Development of Reference Materials for Surface Technology in the Micrometer and Nanometer Range

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Functional surfaces, mostly coated, are of big importance in almost all industrial branches. Application areas are e.g. thermal insulation, corrosion protection, wear protection, decorative and optical coatings and optoelectronic and microelectronic applications. Consequently, quality assurance in surface technology requires reliable testing and analysis procedures from the upper micrometer to the lower nanometer range and the corresponding reference materials. Layer thickness, surface and interface roughness, microstructural features (texture, grain size, phase-composition), stoichiometry and density have to be considered in terms of vertical and lateral resolution and with respect to the uncertainty of measurement.

Reference coatings and films recently developed, qualified or provided by BAM are single and multi-layers such as DLC coatings, TiN-, TiC-, VN-, VC- single, and Ti/Al-, TiO_2/SiO_2- ,CrAlN/CrN- multi-layers. They are applied in mechanical property testing (e.g. scratch test) and depth profiling (e.g. for evaluation of depth resolution of GD-OES, AES, SIMS, SNMS). A cross-section of a GaAs/GaAlAs/InAs multilayer stack provides a nano-scaled strip pattern for the calibration of length scale and the evaluation of the lateral resolution of SEM, AES, XPS and SIMS.

Within this paper, an overview is provided on recent and future activities at BAM in the emerging field of reference coatings. This comprises information on the preparation and the application of such reference materials and the discussion of both destructive (REM, TEM) and non-destructive evaluation and certification techniques by means of Grazing Incidence X-Ray Diffraction (GIXRD), Spectroscopic Ellipsometry (SE) and Surface Acoustic Waves (SAW).

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1. Introduction

The implementation of modern surface technology in production lines requires reliable quality systems. Nowadays, and in particular for surface and film technology from the micrometer to the nanometer range, it is essential to validate analytical and testing procedures. Whereas film thickness, vertical and lateral dimensions are steadily decreasing, the diversity of materials, compounds and artificially designed surfaces, the number of layers and hence interfaces, the complexity of micro- and nano-structural features are increasing to meet the requirements of tailored multi-functional surface properties. Thus, quantitative information on surface topography, chemical composition, morphology, microstructure and physical properties of surfaces prior to and as a result of surface treatment, modification or deposition is required. Therefore, reliable analyzing and testing procedures have to be available for the development of new materials and for the quality control of the production process.

The characterization of surface and interface topography includes the measurement of roughness and the imaging of microstructural features. The determination of surface roughness, either two-dimensional by mechanical or optical stylus techniques or three-dimensional by means of white light interferometry (WLI) or atomic force microscopy (AFM), is a prerequisite for the characterization of micro- and nanotechnological surfaces. Morphology and microstructural features of surfaces, coatings and films can be characterized, mostly at cross-sections, by light microscopy, scanning electron microscopy (SEM) or scanning probe microscopy (AFM, STM). Moreover, layer thickness has to be determined with high reliability even in the presence of surface or interface roughness.

Chemical composition, stoichiometry and density of layers are also key features that have to be characterized with respect to its lateral distribution and as a function of depth. Several techniques of surface chemical analysis such as Glow Discharge Optical Emission Spectroscopy (GD-OES), Secondary Ion Mass Spectrometry (SIMS), Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) are used for depth profiling and chemical mapping. Again, for evaluation of results, surface and interface roughness, layer thickness and analyzing technique related effects have to be considered.

Among the physical properties, coating adhesion and mechanical features (e.g. hardness and modulus) are of big importance independent of the application. Changes in surface topography (surface finish, defects) or chemistry (surface cleaning, gradients) may have substantial impact on the functionality of the entire coating/substrate system. In addition, layer thickness and the morphology of the coating may affect adhesion and mechanical properties of the layer system. There is a variety of testing procedures (e.g. scratch test, instrumented indentation testing (IIT) or surface acoustic waves (SAW) technique) that provide information on mechanical properties. However, in particular for mechanical properties of films and coatings, it is practically difficult (e.g. substrate influence in case of hardness) or in general not possible (e.g adhesion as system quantity) to derive or define intrinsic coating properties.

Hence, reliable testing and analyzing techniques with high precision (repeatability, comparability) and accuracy (absolute numbers, known uncertainty) are needed in particular for coating/substrate systems as mostly system features have to be considered. Reference materials, i.e. reference coatings, are useful for routinely checks and calibration of such analyzing and testing equipment and for the validation of the results. For model-based testing and analysis, reference materials are essential as known reference features may give access to the optimization of testing and analyzing conditions or to the validation of the model for well-defined or almost ideal surfaces or coatings under given experimental conditions. As a result, precision and accuracy can be considerably improved under optimized experimental conditions. Furthermore, the comparability of a specific quantity determined by different testing and analyzing methods can be evaluated and improved only by means of reference materials that are suitable for these techniques. In addition to set-up related issues, surface and interface roughness, layer morpho-logy and thickness, stoichiometry and microstructure may affect depth and lateral resolution and consequently uncertainty of measurement.

Within this paper, an overview is given on recent and future activities at BAM in the emerging field of reference materials. In particular, reference coatings and films developed, qualified or provided by BAM are discussed with respect to preparation methods, certification procedures and application areas. This comprises the discussion of destructive (scanning electron microscopy (SEM), transmission electron microscopy (TEM) at cross-sections) and non-destructive evaluation and certification strategies (grazing incidence X-ray diffraction (GIXRD), spectroscopic ellipsometry (SE) and surface acoustic waves (SAW) techniques at entirely coated substrates). The following examples of reference materials are discussed in more detail:

- Cross-section of a GaAs/AlGaAs/InGaAs layer stack on GaAs substrate for evaluation of lateral resolution in surface chemical analysis, sec. 2.1.
- Single layers of TiN, TiC, VN, VC for evaluation of depth profiling and mechanical property testing on 100Cr6 steel, sec. 2.2.
- Multilayers of TiO_2/SiO_2 and Ti/Al for evaluation of depth profiling and mechanical and optical property testing of coatings, sec.2.3.

2. BAM Certified Reference Materials

2.1 Cross-section of a GaAs/AlGaAs/InGaAs layer stack for the determination of lateral resolution (BAM-L002)

Imaging is a key issue for the analysis of surfaces and the chemical mapping down to the nanometer range. The quality of imaging and mapping, and the reliability and comparability of results are substantially determined by the lateral resolution of the instruments. However, in most cases there is only limited information on the lateral resolution of analysis. This deficiency is mainly due a lack of appropriate reference materials.

In surface chemical analysis, straight edges of slots, mesh bars of copper grids and gold islands are used for the determination of lateral resolution. By now, no reference samples with regular structures with dimensions between lithographic patterns (> 100 nm) and the crystal lattice (< 1 nm) are available. For this reason, BAM developed a new type of certified reference material: "Nanoscale strip pattern for length calibration and testing of lateral resolution" intended to be used for the verification and the validation of surface chemical analysis data.

The strip pattern (Fig. 1) can be used for the calibration of the length scale and for the determination of instrument parameters such as lateral resolution and beam profile. For this reason the pattern includes gratings, isolated narrow strips and sharp edges of wide strips (step transitions). The imaging of narrow lines and step transitions yields the line spread function and the imaging of gratings enables the determination of the contrast transfer function of the instruments used. These functions were used to describe lateral resolution and contrast of imaging instruments.

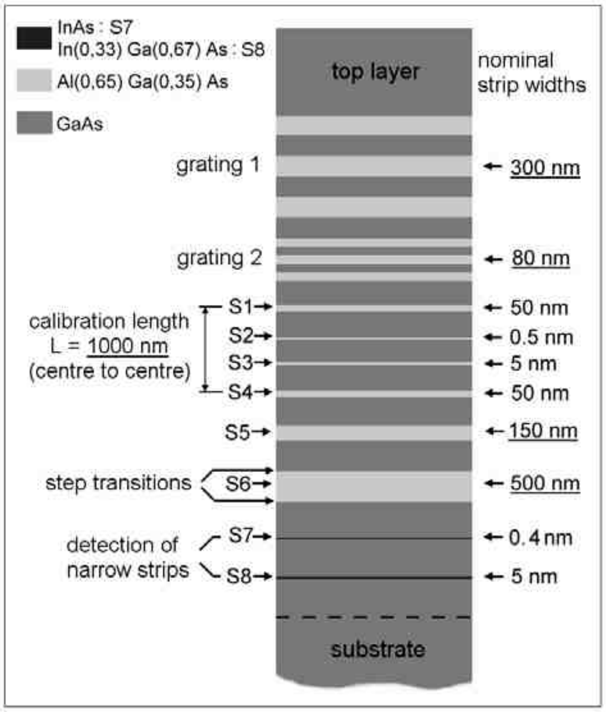


Fig. 1: *Scheme of the strip pattern. Only the underlined nominal values are certified.*

BAM-L002 is applicable to all methods which have enough contrast between the materials forming the semiconductor strip pattern. This includes the analysis using electrons, ions, photons or scanning probes. The application of BAM-L002 in scanning electron microscopy (SEM, Fig. 2), secondary ion mass spectroscopy (SIMS, Fig. 3) and X-ray photo-electron spectroscopy (XPS) has been successfully tested.

The sample is an embedded cross-section of a layer stack of GaAs, AlGaAs and InGaAs on a GaAs substrate. The layer stack was grown by metalorganic chemical vapour deposition (MOCVD). The coated 2-inch wafer was sawed into 5∗5 mm platelets. A coated GaAs platelet and an uncoated GaAs platelet were brought into close contact and embedded together in conductive epoxy. After curing the epoxy block was ground and polished perpendicular to the plane of the two embedded platelets. As a result; the surface of the block shows a cross-section of the layer stack (Fig. 2).

The strip pattern is solely caused by elemental composition and the flat surface shows no substantial three-dimensional structure. The calibration length and four strip widths (underlined in Fig. 1) have been certified by Transmission Electron Microscopy (TEM).

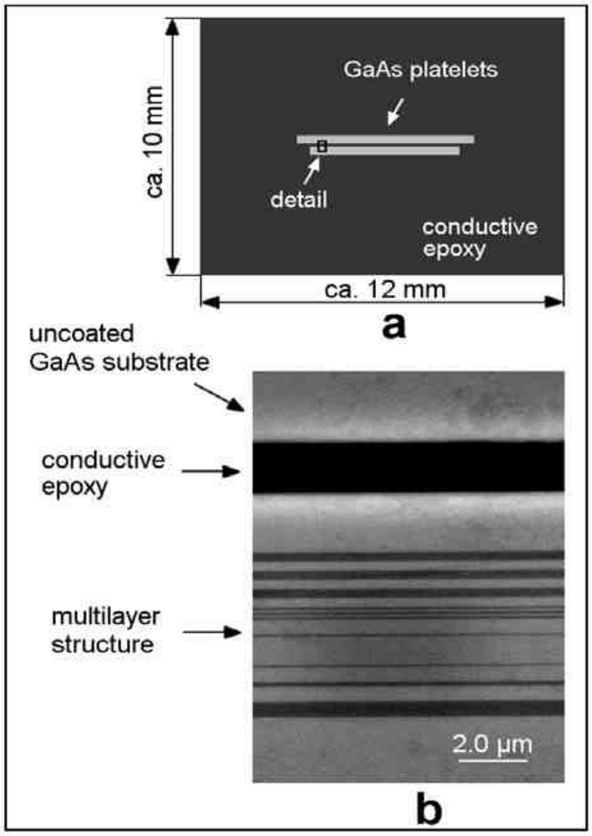


Fig. 2: *(a) Scheme of the whole sample, (b) SEM image of the detail marked in Fig. 2a.*

Fig. 3 shows an example of application. BAM-L002 was imaged with a Time of Flight Secondary Ion Mass Spectrometer (TOF-SIMS IV, IONTOF GmbH, Germany). The element mapping for aluminium shows that grating 1 with its 300 nm strips is clearly resolved and grating 2 with the 80 nm strips is at the limit of resolution. The convolution of the strip pattern with a 150 nm wide Gaussian yield a profile (top) which is very similar to that through the measured aluminium distribution (bottom). Thus it appears that the lateral resolution is much better than the halfwidth of the beam profile, which is often used as a measure of lateral resolution.
The indium distribution shows the clearly detected 5 nm and 0.4 nm wide strips of $In_{0.33}Ga_{0.67}As$ and InAs, respectively. This documents the high capability of SIMS for the detection of small features by chemical mapping.

The combination of gratings, isolated narrow strips and sharp edges of wide strips offers improved possibilities for the calibration of a length scale, the determination of instrument parameters and the “realtime” optimisation of instrument settings.

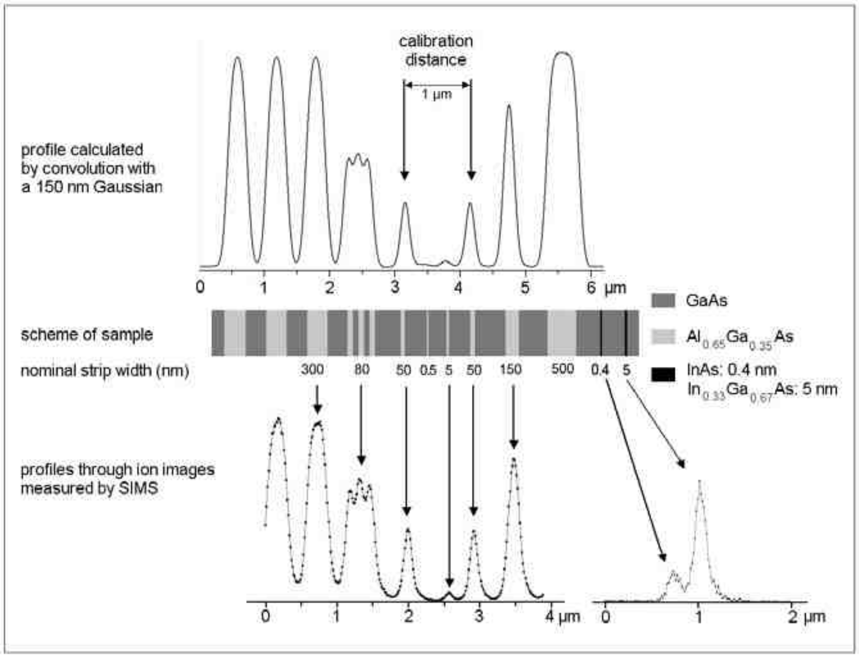


Fig. 3*: Calculated intensity profile (top) and ToF-SIMS analysis (bottom) of BAM-L002. The measured profiles are accumulated from 256 horizontal line scans. The points are measured values (scan points).*

2.2 Single layers of TiN, TiC, VN and VC for depth profiling and mechanical property testing (BAM-L102 – BAM-L105)

Such hard coatings are useful for the evaluation and calibration of depth measurement (sputter rates) and depth resolution (interface to the substrate) of surface analytical methods (e.g. GD-OES, AES, SIMS, XPS). Moreover, the evaluation and optimization of testing conditions for mechanical property testing (scratch test, tribological testing) and the evaluation and calibration of metallographic preparation techniques (e.g. cross-sectioning, ball-grinding) are further application areas. Certified quantity is the layer thickness with additional information on hardness, modulus and surface roughness.

TiN-, TiC-, VN- and VC-coatings with a nominal layer thickness of 2.5 µm have been deposited on polished 100Cr6 steel substrates (discs of 30 mm in diameter and 4 mm thickness) using a PVD UBM sputtering process. To improve adhesion, a Cr inter-layer with a layer thickness of approximately 100 nm was used. For each CRM, a value of the layer thickness d_{CRM} is certified. The certified value d_{CRM} is valid for the central surface area of a diameter of 25 mm.

In case of depth profiling, the intensity (related to an element) vs. time (related to sputtering depth) scale has to be converted into a concentration vs. depth scale. During depth profiling, the shape of the sputter crater is changing, whereas roughness is usually increasing. Moreover, various parameters of the analyzing set-up have to be optimized prior to analysis. To meet these requirements, reference coatings are introduced for routinely system checks, which prove reproducible experimental conditions and provide information on depth resolution. Table 1 gives an overview on BAM layer reference materials.

CRM	layer material	layer thickness (µm)	certification method
BAM-L100	Ti / Al	5 x (0.1 / 0.25)	SEM
BAM-L101	TiO_2 / SiO_2	5 x (0.1 / 0.1)	SEM
BAM-L102	TiN	2,5 µm	SEM
BAM-L103	VN	2,5 µm	SEM
BAM-L104	TiC	2,5 µm	SEM
BAM-L105	VC	2,5 µm	SEM

Table 1: *BAM layer reference materials*

The layer thickness was certified by measuring the average layer thickness over a cross-section using a calibrated scanning electron microscope (SEM). Fig. 4 shows the SEM image and illustrates the determination of layer thickness. For the preparation of cross-sections, either a Cr- or a TiN- top coating was deposited onto the reference coating in order to avoid any mechanical failure at the surface and to enhance the SEM-contrast.

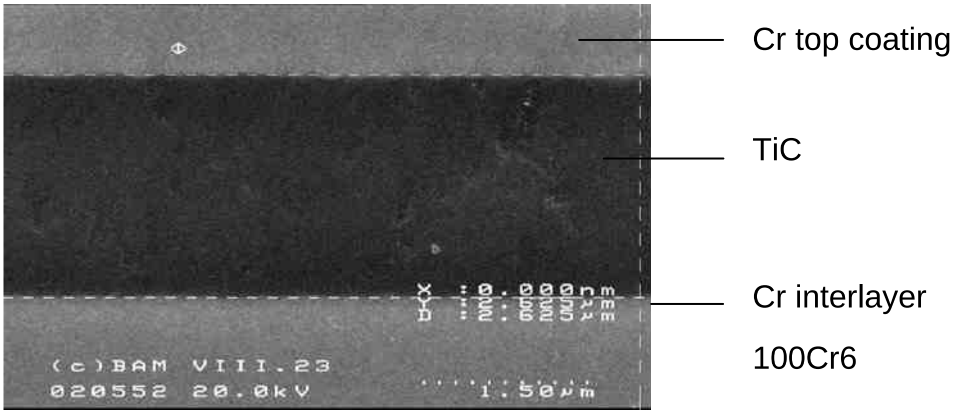


Fig. 4: *SEM image of a cross-section of BAM-L104 (TiC on 100Cr6).*

The strategy of certification was as follows:

1. All reference materials and batch reference samples have been tested non-destructively by means of surface acoustic waves (SAW) and grazing incidence X-ray diffraction (GIXRD). So, a fingerprint of layer thickness, microstructure, texture, Young's modulus, Poisson's ratio and density was taken. Both SAW- and GIXRD-data are sensitively correlated to the mounting level of samples in the deposition chamber.
2. For batch reference samples, destructive testing has been performed additionally. Preparation method (cross-sectioning) and measurement method (SEM) have been validated using reference SiO_2 coatings on Silicon. Prior to destructive testing, the layer thickness of SiO_2 coatings has been determined non-destructively and independently by spectroscopic ellipsometry (SE)
3. The average layer thickness d_a of the reference coating (TiN, TiC, VN, VC) was calculated from measurements at 5 points along the cross-section of the batch reference samples using validated and calibrated preparation and measurement methods described before.
4. The average layer thickness d_a determined for the batch reference samples of each mounting level was identified as the certified value of layer thickness d_{CRM} for samples of identical mounting levels.

The batch homogeneity in terms of a 100% testing of all samples of all four-mounting levels in the deposition chamber has been evaluated non-destructively by means of SAW and GIXRD. It was shown that the uncertainty of the layer thickness within one deposition level is approximately 3%. Exemplarily, the SAW techniques is discussed in some more detail.

For coated materials, the phase velocity of surface acoustic waves depends on the elastic parameters and the density of both the coating and substrate material and the layer thickness. Since the penetration depth of the surface acoustic wave decreases with increasing frequency, the higher frequency range is primarily influenced by the coating whereas the lower frequency range is dominated by the substrate. This results in a dispersion of phase velocity c(f) of the surface acoustic wave. A laser-acoustic technique measures the dispersion of phase velocity as a function of frequency (experimental dispersion curve). By means of a parameterised model (theoretical dispersion curve), the modulus of the coating is derived by fitting the theoretical to the experimental dispersion curve.

Fig. 5 shows the dispersion curves for batch reference samples with a layer thicknesses of 2.14 µm, 2.45 µm and 2.88 µm, respectively. They look similar but their slope increases for higher layer thickness. In addition, a comparison is made with the dispersion curve for bare 100Cr6 steel. In case of the uncoated substrate, the phase velocity of the surface acoustic is nearly constant within the bandwidth of 20 MHz to 60 MHz.

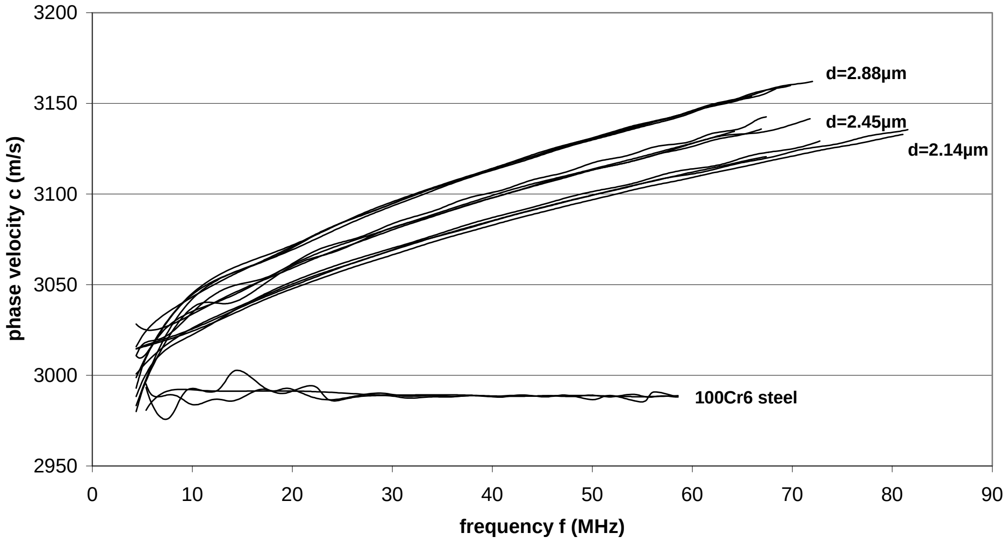


***Fig.5**: Dispersion curves of TiN coatings and bare 100Cr6 steel*

The layer thickness d_{SAW} for each sample is given in Fig. 6 in depen-dence on the mounting level and compared to SEM measurements.

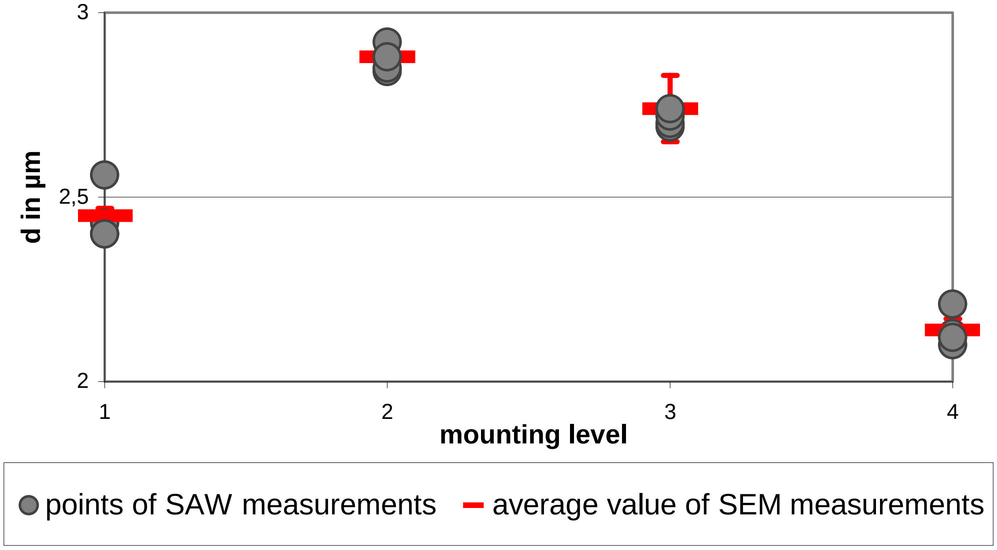
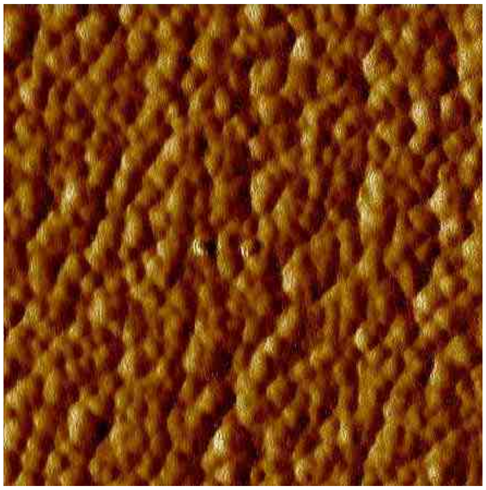


***Fig. 6:** Layer thickness for TiN coatings in dependence on the mounting level in the deposition chamber*

The evaluation of roughness according to DIN EN ISO 4288 with a mechanical profilometer has shown that there is no measurable difference in surface roughness between the coated and uncoated samples (R_a = 0.03 µm; R_z = 0.2 µm). Moreover, the topography of the CRMs was investigated by AFM for the characterization of smaller surface areas (evaluation area was (5 x 5) µm^2). An example is given in Fig. 7.



R_a = 10 nm

R_{max} = 94 nm

R_z = 82 nm

area : (5 x 5) µm²

Fig. 7: *AFM-topography of BAM-L104 (TiC-reference coating)*

Mechanical properties (H_{IT}, E_{IT}), exemplarily shown for BAM-L104 were determined by instrumented indentation tests (F_{max} = 10 mN, h_{max}= 156nm, 100 indentations averaged over an area of (20 x 20) mm^2) according to DIN EN ISO 14577 as follows:

H_{IT} = (30 ± 8) GPa
E_{IT} = (334 ± 72) Gpa

Microstructure and texture of TiC coatings have been evaluated for each reference material and all batch reference samples by means of grazing incidence X-ray diffraction (GIXRD). The stability of the reference material has been evaluated by repeated GIXRD measurements after 400 days. Samples have been stored under ordinary laboratory conditions. One example of these measurements is shown in Fig. 8.

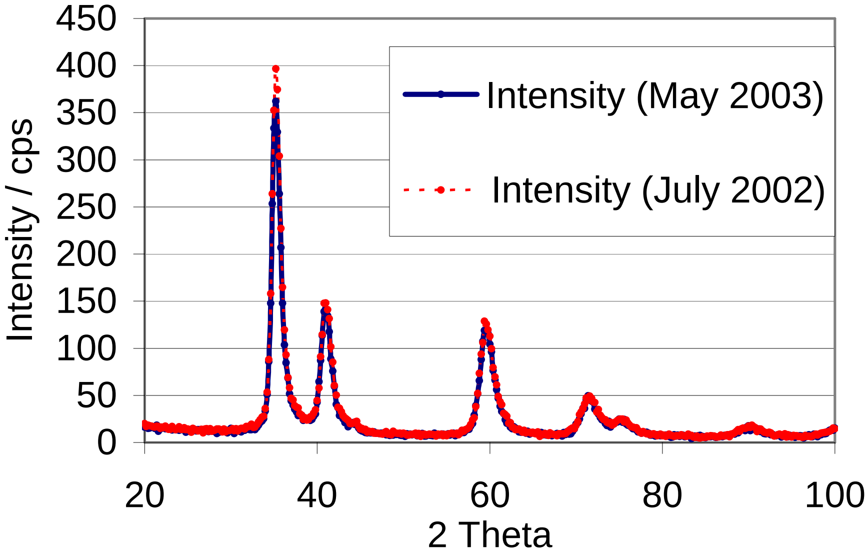


Fig.8: *Repeated GIXRD measurements after 400 days of storage (BAM-L104, TiC)*

2.3 Multilayers of Ti/Al and TiO_2/SiO_2 for evaluation of depth profiling and mechanical property testing (BAM-L100, -L101)

The certified reference material BAM-L100 is a Ti/Al multilayer stack (5 double layers of Ti/Al) with a nominal layer thickness (Ti/Al) of (100/250) nm and 1.75 µm nominal total layer thickness. It has been deposited on polished 100Cr6 steel substrates using the same PVD UBM sputtering process as for single layers. The deposition sequence starts with Ti (layer on the substrate) and ends up with Al (top layer of layer stack).

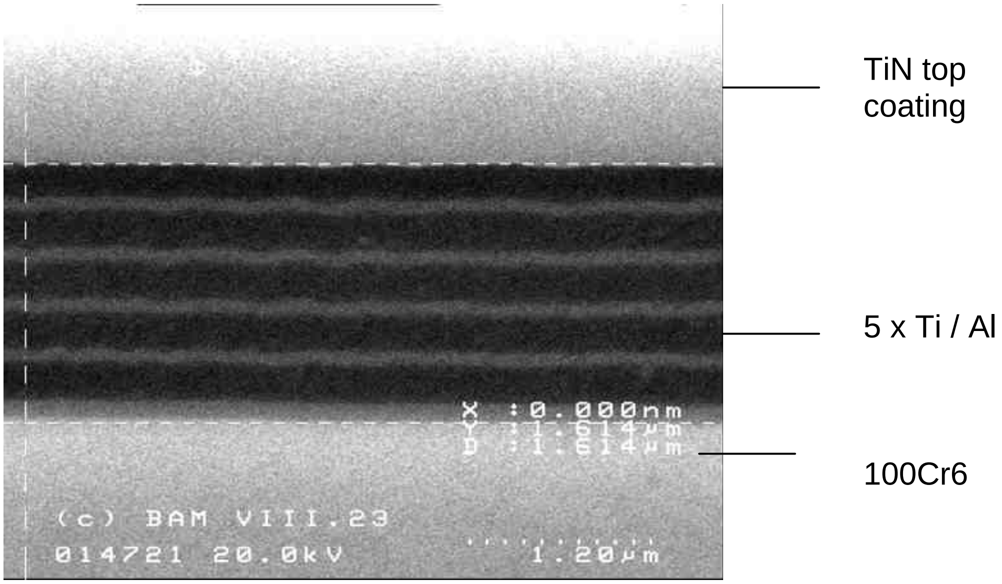


Fig.9: *SEM image of a cross section through the Ti/Al layer stack of BAM-L100.*

Fig. 9 shows a cross-section through the layer stack, again with a TiN top coating for cross-sectioning. Because of the higher waviness of the individual coating interfaces along the measuring length of 5 µm only the total thickness of the layer stack was certified on the basis of the SEM image.

In addition to SAW, for Ti/Al multilayers batch homogeneity has been evaluated non-destructively for each reference material and all batch reference samples by means of grazing angle X-ray diffraction (GIXRD) in terms of a fingerprint technique for stoichiometry, microstructure, density and (total) layer thickness. As described in more detail earlier, normalized intensity ratios of relevant reflexes have been calculated for evaluation of the reproducibility of overall coating quality. The relative intensity deviations PI_n (Fig. 10) correspond to the thickness which itself depends on the mounting level in the deposition chamber.

The surface morphology of Ti/Al coatings is typical of the PVD deposition process. The Ti coatings have a columnar but relatively dense structure with minor defects or droplets, whereas the Al coatings show a dimple fracture morphology which is characteristic of a very ductile material.

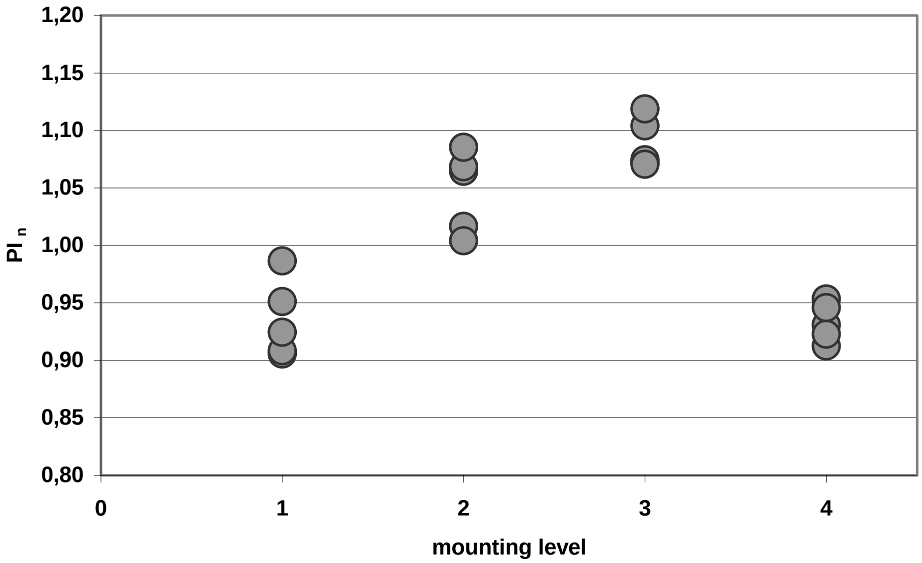
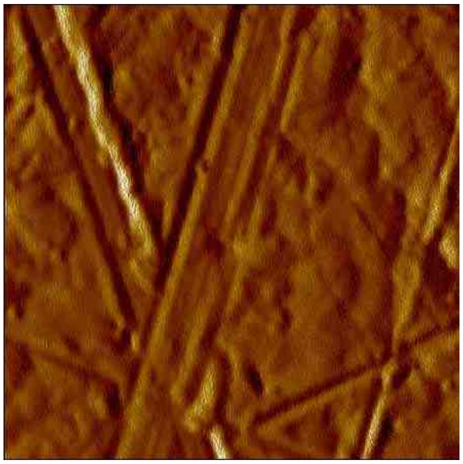


Fig. 10: *Relative GIXRD intensity deviations PI_n in dependence on the mounting level in the deposition chamber*

The evaluation of roughness according to DIN EN ISO 4288 with a mechanical profilometer has shown that there is no measurable difference in surface roughness between the coated and uncoated samples (R_a = 0.03 µm; R_z = 0.2 µm). Moreover, the topography of the CRM´s was investigated by AFM for the characterization of smaller surface areas (evaluation area was (5 x 5) µm^2). An example is given in Fig. 11.



R_a = 7.0 nm

R_{max} = 68.8 nm

R_z = 57.1 nm

area : (5 x 5) µm^2

Fig. 11: *AFM-topography of BAM-L100 (Ti/Al layer stack on 100Cr6 steel)*

The certified reference material BAM-L101 is a TiO_2/SiO_2 multilayer stack (5 double layers of TiO_2/SiO_2) with a nominal layer thickness (TiO_2/SiO_2) of (100/100) nm and 1.0 µm nominal total layer thickness. It has been deposited on polished BK7 glass substrates by ion-assisted electron beam evaporation. The deposition sequence starts with TiO_2 (layer on the substrate) and ends up with SiO_2 (top layer of layer stack).

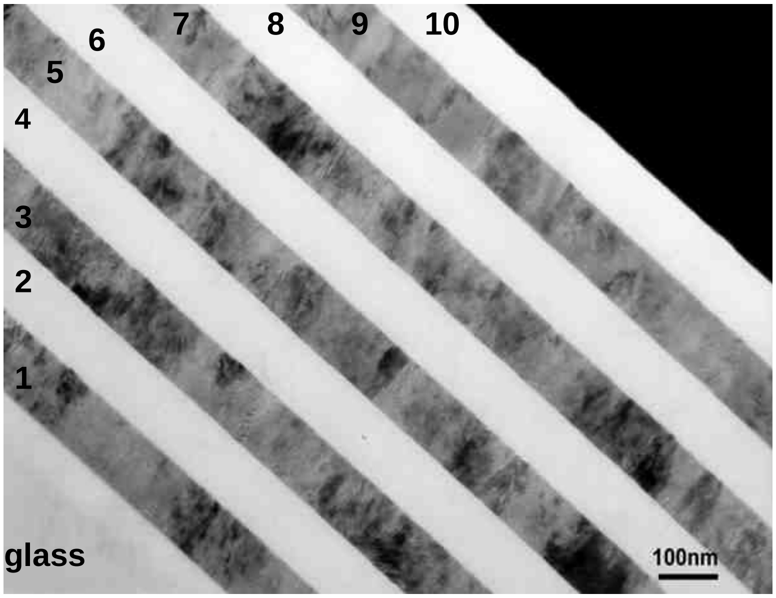


Fig.12: *TEM image of a cross-section through the TiO_2/SiO_2 layer stack of BAM-L101.*

Fig. 12 shows a cross-section through the layer stack. For TEM imaging, a Pt top-coating was applied whereas for the certification by SEM a TiN top-coating was deposited on top. For this transparent layer stack, an independent certification procedure by means of spectroscopic ellipsometry (SE) results in identical values for certified total layer thickness.

Batch homogeneity has been evaluated non-destructively for each reference material by means of SE in terms of a fingerprint technique for stoichiometry, microstructure, density and (total) layer thickness. Ellipsometric quantities (Fig. 13) prove a batch homogeneity of about 1% for total layer thickness and are in agreement with modeling in the same order of magnitude.

The evaluation of roughness by white light interference microscopy (WLIM) has shown that there is no measurable difference in surface roughness between the coated and uncoated samples (R_a = 1 nm;
R_z = 5 nm).

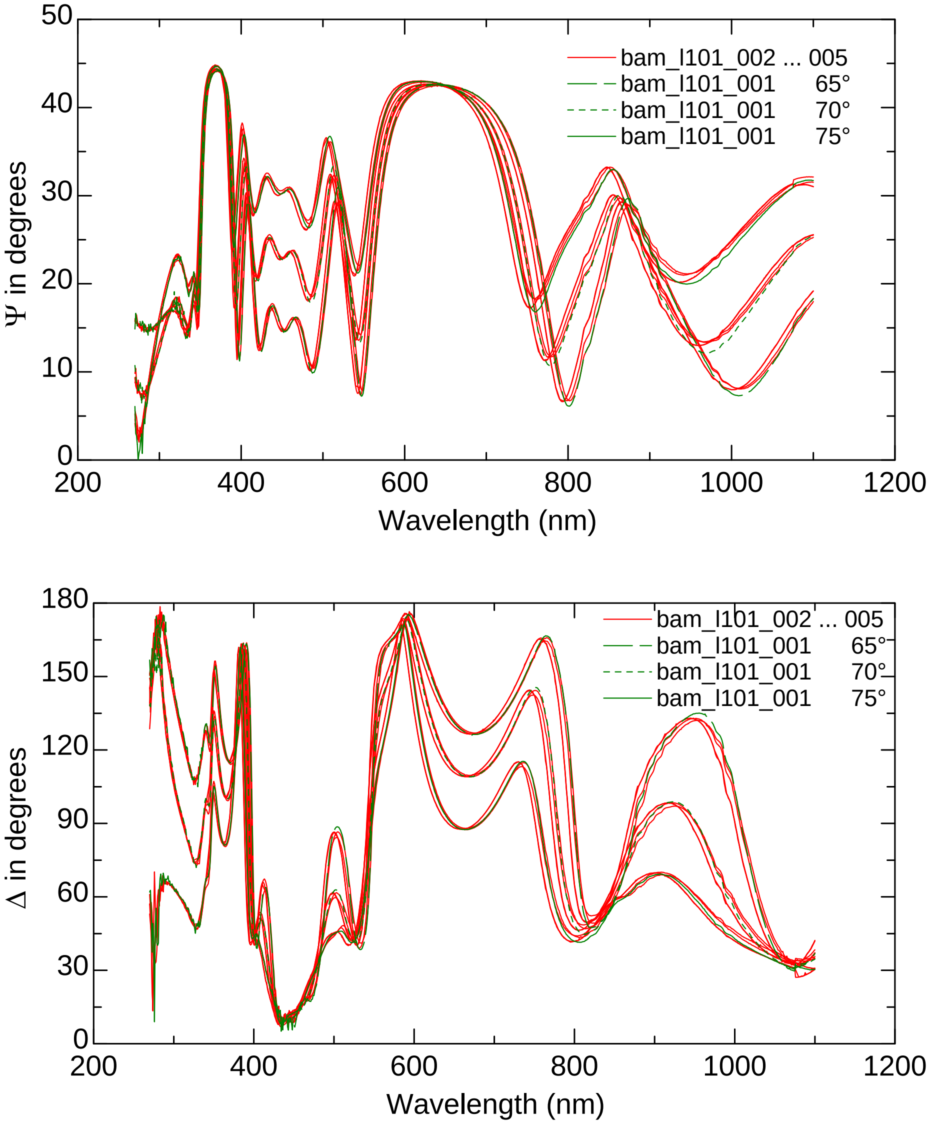


Fig.13: *Ellipsometric quantities as fingerprint for TiO_2/SiO_2 layer stack of BAM-L101.*

For non-conducting layer/substrate systems as BAM-L101, Figs. 14 and 15 demonstrate depth profiles taken within an international inter-laboratory comparison (VAMAS-TWA 22, project A4). In this comparison, as a first step, experimental conditions for SNMS (Fig. 13) and GD-OES (Fig. 14), respectively, have been optimized by using TiO_2/SiO_2 layer systems. Titanium and Silicon as layer elements provide information on the (decreasing) depth resolution. In addition, Boron as substrate element is associated with the crater shape at the interface layer stack to substrate.

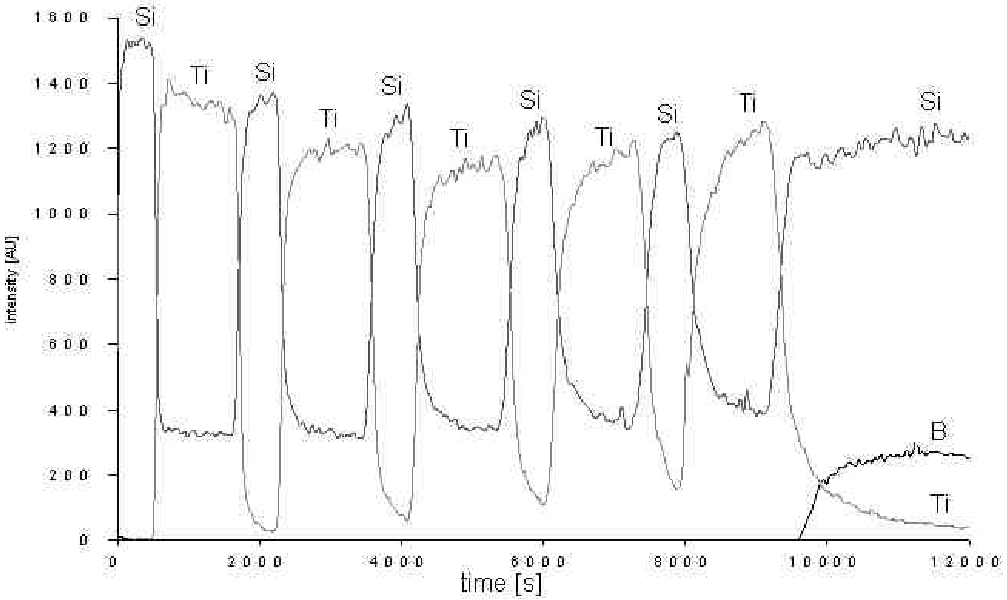


Fig.14: *SNMS spectrum of TiO_2/SiO_2 layer stack of BAM-L101 (VAMAS-TWA22-4), lab 34, optimized conditions*

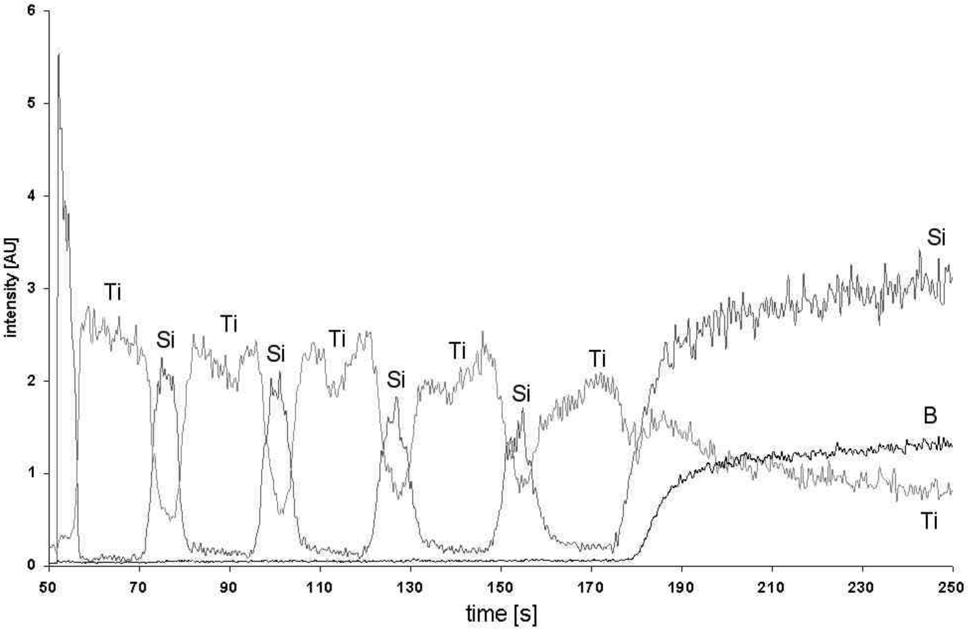


Fig.15: *GD-OES of TiO_2/SiO_2 layer stack of BAM-L101 (VAMAS-TWA22-A4), lab 13, optimized conditions.*

3. Summary and Outlook

Three types of new BAM reference materials useful for surface technology in the micrometer and nanometer range have been developed as follows:

- Cross-section of a GaAs/AlGaAs/InGaAs layer stack for the determination of lateral resolution (BAM-L002)
- Single layers of TiN, TiC, VN and VC for depth profiling and mechanical property testing (BAM-L102 – BAM-L105)
- Multilayers of Ti/Al and TiO_2/SiO_2 for evaluation of depth profiling and mechanical property testing (BAM-L100, -L101)

For development and certification, SEM and TEM at cross-sections (all reference materials), GIXRD (Ti/Al, TiN, TiC, VN, VC), SAW (TiN, TiC, VN, VC) and SE (TiO_2/SiO_2, and SiO_2 reference coatings for the validation of the cross-sectioning technique) have been applied. Certified quantity is the individual (BAM-L002) or total layer thickness (BAM-L100 to L105). For layered materials, additional information is available on surface roughness, mechanical properties, ellipsometric or surface acoustic dispersion curves and X-ray data.

These reference materials have already been used within several international projects and inter-laboratory comparisons (VAMAS-, EU-, national projects). Main application areas are the determination of lateral and depth resolution in surface chemical analysis (imaging and depth profiling). Moreover, layered reference materials can also be used for mechanical property testing (ball-cratering, instrumented indentation testing, surface acoustic waves).

They are available on a commercial basis (www.webshop.bam.de) on customer request.

At present, a funded EU project is dealing with composite coatings for the calibration of energy dispersive X-ray spectrometry (EDS). Further activities refer to the development of advanced reference materials for the evaluation of lateral resolution in chemical surface analysis. In addition, DLC coatings are under investigation for mechanical and optical property testing.