Depolarization sources and their effect on spectroscopic ellipsometric investigation of thin layers

Theses of PhD dissertation

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1. Introduction

Spectroscopic ellipsometry is a non-destructive and accurate tool for measuring the optical and the structural properties of thin layer systems. The method is based on the determination of the polarization change of light upon its reflection from the investigated sample. In most cases during the ellipsometric analysis it is supposed that the light is in a well-defined polarization state. However, there are certain sample- or ellipsometer-related properties, which deteriorate the degree of polarization of light, i. e., depolarize the beam. Such depolarization on one hand can cause inaccuracies in the deduced optical properties and thickness values, but on the other hand it can provide additional information about the sample properties, which could not be obtained by analyzing only the ellipsometric angles (Ψ and Δ). The mathematical description of the depolarized beam and the depolarization sources were elaborated long ago (Stokes-vectors and Mueller-matrices), however, the development of the measurement technique enabled the proper detection of the mixed polarization states only in the last two decades. Although some articles and ellipsometric monographs deal with certain aspects of depolarization, in most cases the effect of depolarization on the evaluation of ellipsometric spectra is neglected.

2. Aims

In this thesis my aim was, besides giving an overview about the properties of the different depolarization sources, to demonstrate their effect on the measured data and on the evaluation of the ellipsometric spectra, and to provide methods for their proper handling. For this purpose, I performed ellipsometric investigations on different sample series which were chosen to fulfill two criteria, namely to represent the wide application range of ellipsometry and to demonstrate as many depolarization sources as possible. Therefore, I have chosen graphene as a promising 2D material and thin carbon layers related to the graphene studies; zinc-oxide layers playing an important role in the photovoltaic industry and possibly having rough surface; and peptide layers from the family of bio-materials, of which coverage and structural properties have a large impact on its applications.

3. Methods and results

First, I performed measurements on graphene and thin carbon layers, which were transferred and deposited onto thick SiO_2 layers, respectively. This sample configuration is favorable for ellipsometric measurements of thin absorbing layers, since it enables the application of the interference enhancement technique. However, I demonstrated, that in such circumstances not only the sensitivity of the measurements is enhanced but also the depolarization caused by the angular spread of the focused beam and by the finite bandwidth of the ellipsometer. I proved that in the case of graphene layers, the neglect of depolarization leads to a thickness error comparable with the thickness of single layer graphene, causing also a notable difference in the deduced optical properties. Applying the same sample structure, I produced thin layers of carbon with different thicknesses using pulsed laser deposition (PLD) technique. I demonstrated with this sample series that for layers having larger thickness than a given threshold value the absorption of the layer can diminish the depolarization. Based on the results of evaluation of the graphene and the PLD carbon layers – both taking into account depolarization and neglecting it – I provided the differences caused by the depolarization effects in the deduced optical data. For materials having similar dispersion behavior (graphite, and differently porous graphite) I determined the thickness ranges where the depolarization can not be neglected in the ellipsometric modeling.

In the second part of the results section I presented my results related to ZnO thin films, which were deposited onto heated Si substrates. These samples contained areas with inhomogeneous layer thickness, and areas with structured surfaces where strong scattering could be observed. I performed measurements at four different sample positions which were i) smooth and homogeneous in thickness, ii) smooth but inhomogeneous, iii) structured but homogeneous, and finally iv) structured and inhomogeneous. Both inhomogeneous layer thickness and scattering are depolarization sources, but they are different: the thickness inhomogeneity is quasi-depolarization (which means that the different spatial parts of the light beam have different polarization state, however, these are well-defined polarization states, and the depolarization can be easily followed) while scattering is random. The Mueller-matrices of the sample with inhomogeneous layer thickness and the sample which randomly depolarizes light had already been elaborated. In my thesis I expressed the combined Mueller-matrix which is capable of describing both the quasi-depolarization and the random depolarization. I showed that by correcting the measured data with a given element of the combined Mueller-matrix the contributions of the random depolarization sources and the quasi-depolarization can be separated. Since the corrected depolarization spectrum contains only the quasi-depolarization, the quasi-depolarization source can be identified and characterized more accurately. As such, the measured datasets can be evaluated with less uncertainty.

Beside the theoretical description, I proved these findings and the correction method experimentally as well.

The final section contained my results achieved on peptide samples. The structure of peptides and their binding affinity have an important role in their future applications. I showed that ellipsometry can provide information on both features, if depolarization character of the samples is thoroughly analyzed. Three models were tested for evaluating the peptide layers, namely the transparent layer approach assuming a homogeneous layer with Sellmeier dispersion, the absorbing layer approach assuming again a homogenous layer with a slight absorption, and the discontinuous layer approach which deals with a Sellmeier-type transparent layer having island-like structure. With the help of depolarization it was shown that from the applied models the last one can describe the actual sample properties the most accurately. The island-like structure of the layers was supported also by atomic force microscopic images. After the comparison of the different models I explained the seeming equivalence – both in the fitting quality and the deduced thickness values – of the absorbing layer approach and the discontinuous layer approach. According to simulation results the layer discontinuity can cause similar distortion in the ellipsometric spectra as the absorption of the layer. As such, the data of the discontinuous layer can be described with an absorbing layer model as well, although the introduced absorption is not physically correct. This result is very important for the accurate evaluation of these peptide layers. By applying these findings the ellipsometric evaluation of peptide layers were performed. I showed that the investigated peptides bind better to p-type silicon and they form an island-like layer in a multilayer assembly.

4. Theses

T1. I demonstrated that the thick dielectric layer applied in the interference enhancement method enhances not only the sensitivity of ellipsometry but also the depolarization effects. I produced samples appropriate for the interference enhancement method by deposition of carbon layers onto thermally grown thick SiO_2 layers. With this sample series I showed, that if the layer thickness exceeds a threshold value, depolarization diminishes due to the absorption of the layer, which finally becomes negligible. Based on simulation results I determined the extinction coefficient-dependent thickness region where notable depolarization occurs for materials having similar dispersion character (graphite and porous graphite) [T1].

T2. By performing ellipsometric modeling both taking into account and neglecting depolarization I demonstrated the effect of depolarization on the deduced optical properties of graphene layers and pulsed laser deposited carbon layers. I provided the differences in the optical properties due to the neglect of depolarization in the different thickness ranges. With the presented results I proved that measuring and handling depolarization is crucial during ellipsometric analysis of 2D materials if the interference enhancement method is applied [T1].

T3. I provided for the first time the Mueller-matrix which is capable of describing the cumulative effect of quasi-depolarization sources and random depolarization. I showed that the correction of the measured spectra with the given element of the Mueller-matrix enables the separation of the contributions of quasi-depolarization and random depolarization. Besides the theoretical description I supported these findings by performing ellipsometric measurements on ZnO layers deposited onto silicon wafers [T2].

T4. By thoroughly analyzing the measured depolarization spectra I showed that the investigated peptide layers form an island-like coating on the silicon substrate. I proved that the ellipsometric model supposing island-like layer structure is capable of describing both the spectra of ellipsometric angles and depolarization if the thickness distribution of the islands is taken into account. Based on the applied ellipsometric model I could demonstrate the multilayer assembly of the peptide layers which were later proved by AFM investigations [T3, T4].

T5. During the analysis of the ellipsometric and depolarization spectra belonging to the peptide layers I showed that the measured data could be fitted both with the island-like layer model and a model supposing absorbing layer in a seemingly equivalent manner. I proved with simulation results that this equivalence can be the consequence of the observation that island-like layer configuration can cause the same distortion of the measured spectra as an absorbing layer; therefore it can appear as quasi-absorption [T4].

5. Publications related to the theses

[T1] **Z. Pápa**, J. Csontos, T. Smausz, Z. Toth, J. Budai. Spectroscopic ellipsometric investigation of graphene and thin carbon films from the point of view of depolarization effects, Applied Surface Science (2016) article in press

[T2] **Z. Pápa**, J. Budai, I. Hanyecz, J. Csontos, Z. Toth. Depolarization correction method for ellipsometric measurements of large grain size zinc-oxide films, Thin Solid Films 571 (2014) 562-566.

[T3] **Z. Pápa***, S. K. Ramakrishnan*, M. Martin, T. Cloitre, L. Zimányi, J. Márquez, J. Budai, Z. Tóth, C. Gergely. Interactions at the Peptide/Silicon Surfaces: Evidence of Peptide Multilayer Assembly, Langmuir 32 (28) (2016) 7250-7258. (* equal contribution)

[T4] **Z. Pápa**, S. K. Ramakrishnan, M. Martin, T. Cloitre, L. Zimányi, Z. Tóth, C. Gergely, J. Budai. Ellipsometric study of peptide layers - island-like character, depolarization and quasi-absorption, Applied Surface Science (2017) article in press

6. Other publications

[1] **Z. Pápa**, J. Budai, B. Farkas, Z. Toth. Investigation of surface roughness on etched glass surfaces, Thin Solid Films 519 (9) (2011) 2903-2906.

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[7] E. Kecsenovity, B. Endrődi, **Z. Pápa**, K. Hernádi, K. Rajeshwar, C. Janáky. Decoration of ultra-long carbon nanotubes with Cu_2O nanocrystals: a hybrid platform for enhanced photoelectrochemical CO_2 reduction, Journal of Materials Chemistry A 4 (8) (2016) 3139-3147.

[8] J. Csontos, Z. Toth, **Z. Pápa**, J. Budai, B. Kiss, A. Börzsönyi, M. Füle. Periodic structure formation and surface morphology evolution of glassy carbon surfaces applying 35-fs–200-ps laser pulses, Applied Physics A 122 (6) (2016) 1-9.

[9] J. Csontos, Z. Tóth, **Z. Pápa**, B. Gábor, M. Füle, B. Gilicze, J. Budai. Ultrafast in-situ null-ellipsometry for studying pulsed laser—Silicon surface interactions, Applied Surface Science (2016) article in press

[10] P. Rácz*, **Z. Pápa***, I. Márton, J. Budai, P. Wróbel, T. Stefaniuk, C. Prietl, J. R. Krenn, P. Dombi. Measurement of Nanoplasmonic Field Enhancement with Ultrafast Photoemission, Nano Letters 17 (2) (2017) 1181-1186. (* equal contribution)

[11] J.-M. Yi, D. Hou, H. Kollmann, V. Smirnov, **Z. Pápa**, P. Dombi, M. Silies, C. Lienau. Probing Coherent Surface Plasmon Polariton Propagation Using Ultrabroadband Spectral Interferometry, ACS Photonics 4 (2) (2017) 347-354.