Qualifications of Si-based Nanocrystalline Structures by Spectroscopic Ellipsometry

PhD thesis booklet

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Motivations and objectives

In these days the nanotechnology is improving intensely and has many applications not only in the semiconductor industry but also in the areas of chemistry, biology and medicine. The application areas are increasing continually due to the observated unique physical and chemical features in the nanoscale. More specific systems can be produced with better and better quality, which can be investigated by better and better measurement techniques due to the improvement of technique.

Ellipsometry is an optical measurement technique which is quite sentitive to surface. This technique is capable of measuring the physical and chemical features or processes, which affect the optical properties of the area near to the surface of sample (several micrometer in depth).

The theory had been knowing for 100 years, even so the technique had been being widespread since nineties, when the computertechnique reached a level which was enough to serve the on-demand computing of ellipsometry. The reason for this is that the characterization method of ellipsometry is an indirect method. The semiconductor industries and the industries who apply thin films and surfaces began utilize the ellipsometry due to the development of computertechnique. At first the ellipsometry was used in the different phases of the production line like quality controller

The method has also developed perpendicular with the increasing of popularization. After the first Null Ellipsometry, the

Rotating-Analyzer Ellipsometry and then the Rotating-Compensator Ellipsometry were realized which provides better measurement precision significantly. The single-wavelength ellipsometry was replaced for the multi-wavelength (spectroscopic) ellipsometry, which used more and more wide range of wavelength from ultraviolet to infrared. Then the scattering ellipsometry and the ellipsometry with more rotating compensators were developed to invenstigate the anisotropic features of sample.

The main objective of the work was to increase the amount of obtained information about the thin layer systems with different types of nanostructure by spectroscopic ellipsometry. After the suitable samples had been choosed, the task was in general the developement of optical models optimized to the correspondent samples. In case of highly complex systems I was also developed a parameter analysing and fitting algorithm.

The silicon is the most popular and most widly used semiconductor in semiconductor industry. The advantages of this material are, that stable oxid layer (i.e. insulator) grows on the top if its in the air ambient, it can be produced in very high purity, single crystalline form, and it can be found in great quantity. Thanks to that some technologies (like solar cell technologie or lighting)are tried to develope primarily based on silicon, or based on silicon too. To reach the required physical properties the silicon is dopped with another materials, or its structure is changed or it is built in the special structure. I have chosen this material due to its wide application area and the plentiful theoretical backgroundknowledge.

Besides this various running projects of the Ellipsometry Laboratory of MFA have revelations to this materialsystem and this subject.

In this work investigations on three silicon-based thin layer systems with different types of nanostructure are discussed. One of the investigated sample groups was the porous silicon prepared by electrochemical etching. Due to the porosity the band structure of bulk material changes accordingly the physical and chemical properties of material also change. Regarding the applications it is also especially important, that the specific surface of material increases. This structure opens the new application possibilities belong semiconductor industry and solar cell technology, for example pharmaceutical industry, optics and sensors.

Researches are going in a wide area about the nanocrystalline silicon structures embedded in a dielectric, especially in the area of non-volatile memory devices, like charge carrying material, silicon based light-emitting diode or sensors. The second sample series had a multilayer structure developed for memory devices where the change of structure caused by annealing was investigated.

Due to the quantum-confinement effect and the electron scattering effect on the grain boundaries the band structure of silicon nanocrystals is different from that of bulk silicon. The band structure shows discrete energy levels in the conduction and valence band that are strongly dependent on silicon nanocrystal size. The electric, the transport and charging properties of nanocrystalls with diameter below 3-5 nm, change and strongly depend on the nanocrystal size.

Analyzing the dielectric function provides valuable information on the band structure, because the imaginary part of the dielectric function is directly proportional to the joint density of electron states in the semiconductor crystal. Finally polycrystalline samples containing nanocrystals with well-defined sizes were investigated. Thanks to that the correlation of the grain size with the dielectric function was able to investigated.

I performed my studies at the Doctoral School of Molecular and Nanotechnologies, University of Pannonia and at the Ellipsometry Laboratory of Photonic department, Research Institute for Technical Physics and Material Science, Research Centre for Natural Sciences . My scientific results are summarized in the theses below:

Theses

1. I have developed a parameter analysing and fitting algorithm, which utilizes both the gradient and grid search methods, furthermore, it uses dynamic ranges for the variable parameters. Due to these features the method is suitable for finding the insensitive and cross-correlating parameters of the system so that they can be fixed at a certain value or coupled to other parameter values. In this manner, the sensitivity of fitted parameters can be significantly increased and the probalitity of finding the global minimum can also be increased in the systems using high number of variable parameters, and the optical model can be simplified and improved

with greater reliability. This method is also exceedingly usefull when there are few or ambiguous information about the layered system, hence wide initial limits for the variable parameters are necessary to be used [T1][T5][T6].

2. I have developed an optical model which provides information about the character and quality of porous silicon films. The refractive index of the porous layers were calculated using the effective medium approximation with two components: single crystalline silicon reference and void. The depth variation of the structure was considered in such a way that the largest possible number of layers was introduced in the optical model without significant cross-correlations. With this model I could determine the properties of porous samples, i.e. the extent and thickness of surface roughness, the thickness of porous layer, the quantity of porosity and the in-depth porosity variation [T1][T5][T6].

3. I have been the first to use the parametric polinom model by Johs-Herzinger to describe the dielectric function of porous silicon. It is revealed that ellipsometry is suitable for the indirect determination of the grain size with the help of a reference measurement method used for the calibration of the grain size and the sensitively varying optical parameters [T1][T5][T6].

4. I have developed an optical model to describe multilayer structures, which consist of two types of layers, and were

annealed at different temperatures. One of the layer type is a non-stoichiometric silicon oxide layer with high silicon concentration (SRO), the other is a stoichiometric silicon oxide layer. The changing of structure and phase transition due to the annealing process were monitored with this optical model by spectroscopic ellipsometry. I have revealed that the multilayer structure, which consists of 10 layer pairs, can be modeled by coupling the thicknesses and optical properties of the layer pairs respectively. With the help of these coupled parameters I have significantly reduced the number of fitted parameters, which was important to avoid high cross-correlation. I have shown, that the shrinking of layer pairs (sintering effect), the decreasing of SRO sublayer thicknesses, the separations of SiO_2 phase, the crystallization of amorphous phase, and the increasing of nanocrystalline grains could be followed with this optical model as a function of annealing temperature [T2][T7][T8][T9].

5. I have developed an optical model using improved effective medium approximation (EMA) to characterize nanocrystalline silicon thin layers with spectroscopic ellipsometry. The samples, featuring systematically varying grain sizes, were prepared by low pressure chemical vapour deposition, followed by oxidation. The nanocrystallinity describing the grain structures was qualified with the ratio of two components, the single crystalline phase and the nanocrystalline phase of the EMA model. The calculated and measured spectra show a good agreement. I have

demonstrated, that the nanocrystallinity determined in such a quantitative way by ellipsometric measurement, revealed a systematic decrease with increasing nanocrystalline layer thickness and with increasing grain size in accordance with the results of reference methods [T3][T4][T10][T11] [T12][T13]

6. An optical model was developed for ellipsometric measurements, which utilizes the model dielectric function of S. Adachi to describe a sample set consisting of different thicknesses of nanocrystalline silicon films. A systemathic method was developed in view of the sensitivity and parameter cross-correlation in order to decrease the number of fitted parameters. The method finds those parameters that can be coupled amongst each other and those that can be pinned down to a fixed value. The dielectric functions of nanocrystalline silicon thin films were determined by fitting the parameters of the oscillators belonging to critical points. Correlation was revealed between the parameters of the absorption peaks and the grain sizes in accordance with the electron scattering on grain boundaries and with the lifetime broadening theories [T3][T9][T11].

This Ph.D. work is based on the following publications

[T1] **E. Agocs**, P. Petrik, S. Milita, L. Vanzetti, S. Gardelis, A. G. Nassiopoulou, G. Pucker, R. Balboni, T. Lohner, M. Fried, *„Optical Characterization of Nanocrystals in Silicon Rich Oxide*

Superlattices and Porous Silicon", Thin Solid Films 519 (2011) 3002, DOI: 10.1016/j.tsf.2010.11.072.

[T2] **E. Agocs**, P. Petrik, M. Fried, A. G. Nassiopoulou, *„Optical characterization using ellipsometry of Si nanocrystal thin layers embedded in silicon oxide"*, MRS Online Proceedings Library, part of Cambridge Journals Online, (2011) DOI: 10.1557/opl.2011949.

[T3] **Emil Agocs**, Androula G. Nassiopoulou, Silvia Milita, Peter Petrik, *„Model dielectric function analysis of the critical point features of silicon nanocrystal films in a broad parameter range"*, Thin Solid Films, 541 (2013) 83-86, DOI: 10.1016/j.tsf.2012.10.126.

[T4] [T4] P. Petrik, **E. Agocs**, „High Sensitivity Optical Characterization of Thin Films with Embedded Si Nanocrystals", ECS Transactions, voulme 53, issue 53, p. 43-52 (2013), DOI: 10.1149/05304.0043ecst

Oral and poster presentations

[T5] **E. Agócs**, P. Petrik, *„Szilícium alapú nanoszerkezetek vizsgálata spektroszkópiai ellipszométerrel"*, 38. Műszaki Kémiai Napok, April 27-29th, 2010, Veszprem, Hungary, *oral presentation.*

[T6] **E. Agócs**, P. Peter, S. Milita, L. Vanzetti, S. Gardelis, G. Pucker, R. Balboni, T. Lohner, M. Fried, and A. G. Nassiopoulou, *„Characterization of Nanocrystals in Silicon Rich Oxide Superlattices and Porous Silicon"*, 5th. International Conference on

Spectroscopic Ellipsometry, May 23-28th, 2010, Albany, NY USA, *oral presentation.*

[T7] **Emil Agocs**, Peter Petrik, Spiros Gardelis and Androula G. Nassiopoulou, *„Ellipsometric investigation of Si nanocrystal thin films within SiO2 prepared by low pressure chemical vapor deposition and oxidation"*, 4th International Conference on Micro-Nanoelectronics, Nanotechnology and MEMS, December 12-15th, 2010, NCSR Demokritos, Athens, Greece, *poszter.*

[T8] **Emil Agocs**, Peter Petrik, Miklos Fried, and Androula G. Nassiopoulou, *„Optical Characterization Using Ellipsometry of Si Nanocrystal Thin Layers Embedded in silicon Oxide"*, MRS Spring Meeting, April 25-29th, 2011, San Francisco, USA, *poszter.*

[T9] **Emil Agocs**, Peter Petrik, Androula G. Nassiopoulou, Spiros Gradelis, and Silvia Milita, *„Ellipsometric investigation of nanocrystalline Si thin films"*, EuroNanoForum, 30 May – 1 June 2011, Budapest, Hungary, *poszter.*

[T10] **Emil Agocs**, Androula G. Nassiopoulou, and Peter Petrik, *„A global search method using parameter analysis in a broad range for silicon nanocrystals"*, 7th. Workshop Ellipsometry, March 5-7th, 2012, Leipzig, Germany, *poszter.*

[T11] **Emil Agocs**, Androula G. Nassiopoulou, and Peter Petrik, *„Model dielectric function analysis of the critical point features of silicon nanocrystal films in a broad parameter range"*, European Materials Research Society, May 14-18th, 2012, Strasbourg, France, *poszter.*

[T12] **Agócs Emil**, Petrik Péter, *„Nanokristályos vékonyrétegek dielektromos függvényének vizsgálata spektroszkópiai ellipszometriával"*, Kálmán Erika Doktori Konferencia, September 18-20th, 2012, Mátraháza, Hungary, *oral presentation.*

[T13] Péter Petrik, **Emil Agócs**, „High sensitivity optical chűaracterization of thin films with embedded Si nanocrystals", 223rd ECS Meeting, May 12-16th, 2013, Toronto, ON, Canada, *oral presentation*.