PERIODIC NANOSTRUCTURES ON LARGE AREAS

PhD thesis

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Introduction

In microelectronics, smaller has always meant better: more components per chip, lower cost, faster response, and lower power consumption. The miniaturisation and production of microelectronic chips has been guided by road maps.

Miniaturization seems also be the trend in a range of other technologies. There are active efforts, for example, to develop magnetic storage media having elements with dimensions of 100 nm, compact disks (CDs) with pit sizes of <50 nm, and of course nanometer-sized sensors or nanoelectromechanical systems (NEMS). The motivation for these improvements is to increase the density of components, lower their cost, and increase their performance per device.

Many materials with minimum dimensions on the nanoscale have properties different than those observed for the bulk material. Fascinating phenomena occur in systems that have a spatial dimension comparable to that of a fundamental physical, chemical, or biological process. The most interesting examples are quantized excitation, Coulomb blockade, single-electron tunnelling, near-field diffraction of visible light, excitation of a collective resonance by light, etc. Revolutionary devices based on these new effects such as arrays of quantum dot lasers, quantum cascade lasers, single-electron transistors, and arrays of nanometer-sized magnets are appearing in prototype forms in research labs.

The fundamental study of phenomena that occur in these structures has already evolved into a new field of research. That is sometimes referred to as nanoscience. In addition to their uses in nanoscience, nanostructures are central to the development of numerous existing and emerging technologies.

Aim of the thesis

The primary aim of the thesis was to develop new methods to prepare nanostructures on macroscopically large areas, preferably without using sophisticated large equipments. My objective was to explore the adequate techniques and combine the available methods, solve the occurring scientific problems.

Preparative and testing methods

To achieve periodic nanostructures on macroscopic silicon substrates I applied one- and two dimensional photoresist gratings prepared by holographic lithography, single and double layer Langmuir-Blodgett (LB) films from Stöber silica particles, and monolayer particulate LB-films structured by photolithography as primary structures. I used these structures as mask for implantation of doping ions. I converted the generated laterally periodic doping distribution to relief structures by electrochemical etching of the silicon. For the qualification of the resulted structures I applied mainly scanning electron microscopy (SEM) and atomic force microscopy (AFM).

For the characterisation of the applied particulate LB-films I chose spectroscopic ellipsometry (SE) because of its time- and cost effective and non-destructive properties. During the evaluation of the SE measurements the possibility has appeared to use the investigated systems – ordered layers of spherical particles with low polydispersity – as model structures to study experimentally the validity limits of the effective medium approximations.

Thesis

1. I have applied first holographically exposured and developed photoresist gratings as mask for the boron ion implantation to generate boron doping distribution with sinusoidal profile in p-type silicon. After electrochemical etching and dissolution of the porous silicon layer were achieved one- and two dimensional diffraction gratings with sinusoidal profile and 375 nm period on large silicon areas. [S1], [S5]

2. First I have applied particulate layers as mask for ion implantation. I have used monolayer and double-layer Langmuir-Blodgett (LB) films from Stöber silica nanospheres of 350 nm diameter as masking layer for boron and phosphorous ion implantation. I converted the achieved laterally periodic doping pattern into relief structure by anodisation. [S2], [S3], [S6]

2.a In case of boron-implanted p- and n-type, phosphorous-implanted n-type silicon applying monolayer LB-film, the samples were preferably anodized in the implanted regions. After removal of the of the porous layer freestanding crystalline pillars remained, where the implanted ions stopped in the masking nanospheres. [S2], [S3], [S6]

2.b In the case of the double-layer masked p-type silicon the boron-ions could reach the substrate through nearly circular windows of diameter ca. 60 nm. The anodisation started here and propagated down and laterally resulting regular hexagonal crystalline honeycomb-like silicon structure after dissolution of the porous regions. [S2], [S3], [S6]

2.c In the case of the monolayer masked boron-implanted n-type silicon the porous etching occurred preferentially in the non-implanted regions terminated by the doped volumes. Where the etching front reached the bottom of the doped layer the anodisation became isotropic. [S2], [S3], [S6]

3. I have applied first photoresist pattern for structuring Stöber silica LB-films. I created streets in the particulate film by dissolving of the photoresist. The structured particulate film and the particulate layer combined with the photoresist pattern served as mask for the boron and phosphorous ion implantation into p- and n-type silicon. I converted the achieved doping pattern into relief structure by anodisation.

4. I have showed experimentally that single layer homogeneous optical model is sufficient for the evaluation of spectroscopic ellipsometric measurements of mono- and multi-layer LB-films from Stöber silica particles and the Maxwell-Garnett effective medium approximation offers more accurate results, than the Bruggeman. [S4]

5. First I have showed experimentally the validity limits of the widely accepted effective medium approximation by using mono- and multi-layer LB films of Stöber silica nanospheres of different diameters. I have introduced the difference threshold between the experimental and from the fitted model generated $\tan \Psi$ and $\cos \Delta$ as new index to derive thresholds wavelengths exactly. I have found linear correlation between the extent of inhomogeneity – i.e. the diameter of the particles – and the reciprocal value of the threshold wavelength. [S4]

6. I have worked out an approximating method to determine average distance between individual particles in the single layer Stöber silica LB-film based on the measured effective porosity values by spectroscopic ellipsometry, assuming a monodisperse size distribution. [S4]

7. I have showed experimentally by using spectroscopic ellipsometry that the relative deviation between the measured and from the monodisperse, ideally close packed model calculated effective thickness values reflects a tendency of saturation around 10% with increasing number of stacked layers (in case of the studied maximum five-layer films). [S4]

Utilisation of the results

The nanostructures prepared by nanoparticulate masks and the preparative technique have interest for basic research (e.g. Brillouin light scattering, Andrejev-microscope) and also for applied research (e.g. solar cells).

In case of ellipsometric measurements the use of particulate LB-films as model structure is one of my important innovations (e.g. for development of new models and methods). On the other hand the application of these layers as primary structure seems also useful to prepare model structures (e.g. applying material deposition or ion implantation).

Publications related to the thesis

[S1] N. Nagy, J. Volk, A. Hámori, I. Bársony:
Submicrometer period silicon gratings by porous etching
Physica Status Solidi (a) **202** p.1639–1643 (2005) [impact factor: 1,041]

Independent citations:

L. Naszályi, A. Deák, E. Hild, A. Ayral, A.L. Kovács, Z. Hórvölgyi:
Langmuir–Blodgett films composed of size-quantized ZnO nanoparticles: Fabrication and optical characterization
Thin Solid Films **515** p.2587–2595 (2006)

[S2] N. Nagy, A. E. Pap, A. Deák, J. Volk, E. Horváth, Z. Hórvölgyi, I. Bársony:
Regular patterning of PS substrates by a self-assembled mask
Physica Status Solidi (c) **4** p.2021–2025 (2007)

[S3] N. Nagy, A. E. Pap, A. Deák, E. Horváth, J. Volk, Z. Hórvölgyi, I. Bársony:
Large area self-assembled masking for photonics applications
Applied Physics Letters **89** 063104 (2006) [impact factor: 3,977]

Independent citations:

P. Petrik:
Ellipsometric models for vertically inhomogeneous composite structues
Physica Status Solidi (a) **205** p.732–738 (2008)

[S4] N. Nagy, A. Deák, Z. Hórvölgyi, M. Fried, A. Agod, I. Bársony:
Ellipsometry of silica nanoparticulate LB films for the verification of the validity of EMA
Langmuir **22** p.8416–8423 (2006) [impact factor: 3,902]

Independent citations:

J. Meunier:
Optical reflectivity of thin rough films: Application to ellipsometric measurements on liquid films
Physical Review E **75** 061601 (2007)

T.N. Hunter, G.J. Jameson, E.J. Wanless:
Determination of contact angles of nanosized silica particles by multi-angle single-wavelength ellipsometry
Australian Journal of Chemistry **60** p.651–655 (2007)

D. Grigoriev, D. Gorin, G.B. Sukhorukov, A. Yashchenok, E. Maltseva, H. Möhwald:
Polyelectrolyte/magnetite nanoparticle multilayers: Preparation and structure characterization
Langmuir **23** p.12388–12396 (2007)

P. Petrik:
Ellipsometric models for vertically inhomogeneous composite structues
Physica Status Solidi (a) **205** p.732–738 (2008)

[S5] Nagy N., Volk J., Tóth A. L., Hámori A., Bársony I.:
Optikai érzékelők nanoszerkezetű szilíciumból
(*Porous silicon optical sensors)*
Élet és Tudomány **36** p.1130–1133 (2006)

[S6] Nagy N., Pap A. E., Deák A., Horváth E., Hórvölgyi Z., Bársony I.:
Periodikus nanostruktúrák makroszkopikusan nagy felületeken
(Periodic nanostructures on macroscopically large areas)
Fizikai Szemle **9-10** p.314–319 (2007)

Further publications

[S7] J. Volk, N. Norbert, I. Bársony:
Subquart micron period laterally stacked porous silicon multilayer for UV grating
Physica Status Solidi (a) **202** p.1707–1711 (2005) [impact factor: 1,041]

Independent citations:
L. Naszályi, A. Deák, E. Hild, A. Ayral, A.L. Kovács, Z. Hórvölgyi:
Langmuir–Blodgett films composed of size-quantized ZnO nanoparticles: Fabrication and optical characterization
Thin Solid Films **515** p.2587–2595(2006)

[S8] A. Agod, N. Nagy, Z. Hórvölgyi:
Modeling the structure formation of particulate Langmuir films: the effect of polydispersity
Langmuir **23** p.5445–5451 (2007) [impact factor in 2006: 3,902]

[S9] N. Nagy, A. Deák, A. Hámori, Z. Hórvölgyi, M. Fried, P. Petrik, I. Bársony:
Comparative investigation of Stöber silica Langmuir-Blodgett films as optical model structures
Physica Status Solidi (a) **205** p.936-940 (2008) [impact factor in 2006: 1.221]

[S10] P. Kozma, N. Nagy, S. Kurunczi, P. Petrik, A. Hámori, A. Muskotál, F. Vonderviszt, M. Fried, I. Bársony:
Ellipsometric characterization of flagellin films for biosensor applications
Physica Status Solidi (c) **5** p.1427–1430 (2008)

[S11] A. Hámori, N. Nagy:
Submicrometer period refractive index diffraction grating couplers
Third IEEE International Conference on Sensors, IEEE Sensors 2004
ISBN: 0-7803-8693-0; Catalog Number: 04CH37603C; p.1333–1336 (2004)

Independent citations:
J.S. Maikisch, T.K. Gaylord:
Optimum parallel-face slanted surface-relief gratings
Applied Optics **46** p.3674–3681 (2007)

[S12] Nagy N.:
Integrált optikai interferométer előállítása fotoreziszt modellanyagként történő felhasználásával
(Integrated optical interferometers made of photoresist as a model material)
Diploma piece, Budapest University of Technology and Economics (2002)

[S13] Hámori A., Nagy N.:
Eljárás többcsatornás optikai hullámvezető fénymódus spektroszkópiai mérések elvégzésére
(Method of measurement of multi-channel optical waveguide lightmode spectroscopy)
Hungarian patent