two-substrate method, where the calculated values of ν_f and E_f markedly depended on the substrate, i.e., on the value of α_s inserted in

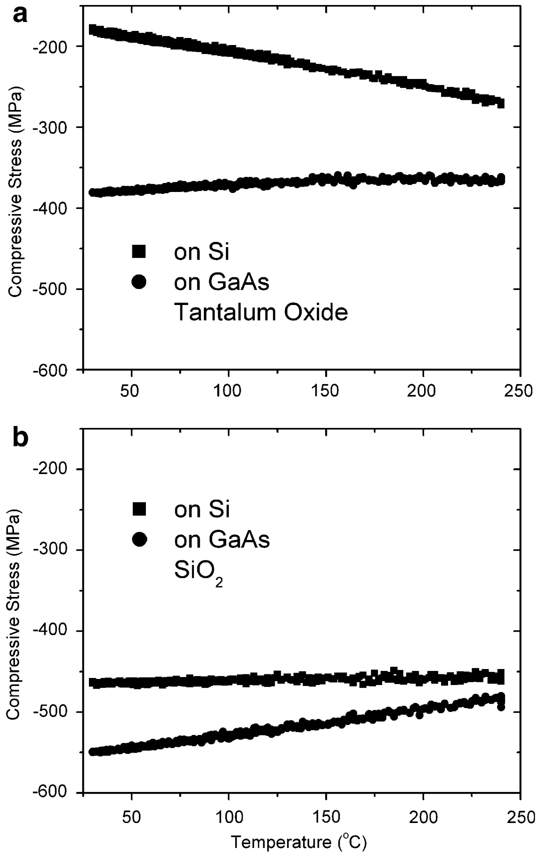

Fig. 1 $\sigma - T$ plots of tantalum oxide (**a**), silicon dioxide (**b**) films

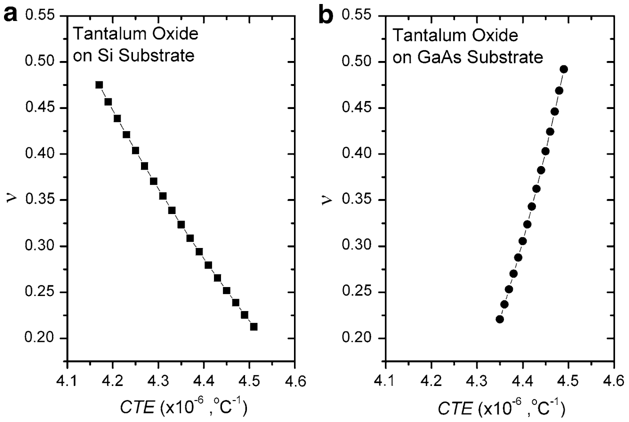

Fig. 2 Plots of calculated ν_f as a function of CTE of tantalum oxide films deposited on Si (**a**) and GaAs (**b**) substrates

Table 1 CTE, ν_f, and E_f of silicon dioxide, tantalum oxide, and niobium oxide films determined with the one-substrate method

Film	Substrate	ν_f	CTE ($\times10^{-6}$) (°C^{-1})	E_f (GPa)
Silicon dioxide	Si	0.19	2.1	91
	GaAs	0.12	2.1	91
Niobium oxide	Si	0.26	4.8	136
	GaAs	0.30	4.8	101
Tantalum oxide	Si	0.33	4.4	138
	GaAs	0.25	4.4	137

Table 2 CTE, ν_f, and E_f of silicon dioxide, tantalum oxide, and niobium oxide films determined with the two-substrate method

Substrate	Parameters	Silicon dioxide	Niobium oxide	Tantalum oxide
E_r (on Si)	CTE ($\times10^{-6}$) (°C^{-1})	2.1	4.85	4.42
	ν_f	0.11	0.22	0.27
	E_f (GPa)	93	139	143
E_r (on GaAs)	CTE ($\times10^{-6}$) (°C^{-1})	2.1	4.85	4.42
	ν_f	0.13	0.60	0.35
	E_f (GPa)	91	71.1	128

Eq. (6.1). In fact, as shown in Table 2, the values of ν_f and E_f determined by the two-substrate method were more sensitive to the values of the substrate parameters than in the case of the one-substrate method. In addition, it should be noted that the substrate has an impact on the microstructure of the film, and this is another important advantage of using the one-substrate method over the two-substrate method in which the mechanical properties and the microstructure of the films can differ when the films are deposited on different substrates.

The proposed one-substrate method, like the two-substrates method, is limited by requiring a linear dependence of σ_f on temperature, i.e., to have a constant $d\sigma_f/dT$ in Eq. (3). This requirement is fulfilled when the five parameters σ_i, α_s, E_f, α_f, and ν_f of Eqs. (2, 3) do not depend on T in the investigated temperature range. As the observed $d\sigma_f/dT$ is constant to a high approximation, it is expected, from a probabilistic standpoint, that the values of the five parameters σ_i, α_s, E_f. α_f, and ν_f do not depend coherently on T. Furthermore, it is hardly conceivable that the values of these parameters vary in such correlated way to produce the observed linearity of σ_f as function of T. Consequently, when $d\sigma_f/dT$ is constant, the basic assumption of the two-substrates and one-substrate methods is justified. This requirement of $d\sigma_f/dT$ excludes the application of the two methods whenever σ_f (T) is not linear with T, as could be the case when the substrate is a polymer.

The proposed method is also limited by the required nanoindentation of the film. The film thickness should be at least few hundreds of nanometers thick to eliminate the influence of the substrate on the measured data. For the same reason, it is also required that the indenter penetration depth should not exceed 10% of film thickness. Consequently, the one-substrate and the two-substrate methods are not appropriate to determine the mechanical characteristics of thinner films; however, in such case, the present model can be applied using other techniques, e.g., AFAM which can be accurately used with thinner films.

In conclusion, the CTE, ν_f, and E_f of silicon oxide, niobium oxide, and tantalum oxide thin films could be determined using one-substrate by measuring the dependence of the film stress on temperature and the reduced Young's modulus of the film by nanoindentation. The procedure can be applied when the dependence of ν_f on α_f is close to linear. The CTEs of the studied oxide films that were obtained by the one-substrate method were very close to those obtained by the two-substrate method. However, the values of ν_f and E_f determined by both methods depended on the CTE of the substrate material. The application of the one-substrate method is semi-empirical, and has the advantage of requiring only one substrate in order to determine the CTE, ν_f, and E_f of some thin films. Its applicability, however, should be examined by studying the dependence of σ_f on T, and the dependence of ν_f on α_f as calculated with Eq. (6.1).

Acknowledgement This work was performed in the Engineering Physics Department at Ecole Polytechnique of Montreal, Canada. The author would like to thank Prof. S. Goldsmith and Prof. R.L Boxman for a critical reading of the manuscript and helpful discussions.

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