Optik - International Journal for Light and Electron Optics 173 (2018) 271–278

Contents lists available at ScienceDirect

Optik

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

Original research article

Porosity and roughness determination of porous silicon thin films by genetic algorithms

C.F. Ramirez-Gutierrez[a,b,*], J.D. Castaño-Yepes[c], M.E. Rodriguez-Garcia[d]

[a] *Posgrado en Ciencia e Ingeniería de Materiales, Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México Campus Juriquilla, C.P. 76230 Qro., Mexico*

[b] *Ingeniería Física, Facultad de Ingeniería, Universidad Autónoma de Querétaro, C.P. 76010 Querétaro, Qro., Mexico*

[c] *Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, México Distrito Federal, C.P. 04510, Mexico*

[d] *Departamento de Nanotecnología, Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México Campus Juriquilla, C.P. 76230 Qro., Mexico*

A R T I C L E I N F O

Keywords:
Effective medium approximation
Optimization
Refractive index
Reflectance
Optical admittance

A B S T R A C T

The problem of determining the porous silicon (PSi) optical constants, thickness, porosity, and surface quality using just reflectance data is board employing evolutionary algorithms. The reflectance measurements were carried out of PSi films over crystalline silicon (c-Si) substrate, and the fitting procedure was done by using a genetic algorithm (GA). The PSi is treated as a mixture of c-Si and air. Therefore, its effective optical constants can be correlated with the porosity through effective medium approximation (EMA). The results show that genetic fitting has a good match with the experimental measurements (near UV–vis reflectance) and the thickness obtained by scanning electron microscopy (SEM).

1. Introduction

Porous silicon (PSi) is a nanostructured material [1] obtained by electrochemical etching of crystalline silicon (c-Si). In the case of p-type c-Si, microporous can be obtained (< 2 nm) if the resistivity of the sample is more than 0.1 Ω cm, mesoporous (2–50 nm) for heavy doped c-Si with resistivity between 0.1 and 0.001 Ω cm [2]. For n-type c-Si with 0.1–0.01 Ω cm mesoporous are formed, while for more resistive n-Si macroporous formation (> 50 nm) is present [2].Therefore, it is possible to tune the PSi electrical and optical properties through the porosity by using a combination of fabrication parameters such as the current density, electrolyte composition, temperature [2–6], thermal oxidation [1], among others extrinsic and extrinsic parameters.

PSi has a high surface area, diverse surface chemistry [7], porous morphology [8], high-efficiency photo- and electro- luminescence [5,9], as well as piezoelectric [10] and piezooptic properties [11]. Furthermore, PSi has effective optical properties that depend on the material that can fill the pores. The characteristics mentioned above make the PSi an interesting material for chemical sensing [12], biological applications, photonics, and optoelectronics [13].

It is common to use ex situ techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM) [1], profilometry, and gravimetry [14] to characterize PSi properties. In some cases, the probe can be destructive. Other works are focused on describing the kinetics of the chemical reaction and following the formation of the porous film in real time to determine some properties of PSi in-situ [3–6,14–16]. For any application of the PSi, a completed knowledge of PSi optical properties is required, interface quality, thickness, and porosity. Optical transmittance and reflectance are good options because they are non-destructive

* Corresponding author.
E-mail address: cristianframirezg@gmail.com (C.F. Ramirez-Gutierrez).

https://doi.org/10.1016/j.ijleo.2018.08.019
Received 6 June 2018; Received in revised form 10 August 2018; Accepted 11 August 2018
0030-4026/

techniques and provide rapid and accurate information of optical properties of c-Si and PSi in the visible range [17].

The calculation of the optical constants (refractive index $n(\lambda)$, and extinction coefficient, $k(\lambda)$) is usually made by fitting the reflectance or transmittance spectra. However, the methods are not trivial, in fact, they represent an inverse problem. This problem of estimating optical constants and thickness using only transmittance or reflectance data has been addressed by using fitting procedures and optimization algorithms. However, in the case of PSi, due to the nature of the random porous formation, it is necessary to consider other parameters such as porosity and interface roughness because this variety of inhomogeneities causes light scattering. These inhomogeneities and roughness are no longer negligible, and they can introduce a significant error in the determination of the optical constants [18].

Optimization algorithms solve this kind of problems, especially evolutionary algorithms because they can avoid local minima following many search pats simultaneously [19–22]. Torres-Acosta et al. [19] used a self-adaptive genetic algorithm (GA) to determine optical constants and thickness of PSi films in the visible range (400–800 nm). However, the fitting procedure used a parameterization of the real part of the refractive index, and it did not consider the porosity and roughness of the PSi film because the experimental setup includes an integrating sphere. On the other hand, Peña and Torres [23] propose to determine the optical constants of PSi films using diffuse and specular reflectance simultaneously. The comparison between the scattering and specular spectrum allows an estimation of film roughness. However, this methodology fails in the ultraviolet region due to the difficulty to extrapolate the refractive index and the high absorption contribution in this region. Nevertheless, it is possible to use the same methodologies to introduce the porosity and interface roughness, and fit the specular reflectance spectrum to determine the thickness, optical constants, porosity, and interfacial roughness simultaneously.

To add the porosity percentage and roughness interface, the electrical permittivity of PSi can be described as an effective medium. This method takes into account the system as a mixture composed by a host medium with $\hat{\varepsilon}_m$ (c-Si) with inclusions within it, characterized by $\hat{\varepsilon}_i$, which allows the determination of the optical properties in the linear regimen. Thus, the PSi is modeled as an effective medium [24,25] that is the result of a mixture of c-Si and the material that fill the pores that can be a gas or liquid.

To overcome this problem, this work proposes a methodology based on genetic algorithms to fit the near-specular reflectance (6° incidence) spectrum of single films of PSi over the c-Si substrate. A simultaneous determination of PSi properties such as optical constants, thickness, porosity, and interface roughness is made only by using reflectance measures. The system is considered as a silicon (c-Si) single crystal, and by using an effective medium approximation (EMA) the algorithm can determine the refractive index $\eta(\lambda)$, extinction coefficient $\kappa(\lambda)$, PSi thickness, interfaces RMS roughness (σ) (Air/PSi and PSi/Si substrate) and the porosity. The model is tested by using several films of p-type Si fabricated with different anodization times. Also, the thickness of the PSi samples was determined by the genetic fit and compared with the thickness obtained by electron scanning microscopy (SEM) images.

2. Experimental section

2.1. Porous silicon fabrication

A heavy boron doped Si (p^{++}) with 0.005 Ω cm of resistivity and [100] crystalline orientation it was used. The samples were cut into squares of 14 mm in length, and cleaned by the RCA standard method. Four PSi films were fabricated by electrochemical etching using 40% aqueous hydrofluoric acid (HF) diluted with 99.67% ethanol. The electrolyte composition was 3:7 (HF/ethanol) in volume ratio, and a regimen of a constant current of 20 mA/cm^2 was applied. The porous formation was followed by photoacoustic using the methodology proposed by Ramirez-Gutierrez et al. [3–6]. Each sample was fabricated under the same conditions (current density, temperature, and electrolyte composition). The etching time was the changed parameter. Sample S1 was etched for 28 s, S2 for 56 s, S3 for 84 s, and S4 for 112 s. The etched area is a disk of 10 mm of diameter.

2.2. Near specular reflectance

Optical characterization of PSi films was carried out using a Perkin Elmer UV-Vis Spectrophotometer Lambda 35 in the near-normal (6°) relative specular reflectance mode from 1100 to 210 nm range. The spectrophotometer was self-calibrated using an aluminum mirror, and the samples were measured over the Si substrate. It means that the reflectance is the optical response of the PSi thin film Si substrate (PSi/Si structure).

The spectra were corrected following Eqs. (1 and 2) to obtain the absolute reflectance.

$$R(\lambda) = R_{\text{relative}}(\lambda) R_{\text{transfer}}(\lambda), \tag{1}$$

$$R_{\text{transfer}}(\lambda) = \frac{R_{\text{Teo}}^{(\text{Si})}(\lambda)}{R_{\text{relative}}^{(\text{Si})}(\lambda)}, \tag{2}$$

where $R(\lambda)$ is the absolute reflectance of the sample (PSi/Si-structure), $R_{transfer}$ is the transfer function of the spectrophotometer built through theoretical reflectance of Si ($R_{\text{Teo}}^{(\text{Si})}$) and the measured reflectance of a Si substrate ($R_{\text{relative}}^{(\text{Si})}$).

2.3. Morphological studies

After the optical characterization, the samples were cut to determine the films thickness. A MIRA3 TESCAN microscopy was used with a 5.0 kV electron acceleration voltage. Before the analysis, samples were fixed on the holder with copper tape. The samples were