T4 - Real structure - Thin Films

T4 - P81

ANISOTROPIC INTRINSIC AND EXTRINSIC STRESSES IN GAN THIN FILM ON LiAlO$_2$ (100)

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Temperature dependencies of residual stresses and unstrained lattice parameters are evaluated in hexagonal GaN (100) thin films using elevated-temperature X-ray diffraction (XRD). The films with a thickness of about 150 nm are deposited on single crystalline LiAlO$_2$ (100) by ion beam assisted molecular beam epitaxy (IBA-MBE).

The diffraction measurements are performed using a four circle X-ray diffractometer (Seifert PTS 3000) in the temperature range from 25°C to 600°C with a step width of 50°C, applying the heating stage DHS 900 (provided by Anton Paar Ltd).

The GaN thin film is grown with (100) crystallographic parallel to the substrate surface. Therefore the mechanical and thermal behaviour of the thin film is predetermined by the anisotropic nature of the (100) plane resulting in the anisotropic in-plane residual stresses and thermal expansion coefficient (TEC) mismatch.

These anisotropic in-plane TEC mismatches results in the anisotropic temperature development of the residual stresses. Moreover, since no sign of plastic flow is detected, the temperature dependencies of the (extrinsic) stresses allow extrapolating of the anisotropic intrinsic stresses formed in the film during the deposition. This (for the first time observed behaviour) indicates an anisotropic nanostructure development of the film during the growth.

T4 - P82

INFLUENCE OF SOME MAGNETRON SPUTTERING CONDITIONS ON PARAMETERS OF TIN COATINGS ON STEEL SUBSTRATE

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Magnetron sputtering has become the process of choice for deposition of a wide range of industrially important coatings. The driving force for the very active development of this modern surface engineering method recently is permanently increasing demand for high – quality functional films in many industrial and market sectors.

In the basic sputtering process, a target (acting as a cathode) plate is bombarded by energetic ions generated in a glow discharge plasma. The ion beam bombardment causes removal, i.e., 'sputtering', of target atoms, which may then condense on a substrate as a thin film. During the bombardment secondary electrons are also emitted from the target and they play an important role in maintaining the plasma. However, in its original version this technique has some disadvantages connected with the low deposition rates, relatively low ionization efficiencies in the plasma and high substrate heating effects [1]. An improved version of this very promising ion beam method is so called unbalanced magnetron sputtering described in details in Ref. [1,2,3].

Titanium nitride TiN films on steel have found permanently growing acceptance in industry due to the unique properties of this material, including high hardness, good wear and corrosion resistance parameters observed over quite a large temperature interval. These superior mechanical properties of magnetron sputtered TiN films are a function of their phase composition, stoichiometry, microstructure parameters, crystallinity, density, availability of transition Ti layers, thickness, etc.

In the present investigation TiN films with 4 m thickness have been applied by unbalanced magnetron sputtering. During the sputtering procedure M2 tool steel substrates have been biased with -50V biased voltage. Three films differing by the applied direct currents during their deposition namely 4, 6 and 8A have been produced by the equipment available at the Centre for Advanced Materials and Surface Engineering, University of Salford, UK.

The parameters of the so prepared three films have been analysed by X – ray diffraction with Cu K radiation applying Asymmetric Grazing Incidence geometry method

(AGIB) [4]. Phase composition, lattice parameters and imperfections, crystallographic texture and residual macro stresses have been investigated. Depth profile analyses at different incident angles of the falling X-ray beam have also been performed. The anisotropy of texture and residual stresses in the films' surface have also been between the analyzed parameters.

And finally, the relationship between the micro- and substructure parameters and wear resistance results of the investigated films and their dependences on the value of the direct current applied during the films' application have also been analyzed.

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T4 - P83

STRUCTURE OF ELECTRO-SPARK COATINGS AFTER PULSE TREATMENT

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The phase and a structural-stress state of spark-erosion coats and nearsurface layers of iron- and titanium-based alloys under an operation of combined spark-erosion treatment have been investigated.

By means of direct structural methods it is shown that structural-phase state of spark-erosion coats on the steel U8 is determined by a dissociation of carbide WC into such components as W_2C and W and their consequent erosion, the following interaction of erosion products with elements of interelectrode medium (carbon, nitrogen, oxygen), an interdiffusion of elements of a coat and a steel undercoat, and also an uprising diffusion of carbon from nearsurface layers of the liner.

The analysis of a structural-stress state of the system have showed that in compound on the base of TiC stretching residual stresses have been formed, and in coat components W_2C, W and the liner component Fe squeezing residual stresses have been registered. In high-carbon austenitic interlayer of the liner residual stresses were practically relaxed, that promoted stress gradient reduction on a phase boundary and an increase of thickness of a coat.

It was determined that laser heating of spark-erosion coat improved exploitation properties at the expense of assimilation of nitrogen with the increase of a nitride TiN fraction in TiCN carbonitride, additional secondary tungsten carbidization with formation of high-strength carbide W_2C and a selective relaxation of weaken stretching stresses with conservation of reinforcing contracting residual stresses.

T4 - P84

CHALCOGENIDE FILMS AS ATTENUARS OF X-RAY RADIATION ON GLASSY COATS

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Multicomponent chalcogenide glasses are widely applicable in the field of semiconductor techniques. The great interest of these materials is due to their simply obtaining technology in bulk forms and thin films; chemical and radiation durability; relatively good thermal and mechanical properties; low optical losses; their transparency and photosensitivity in IR and VIS spectral regions, as well as the possibility of wide varying of properties with composition. That determines the possibilities for their practical application for pulse generation of acoustic and optical radiation. Thin films deposited from chalcogenide glasses are applicable in opto- and microelectronics for different purposes – electrical switches, data recording, protective, passivity and optical coatings [1-5].

Many investigations showed the interesting behaviors that can be obtained with introduction of transition metals into the matrix of chalcogenide glasses. The great variations of important glass characteristics are achieved by introducing of Cu, Ag or Cd atoms into chalcogenide systems. It has been found that the presence of Cu in amorphous arsenic-selenides leads to the increase of density, microhardness, softening temperature and to the decrease of activation energy of electroconductivity. Besides known good mechanical, thermical, magnetic or changeable electrical features, investigations were also oriented to emphasize the optical features of glasses with introduction of copper in its matrix [6].

It is well known that X-rays include vawe lengts in electromagnetic spectra, with possible negative effects on human health. With energies around 1.2 keV, they are not extremely hard radiation, which means that lower intensities in short periods, which are used in medical diagnostic tests, or special X-ray examins, which are based on different absorption in healty and unhealthy tissues and bones, make acceptable doses in most cases.

Standard transparent glasses do not have high absorption, i.e. significant attenuation of scattered vawes. This was a reason for the begining of investigation of syntesis of new glass systems, which will be sutable, according to their transsparency, stability and other characteristics, for reduction of negative affects of X-rays.

This paper presents the results of investigation of possibility of X-ray attenuation in standard glasses K-8, by coating them with thin chalcogenide films. These investigations are of great importance for X- ray radiation and its negative influence in diagnostic centers in cities and urban areas.

The X-ray diffraction (XRD) measurements were performed on a conventional X-ray diffractometer PW 1373-PW 1065/50 (Philips) and non-monochromatized CuK radiation.

Thin-film samples were prepared by thermal evaporation in vacuum of powdered previously synthesized complex glasses. The investigated glasses of $Cu_xAs_{50}Se_{50-x}$ type, with various concentration of Cu (5, 10 and 15 at %), were synthesized from high-purity elemental component by fast cooling from the melt. The proces was carried out in semiautomatic horizontal tube furnaces Carbolite, Model CTF 12/65, with a temperature controller Eurotherm 91-3, according to the empirically defined cascade regimes. Cooling at a rate of 800 ^{0}C/min resulted in amorphous samples. Condensation was carried out on the substrates made of the standard glass K-8 of the known index of refraction,

kept at room temperature ("cold" substrates). Film thickness in the course of evaporation was controlled by optical method on the basis of the interference of reflected laser beam. It was 1.24, 0.86 and 0.97 m, for film with 5, 10 and 15 at % Cu, respectively. Supstrate thickness was 0.133 cm.

Dependence of protection level on thin films thickness and values of linear attenuation coefficient were determined. Influence of glass composition on relevant parameters was also investigated.

It has been determined that chalcogenide coats significantly increase the absorption power of investigated system, i.e. those linear absorption coefficients increase in interval: 30.6%-42.6%. In coats from investigated system copper content has a great influence on absorption coefficient increase.

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T4 - P85

STRUCTURAL AND MICROSTRUCTURAL CHARACTERISATION OF ZrN COATINGS FOR DECORATIVE APPLICATIONS

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Residual stresses play a primary role in the mechanical behaviour of the protective coating and thus in the lifetime of the coated component. Indeed, stresses can also compromise the corrosion resistance of the film and hence the substrate. In this paper we studied ZrN coatings applied to manufact for decorative industry. We will present the results of structural characterization of ZrN coating deposited on different substrates. In particular the correlations among substrate, surface morphology and residual stress

will be discussed together with the advantages of this coating compared to the more popular TiN. For this work a new method (DRAST) [1] to evaluate residual stress based on the analysis of 2D diffraction images collected by a laboratory X-Ray microdiffractometer equipped with an image plate detector was applied.

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T4 - P86

EFFECT OF ANNEALING CONDITIONS ON STRUCTURAL TRANSFORMATION OF ZnS THIN FILM

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The necessity of full-color displays fabrication results in the further development and investigation of an efficient emitting material. One of such materials is well known ZnS. With Cu doping it can be used as green and blue emitting active layer. However, by the reason of the fast degradation and relatively low brightness of ZnS:Cu alternating-current thin film electroluminescent (ACTFEL) devices these films are still not adequate for practical purposes. The crystalline structure of the films, concentration of dopant and the effect of Cu incorporation into the lattice of ZnS influence on the operating parameters and degradation stability of ACTFEL devices. A new method of annealing at atmospheric pressure for the improvement of electroluminescent (EL) characteristics of ZnS:Cu films was developed [1]. It was also reported that effective powder EL material must contain both sphalerite and wurtzite phases [2,3].

In the present work the effect of an original non-vacuum annealing of ZnS thin films according to the annealing conditions and type of substrate on film's crystalline structure and surface morphology was investigated.

ZnS thin films were grown by electron-beam evaporation method on $BaTiO_3$ ceramic (polycrystalline) and glass (amorphous) substrates heated up to 150 200° C. Three types of targets such as ZnS, ZnS-Cu and ZnS-Cu, Al were used. The film thickness varied from 0.6 m to 1 m. As-deposited films were annealed at the atmospheric pressure at 600 950° C during one hour. The annealing S_2-rich atmosphere was prepared by decomposition of sulfur containing compound. Different annealing conditions were used: 1) in the pure ZnS powder at 600 800 C; 2) in the ZnS-Cu, Cl powder at 600 800 C; 3) in the S_2-rich atmosphere with additional vapors of Ga at 800 950 C; 4) two steps of annealing: a) in the ZnS-Cu, Cl powder at 650 C, b) in the S_2-rich atmosphere with additional vapors of Ga at 800 950 C. The structural analysis was carried out with a Siemens D500 X-ray diffractometer using Co K radiation and also with a D8 Advance Bruker diffractometer using Cu K radiation for determination of grain size and residual stresses. Surface morphology of the films was investigated by atomic force microscopy (AFM) (Park Scientific).

The XRD patterns of ZnS/glass and $ZnS/BaTiO_3$ structures deposited from three types of the targets revealed that ZnS films had only cubic crystal structure with preferred orientation in o direction. For two types of the ZnS:Cu, Cl/glass films prepared from ZnS films by annealing in the ZnS-Cu, Cl powder with different ratio of Cu and Cl at 600 C a phase transformation and change in the texture were not observed. The XRD patterns of $ZnS/BaTiO_3$ and $ZnS:Cu/BaTiO_3$ films annealed in S_2-rich atmosphere with and without Ga vapors at 950 C did not show any changes in crystal structure, though the annealing temperature was very close to the ZnS phase transformation temperature of 1020 C. Strong phase transformation for ZnS:Cu, $Cl/BaTiO_3$ film was observed after the annealing in the ZnS-Cu, Cl powder at 800 C. After two steps of annealing the phase transformation for ZnS:Cu, Cl, Ga film was also observed. The fraction of grains, which were transformed, depends on the temperature of the second annealing in the S_2-rich atmosphere with Ga vapors. After the second annealing at the higher temperature of 950 C the film has the hexagonal structure with preferred orientation in d direction almost in whole volume.

The investigations of the surface morphology by AFM showed an enlargement of grain size for the film deposited from the ZnS:Cu, Al target. After the annealing of ZnS film in the S_2-rich atmosphere at 600 C some increase of grain size is observed. The increase of grain size after annealing in the ZnS-Cu, Cl powder at 600 C depends on the ratio of Cu and Cl concentrations. Annealing of the ZnS film in S_2-rich atmosphere with Ga vapors at 950°C does not lead to substantial distinction of surface morphology comparing to the annealing in the S_2-rich atmosphere. After annealing of ZnS:Cu film in S_2-rich atmosphere with Ga vapors at 950°C the grains are enlarged and clearly separated. Major changes of surface morphology such as clearly separated smooth grains with largest grain size (1 m) are observed for ZnS:Cu, Cl, Ga films after two steps of annealing. The vapors of Ga with atoms of Cu and Cl influence not only on the phase transformation, but also induce strong grain growth processes.

The temperature of the ZnS phase transformation from the sphalerite to wurtzite structure depends on the presence, type and ratio of additional impurities. It was clarified that Ga and Cl act not only as co-dopants to improve the luminescent properties, but also as activators of recrystallization processes.

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T4 - P87

MICROSTRUCTURE AND MAGNETISM OF UN AND US SPUTTER-DEPOSITED LAYERS

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Strongly magnetic materials belong mostly to the group of lanthanide ($4f$) metals or transition ($3d$) metals. Besides them, there is emerging a third specific group of magnetic materials, based on actinides, with very intriguing properties. Magnetic properties of nanocrystalline and amorphous systems have been so far studied for the first two groups. Actinide systems remain largely unexplored. Studies of nanocrystalline materials bring information on the influence of atomic disorder and microstructure details on magnetism of actinide compounds. Few studies undertaken so far reveal very dramatic effects. The changes in microstructure details lead to the suppression of ordering temperatures and magnetic moments or even to the vanishing of magnetic ordering.

In our studies we have concentrated on two compounds crystallizing with the cubic NaCl structure type: UN and US.

As we reported previously [1], systematic investigation of sputter-deposited (reactive sputtering) thin layers of UN revealed preferred orientation with the direction {111} perpendicular to the substrate, which gets more pronounced at lower deposition temperature T_d. Though magnetic susceptibility of UN (antiferromagnet in bulk) is normally characterised by a pronounced maximum at $T_N = 53$ K, the layers do not exhibit any anomaly around 50 K. Instead, the magnetic behaviour of the deposited layers tends to weak ferromagnetism and strongly depends on the conditions of their synthesis. The layers deposited at $T_d = 20 – 300$ C exhibit a small ferromagnetic component developing gradually below T 100 K, which can be attributed to not fully compensated antiferromagnetic moments at grain boundaries and/or at numerous defects. Decreasing T_d leads to the suppression of the ferromagnetic component, which can be explained as due to the suppression of the local magnetic moments of uranium. For $T_d = 400$ C an anomaly appears around $T = 50$ K, which can be associated with incipient bulk antiferromagnetism of UN.

Our most recent research is focused on the compound US. The US layers (thickness $0.1 – 0.3$ m) were sputtered in Ar atmosphere from a US target. The quartz glass substrates were used for deposition. In order to study the influence of microstructure on magnetic properties of the deposited layers, T_d was varied in the range $25 – 300$ C. The stoichiometry was checked by in-situ XPS. A very weak oxygen contamination and the absence of other elements prove that we deal indeed with a special form of US.

The microstructure studies of US thin films were performed by means of glancing angle X-ray diffraction (GAXRD) at the angle of incidence of the primary beam of 3° using the Cu radiation (= 1.5418 Å). The US thin films under study consist probably of a mixture of "nanocrystalline" and "amorphous" parts, as can be seen from a strong diffuse scattering in the low-angle region of the XRD patterns. The crystallite size in the nanocrystalline parts is approximately 100 Å. In all samples, a large anisotropy of the lattice parameters was observed. This anisotropy is extremely strong in the samples deposited at room temperature at lower deposition rates and at $T_d = 200$ C. In all samples anisotropy is related to the easy deformation direction {111} and is typical also for other nitrides crystallizing with the NaCl structure, e.g. TiN or UN.

The anisotropy of the lattice parameters is usually enhanced by a large compressive residual stress and by a strong preferred orientation of crystallites. The compressive residual stress was found in all samples, but the values are below –3 GPa in most samples (see Table 1). The samples are rather texture-free (or have a very weak preferred orientation of crystallites) with the exception of the sample deposited at the room temperature at the lowest deposition rate, which shows the {100} texture. The stress-free lattice parameters are below those tabulated for the intrinsic uranium sulfide (a = 5.484 Å). A possible reason could be a slight departure from the expected stoichiometry of the samples or an incorporation of the structure defects into the host structure of the US.

The strong anisotropy of the lattice deformation in these samples could be explained assuming a plastic deformation of crystallites, which leads to a relaxation of the overall residual stress – thus the relative low residual stresses were observed. However, a part of the mechanical interaction must remain frozen in the crystallites, as it is responsible for the anisotropy of the lattice deformation. This phenomenon can again be related to the bimodal microstructure of the films containing the nanocrystalline and the amorphous parts; the latter is probably created during the plastic deformation.

The layers were subjected to magnetic measurements. The AC susceptibility (to determine T_C in low magnetic fields) was measured using the PPMS system from Quantum Design. The squid magnetometer (Quantum Design) was used to study DC susceptibility. It turned out that for US thin films the magnetism tends to be suppressed comparing to the bulk US, which is a band ferromagnet with $T_C = 177$ K [2]. No anomaly is observed at this temperature for any of the samples prepared. Instead we found ferro-

magnetism at lower temperatures, depending on T_d. T_C decreases down to 85-105 K for the layers deposited at room temperature (depending on the rate of deposition) and grows with the increase of T_d (see Table 1). The temperature dependence of magnetic susceptibility has a character of two-phase system where one phase is a temperature-independent paramagnet (presumably amorphous), while other one is ferromagnetic with ordering temperature lower than in the bulk sample.

Spontaneous magnetization in the ordered state is considerably suppressed for the deposited layers: its value is below 0.1 μ_B/f.u. for all samples studied (compare with 1.55 μ_B/f.u. for bulk US [2]), but there is a relatively large high-field susceptibility. We may assume that only part of the suppression is due to the presence of amorphous non-magnetic phase.

Based on the results obtained we can conclude:

US thin layers consist of two phases – nanocrystalline, which is ferromagnetic, and a morphous, which is presumably nonmagnetic;

Largely reduced magnetization at low temperatures points to reduction of uranium moments even in the nanocrystalline phase and glassy character of magnetism (frustration due to large microstrain);

Unlike UN, for which the evolution of 5f magnetism is a function of deviation from the ideal crystallinity, in the case of US the direct dependence of the Curie temperature on the microstructure parameters has not been established yet.

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Table 1. Microstructure and magnetic parameters of US thin films depending on temperature of deposition (T_d) and ion current of the deposition (I). T_C is the Curie temperature.

T_d (°C)	Stress-free lattice parameter (Å)	Residual stress (GPa)	Crystallite size (Å)	Microstrain (10^{-3})	T_C (K)
25 (I = 1.10 mA)	(5.389 ± 0.006)	– (2.3 ± 1.0)	90	7.6	105
25 (I = 0.50 mA)	(5.469 ± 0.035)	– 3 GPa (?)	80	6.2	94
25 (I = 1.35 mA)	(5.447 ± 0.048)	–1 GPa (?)	180	16.5 (?)	85
200 (I = 0.45 mA)	(5.430 ± 0.018)	– (2.8 ± 2.0) (?)	95	9.1	113
300 (I = 0.50 mA)	(5.439 ± 0.006)	– (2.2 ± 1.0)	100	8.5	117
Bulk	5.484	–	–	–	177

T4 - P88

ULTRASHORT PERIOD Cu/Si AND Ni/C MULTILAYERS FOR X-RAY MIRRORS

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Interference multilayer mirrors have become an indispensable part of instrumentation in astronomy, lithography, plasma diagnostics, at synchrotron storage rings and in other fields. Being a periodic stack of layers, they may be viewed as one dimensional crystals. The layer thicknesses are freely adjustable at deposition which enables us to obtain arbitrary periods, not available in natural crystals. Therefore application of such mirrors covers a broad wavelength range from hard X-rays up to DUV region. Compositionally sharp and geometrically smooth interfaces are required. Multilayers with ultrashort period approaching 2 nm or less represent a true challenge for nanotechnology as the layer thicknesses become comparable with the interface width which deteriorates the optical performance severely. Such ultrashort periods are inevitable both in soft X-ray normal incidence optics, such as for "water window" region (2.5-4.5) nm, and grazing incidence hard X-ray optics, such as in telescopes working close to 100 keV.

The contribution is devoted to Cu/Si and Ni/C ultrashort period multilayers which are applicable above 80 keV where W- and Pt-based mirrors exhibit a strong absorption. Ni/C multilayers are of interest also for the X-ray microscopy in the "water window" just below K absorption edge of carbon. Both types of mirrors have been prepared mainly by sputtering or by pulsed laser deposition. The e-beam evaporation was tried only in a few cases and always with an in situ ion-beam polishing of metal layers to suppress the interface roughness [1]. Evaporation in comparison with other two techniques produces generally less energetic adatoms which may supress unwished mixing at the interfaces. In our contribution, we study the possibility to prepare ultrashort period multilayers by e-beam evaporation with in situ substrate heating. Such a heating is a simpler and cheaper way of modifying the interfaces than ion beam polishing. A slightly increased adatom mobility by substrate heating may heal the interface roughness established as a ballance between the kinetics of the deposition process and the thermodynamics of the given element couple.

The multilayers were deposited on silicon wafers and contain typically 10-15 periods (basic bilayers) which scaled between 2 nm and 3.2 nm in different samples. The deposition at various elevated temperatures up to 160 C was tried. The interface quality was examined in terms of the total width $_{eff}$, geometrical roughness $_{geom}$, interdiffusion, lateral ($_{lat}$) and vertical ($_{vert}$) correlation lengths and scaling properties by specular and non-specular X-ray reflectivity (XRR). Randomly rough interfaces were supposed. Such interfaces are typical for amorphous or polycrystalline layers which were identified in our samples by X-ray diffraction. All X-ray measurements were performed at CuK wavelength. The specular and non-specular XRR measurements were evaluated within Fresnel optical theory and distorted-wave Born approximation, respectively.

The multilayers deposited at 80 C exhibited the highest reflectivity and the best developed oscillations in the XRR curves in both types of multilayers. A comparison of the interface parameters extracted from the XRR simulations for this deposition temperature is shown in Table 1. It can be seen that Cu/Si multilayers are superior to Ni/C ones in terms of a smaller total interface width and geometrical interface roughness as well as a smaller degree of intermixing induced by the deposition. On the other hand, Ni/C multilayers exhibit generally weaker correlations of interface profiles which is advantageous for imaging applications. C-on-Ni interfaces are rougher than Ni-on-C ones so that Ni layer growth seems to be a limiting factor for obtaining good reflectivity which determines also the optimum deposition temperature. Another important issue to consider is thermal stability as the steep concentration gradient at the interfaces may bring about an interface degradation and reflectivity loss under intense beam irradiation. Here Cu/Si multilayers showed to be less resistant as already a single 280 C/1h vacuum annealing resulted in a complete degradation of the interfaces and a rather homogeneous monoloyer was formed. This degradation is presumably connected with the diffusion of Si into Cu layers and formation of '(Cu,Si) phase which has been detected above 100 C. Ni/C multilayers collapsed completely at 350 C after a set of successive cummulative 4h annealings with 50 C step. Therefore the intermixed regions formed at the interfaces during the deposition do not spread in Ni/C multilayers while opposite is the case in Cu/Si ones, though being thinner here at the beginning. A 10% expansion of the multilayer period in Ni/C multilayers was observed before multilayer collapse which may be attributed to a gradual graphitization of the C layers and/or carbide crystallization visible by XRD at 300 C. Similar effect was found in Ni/C multilayers prepared by sputtering [2] or pulse laser deposition [3]. In conclusion, our results show that e-beam evaporation with in situ substrate heating is a promising alternative for preparation of good-quality and thermally stable Ni/C interference mirrors. Cu/Si mirrors may be prepared with still narrower interfaces by this technique, however, suffer from a limited thermal stability. This feature is due to thermodynamical properties of this

element couple and thus poses a general problem regardless the deposition technique.

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sample	D (nm)	$d_{Cu(Ni)}$ (nm)	$d_{Si(C)}$ (nm)	eff (nm)	geom (nm)	lat (nm)	vert (nm)
Cu/Si	3.17	1.27	1.9	0.45-0.5	0.25-0.3	10	30
Ni/C	3.10	1.24	1.86	0.7-0.8	0.3-.4	5	10

T4 - P89

X-RAY DIFFRACTION LINE BROADENING IN THIN LAYERS OF QUATERPHENYL ON C-COVERED GOLD (111)

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Thin films of crystalline organic semiconductors (conjugated molecules) offer promising prospects for future developments in electronic and opto-electronic devices. Defined interfaces, the specific molecular orientation within a crystalline film and large domain sizes are required to enhance the performance of such devices [1-3]. As it is well-known that various conjugated molecules form highly regular structures on metal surfaces, the role of the organic/substrate interactions in determining the final interface- and film-structure is very important and influences the resulting microstructure of the film.

X-ray diffraction line profile analysis is a powerful method to obtain microstructural characteristics [4,5]. Usually applied to thin films of inorganic materials like high T_c superconductors, Indium Tin Oxide (ITO) or coating materials (e.g. see [6]), line profile analysis on organic thin films is a difficult task. The problem is that diffraction peaks of sufficient intensity can only be observed at high d-values (low 2 -angles), and that no standards for the determina-
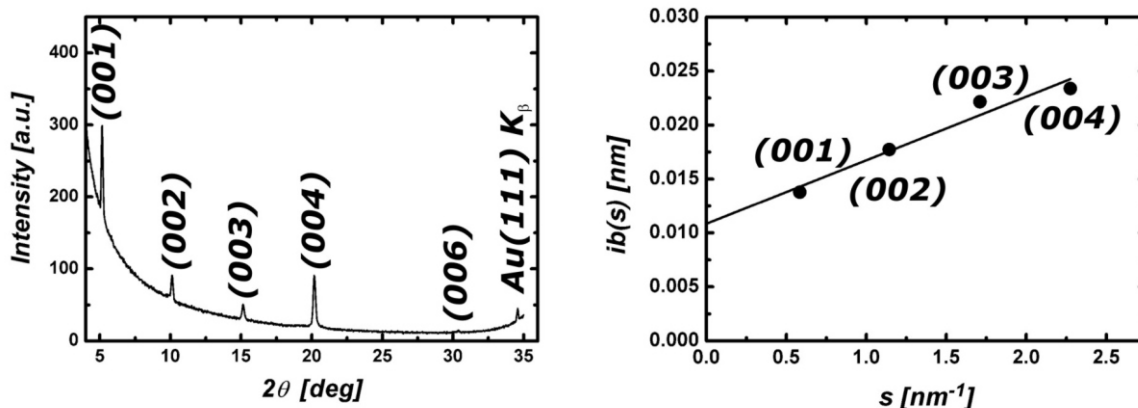
Figure 1: Left panel: /2 scan of the 4P film deposited on C-covered Au(111). Right panel: Williamson-Hall plot of the (00l)-peaks. Only the peaks (001) to (004) could provide enough intensity for a peak shape analysis. The line is a linear least squares fit.

tion of the instrumental broadening are available in this region. Another problem is the low diffracted intensity of thin films, especially as the organic material consists of matter with low atomic mass which have low scattering cross sections.

In this study we concentrate on the system *para*-quaterphenyl ($C_{24}H_{18}$, 4P) on C-covered Au(111). The films were prepared at room temperature with a rate of 0.3 nm/min with a thickness of about 30 nm. The mean film thickness was monitored by a water-cooled quartz crystal microbalance during the evaporation process [7-9]. The diffraction pattern were collected with a Siemens D501 diffractometer with copper K radiation and a secondary graphite monochromator in Bragg-Brentano geometry. Only reflections of net planes parallel to the surface of the substrate can be detected in this geometry. The line profile analysis of these recorded pattern reveal size and strain information perpendicular to the substrate surface. The morphology of the films is studied by atomic-force microscopy (AFM) using a Nanoscope IIIa system (Digital Instruments, Santa Barbara, CA) in tapping mode. Both, the x-ray and the AFM measurements were performed *ex situ* under ambient conditions.

The accuracy of the line profile analysis depends crucially on the separation of the instrumental broadening from the intrinsic sample generated broadening. Lanthanum hexaboride (LaB_6 - NIST, Standard Reference Material 660a) was used to determine the instrumental broadening. For an analytical expression of the broadening the Caglioti *et. al.* model [10] was adopted to the LaB_6 reference material. The instrumental broadening is taken into account in order to obtain the pure fraction of the investigated sample. This remaining broadening consists of two different contributions: size and strain. To separate them the Williamson-Hall analysis [11] is applied:

$$b(s) \quad \frac{1}{\langle l \rangle_V} \quad \sqrt{2 \langle {}^2 \rangle} s$$

With: s the length of the scattering vector, $b(s)$ the integral breadth of the peak. $< l >_V$ the volume weighted column length, which is in this case the volume weighted crystal size perpendicular to the surface. $< {}^2 >$ is the mean square (local) strain, whereas the whole root expression is the root mean square strain (rms strain).

Figure 1 shows the x-ray diffraction pattern of the sample. Scattered intensity is detected for the net plane (001) and its higher order reflections. All single peaks are fitted with pseudo-Voight shaped profile functions and the instrumental broadening is considered (for more details see e.g. [12,13]), as this task is essential for this method. Figure 2 is a Williamson-Hall plot of all (00l) peaks with reasonable intensity. The results of the Williamson-Hall analysis are: $1/< l >_V = (0.011 \pm 0.001)$ nm and $= 0.006 \pm 0.001$. This results in a volume weighted crystal size of around 90 nm. The value for the rms strain is typical for vapour deposited organic films [4,5].

4P forms a layer-like, continuous film with a granular morphology (see Figure 2). The grain structures have lateral dimensions in the length scale of 1 ěm. These AFM images give us a hint towards the lateral surface dimension of the 4P structures that is not the true lateral dimension of the crystallites. Comparing the mean film thickness of 30 nm (obtained by the microbalance measurement) and the vertical roughness of the surface, it can be concluded that the local thickness of the film can range from several nm up to a few hundred nm. These values match the value obtained from the Williamson-Hall analysis, because the 90 nm are volume weighted crystal sizes, where the contribution of bigger crystallites is more pronounced than smaller crystallites. As AFM is a pure surface technique it is impossible to decide if the crystallites extend down to the substrate, but on the other side there can only be very few crystallites on top of each other. In this context the value of 90 nm seems representative for the investigated film and shows the applicability of this method for organic thin layers.

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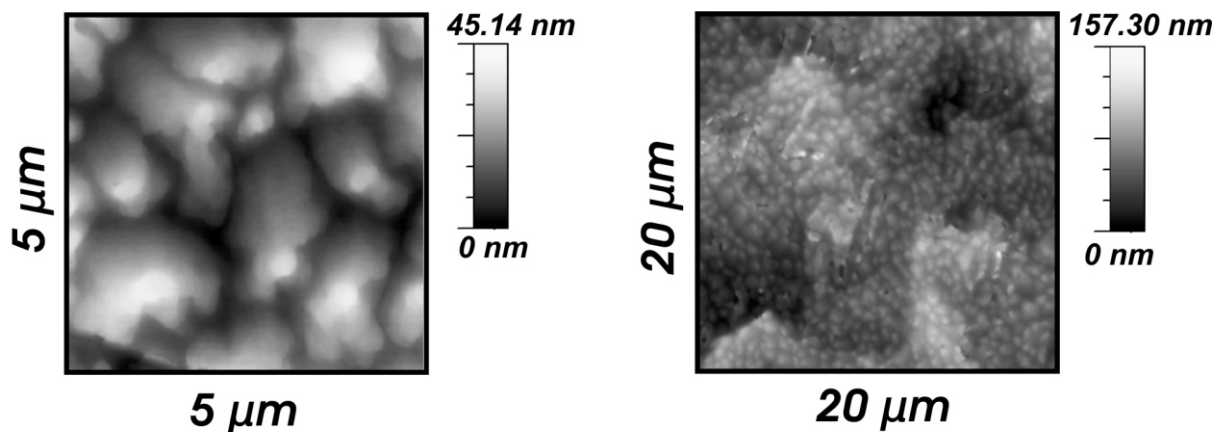
Figure 2: AFM results: The left image is a magnification of the overview scan shown at the right side. The morphological structure seems to be uniform over a large area of the sample.

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T4 - P90

X-RAY RESIDUAL STRESS MEASUREMENT IN TITANIUM NITRIDE THIN FILMS

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Thin polycrystalline layers plays substantial role in many of technical applications nowadays. The aim of our study was sintered tungsten carbide material coated with thin layers of TiN, prepared by CVD method. Such materials are extensively used as different kinds of drills and cutting tools because of its specific mechanical, physical and chemical qualities. One of the principal parameter, which reflects in mechanical properties, is presence and magnitude of residual stress.

The samples were characterized using the x-ray diffraction, which is method appropriate for thin layers investigation. The x-ray diffraction measurements were performed using diffractometer (goniometer equipped with an Eulerian cradle) and Cu K radiation. Measure data were corrected for experimental aberrations, using Si standard.

Current work discusses and compares different techniques that are commonly used for x-ray diffraction stress measurements. The residual stress calculations were performed using both - methods based on the diffraction elastic constants and mechanical elastic constants as well.

We also discuss various grain interaction models (Reuss, Voigt and Neerfeld-Hill) and its influence on calculated results.

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T4 - P91

DIFFUSE SCATTERING FROM GAN THIN FILMS

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Nowadays, electronic devices based on thin films of GaN are especially used for blue-light lasers. Thin films of galium nitride are grown on different substrates - SiC, sapphire, bulk GaN for instance. During the growth proccess, even on bulk GaN, misfit and threading dislocations are formed. These defects strongly affect electronic properties, namely a carrier mobility.

Concentration of mentioned defects can be determined either by transmission electron microscopy either from diffuse x-ray scattering. The later method has a big advantage comparing to TEM it is a nondestructive method.

Theory of diffusively scattered x-ray's caused by randomly distributed defects was developed by Krivoglaz [1]. Intensity of diffuse scattering is given by

$$I(q_x, q_z) \quad dx \int_t^0 dz \int_t^0 dz' \exp[i(q_x x \quad q_z(z \quad z'))]$$
$$\exp[\quad T(x; z, z')] \qquad (1)$$

where t denotes thickness of the film and $T(x;z,z')$ is the so-called correlation function which is defined by a displacement field due to defect:

In (2), we sum over all types of defects , u (**r**) denotes the displacement field caused by defect at the origin at

$$T(|\mathbf{r} \quad \mathbf{r}'|; z, z') \qquad\qquad d\mathbf{r}''\{1 \quad \exp[\quad ih \quad (u \quad (\mathbf{r} \quad \mathbf{r}'') \quad u \quad (\mathbf{r}' \quad \mathbf{r}''))]\} \qquad\qquad (2)$$

point **r**. Formulas for displacement fields from strait dislocations can be found elsewhere [2].

In our work we present analysis of reciprocal space maps measured on thin films of GaN grown on different substrates, SiC and sapphire. All measurements were provided utilizing X'Pert MRD high resolution diffractometer. Densities of screw threading dislocations with Burgers vector **b** || [001] and of edge dislocations (**b** || [110]) were determined.

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