Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Spectroscopic ellipsometry data inversion using constrained splines and application to characterization of ZnO with various morphologies

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ARTICLE INFO

Article history:
Received 5 July 2016
Received in revised form
20 September 2016
Accepted 21 September 2016
Available online xxx

Keywords:
Ellipsometry
Inversion
Optical constants
Dielectric function
Thin films
Optical properties
ZnO

ABSTRACT

An original method of ellipsometric data inversion is proposed based on the use of constrained splines. The imaginary part of the dielectric function is represented by a series of splines, constructed with particular constraints on slopes at the node boundaries to avoid well-know oscillations of natural splines. The nodes are used as fit parameters. The real part is calculated using Kramers–Kronig relations. The inversion can be performed in successive inversion steps with increasing resolution. This method is used to characterize thin zinc oxide layers obtained by a sol–gel and spin-coating process, with a particular recipe yielding very thin layers presenting nano-porosity. Such layers have particular optical properties correlated with thickness, morphological and structural properties. The use of the constrained spline method is particularly efficient for such materials which may not be easily represented by standard dielectric function models.

1. Introduction

Ellipsometry is a technique of predilection to characterize thin films. It uses detection of polarization state which can be measured with great accuracy using modulation techniques. Because the polarization response is sensitive to structure, thicknesses, surface states and optical properties, a large range of information can be extracted from the measurements. Its applicability has been demonstrated through years in larger and larger fields [1–3]. However the drawback of these considerable advantages is that ellipsometry should be qualified as an indirect technique. It measures the well known but hardly intuitively understandable Ψ and Δ angles characteristic of the change of polarization of light after reflection on the sample; and it requires a work of coupled modeling and data processing to extract the interesting information.

All ellipsometric inversion methods are based on the use of a model of the sample made of a representative stack of thin films and on the use of an inversion procedure to extract optical data, thicknesses and additional structural parameters. A first general strategy in spectroscopic angles processing consists in representing the unknown materials by dispersion functions and adjust the dispersion parameters and unknown thicknesses to fit generated to experimental data [4]. This approach allows to directly cope measured quantities with physically meaningful models and allows the determination of characteristic parameters figuring in the model dielectric functions such as, for instance in the case of semiconductors, bandgap energy, excitonic energy and broadening or coupling parameters. This task is however not always easy and successful because of complexity of materials that cannot always be represented by theoretical laws.

A second general strategy in spectroscopic angles processing consists in treating independently the points of the spectrum and extract, by the use of numerical techniques, interesting information such as thickness, refractive index or extinction coefficients for each point of the spectrum regardless of correlation to other points. For each point of the spectrum, two quantities can be extracted such as thickness and refractive index in the case of transparent using the McCrackin and derived methods [5–9]; or refractive index and absorption coefficient provided that thickness is known using the point-by-point and derived methods [10–15]. This approach does not require a priori knowledge of shape, type or parameters of the dispersion functions. It can really be efficient in cases where the optical properties have really complex features. However its use should be associated to a careful examination of associated errors and possibility of multiple solutions [16,17]. It furthermore ignores information lying in the continuity between neighboring points of

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http://dx.doi.org/10.1016/j.apsusc.2016.09.106

Please cite this article in press as: M. Gilliot, et al., Spectroscopic ellipsometry data inversion using constrained splines and application to characterization of ZnO with various morphologies, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.09.106

the spectrum and does not guarantee Kramers–Kronig consistency of the extracted optical data.

A less known alternative to these standard methods is the use of basis Kramers–Kronig consistent mathematical functions which coefficients are used as fitting parameters. Various such approaches have been reported. In the natural spline approach, the imaginary part of the dielectric function spectrum or equivalently the imaginary part of the complex refractive index spectrum is represented by a set of points interpolated by natural cubic spline, and the values of the node points are fitted [18]. A variation of this approach is the combination of the natural cubic spline with harmonic oscillators [19]. In the variational analysis the dielectric function is represented by a huge number of oscillators located at each node of a dense anchor frequency mesh and the amplitudes of these oscillators are fitted [20]. In the parametric optical constant model, Gaussian-broadened polynomials of degree four centered on critical point structures are used and particular control points are fitted [21]. In the B-splines approach, a series of polynomial segments maintaining continuity up to a certain number of derivative orders are constructed by a recursion process to represent dielectric function of semiconductors [22]. In the present work, we would like to focus on the particular case of the cubic spline approach. We propose an original formulation of the spline approach using particular mathematical conditions in the construction of the imaginary part of the dielectric function. This approach reveals to be particularly suitable to represent semiconductors optical data with a reduced number of fitting parameters. In this paper we give details about calculation of the spline series, details about their practical implementation and examples of use in the case of zinc oxide thin layers presenting different optical properties. The present method is particularly adequate for these particular layers with particular morphologies and dielectric functions which do not always fit the standard dielectric function models.

2. Theory

We address the problem of a stack of thin films with one unknown material inside this stack. This material is represented by its complex refractive index $N = n - i\,k$ or equivalently by its dielectric function $\epsilon = \epsilon_r - i\epsilon_i$ as a function of incident photon energy ω, the real parts being related to propagation and the imaginary parts related to absorption. Thicknesses may also be unknown. In order to determine these unknown parameters, ellipsometric spectra expressed by the Ψ and Δ angles as a function of ω are measured between two ω_0 and ω_N bounds and treated using a spline inversion procedure.

2.1. Constrained spline formulas

In order to determine the unknown dielectric function, the imaginary part of the dielectric function ϵ_i is represented by a collection of connected splines, the real part of the dielectric function ϵ_r being calculated by Kramres–Kronig relations. The principle of the spline representation of dielectric function is shown in Fig. 1. ϵ_i is constructed over a set of $(N+1)$ points referred in this work as nodes located at energies of the spectrum ω_k and having values y_k which may be used as fitting parameters. The spectrum between the two ω_0 and ω_N bounds, is divided into N independent parts associated to N independent splines referred as ϵ_{ki} $(k = 1, \ldots, N)$. The ϵ_{ki} splines are regular functions given by third order polynomials between the two ω_{k-1} and ω_k energies as:

$$\epsilon_{ki} = \begin{cases} a_{3k}\omega^3 + a_{2k}\omega^2 + a_{1k}\omega + a_{0k} & \text{if} \quad \omega \in [\omega_{k-1}, \omega_k] \\ 0 & \text{if} \quad \omega \notin [\omega_{k-1}, \omega_k] \end{cases} . \qquad (1)$$

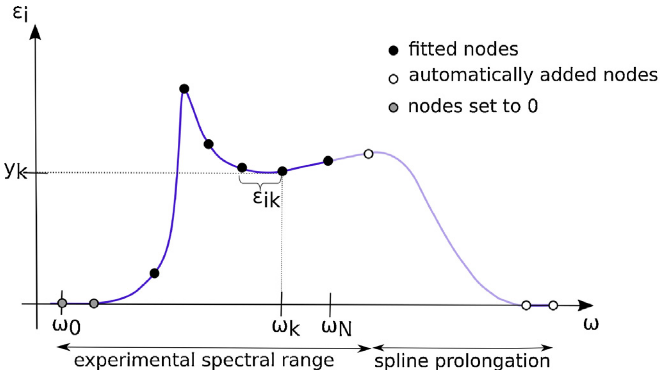

Fig. 1. Representation of the imaginary part of the dielectric function using constrained splines showing nodes set to zero in the transparency range, nodes used as fit parameters, and nodes automatically added outside the experimental spectral range to terminate the spline.

The ϵ_{ki} spline is determined by the four a_{3k}, a_{2k}, a_{1k} and a_{0k} coefficients. These coefficients are determined by a number of $4N$ mathematical relations. In natural cubic splines, these relations are given as: (i) the values of interpolation points at each spline boundaries yielding two relations for each spline or in total $2N$ relations, (ii) the continuity of first derivatives between two adjacent splines, which adds a number of $N - 1$ mathematical relations, (iii) the continuity of second derivatives between two adjacent splines, which adds a number of $N - 1$ mathematical relations, (iv) and finally imposed values for the first derivatives at the ω_0 and ω_N boundaries, which adds 2 more relations to completely define the spline coefficients. This approach is however not satisfactory for the representation of physical dielectric functions because of the natural trend of these splines to adopt a non-physical oscillating behavior, especially for close interpolating points. In order to avoid theses oscillations we use an other form of splines, referred as constrained splines, where the condition on second derivatives is not used but more constraining relations on the first derivatives are used according to:

$$\epsilon_{ki}(\omega_k) = a_{3k}\omega_k^3 + a_{2k}\omega_k^2 + a_{1k}\omega_k + a_{0k} = y_k \qquad (2)$$

$$\epsilon_{ki}(\omega_{k-1}) = a_{3k}\omega_{k-1}^3 + a_{2k}\omega_{k-1}^2 + a_{1k}\omega_{k-1} + a_{0k} = y_{k-1} \qquad (3)$$

$$\frac{d\epsilon_{ki}}{d\omega}(\omega_k) = 3a_{3k}\omega_k^2 + 2a_{2k}\omega_k + a_{1k} = s_k \qquad (4)$$

$$\frac{d\epsilon_{ki}}{d\omega}(\omega_{k-1}) = 3a_{3k}\omega_{k-1}^2 + 2a_{2k}\omega_{k-1} + a_{1k} = s_{k-1} \qquad (5)$$

where the special values for the slopes are given by [23]:

$$s_{k \neq \{0,N\}} = \begin{cases} \dfrac{2}{\dfrac{\omega_{k+1} - \omega_k}{y_{k+1} - y_k} + \dfrac{\omega_k - \omega_{k-1}}{y_k - y_{k-1}}} & \text{if} \quad (y_{k+1} - y_k)(y_k - y_{k-1}) > 0 \\ \dfrac{1}{2}\left(\dfrac{y_{k+1} - y_k}{\omega_{k+1} - \omega_k} + \dfrac{y_k - y_{k-1}}{\omega_k - \omega_{k-1}}\right) & \text{if} \quad (y_{k+1} - y_k)(y_k - y_{k-1}) < 0 \\ 0 & \text{if}\, (y_{k+1} - y_k)(y_k - y_{k-1}) = 0 \end{cases} \qquad (6)$$

$$s_0 = \frac{y_1 - y_0}{\omega_1 - \omega_0} \qquad (7)$$

$$s_N = \frac{y_N - y_{N-1}}{\omega_N - \omega_{N-1}}. \qquad (8)$$

In this set of equations, the two first relations express the interpolation values the boundaries of each spline, whereas the other relations express the particular constraint of slopes between two adjacent splines. It distinguishes the different cases where slopes at both parts of the considered point have the same sign, or have different signs or one of the two slopes is zero. It sets the slope to be between the slopes of the adjacent straight lines, and should

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