Krzysztof DORYWALSKI[1], Aleksy PATRYN[1], Bohdan ANDRIYEVSKY[1], Christoph COBET[2], Norbert ESSER[3]

Koszalin Univeristy of Technology, Koszalin, Poland (1), Johannes Kepler Uniweristät Linz, Linz, Austria (2), Leibniz-Institut für Analytische Wissenchaften – ISAS, Berlin, Germany (3)

Synchrotron-based VUV spectroscopic ellipsometry system in application to optical properties studies of wide-bandgap materials for optoelectronics

Abstract. *The paper presents the implementation of spectroscopic ellipsometry measurements in the vacuum-ultraviolet spectral range with use of synchrotron radiation as a light source. Current status of VUV ellipsometer and the principle of its operation is described. The procedure of measurements and ellipsometric data evaluation taking into account surface roughness of the measured specimen of optically uniaxial wide-bandgap single crystal is presented through the example of* $Sr_{61}Ba_{39}Nb_2O_6$ *ellipsometric characterization. Complex dielectric function* $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$ *for* $Sr_{61}Ba_{39}Nb_2O_6$ *was obtained in the spectral photon energy range 2–25 eV for polarization direction along* b *and* c *crystallographic axes.*

Streszczenie. *W artykule przedstawiono implementację techniki spektroskopii elipsometrycznej z wykorzystaniem promieniowania synchrotronowego jako źródła światła do zakresu widmowego nadfioletu próżniowego. Zaprezentowano obecny status VUV systemu elipsometrycznego oraz opisano sposób jego funkcjonowania. Poprzez charakteryzację optyczną kryształu* $Sr_{61}Ba_{39}Nb_2O_6$*, przedstawiono procedurę analizy elipsometrycznych danych pomiarowych dla optycznie jednoosiowego monokryształu z uwzględnieniem anizotropii optycznej oraz niejednorodności powierzchni badanej próbki. Uzyskano zależności dyspersyjne tensora zespolonej przenikalności dielektrycznej* $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$ *dla kryształu* $Sr_{61}Ba_{39}Nb_2O_6$ *w szerokim zakresie widmowych 2–25 eV, dla kierunków wzdłuż osi krystalograficznych* b *oraz* c*. (**System spektroskopii elipsometrycznej z promieniowaniem synchrotronowym w zastosowaniu do badań własności optycznych szerokopasmowych materiałów dla optoelektroniki**).*

Keywords: VUV ellipsometry, synchrotron, SBN, optical.
Słowa kluczowe: VUV elipsometrii, synchrotron, SBN, optyczne.

doi:10.12915/pe.2014.03.56

Introduction

The designing of novel and the optimization of current optoelectronic devices requires data on the optical parameters of materials used for its construction, i. e. the dispersion of complex refractive index, the bandgap value etc., while dynamic progress in the field of optoelectronics materials is closely associated to the developments of novel techniques for its manufacturing and characterization.

Since its invention by Paul Drude more than 120 years ago [1] and later rapid developments ranging from 70's (which are closely related to advances in computer technology), ellipsometry technique has matured as tool-of-excellence in almost all materials research areas. Today, spectroscopic ellipsometry (SE) is a well-established non-destructive technique known for its efficiency in optical characterization of various materials [2]. The main benefit of ellipsometric measurements, compared to other optical methods, is the direct evaluation of both real and imaginary parts of complex refractive index $N = n + ik$ without need of Kramers-Kronig transformation. High sensitivity of this method makes it attractive in particular for investigation of thin films, stacked layered systems and surfaces.

Typical ellipsometers, however, are limited in the UV region due to ambient air absorbing wavelengths shorter than 190 nm. This disadvantage prevents use of a typical instruments in a lot of major application including studies of the optical properties of thin films and bulk materials at short wavelengths for development of new lithographic processes, new fundamental science, and new metrology in the semiconductor, optical and data storage industries as well as study of wide bandgap materials for blue lasers and detectors and others.

The implementation of ellipsometry measurements in the vacuum-ultraviolet (VUV) spectral range is difficult in view of lack of efficient conventional light sources as well as transparent crystalline polarizers in this range. The above difficulties were overcome by designing of a world-unique VUV ellipsometric system using a synchrotron radiation as a light source [3, 4]. This setup allows ellipsometric measurements in the wide photon energy range E = 3–35 eV, thus allowing the optical characterization of wide-bandgap semiconductors and dielectrics in the range of valence and deep-level electronic excitation [3–6]. In this work, we present the current status of VUV ellipsometric system and results of its use to optical properties studies of optically uniaxial material.

The paper is organized as follows: section "Ellipsometry principles" provides the ellipsometry basics and briefly discuss main ellipsometry features. Section "The Bessy VUV ellipsometry system" presents the current status of the ellipsometric system which employs synchrotron radiation. In section "UV–VUV ellipsometry on $Sr_{61}Ba_{39}Nb_2O_6$ crystal", implementation of synchrotron-based ellipsometry to the optical properties studies of wide-bandgap material is presented through the example of $Sr_{61}Ba_{39}Nb_2O_6$ single crystal optical characterization.

Ellipsometry principles

Ellipsometry determines the change of the polarization state of an electromagnetic plane wave after interaction with a measured sample. In spectroscopic ellipsometry (SE), ellipsometric parameters (Ψ, Δ) spectra are measured by changing the wavelength of light (usually from infrared to visible/ultraviolet region). The principle of ellipsometry is based on the fact that the different polarization states of an electric field, parallel E_p and perpendicular E_s to the plane of incidence, are reflected with different intensities. Consequently, the resulting polarization state is generally elliptic and hence the name *ellipsometry*. This elliptically polarized light is normally expressed in terms of two parameters, Ψ and Δ [2, 5]:

$$(1) \qquad tan\,\Psi e^{i\Delta} = \frac{r_p}{r_s} = \rho$$

where r_p and r_s are the complex Fresnel reflection coefficient of the sample for p- (in the plane of incidence) and *s*- (perpendicular to the plane of incidence) polarized light, as illustrated in Figure 1.

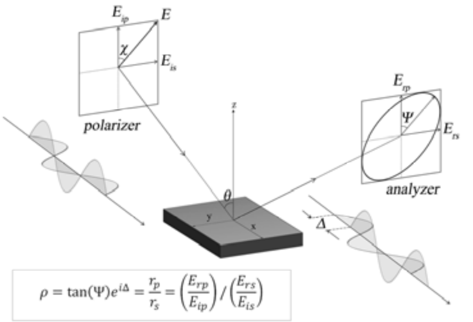

Fig.1. Measurement principle of ellipsometry

Because ellipsometry measures the ratio of two values, it can be highly accurate and very reproducible. Moreover, the calculation of both real and imaginary parts of a complex refractive index is possible following one principal measurement. The change of polarization state of light after reflection with sample surface is generally related to the optical properties of a material measured. Accordingly, ellipsometry is mainly used for the optical characterization of a materials. The determination of the complex optical constants enables the investigation of a material structural properties, thus the application area of SE is quite wide ranging from studies of optical by electrical to mechanical parameters.

Likely the main disadvantage of SE measurements comes from its indirect character, namely the optical response of the investigated sample has to be deduced using the optical model representing the sample in a fitting procedure that minimizes the mean square error MSE [2, 5]. The one exception is the case of an isotropic sample, where only the air/sample interface is considered (semi-infinite bulk sample with perfectly smooth and clean surface). In this case the optical constants can be directly calculated from the ellipsometric parameters using formula:

$$(2) \qquad <\varepsilon> = \sin^2\theta_i\left[1+\tan^2\theta_i\left(\frac{1-\rho}{1+\rho}\right)^2\right]$$

where θ_i is an incidence angle and ρ is given by Equation 1.

The above representation of the ellipsometric data, referred to as a pseudo-dielectric function, is commonly used even for more complicated cases (anisotropy, non perfect surface, layered systems) to get “rough” results. For a detailed review about the application area of SE, principles and data analysis procedures for the ellipsometric measurements see e. g. excellent Fujiwara’s textbook [2].

The Bessy VUV ellipsometry system

Ellipsometry measurements in the VUV region were first briefly demonstrated in 1970 at DESY synchrotron in Hamburg [6]. After that, no further attempts was made till the mid-1980s, when the development began on a VUV ellipsometer at the BESSY I storage ring in Berlin [3, 4]. Despite of the latest developments in a commercial VUV ellipsometers, this instrument, after continuous modifications, is still sole for the measurements above the photon energy range $E > 10$ eV.

Today, described system is installed at the beamline of BESSY II storage ring, successor of the BESSY I. The system works in rotating-analyzer (RAE) configuration. The arrangement of the instrument with all principal components is shown in Figure 2. The components are mounted in a UHV chambers and, in order to meet different vacuum requirements, the system is separated into several differentially pumped section.

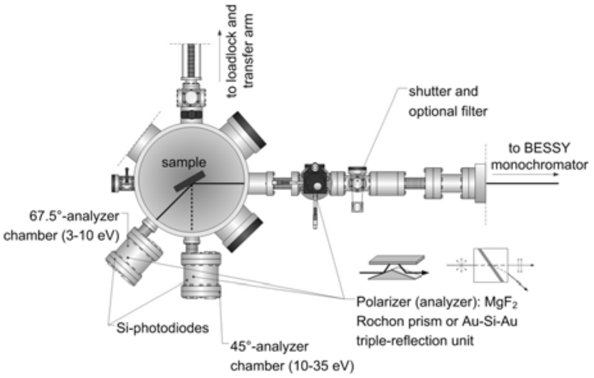

Fig.2. Sketch of the VUV ellipsometer

First, the incoming synchrotron light passes through a small chamber which includes optical filters and shutters for the repeated measurement of the dark current, and subsequently reaches next chamber which contains polarizers. Even though synchrotron radiation is already highly polarized, additional polarizers, namely MgF_2 rochon prism (Au-Si-Au reflection type polarizer) for spectral range up to 10 eV (above 10 eV), are used to ensure a satisfactory degree of polarization of the incoming light. With these polarizers, a degree of polarization of 99.998% (95%) can be obtain for the range $E < 10$ eV ($E > 10$ eV). In that conditions, measurements in the spectral range from 3 to 35 eV are possible depending on the actually used Bessy monochromator.

Further, the incoming light is reflected on the sample surface, which is mounted on the manipulator in the main chamber. Recently installed manipulator allows temperature measurements in the range from liquid helium temperatures (~ 6K) up to the temperatures far above ambient temperatures (~ 900 K), when other manipulator is used. The set of rotary pumps and turbomolecular pumps ensure the base pressure in the sample chamber around 2×10^{-10} mbar. Reflected light finally reaches one of two different analyzer chambers under an angle of incidence of either 45° or 67.5°, for the measurements in spectral range $E > 10$ eV and $E < 10$ eV, respectively.

As was already mentioned, the system works in RAE configuration. Polarizer, which now acts as a analyzer, is mounted inside a rotating drum driven via friction wheel by a tachogenerator-stabilized *dc* motor. The angular orientation α of the analyzer is measured with an angle encoder mounted directly on the drum (1000 pulses per revolution). The pulses from the encoder trigger the readout of the detector mounted behind rotated analyzer 50 times per optical cycle and the polarization ellipse is converted into a modulated intensity I_{det} having form of a sinusoidal curve on *dc* background which can be written as:

$$(3) \qquad I_{det} = const\left(1 + a_1\cos 2\alpha + a_2\sin 2\alpha\right)$$

Afterwards, the coefficients a_1 and a_2 are evaluated using of a Fourier analysis and later optical constants of a material under study can determined numerically from these two parameters. After initial use of GaP Schottky diodes [4], Si-photodiodes are used as a detectors for both lower and higher photon energy range. These photodiodes was gradually exchanged along with improvements to their parameters. All the components are controlled in a measuring procedure by dedicated software.

Before each measurements cycle starts, a calibration of optical elements is necessary, namely the 0° positions of optical elements have to be adjusted accurately to the coordinates of p- and s-polarizations. For this purpose, the residual calibration method is used [7]. In order to perform such calibration, the whole chamber of the instrument can be rotated with respect to the plane of incidence. Accordingly, the theoretical equation for the light intensity at the detector, I_{det}, is given by rewriting Equation 3 as follows [7]:

$$(4)\quad I_{det} = const\left[1 + \eta a_1 \cos 2(\alpha - A_s) + \eta a_2 \sin 2(\alpha - A_s)\right]$$

where A_s indicates a deviation from 0° of the starting position for readout of the light intensity and η is a correction coefficient that represents nonideal behavior of the detector (the attenuation of the ac components relative to the dc component).

UV–VUV ellipsometry on $Sr_{61}Ba_{39}Nb_2O_6$ crystal

Since its first demonstration, the VUV ellipsometric system has been extensively used to develop both instrumentation and experiments on optical characterization of various materials, such as the group III–V semiconductors [8-11] or ferroelectrics [12-14]. Here we demonstrate application of the system to ellipsometric study in the range of electronic excitations (2–25 eV) of strontium barium niobate (SBN) single crystal with the congruently melting composition $Sr_{61}Ba_{39}Nb_2O_6$.

The SBN, due to many promising properties like electro-optic [15], pyroelectric [16] and piezoelectric ones [17], is considered as very attractive material for new optoelectronic and electrical devices. Special interest is devoted to high photorefractive sensitivity and large electro-optic coefficient r_{33}, which makes it applicable in different fields of optoelectronics [18] including optical storage [19], optical data processing and optical conjugation [20-22]. The further use of the material requires a knowledge of its optical features related to the band structure parameters within the spectral range covering fundamental inter-band transition range. Moreover, such data are crucial as a reference for the theoretical studies of the structural properties.

Early data on SBN crystals in the energy region 1 to 35 eV are available based on the near-normal incidence reflectance measurement combined with a Kramers-Kronig transformation [23]. These data however do not include congruently melting composition of SBN, which is the most important for applications because of its easiest growing comparing to other compositions. Our recent ellipsometric studies of SBN crystals in the spectral range of 2–10 eV [12, 13, 24] shows, that the optical spectra of congruently melting composition reveals distinct differences with respect to other compositions.

In the above studies, the ellipsometric data were evaluated by means of two-phase ambient-material model and presented in the form of pseudo-dielectric functions (see Eq. 2). However, the SBN belongs to the tetragonal part of symmetry, therefore an anisotropy of optical response should be taken into account as well as non-perfect surface (roughness) of the measured specimen in order to get more accurate optical spectra. All this leads to necessity of ellipsometric data evaluation by three-phase model: ambient/surface rough layer/anisotropic bulk material.

In the measurements we used fact, that our [100]-cut platelet-shaped SBN sample can be oriented in such a way that the principle axes of optical indicatrix n_1, n_2, n_3 coincide well with surface plane and the plane of incidence, respectively. In this situation, the light reflection can be simplified to the description derived from the extended Fresnel equations for anisotropic materials [5]. Following this approach, a-cut uniaxial SBN sample was measured for two different azimuthal orientations with c-axis parallel and perpendicular to the plane of incidence. All the measurements were performed at ambient temperature (295 K) and with standard spectral resolution 0.02 eV and 0.05 eV for spectral range E < 10 eV and E > 10 eV, respectively. For the measurements in the region E = 2–5 eV, conventional ellipsometer (SENTECH) was also used.

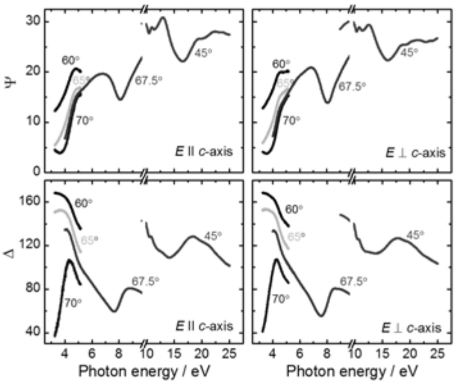

Fig.3. Ellipsometric spectra for $Sr_{61}Ba_{39}Nb_2O_6$ crystal for extraordinary (left graphs) and ordinary (right graphs) light polarization recorded for five angles of incidence: 60°; 65°; 70° (conventional ellipsometer) and 67.5°; 45° (VUV ellipsometer)

The measured ellipsometric spectra are shown in Fig. 3. These data were further evaluated starting with the description by a Cauchy dispersion relation for the real part of the complex dielectric function when assuming no absorption in the photon energy range 2–3.2 eV. The roughness of the surface was approximated by effective medium theory according to Bruggeman [2], assuming 50% voids in a matrix of SBN. The thickness of the rough layer and the Cauchy dispersion model parameters were the starting fitting factors. The determined thickness of the rough layer is equal to 5.2 nm, which is in good agreement with rms value obtained with use of atomic force microscopy.

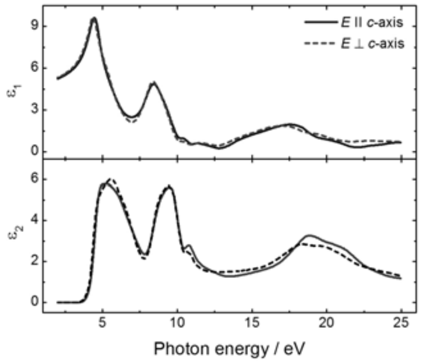

Fig.4. Real (ε_1) and imaginary (ε_2) components of the complex dielectric function for $Sr_{61}Ba_{39}Nb_2O_6$ single crystal. Solid lines correspond to extraordinary, while dashes to ordinary light polarization, respectively

Having determined the roughness thickness, the ellipsometric spectra were fitted in the whole spectral range, separately at each experimental spectral point. Resulting real and imaginary parts of the complex dielectric functions obtained for the polarization direction along b and c crystallographic axes of SBN following data evaluation procedure described above, are shown in Figure 4. The $\varepsilon_2(E)$ spectra are dominated by two wide bands centered around 5 and 9.5 eV and additional smaller third band around 18 eV, all having a complex structure.

In the formation of band structure and corresponding UV-VUV absorption spectra of such materials like SBN (oxygen-octahedral ABO_3-type ferroelectrics) fundamental significance have NbO_6 groups [12, 24]. Flat spectral bands, which should be considered as involving more than one critical point or critical line in the Brillouin zone, indicate the relatively weak wave vector dispersion of valence electronic levels. Differences observed for spectra polarized along b and c axes clearly prove optical anisotropy. Detailed analysis of the spectra features and corresponding electronic properties will be possible after theoretical band structure calculations, which will be done elsewhere.

Summary

In this paper, the description of state of the art VUV ellipsometric measurements using synchrotron radiation as a light source was demonstrated through the measurements on photorefractive SBN single crystal. Current status of the VUV ellipsometer and principle of its operation was presented. The procedure of ellipsometric measurements and data analysis taking into consideration an unintentional surface roughness and optical anisotropy of optically uniaxial bulk crystal was introduced. Demonstrated are capabilities of the VUV ellipsometric system for the precise measurements of polarized optical spectra of wide-bandgap semiconductors and dielectrics in the spectral range of valence electronic excitations.

The spectra derived for polarization along b and c crystalographic axes for SBN crystal revealed some differences with respect to each other, which are related to optical anisotropy. Results presented in this work extend optical data available for $Sr_{61}Ba_{39}Nb_2O_6$ crystal above photon energy E > 10 eV.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n.°226716. We also want to thank the BESSY GmbH for help and support. K. D. appreciate the financial support of German Academic Exchange Service (DAAD) under grant no A/10/82079

REFERENCES

[1] Vedam K., Spectroscopic ellipsometry: a historical overview, *Thin Solid Films*, 313-314 (1998), 1-9

[2] Fujiwara H., Spectroscopic Ellipsometry, Principles and Applications, *John Wiley & Sons Ltd,* 2007

[3] Barth J., Johnson L.R., Logethetidis S., Cardona M., Spectroscopic Ellipsometry with synchrotron radiation: latest developments, *SPIE Proc.*, 733 (1986), 265-271

[4] Barth J., Johnson L.R., Cardona M., in: Handbook of Optical Constants of Solids II, ed. Palik, *Academic Press,* San Diego, pp. 213-246, 1998

[5] Azzam R.M.A., Bashara N.B., Ellipsometry and Polarized Light, *North-Holland Personal Library,* New York, 1987

[6] Schledermann M., Skibowski M., Determination of the ellipticity of light and of optical constants by use of two reflection polarizers, *Appl. Opt.,* 10 (1971), 321-326

[7] Aspnes D.E., Studna A.A., High precision scanning ellipsometer, *Appl. Opt.*, 14 (1975), 220-228

[8] Feneberg M., Roppisher M., Cobet C., Esser N., Schormann J., Shupp T., As D.J., Horich F., Dlasing J., Krost A., Goldhahn R., Optical properties of cubic GaN from 1 to 20 eV, *Phys. Rev. B*, 85 (2012), 155207

[9] Cobet C., Goldhahn R., Richter W., Esser N., Identification of van Hove singularities in the GaN dielectric function: a comparison of the cubic and hexagonal phase, *Phys. Status Solidi B*, 246 (2009), 1440-1449

[10] Esser N., Rakel M., Cobet C., Schmidt W.G., Braun W., Cardona M., VUV-ellipsometry on GaN: Probing conduction band properties by core level excitations, *Phys. Status Solidi B*, 242 (2005), 2601-2609

[11] Cobet C., Schmidtling T., Drago M., Wollschläger N., Esser N., Richter W., Feenstra R.M., Kampen T.U., Surface termination during GaN growth by metalorganic vapor phase epitaxy determined by ellipsometry, *J. Appl. Phys.*, 94 (2003), 6997-6999

[12] Andriyevsky B., Patryn A., Dorywalski K., Cobet C., Piasceki M., Kityk I., Esser N., Łukasiewicz T., Dec J., Electronic and optical properties of strontium barium niobate single crystals, *Ferroelectrics*, 426 (2012), 194-205

[13] Andriyevsky B., Dorywalski K., Kityk I., Piasecki M., Łukasiewicz T., Świrkowicz M., Patryn A., Dec J., Esser N., Cobet C., Spectral ellipsometry study of SBN single crystals in visible and ultraviolet region, *Ferroelectrics*, 417 (2011), 14-19

[14] Andriyevsky B., Patryn A., Cobet C., Przesławski J., Kosturek B., Esser N., Dorywalski K., Electronic properties of KDP and DKDP crystals: ab-initio calculations and spectral ellipsometry experiment, *Ferroelectrics*, 417 (2011), 20-24

[15] Lenzo P.V., Spencer E.G., Ballman A.A., Electro-optic coefficients of ferroelectric strontium barium niobate, *Appl. Phys. Lett.*, 11 (1967), 23-24

[16] Glass A.M., Investigation of the electrical properties of $Sr_{1-x}Ba_xNb_2O_6$ with special reference to pyroelectric detection, *J. Appl. Phys.*, 40 (1969), 4699-4713

[17] Neurgaonkar R.R., Cory W.K., Oliver J.R., Growth and applications of ferroelectric tungsten bronze family, *Ferroelectrics*, 51 (1983), 3-8

[18] Günter P., Huignard J.P., Photorefractive materials and their applications 3, *Springer,* 2007

[19] Wood C., Salamo G.J., Goff J., Wood G.L., Anderson R.J., McGee D.J., Fixed three-dimensional holographic images, *Appl. Opt. Am,* 41 (2002) 6796-6801

[20] Wolfersberger D., Tranca D., 2D infrared self-focusing in bulk photorefractive SBN, *Opt. Mater. Express,* 1 (2011), 1178-1184

[21] Zhang P., Zhao J.L., Lou C., Tan X.Y., Gao Y.H., Liu Q., Yang D.X., Xu J.J., Chen Z.G., Elliptical solitons in nonconventionally biased photorefractive crystals, *Opt. Express,* 15 (2007), 536-544

[22] Horn W., Bassewitz J., Denz C., Slow and fast light in photorefractive SBN:60, *J. Opt.*, 12 (2010), 104011.

[23] Mamedov A.M., Shilnikov V.I., Mehdiev T.R., Bragimova I.S., Optical-properties of ferroelectrics with the tetragonal potassium tungsten bronze structure in the fundamental absorption-band, *Physica 123B*, (1984), 156-168

[24] Dorywalski K., Andriyevsky B., Cobet C., Piasecki M., Kityk I.V., Esser N., Łukasiewicz T., Patryn A., Ellipsometric study of near band gap optical properties of $Sr_xBa_{1-x}Nb_2O_6$ crystals, *Optical Materials*, 35 (2013), 887-892

Authors:
Krzysztof Dorywalski, Koszalin Univeristy of Technology, Institute of Technology and Education, Śniadeckich Str. 2, PL-75-453 Koszalin, Poland, E-mail: krzysztof.dorywalski@tu.koszalin.pl;
prof. Aleksy Patryn, prof. Bohdan Andriyevsky, Koszalin Univeristy of Technology, Faculty of Electronics and Computer Sciences, Śniadeckich Str. 2, PL-75-453 Koszalin, Poland, E-mail: patryn@ie.tu.koszalin.pl; bohdan.andriyevskyy@tu.koszalin.pl;
dr Christoph Cobet, Johannes Kepler Uniwerität Linz, Zentrum für Oberflächen und Nanoanalytik (ZONA), Altenberger Str. 69, 4040 Linz, Austria, E-mail: christoph.cobet@jku.at;
prof. Norbert Esser, Leibniz--Institut für Analytische Wissenchaften – ISAS – e. V., Department Berlin, Albert-Einstein-Str. 9, 12489 Berlin, Germany, E-mail: norbert.esser@isas.de.