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SPECTROSCOPIC ELLIPSOMETRY*

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Abstract. Spectroscopic ellipsometry (SE) is an optical technique which measures the change of polarization upon reflection or transmission. It is a non destructive technique used frequently for optical and structural characterization of thin films and substrates. Thin films of Ni YSZ5% and Ni YSZ10% deposited by PLD technique with ArF excimer laser (193 nm) on Si (100) and Pt/Si (100) substrate temperature (600ºC) were characterized with spectroscopic ellipsometry method. It is described the potential of S.E measurements and a complex application in optical and structural characterization of Ni-YSZ thin films, by operating an advanced VASE system.

Key words: SE, WVASE32, Optical Models, EMA, Ni-YSZ, PLD.

1. INTRODUCTION

Recent progress in the field generated a new type of instruments – VASE-Variable Angle Spectroscopic Ellipsometry with advantage in extension the limits of applications of classical configurations like multilayer, anisotropic samples, non-uniform thin films etc. The measurements are limited by hardware capabilities; as a result, the last generations of SE instruments are focused on improving the precision of ellipsometric parameters, high speed in operation and extension of spectral band from 140 nm and 200 μm [2, 3]. For monitoring the technological process, in situ real time SE is developed into a customized configuration (characterization of thin film growth, progress diagnoses including etching and thermal oxidation). There are two general restrictions on SE measurements: 1) Surface roughness should be bellow ~ 30% of the probe wavelength, because errors generally increase, although this effect depends completely on the type of instrument (VASE configuration is equipped with specific compensator or autoretarder); 2) The measurement must be performed at oblique incidence, because at normal incidence the measurements becomes impossible, since *p* and *s*

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polarizations can not be distinguished. The incidence angle is chosen to maximize the sensitivity of measurements, and varies according to the optical constants of samples. The one inherent draw back of the SE technique is the indirect nature of this characterization method; SE data analysis requires an optical model defined by optical constants and layer thickness of the sample. In the case of VASE systems, the data analysis is made by WVASE32 software that acts manly like a simulator of sample, being very useful in research activities. WVASE 32 included a data base with refractive index for a large number of materials. Because it can be applied also in VUV, it is useful for researches, because many materials present absorption in VUV that can not be explained by physics or chemically.

2. FEATURES OF SPECTROSCOPIC ELLIPSOMETRY

Ellipsometry is an optical measurement technique that characterizes light reflection (or transmission) from samples [1, 2]. The key feature of ellipsometry is that it measures the change in polarized light upon light reflection on a sample (or light transmission by a sample), Fig.1

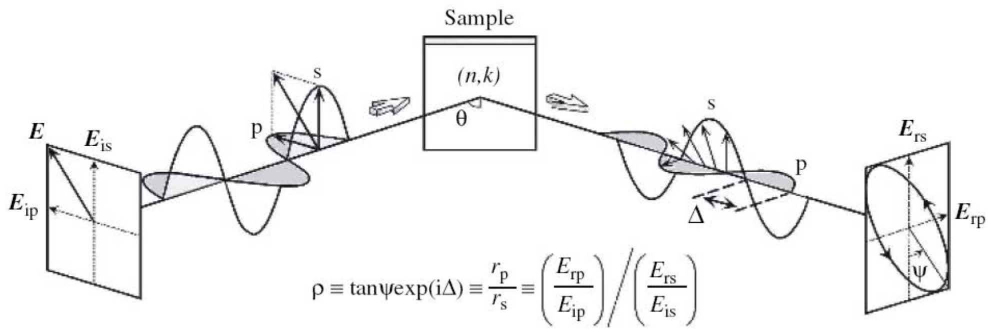


Fig. 1 – Measurement principle of ellipsometry [1].

Ellipsometry measures the two values (Δ,Ψ). Ψ represent the rate of amplitude Fresnel coefficients r_p and r_s for the light waves polarized in the plane p (parallel with plane of incidence) and s (perpendicular on plane of incidence); Δ is the phase difference between the mentioned plane p and s. In spectroscopic ellipsometry, (Δ,Ψ) are measured by changing the wavelength of light in our applications developed on VASE this is limited at the field of 250–1 700 nm that means ultraviolet, visible and near infrared region. Application area of spectroscopic ellipsometry is very large: semiconductor thin films, dielectric gates, high $-k$ dielectric films like YSZ, characterization of photoresist in UV; optical coating-thermal barrier coating with YSZ thin films for turbo reactor blades; chemistry-polymer thin films; self-assembled monolayer, DNA; real-time monitoring (*in situ*) of technological process like chemical vapor deposition (CVD).

3. ADVANTAGES AND DISADVANTAGES OF SPECTROSCOPIC ELLIPSOMETRY

It is a non-contact and non-destructive measurement with a fast measurement and data acquisition (in the case of SE assisted by computer). It has a wide application mainly in the field of scientific research (ex situ technique), because of large possibilities to generate and simulate the applications models for a great variety of materials, including unknown combination. For example software package WVASE 32. The data analysis is complicated because of a great variety of problems (transparent films, films with high absorption, isotropic and anisotropic structure, one and many phases/ constituents) that involve the application of EMA (Effective Medium Approximation).

The spot size of the light beam used in spectroscopic ellipsometry is typically several millimeters that means a low spatial resolution of the measurement. There are difficulties in characterization of thin films with thickness < 10 nm, because is not possible to make a difference between layer and substrate. Also the characterization at small absorption coefficient (α < 100 cm^{-1}) is rather difficult, mainly in ultraviolet region. Other limitation is generated by the roughness of thin film surface; the value of roughness must be limited to avoid the depolarization of light and to be in position for applying the EMA, in Bruggeman approximation. Measurement has to be performed at oblique incidence (in the case of semiconductor the field of angle is 70º–80º. The optimization of incidence angle is hard to determine at materials with multiple phases, amorphous materials etc. Measurements around the values Δ= 0º and Δ= 180º; in the case of transparent sample can implement errors and the result Woollam Co. developed a special optical device-retarder, assisted by computer that introduces a shift in the phase. To apply spectroscopic ellipsometry is important like the interfaces to be plane – parallel, mainly to measure the roughness. Also, the thin films must be uniform in the thickness. In the case of multilayer samples, it is necessary to know in advance some optical constants for the first iteration, because the use of dielectric functions in this case is more complex [2, 3].

4. CHARACTERIZATION OF PHYSICAL PROPERTIES BY SPECTROSCOPIC ELLIPSOMETRY

Figure 2 shows various physical properties that can be determinate from spectroscopic ellipsometry; in an ex situ measurement. As shown in Fig. 2, spectroscopic ellipsometry measure (Ψ, Δ) spectra for wavelength λ. To analyze (Ψ, Δ), it is constructed an optical model. From this data analysis, physical properties can be extracted. All mentioned applications are possible to run on

V-VASE, in the spectral range 250–1 700 nm, angle of incidence 45°,75° for reflection mode and 90° for transmission mode, with a precision of 0.01°, for a rate of acquisition of 0.1–3 s/λ, that is a function of the grade of reflection on the sample.

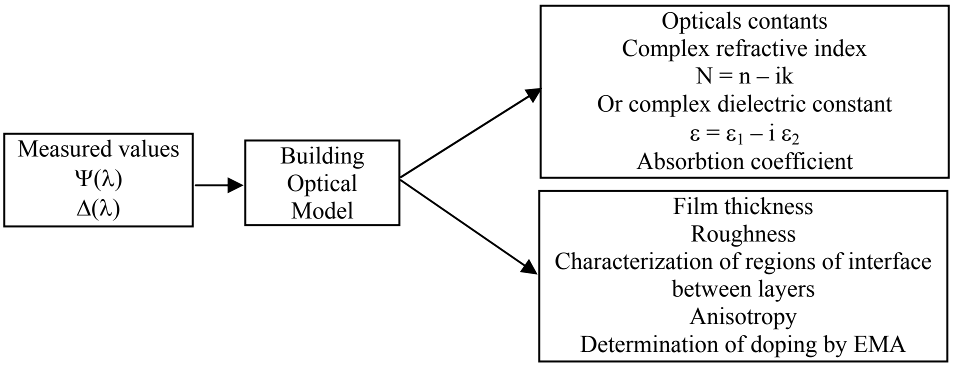


Fig. 2 – Characterization of physical properties by spectroscopic ellipsometry [1].

Because (Ψ, Δ) are function to the degree of polarization of the reflected light, in the optical model must be incorporated depolarization effects, for example, depolarization induced by backside reflection. By optimize the sample structure; the optical model can be simplified. For depolarized sample with backside reflection on the bottom surface of transparent substrate is necessary to polish this surface to avoid such effect. In operation of V-VASE it is observed the difficulties in characterization of samples with a non uniformity thickness of ~2% at a total thickness of ~1µm. In this case it is possible to build more layers or to use an approximation for interpretation.

Like an example, Fig. 3 presents configurations of ellipsometric parameters Ψ and Δ acquired at three angle of incidence (45°, 60°, 75°), on sample of 5Ni:YSZ and 10Ni:YSZ thin films, deposited by pulsed laser deposition [4].

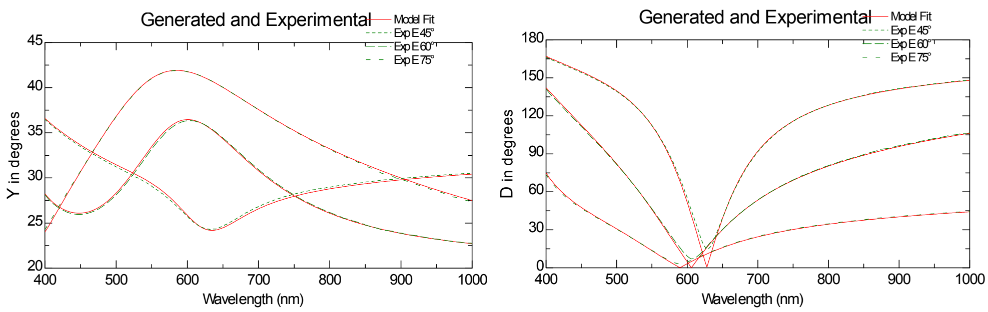


Fig. 3 – Ψ and Δ configurations for 5Ni: YSZ and 10 Ni:YSZ thin films [4].

5. DIELECTRIC FUNCTION MODELS

If the dielectric function [1] of a sample is not known, it is necessary to model it, by selection an appropriate model according to optical properties of the sample. For the dielectric function model in transparent region ($\varepsilon_2 \sim 0$) the Sellmeier or Cauchy model is used [3].

Cauchy model implemented in software package WVASE 32 is described by equation:

For the sample with absorption, in some region of spectrum it is used Cauchy-Urbach model, by adding following function:

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4}, \tag{2}$$

$$k(\lambda) = A_k \cdot e^{B(E - E_b)}, \tag{3}$$

where:

$$E \cong \frac{1\,240}{\lambda} \text{ and } E_b \approx \frac{E_b}{\lambda_b}.$$

The Tauc-Lorentz model has been employed to model the dielectric function of amorphous materials and transparent conductive oxides. Optical constants ε_1 and ε_2 are not independent of each other and if ε_1 varies, ε_2 also changes. The relation between ε_1 and ε_2 is described by Kramer-Kronig relations. If Tauc-Lorentz model satisfy this condition, it means that model is correct physically. The Drude model has been applied to examine free-carrier absorption in semiconductors.

With WVASE 32 it is possible to make an analysis Kramer-Kronig, the most frequent procedure is like this: a) it is collected (Ψ, Δ) for an unknown sample; b) use Cauchy model, to fit data in a limited region of spectra, where $k = 0$ (or can be calculated with Urbach equation); c) by fixing the thickness at the value determined at b) it is made a fitting necessary to generate ε_1 and ε_2.

6. EFFECTIVE DIELECTRIC MEDIUM APPROXIMATION THEORIES (EMA)

EMA is applied to characterize the composite structure with a number of phases. It is applied mainly for determination the complex refractive indices of surface roughness interface layers and volume fractions in composite materials.

There are three theories that can be presented into a uniform equation:

$$\frac{\langle \varepsilon \rangle - \varepsilon_h}{\langle \varepsilon \rangle + \gamma \varepsilon_h} = \sum f_j \frac{\varepsilon_j - \varepsilon_h}{\varepsilon_j + \gamma \varepsilon_h} \tag{4}$$

where: $\langle\varepsilon\rangle$ is the dielectric functions of effective medium; ε_h is the dielectric function for basic material; f_j is the fraction of phase; γ is a depolarization coefficient and has the value $\gamma = 2$.

The only difference between EMA models consists in selection of basic phase ε_h:

a) Lorentz- Lorentz: $\varepsilon_h = 1$ (air);

b) Maxwell – Garnett: $\varepsilon_h = \varepsilon_j$, where ε_h is the phase with highest fraction. This approximation is the most realistic ones, when the inclusion fraction (carriers, voids) is more reduced than the basic phase;

c) Bruggeman: $\varepsilon_h = \langle\varepsilon\rangle$ in which the dielectric function of basic material is just EMA function.

The roughness of surface is modeled mainly with Bruggeman approximation made by ~50% voids and ~50% material.

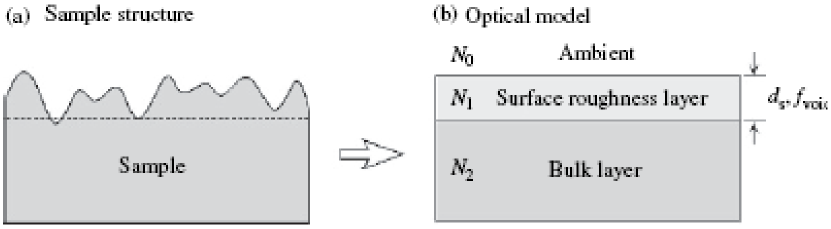


Fig. 4 – a) Sample with surface roughness; b) optical model composed of surface roughness and bulk layers. In (b), d_s and f_{void} represent the thickness of the surface roughness layer and the volume fraction of the ambient (voids) present within the surface roughness layer, respectively [1, 3].

If the roughness has a great thickness, it is necessary to insert a number of layers, with different fractions of voids and materials. EMA [1] can be applied in the following conditions:

a) The size of phases in composite materials is higher than neighboring atoms, but lower than $\lambda/10$ of wavelength for exploration;

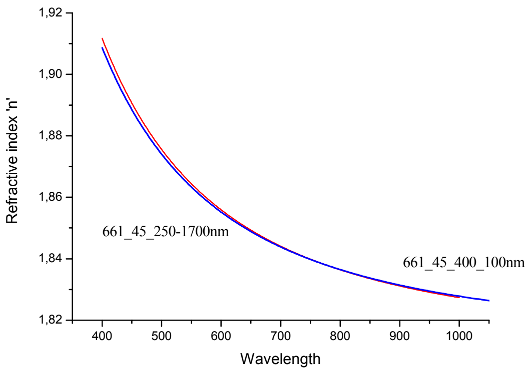
b) The dielectric functions of phases are independent of size and shape.

7. DATA ANALYSIS

Data analysis is performed by using linear regression analysis, and optical constants and film structures are determined by minimizing fitting errors MSE.

The dielectric functions show significant changes mainly by effects of doping, type of crystalline structure, chemical composition of thin films, surface temperature of the substrate during deposition, type of deposition, the quality of surface (roughness). Data were acquired using a J. A. Woolam Company VASE ellipsometer. Optical modeling and data analysis were done using WVASE 32 soft – ware package [2]. Ellipsometric parameters Ψ and Δ were acquired at three angle of incidence (45°, 60°, 75°) over the spectral range 250–1 700 nm and 400–1 700 nm; higher incident angles generates less rough, because the roughness value, follows a cosine dependence. To determine an approximate films thickness and refractive index and to maintain controllability in fitting process it was started to find a region of the spectral range where the film is transparent (or nearly so). This allows generation the models with fewer parameters to be used in fitting the data [4]. In the case of study presented on Ni:YSZ, being an high –*k* dielectric transparent in UV-VIS and NIR refractive index was described using Cauchy dispersion relation and k =0 at all measured wavelengths where A_n, B_n, C_n are fit coefficients. A_n is a constant that has a great contribution in configuration the curve and in most cases, it is necessary to make a first approximation. In the last version of VVASE 32 it is adopted $C_n = 0$.

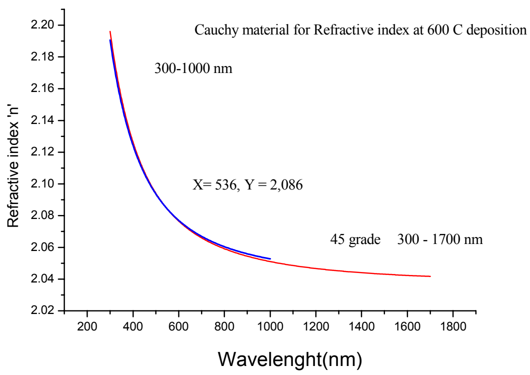
The substrate optical constant is taken from literature [2] and is not allowed to vary during the fit. Once an acceptable fit is achieved for part of spectrum, the spectral range is slowly extended to include longer and sorter wavelengths Refractive index variation for samples YSZNi5% and YSZNi10 % are presented in Fig. 5 [4].



MSE = 7.349	
Thick.1	101.686±0.147
An.1	1.8152±0.000882
Bn.1	0.0082874±0.0003
Thick.2	10.576±0.313
ThkUni	4.5116±0.143

2	srough	10.576 nm
1	cauchy_661_45_250_1700	101.686 nm
0	si_jaw	1 mm

a



MSE=11.88
Thick.1 75.558±0.0738
An.1 2.0461±0.001
Bn.1 0.010841±0.000267
Thick.2 13.983±0.162

2	srough	13.983 nm
1	cauchy785_25-1700_400-1000_45	75.558 nm
0	si_jaw	1 mm

b

Fig. 5 – a, b. Experimental data and analysis and refractive index for: a) 5Ni:YSZ; b) 10 Ni:YSZ thin films at room temperature and 600°C.

7. CONCLUSIONS

The present study demonstrates the limits of performance in thin films characterization by VASE-SE. Powerful data analysis techniques implemented in WVASE 32 software package are extremely important in extracting optical constants and structural parameters from a wide range of λ. The ability to acquire Ψ and Δ and quantitative characterization are presented in the case of Ni-YSZ thin films, a high-*k* dielectric material.

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