Thin Solid Films xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

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

Characterization of highly anisotropic three-dimensionally nanostructured surfaces

Daniel Schmidt

Department of Electrical Engineering and Center for Nanohybrid Functional Materials, University of Nebraska-Lincoln, Lincoln, NE 68588-0511, USA

ARTICLE INFO

Available online xxxx

Keywords:
Generalized ellipsometry
Glancing angle deposition
Atomic layer deposition
Sculptured thin films
Biaxial anisotropy
Effective medium approximations

ABSTRACT

Generalized ellipsometry, a non-destructive optical characterization technique, is employed to determine geometrical structure parameters and anisotropic dielectric properties of highly spatially coherent three-dimensionally nanostructured thin films grown by glancing angle deposition. The (piecewise) homogeneous biaxial layer model approach is discussed, which can be universally applied to model the optical response of sculptured thin films with different geometries and from diverse materials, and structural parameters as well as effective optical properties of the nanostructured thin films are obtained. Alternative model approaches for slanted columnar thin films, anisotropic effective medium approximations based on the Bruggeman formalism, are presented, which deliver results comparable to the homogeneous biaxial layer approach and in addition provide film constituent volume fraction parameters as well as depolarization or shape factors. Advantages of these ellipsometry models are discussed on the example of metal slanted columnar thin films, which have been conformally coated with a thin passivating oxide layer by atomic layer deposition. Furthermore, the application of an effective medium approximation approach to *in-situ* growth monitoring of this anisotropic thin film functionalization process is presented. It was found that structural parameters determined with the presented optical model equivalents for slanted columnar thin films agree very well with scanning electron microscope image estimates.

1. Introduction

With sophisticated deposition techniques and growth processes it is possible to bottom-up fabricate self-organized three-dimensional nanostructures, which render an artificial material class with intriguing optical, magnetic, mechanical, electrical or chemical properties. One of these technologies is a physical vapor deposition process called glancing angle deposition, which, due to the particular growth geometry and conditions combined with dynamic substrate movement, allows for *in-situ* sculpturing of self-organized, highly spatially coherent, three-dimensional achiral and chiral geometries at the nanoscale. The resulting sculptured thin films (STFs) exhibit columnar characteristics and physical film properties can be tailored by choice of material and controlling nanostructure geometry and film porosity [1–3]. In subsequent fabrication steps the nanostructure scaffolds may be further enhanced by surface functionalization. Atomic layer deposition (ALD) is an excellent technique to conformally coat such complex nanostructures with protective oxide coatings and ferromagnetic shells, for example [4,5].

Such engineered nanostructured materials constitute a new realm of solid state materials, and carry a huge potential for applications in the fields of nano-photonics [6], nano-electromechanics [7], nano-electromagnetics [8], nano-magnetics [9,10], nano-sensors [11–14], and nano-hybrid functional materials [15].

In order to systematically utilize STFs in future applications, physical properties of these nanosized objects need to be evaluated and understood such that targeted geometry engineering with tailored properties from selected materials and material combinations will be possible. Non-invasive and non-destructive optical techniques are preferred, however, due to the complexity of STFs, optical characterization is a challenge. Spectroscopic generalized ellipsometry within the Mueller matrix formalism is a polarization-dependent linear-optical spectroscopy approach and provides an excellent tool to determine the dielectric functions of anisotropic optical systems. Generalized ellipsometry has been shown to be an excellent optical technique to determine anisotropic optical properties of STFs of arbitrary geometry and materials upon analyzing the anisotropic polarizability response [16]. Structural parameters such as thickness and void fraction can be derived from best-match model analysis [17–19]. It is also possible to determine multiple film constituents within slanted columnar thin films (F1-STFs) and this has been recently shown for thin conformal passivation layers grown by ALD and *in-situ* quantification of organic adsorbate attachment analysis [4,13].

However, since ellipsometry is an indirect measurement technique, adequate optical models have to be chosen to evaluate experimental data in order to obtain reliable optical and structural properties of anisotropic samples. The film structure of metal STFs, which are in the simplest case homogeneous anisotropic lossy composite materials

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.10.119

consisting of slanted columns of regular shape and common orientation (F1-STFs), induces form-birefringence and dichroism. Appropriate mixing formulas and effective medium homogenization approaches need to be applied to calculate an effective anisotropic dielectric medium response that renders the effects of the measured anisotropy [16,20].

In case of a biaxially anisotropic composite material, the classic ellipsometry model approach is to individually determine the three major axes dielectric functions without any implications on the kind of constituents and constituent fractions of the composite. This homogeneous biaxial layer approach can deliver structural information from a thickness parameter and Euler angles [21,22]. If constituent fractions and information about the shape of the constituents are desired results, homogenization approaches based on Bruggeman, for example, can be applied such that the three major axes dielectric functions can be constructed from a composite model that describes the effects of shape, average constituent fraction and the use of constituent bulk-like optical constants for the materials of the building blocks (in general ellipsoidal inclusions) [23].

The objective of this manuscript is to briefly summarize optical model strategies to analyze the polarization-sensitive optical response of ultrathin STFs with simple and complex geometries based on the homogeneous layer approach. The example of cobalt F1-STFs conformally coated with alumina by ALD is used as a reference to illustrate how two different generalized effective medium approximations derived from Bruggeman's original formalism compare with the homogeneous layer approach and estimates obtained from scanning electron microscopy (SEM) images. Furthermore, *in-situ* growth monitoring of conformal oxide coatings on permalloy ($Ni_{80}Fe_{20}$) F1-STFs by analysis of Mueller matrix spectra is presented.

2. Generalized ellipsometry

Generalized ellipsometry (GE), a non-destructive and non-invasive optical technique, has proven to be highly suitable for determining optical and structural properties of highly anisotropic nanostructured films from metals such as F1-STFs or even helical (chiral) STFs [21,24,16]. Measurements of the complex ratio ρ of the *s*- and *p*-polarized reflection coefficients are presented here in terms of the Stokes descriptive system, where real-valued Mueller matrix elements M_{ij} connect the Stokes parameters before and after sample interaction [25,26]. The linear polarizability response of a nanostructured thin film due to an electric field $\mathbf{E}$ is a superposition of contributions along certain directions: $\mathbf{P} = \varrho_a(\mathbf{a} \cdot \mathbf{E})\mathbf{a} + \varrho_b(\mathbf{b} \cdot \mathbf{E})\mathbf{b} + \varrho_c(\mathbf{c} \cdot \mathbf{E})\mathbf{c}$ [27]. In the laboratory Cartesian coordinate system the F1-STF is described by the second rank polarizability tensor χ and $\mathbf{P} = (\varepsilon - 1)\mathbf{E} = \chi\mathbf{E}$. The Cartesian coordinate system (x, y, z) is defined by the plane of incidence (x, z) and the sample surface (x, y). This Cartesian frame is rotated by the Euler angles (φ, θ, ψ) to an auxiliary system (ξ, η, ζ) with ζ being parallel to $\mathbf{c}$ [25,28]. For orthorhombic, tetragonal, hexagonal, and trigonal systems a set of φ, θ, ψ exists with χ being diagonal in (ξ, η, ζ). For monoclinic and triclinic systems an additional projection operation $\mathbf{U}$ onto the orthogonal auxiliary system (ξ, η, ζ) is necessary, which transforms the virtual orthogonal basis into a non-Cartesian system [29]:

$$\mathbf{U} = \begin{pmatrix} \sin\alpha & \dfrac{\cos\gamma - \cos\beta\cos\alpha}{\sin\alpha} & 0 \\ 0 & \left[\sin^2\beta - \left(\dfrac{\cos\gamma - \cos\beta\cos\alpha}{\sin\alpha}\right)^2\right]^{\frac{1}{2}} & 0 \\ \cos\alpha & \cos\beta & 1 \end{pmatrix}. \qquad (1)$$

Additional internal angles α, β, γ are introduced into the analysis procedure, and which differentiate between orthorhombic ($\alpha = \beta = \gamma = 90°$), monoclinic ($\beta \neq 90°$), or triclinic ($\alpha \neq \beta \neq \gamma$) biaxial optical properties.

Ellipsometric data analysis for anisotropic thin film samples requires nonlinear regression methods, where measured and calculated GE data are matched as close as possible by varying appropriate physical model parameters [25,28]. The quality of the match between model and experimental data can be measured by the mean square error (MSE) [30]. The major axes polarization response functions ϱ_a, ϱ_b, ϱ_c can be extracted on a wavelength-by-wavelength basis, *i.e.*, without physical lineshape implementations and Kramers–Kronig consistency tests can then be done individually for dielectric functions along each axis [27]. However, a generally more robust procedure is matching parameterized model dielectric functions to experimental data simultaneously for all spectral data points. Parametric models further prevent wavelength-by-wavelength measurement noise from becoming part of the extracted dielectric functions and greatly reduce the number of free parameters.

3. Homogeneous biaxial layer approach

The homogeneous biaxial layer approach (HBLA) assumes that a given composite material can be described as a homogeneous medium whose anisotropic optical properties are rendered by a spatially constant dielectric function tensor. This dielectric function tensor must be symmetric since no magnetic or other non-reciprocal properties are considered. The dielectric function tensor, in general, comprises three effective major axes dielectric functions $\varepsilon_j = 1 + \varrho(\omega)_j$ as described in Eq. (2), and may represent an anisotropic material resembling either orthorhombic, monoclinic, or triclinic optical symmetries.

Applied to a F1-STF, the optical equivalent can be, in the most simple case, a single biaxial layer described by the HBLA. This biaxial layer comprises then an optical thickness *d*, corresponding to the actual thickness of the nanostructured thin film as well as external Euler angles (φ, θ, ψ) and internal angles (α, β, γ) determining the orientation of the columns and sample during a particular measurement and biaxial properties, respectively [31]. Furthermore, there are three independent, complex, and wavelength-dependent functions $\varrho(\omega)_j$, pertinent to major polarizability axes $j = \mathbf{a}, \mathbf{b}, \mathbf{c}$ [21,22,16].

Explicitly, the dielectric tensor ε_t for a triclinic material takes the form

$$\varepsilon_t = \mathbf{AU}\begin{pmatrix} \varrho(\omega)_a & 0 & 0 \\ 0 & \varrho(\omega)_b & 0 \\ 0 & 0 & \varrho(\omega)_c \end{pmatrix}\mathbf{U}^{\mathrm{t}}\mathbf{A}^{\mathrm{t}}, \qquad (2)$$

where $\mathbf{A}$ is the real-valued Euler angle rotation matrix and $\mathbf{U}$ is the projection matrix [16]. Note that here the superscript “t” refers to the transpose of the respective matrix.

The HBLA does not allow to determine fractions of constituents within the composite material, nor the constituent bulk-like optical properties of the building blocks. However, the HBLA has several advantages over other effective medium approximations: (i) no initial assumptions such as optical parameters of the constituents or material fractions are necessary, (ii) it is valid for absorbing and non-absorbing materials, and (iii) it does not depend on the structure size. Note that the actual structure size is disregarded in this homogenization approach. This procedure is considered valid since the dimensions and especially the diameter of the nanostructures under investigation are much smaller than the probing wavelength. Care must be taken when properties at shorter wavelengths are evaluated, because diffraction and scattering phenomena may be present.

In general, it is presumed that the HBLA method together with the assumption of one effective optical thickness *d* applied to match experimental data for a F1-STF delivers the best possible dielectric tensor ε, *i.e.* $\varepsilon_{\mathrm{eff}}$, *j* are considered the true effective major axes dielectric functions and therefore target functions for other effective medium approximations.

Please cite this article as: D. Schmidt, Thin Solid Films (2013), http://dx.doi.org/10.1016/j.tsf.2013.10.119