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Characterization of ZnO structures by optical and X-ray methods

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ABSTRACT

ZnO thin films doped by Ga and In as well as multilayer structures of ZnO/Al_2O_3 have been investigated by X-ray fluorescence, Raman spectrometry, spectroscopic ellipsometry and vacuum ultra violet reflectometry. Systematic changes in the optical properties have been revealed even for Ga concentrations below 1%. The Raman active phonon mode of Ga doping at $580\,cm^{-1}$ shows a correlation with the Ga concentration. Optical models with surface nanoroughness correction and different parameterizations of the dielectric function have been investigated. There was a good agreement between the dielectric functions determined by the Herzinger–Johs polynomial parameterization and by direct inversion. It has been shown that the correction of the nanoroughness significantly influences the accuracy of the determination of the layer properties. The band gap and peak amplitude of the imaginary part of the dielectric function corresponding to the excitonic transition changes systematically with the Ga-content and with annealing even for low concentrations.

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1. Introduction

The manufacturing of optoelectronic thin films is of key importance, because a significant number of industries rely on such structures. ZnO is one of the most intensively investigated optoelectronic materials for applications as a transparent conductive oxide or complex semiconductor with different doping, defect budget and varying preparation parameters [1]. Thin ZnO layers can be prepared using a range of methods including sputtering [2], atomic layer deposition (ALD) [3], pulsed laser deposition [4–6], spin coating from nanoparticulates [7], or spray pyrolysis [8]. Optical techniques such as ellipsometry can be used for the sensitive, quick and non-destructive determination of a range of material and structural parameters such as thickness, surface nanoroughness, interface quality, density, homogeneity, band gap and exciton strength (which makes possible the indirect determination of electrical properties) [9–11].

The aim of the studies was the improvement (development of sophisticated models and evaluations) and comparison of optical and X-ray metrologies for the characterization of ZnO structures in single layer as well as in multi-layer stacks prepared by sputtering and ALD. This study is intended to be a step toward the establishment of validated reference methodologies for a reliable characterization of key optoelectronic materials, as a part of the joint research project for optoelectronic thin film characterization (IND07, "Metrology for the manufacturing of thin films") in the European Metrology Research Program of EURAMET. Furthermore, our investigations aim for the development of reference samples with controlled defect concentration and morphology as well as methods for elemental depth profiling.

2. Experimental details

Dual-target sputtering was used to prepare InGaZnO samples on oxidized (10 nm SiO_2) single-crystalline silicon wafers in thicknesses of nominally 50 nm (for X-ray, ellipsometric and reflectometric measurements) and 500 nm (for Raman spectrometry). The parameters of preparation and numbering of samples used in this study are summarized in Table 1.

ZnO/Al_2O_3 multi-layer structures of $n\times\{ZnO\ (10\,nm)/Al_2O_3\ (3\,nm)\}/ZnO\ (10\,nm)$ have been prepared for $n = 1, \ldots, 3$ using ALD

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Table 1
Parameters of preparation and numbering of samples investigated in this study. Notations of 'X' and 'R' were used for X-ray/optical (with nominal thicknesses of 50 nm) and Raman (with nominal thicknesses of 500 nm) measurements, respectively.

Ga (%)	Not annealed	Annealed
0.00	X1, R1	X9, R9
0.17	X5, R5	X13, R13
0.34	X7, R7	X15, R15

[12]. The ALD process took place in a flow type Picosun SUNALE TM R-100 type ALD reactor. Nitrogen was used as purging gas and diethyl-zinc, trimethyl-aluminum and H_2O as precursors. The precursors were of electronic grade purity manufactured by SAFC Hitech. The deposition temperature was 300 °C, the flow rates were 150 sccm. The pulse time for all precursor injections was 0.1 s, while the purging time after each metalorganic precursor pulse was 3 s, and 4 s after the water pulses. The substrates were cleaned in cc.HNO_3 and high resistivity water.

Ellipsometric measurements were performed using a SOPRA SE5 multichannel rotating polarizer and a Woollam M-2000DI multichannel rotating compensator spectroscopic ellipsometer in the wavelength range of 193–1690 nm. The spot size was 2–3 mm in both cases. The measurement time of one spot was in the several seconds range.

The X-ray fluorescence (XRF) measurements on the Ga- and In-doped ZnO samples have been carried out at a four-crystal monochromator (FCM) beamline [13] in the PTB laboratory at the synchrotron radiation facility BESSY II. This beamline provides monochromatic radiation from a bending magnet in the energy range between 1.75 eV and 11 keV. The originating measurements shown here were performed at 11 keV at an angle of incidence of 1°. A toroidal mirror in the front and a cylindrical behind of the FCM ensures a beam diameter in the focal plane of about 280 μm.

As a possible end station at the FCM beamline, an ultra high vacuum (UHV) chamber optimized for X-ray spectrometry measurements in different geometries was placed in the focus. So, each of the samples can be adjusted in the center of the chamber, were the focus is located. For detecting the fluorescence radiation an energy dispersive Silicon Drift Detector (SDD) is placed perpendicular to the incoming beam. The detector response function for the respective energies and the efficiency are well-known [14,15]. The solid angle of detection was determined exactly and the incoming photon flux was measured by means of calibrated photodiodes. The knowledge of the experimental details is necessary for a reference-free quantification of the mass deposition of thin layered structures [16].

The Raman spectrometric measurements were performed using a LabRAM Aramis Raman microscope and LabSpec 5.0 Software (Horiba Jobin-Yvon). The instrument was equipped with a 1200 grooves/mm holographic grating and an excitation laser using a wavelength of 532 nm. The laser power was set to 2 mW. The microscope was used in non-confocal mode with an 50× objective (NA 0.75). Calibration of the spectral line position was carried out prior to each acquisition using the crystalline silicon mode at 520 cm^{-1}. The integration time was 400 s. As the thin films were sputtered on a c-Si wafer with 30 nm of thermal oxide on top, the spectra of c-Si and c-Si coated with thermal oxide were also acquired and used for baseline subtraction.

Vacuum ultra-violet (VUV) reflectometry has been done using a Metrosol VUV 7000 equipment in the wavelength range of 120–800 nm with a spot size of 35 μm. The spot size can be important when checking lateral inhomogeneity, but it was not utilized in this study.

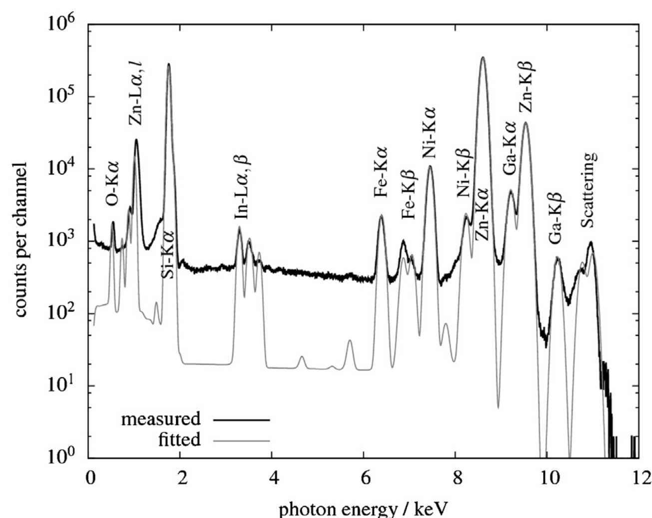

Fig. 1. X-ray fluorescence spectrum of the sample X7. The excitation energy was set to 11 keV. The black line is the measured spectrum and the gray line is the fitted spectrum of the convolution of the fluorescence lines energies with the detector response function.

3. Results and discussion

The samples X1, X7, X13 and X15 were analyzed regarding their chemical composition by means of reference-free X-ray fluorescence analysis [16]. This approach allows for a determination of the mass deposition of the elements and if the density is known the thickness of the layer can be concluded. The photon energy was set to 11 keV in order to excite the main element of the layer (Zn) and the implanted Ga and In atoms.

The analysis of XRF data is based on the deconvolution of the respective spectra by means of detector response functions. The outcome of this is the net count rate for the respective fluorescence lines. Considering the detector efficiency the count rate can be converted into an intensity. For the calculation of the mass deposition m/F (m denoting the mass and F the unit area) only primary excitation are taken into account because no secondary effects are to be expected. The description of the used relation between fluorescence intensity and the number of atoms and mass is described in detail elsewhere [16,17]. This approach requires among the experimental parameters atomic fundamental parameters as photo-electron absorption cross sections, mass attenuation coefficients and fluorescence yield. In this work, the data for the cross sections were taken from data bases of Elam et al. [18] and Ebel et al. [19].

Fig. 1 shows a measured XRF spectrum (black line) and the respective fitted spectrum with detector response function of sample X7 (gray line). This XRF spectrum exhibits the main matrix element fluorescence lines of the single layer Zn Kα, β, the substrate material silicon Si Kα, the dopants Ga Kα, β and In Lα, β as well as contamination as nickel Ni Kα, β and iron Fe Kα, β. For the further evaluation the fluorescence lines of Zn, Ga and In have been considered. In Fig. 2 a selection of the recorded XRF spectra are plotted. Focusing on the dopant's fluorescence lines Ga Kα, β and In Lα, β the intensity is considerably increased when increasing the dopant concentration of these elements. All other fluorescence intensities remain almost constant. Considering the intensities of respective fluorescence lines the mass deposition (m/F) of Zn, In and Ga can be determined and the results are shown in Table 2. Considering the presented results in Table 2 the stoichiometry of these samples can also be determined by XRF. The results are listed in Table 3.

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