UNIVERSITY OF PÉCS

Doctoral School of Physics
Nonlinear optics and spectroscopy program

Ellipsometric study of nanostructured silicon materials

PhD Thesis

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Background and aims

The incredible development in miniaturization of the last century has lead us today to the domain of nanotechnology. These miniaturization steps to obtain smaller, faster, lighter, denser, and cheaper devices are closely interweaved with the advancement attained in characterization techniques. The ellipsometric technique has followed such a path, with most ellipsometers today being spectroscopic. Ellipsometry is an optical method based on the measurement of the change of polarization upon reflection from, or transmission through a sample [1]. By measuring the polarization change, we obtain not only amplitude, but also phase information of the light interacting with the sample. This remarkable property enables an incredible sensitivity to the properties of thin layers, with a sub-nanometer precision, hence valued in industrial processes as an *ex situ* feedback between process steps with more and more demand for even *in situ* measurements. Being an optical technique, spectroscopic ellipsometry (SE) is non-destructive with relatively fast measurements compared to other probing methods. However, it is an indirect technique, meaning that any information on the sample is obtained through the modelling and inversion of the ellipsometric response, often through simulation and iterative fitting [2].

In electronics miniaturization, silicon-based semiconductor technology is approaching its theoretical limits, but silicon industry has grown to such an extent, that it would be hard to imagine the near future without the basic building block of monocrystalline silicon (c-Si). Many different c-Si based nanostructures have emerged in the last two to three decades, that are finding (potential) applications, but industrial ellipsometric characterizations remains limited because the development of highly complex optical models is challenging and often limited to academic research.

In my thesis, I aim to show the versatility of SE characterization for some c-Si-based nanostructured materials. I not only wish to increase the understanding of the fundamental properties and formation mechanisms of these materials but also hope to boost their spreading for industrial productions in any modest way by the development of ellipsometric models.

Methods

I studied by SE the near surface cavities formed in c-Si due to He-implantation [3] through a screening oxide layer followed by an annealing step. I compared the results to those obtained from the analyses of transmission electron microscopic images. I characterized with optical and infrared SE as-prepared and post-oxidized porous silicon (PSi) layers formed by electrochemical etching [4]. I also investigated the anisotropic behavior of PSi thin layers [5] and of silicon nanowires [6]. Lastly, I studied the relationship between the parameters describing surface roughness and the effective layer thickness commonly determined by SE [7] by simulating the ellipsometric spectra with finite element method.

For all the studied cases, I applied some variant of an effective medium theory based model, as they are the most widely accepted methods to obtain structural information about thin films. A multilayered structure composed of isotropic Bruggeman effective medium approximation (B-EMA) based layers well described the in-depth variation of the implantation caused cavities [8]. The PSi layers were characterized by a two- or a three-component isotropic or anisotropic multilayered B-EMA based structure [9,10], while the nanowires were best described by a multilayered structure based on anisotropic Maxwell-Garnett effective medium theory. The finite element simulated ellipsometric spectra of silicon surface roughness was fitted with a simple B-EMA having only its thickness value as free parameter.

New scientific results

The following theses summarize the results supported by publications as my own contribution to the present PhD work:

1. I had developed a multilayer, multi-parametric optical model that I successfully used to determine the influence of the masking

oxide layer, fluence and heat treatment on the depth distribution of cavities formed in helium implanted single-crystalline silicon. I have shown that spectroscopic ellipsometry is suitable for determining the depth distribution of cavities in a resolution comparable to or greater than electron microscopy and thereby suitable for rapid, high-sensitivity and non-destructive testing of these samples. I have found that the total volume of the cavities greatly increases with increasing ion fluence, while the peak density of the cavity distribution becomes more localized to the surface region. [T4, T8].

2. I had developed optical models for ultraviolet-near-infrared (191–1690 nm) and mid-infrared (1.7–16.7 μm) wavelength range, with which I was able to determine the thickness, average porosity, in-depth porosity distribution, lateral inhomogeneity, oxidation level and surface roughness of porous silicon (PSi) layers of a broad thickness range (0.7–52 μm). I showed with ellipsometry the uneven in-depth porosity distribution of thick PSi layers (25–52 μm). By analyzing the volume ratio of porous and oxidized content, I have shown that the oxidation of the porous structure reproduces the same volume expansion as would be obtained when oxidizing plane wafers [T3, T7].

3. I had created optical models and a qualification procedure based on them for anisotropic porous silicon (PSi) and silicon nanowire (SiNW) layers, with which I revealed that the optical

behavior of PSi layers etched with low current density (2–40 mA/cm^2) is dominated by the in-depth gradient of the porosity (beyond the average porosity and the layer thickness), but in the case of the samples created at high current density (200–800 mA/cm^2), anisotropy becomes the dominant feature. I have also shown that the SiNW layers are highly anisotropic and the fibrous structure revealing the best orientation is obtained for the 1 μm wire length. I have shown that the SiNW layers formed up to a thickness of ~4 μm can be described by effective medium approximation-based models, above this thickness, light scattering from the layers is significant in the visible, near-infrared range [T1, T5].

4. I have shown that ellipsometric spectra of rough surfaces simulated by finite element method and by effective medium approximation are in good agreement for random surfaces with a Gaussian distribution if the wavelength of illumination is much larger than the root-mean-square height. I revealed quadratic relations between the root-mean-square heights and the effective medium layer thickness for given auto-correlation lengths. I have shown that these quadratic relations can be expressed as a linear relationship between the effective medium thickness and the product of the root-mean-square height (in case it is less than 5 nm) and the average surface slope [T2, T6].

List of publication

Publications strictly related to the thesis

Articles published in peer-reviewed journals:

[T1] **B. Fodor**, T. Defforge, E. Agócs, M. Fried, G. Gautier, P. Petrik , "Spectroscopic ellipsometry of columnar porous Si thin films an Si nanowires", Applied Surface Science, 421 (2017) 39, DOI: 10.1016/j.apsusc.2016.12.063.

[T2] **B. Fodor**, P. Kozma, S. Burger, M. Fried, P. Petrik, "Effective medium approximation of ellipsometric response from random surface roughness simulated by finite-element method", Thin Solid Films 617 (2016) 20, DOI: 10.1016/j.tsf.2016.01.054.

[T3] **B. Fodor**, E. Agocs, B. Bardet, T. Defforge, F. Cayrel, D. Alquier, M. Fried, G. Gautier, P. Petrik, "Porosity and thickness characterization of porous Si and oxidized porous Si layers – an ultraviolet-visible-mid infrared ellipsometry study", Microporous and Mesoporous Materials 127: (2016) 112, DOI: 10.1016/j.micromeso.2016.02.039.

[T4] **B. Fodor**, F. Cayrel, P. Petrik, E. Agocs, D. Alquier, M. Fried: "Characterization of in-depth cavity distribution after thermal annealing of helium-implanted silicon and gallium nitride”, Thin Solid Films 571 (2014) 567, DOI: 10.1016/j.tsf.2014.02.014.

Results presented at conferences:

[T5] **B. Fodor**, T. Defforge, B. Bardet, E. Agócs, F. Cayrel, M. Fried, G. Gautier, P. Petrik, “Spectroscopic Ellipsometry of Columnar Porous Si Thin Films and Si Nanowires”, ICSE-VII (7th International Conference on Spectroscopic Ellipsometry), poster presentation, 2016.06.06–10, Berlin, Germany.

[T6] **B. Fodor**, P. Kozma, S. Burger, M. Fried, P. Petrik, “Comparison of effective medium and finite element methods for photonic structures”, EMRS 2015 Spring, oral presentation, 2015.05.11–15, Lille, France.

[T7] **B. Fodor**, E. Agocs, G. Gautier, T. Defforge, B. Bardet, D. Alquier, M. Fried, P. Petrik, “Ellipsometric Characterization of Porous Silicon and Oxidized Porous Silicon Layers within a Wide Spectral Range”, EVC13 (13th European Vacuum Conference), poster presentation, 2014.09.08–12, Aveiro, Portugal.

[T8] **B. Fodor**, F. Cayrel, P. Petrik, E. Agocs, D. Alquier, M. Fried, “Characterization of in-depth cavity distribution after thermal annealing of helium-implanted silicon and gallium nitride”, ICSE-VI (6th International Conference on Spectroscopic Ellipsometry), poster presentation, 2013.05.26–31, Kyoto, Japan.

Other publications

Articles published in peer-reviewed journals:

[O1] E. Agocs, Z. Zolnai, A.K. Rossall, J.A. van den Berg, **B. Fodor**, D. Lehninger, L. Khomenkova, S. Ponomaryov, O. Dugymenko, V. Yukhymchuk, B. Kalas, J. Heitmann, P. Petrik, “Optical and structural characterization of Ge clusters embedded in ZrO2”, Applied Surface Science, 421 (2017) 283, DOI: 10.1016/j.apsusc.2017.03.153.

[O2] E. Agócs, P. Kozma, J. Nádor, A. Hámori, M. Janosov, B. Kalas, S. Kurunczi, **B. Fodor**, E. Ehrentreich-Förster, M. Fried, R. Horvath, P. Petrik, “Grating coupled optical waveguide interferometry combined with in situ spectroscopic ellipsometry to monitor surface processes in aqueous solutions”, Applied Surface Science, 421 (2017) 289, DOI: 10.1016/j.apsusc.2016.07.166.

[O3] P. Petrik, E. Agocs, B. Kalas, **B. Fodor**, T. Lohner, J. Nador, A. Saftics, S. Kurunczi, T. Novotny, E. Perez-Feró, R. Nagy, A. Hamo-ri , R. Horvath, Z. Hózer, M. Fried, “Nanophotonics of biomaterials and inorganic nanostructures”, J. Phys.: Conf. Ser 794 (2017) 012004, DOI: 10.1088/1742-6596/794/1/012004.

[O4] B. Lu, T. Defforge, **B. Fodor**, B. Morillon, D. Alquier, G. Gautier, “Optimized plasma-polymerized fluoropolymer mask for local porous silicon formation”, Journal of Applied Physics, 119 21 (2016) 213301, DOI: 10.1063/1.4953088.

[O5] P. Petrik, N. Kumar, M. Fried, **B. Fodor**, G. Juhasz, S. F. Pereira, S. Burger, H. P. Urbach, “Fourier ellipsometry - An ellipsometric approach to Fourier scatterometry”, JEOS:RP 10 (2015) 15002, DOI: 10.2971/jeos.2015.15002.

[O6] P. Petrik, E. Agocs, B. Kalas, P. Kozma, **B. Fodor**, J. Nador, C. Major, M. Fried, “Multiple angle of incidence, spectroscopic, plasmon-enhanced, internal reflection ellipsometry for the characterization of solid-liquid interface processes”, Proc. SPIE - Int. Soc. Opt. Eng., 95290W (2015), DOI: 10.1117/12.2184850.

[O7] P. Petrik, **B. Fodor**, E. Agocs, P. Kozma, J. Nador, N Kumar, J. Endres, G. Juhasz, C. Major, S.F. Pereira, T. Lohner, H.P. Urbach, B. Bodermann, M. Fried, “Methods for optical modeling and cross-checking in ellipsometry and scatterometry”, Proc. SPIE - Int. Soc. Opt. Eng., 95260S (2015), DOI: 10.1117/12.2184833.

[O8] J. Landwehr, R. Fader, M. Rumler, M. Rommel, A. Bauer, L. Frey, B. Simon, **B. Fodor**, P. Petrik, A. Schiener, B. Winter, E. Spieker, „Optical polymers with tunable refractive index for nanoimprint technologies”, Nanothechnology (2014) 25 505301, DOI: 10.1088/0957-4484/25/50/505301.

[O9] E. Agocs, **B. Fodor**, B. Pollakowski, B. Beckhoff , A. Nutsch, M. Jank, P. Petrik “Approaches to calculate the dielectric function of ZnO around the band gap”, Thin Solid Films (2014), DOI: 10.1016/j.tsf.2014.03.028.

[O10] P. Petrik, E. Agocs, J. Volk, I. Lukacs, **B. Fodor**, P. Kozma, T. Lohner, S. Oh, Y. Wakayama, T. Nagata, M. Fried, „Resolving lateral and vertical structures by ellipsometry using wavelength range scan”, Thin Solid Films (2014), DOI: 10.1016/j.tsf.2014.02.008.

[O11] P. Petrik, N. Kumar, G. Juhasz, C. Major, **B. Fodor**, E. Agocs, T. Lohner, S.F. Pereira, H.P. Urbach, M. Fried, “Optical characterization of macro-, micro- and nanostructures using polarized light”, J. Phys.: Conf. Ser 558 (2014) 012008,
DOI: 10.1088/1742-6596/558/1/012008.

[O12] A. Saftics, E. Agócs, **B. Fodor**, D. Patkó, P. Petrik, K. Kolari, T. Aalto, P. Fürjes, R. Horvath, S. Kurunczi, “Investigation of thin polymer layers for biosensor applications”, Applied Surface Science (2013), DOI: 10.1016/j.apsusc.2012.12.042.

[O13] Szekeres, S. Alexandrova, P. Petrik, **B. Fodor**, S. Bakalova, “Ellipsometric study of crystalline silicon hydrogenated by plasma immersion ion implantation”, Applied Surfac Science (2013), DOI: 10.1016/j.apsusc.2012.12.024.

[O14] P. Petrik, T. Gumprecht, A. Nutsch, G. Roeder, M. Lemberger, G. Juhasz, O. Polgar, C. Major, P. Kozma, M. Janosov, **B. Fodor**, E. Agocs, M. Fried, “Comparative measurements on atomic layer deposited Al2O3 thin films using ex situ table top and mapping ellipsometry, as well as X-ray and VUV reflectometry”, Thin Solid Films (2013), DOI: 10.1016/j.tsf.2012.12.091.

[O15] P. Kozma, **B. Fodor**, A. Deak, P. Petrik, "Optical Models for the Characterization of Silica Nanosphere Monolayers Prepared by the Langmuir-Blodgett Method Using Ellipsometry in the Quasistatic Regime", Langmuir (2010), DOI: 10.1021/la1028838.

Results presented at conferences:

[O16] **Fodor B.**, Petrik P., „Szilika nanogömbökből álló vékonyrétegek tanulmányozása ellipszometriával", MTA TTK Doctoral Conference, oral presentation, 2014.12.10–12, Budapest, Hungary.

[O17] **B. Fodor**, P. Petrik, J. Volk, I. Lukacs, S. Oh, Y. Wakayama, T. Nagata, M. Fried, "Mueller Matrix Ellipsometry of Two-Dimensional Periodic Submicron Structures", EMRS 2012 Fall, poster presentation, 2012.09.17–21, Warsaw, Poland.

[O18] **B. Fodor**, P. Kozma, N. Nagy, Z. Zolnai, P. Petrik, M. Fried, "Ellipsometric Characterization of Ion Irradiated Monolayers Prepared from Submicron Silica Particles", EMRS 2012 Spring, oral presentation, 2012.05.14–18, Strasbourg, France.

[O19] **B. Fodor**, P. Kozma, A. Deak , N. Nagy , Z. Zolnai , P. Petrik , M. Fried, “Spectroscopic Ellipsometry Investigation of Silica Nanosphere Monolayers before and after Ion Irradiation-induced Shape Transformation”, EuroNanoForum, poster presentation, 2011.05.30–06.01, Budapest, Hungary.

[O20] **B. Fodor**, P. Kozma, A. Deak, Z. Zolnai, P. Petrik, M. Fried, “Optical Models for the Characterization of Silica Nanosphere Monolayers investigated by Spectroscopic Ellipsometry”, 6th Workshop Ellipsometry, oral presentation, 2011.02.21–24, Berlin, Germany.

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