

537th WE-Heraeus-Seminar

HZDR

Physics of Ionized and Ion-Assisted PVD: Principles and Current Trends

June 26 to June 28 2013

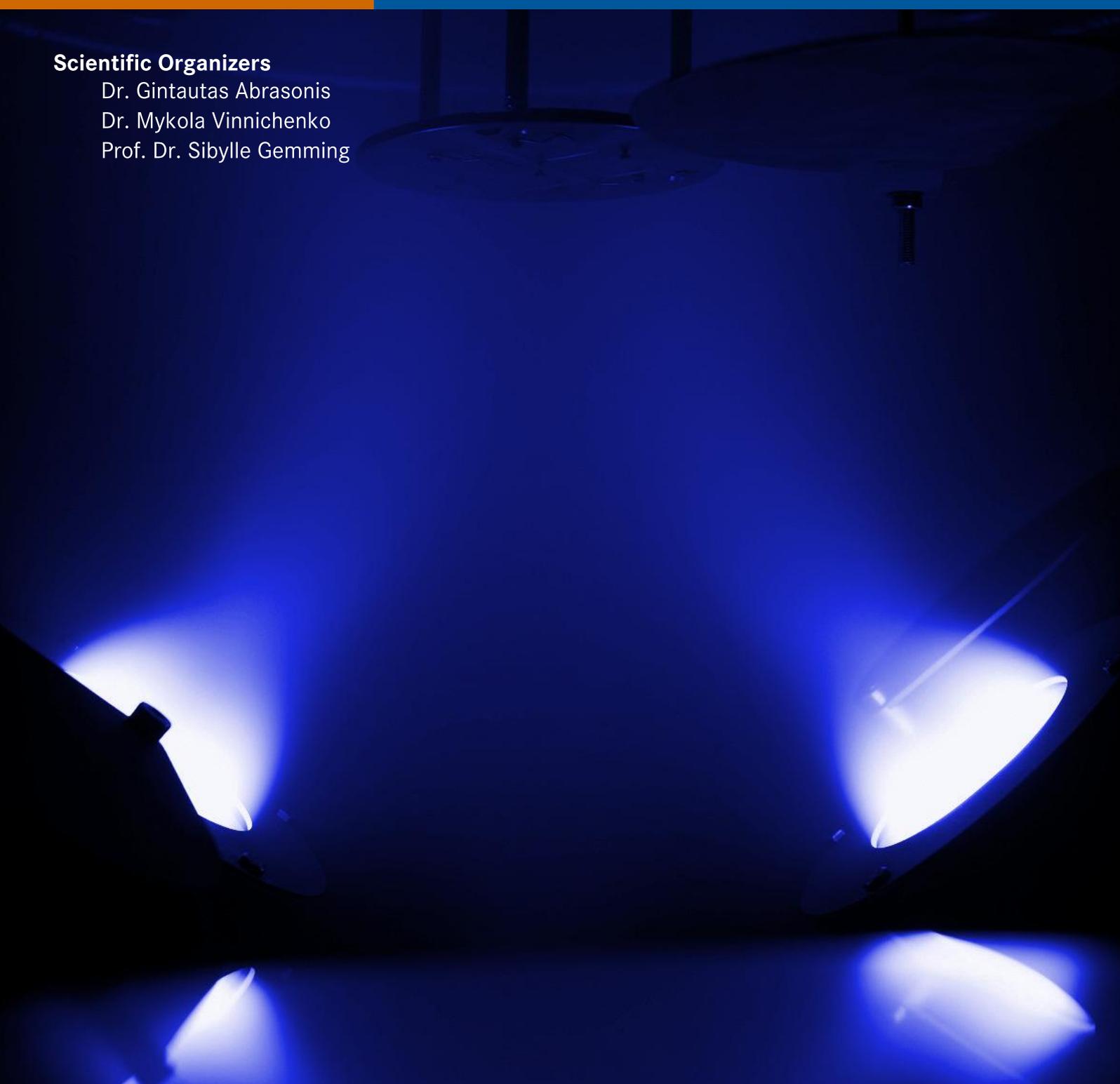
 **HELMHOLTZ
ZENTRUM DRESDEN
ROSSENDORF**



Program | Talks | Posters | Participants

Scientific Organizers

Dr. Gintautas Abrasonis
Dr. Mykola Vinnichenko
Prof. Dr. Sibylle Gemming



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Contents

1 Program	3
2 List of Talks	4
3 List of Posters	5
Poster flash I	5
Poster flash II	7
4 Abstracts of Talks	10
Wednesday, June 26	10
09:00 Ion-Surface Interactions in Thin Film Processing	10
10:30 Generation and properties of highly ionized plasmas for thin film deposition	12
11:15 Plasma Diagnostics in i-PVD	14
14:00 Ion-assisted Deposition	16
15:30 Ion Beam Assisted Deposition	22
16:15 i(a)-PVD of functional oxide materials: magnetron sputtering of transparent conductive oxides	24
17:00 Ion-Beam Induced Crystalline Alignment during Film Growth	28
Thursday June 27	30
09:00 Basic processes in ionized-PVD	30
10:30 HiPIMS - Basics	32
11:15 High-rate reactive deposition of oxide and oxynitride films using high-power impulse magnetron sputtering	34
12:00 HiPIMS for ice free windshield applications	36
14:00 Introduction to Pulsed Laser Deposition (PLD) as a versatile prepara- tion method	38
15:30 Combinatory epitaxy of oxides films made by laser ablation: from single crystals to polycrystalline substrates	42
16:15 Hybrids of Pulsed Laser Deposition with PVD methods for Nanocom- posite Film Growth	44
Friday, June 28	48
10:30 Cathodic Arcs	48
11:15 Vacuum Arc Deposition and its Applications	50
5 Abstracts of Posters	52
6 Other participants	86
7 List of Participants	92

1 Program

Timetable for the WE-Heraeus-Seminar, Dresden, 06-26-2013 – 06-28-2013

Time	Tue 06-25	Wed 06-26	Thu 06-27	Fri 06-28	
		7:45 Bus transfer to HZDR	8:00 Bus transfer to HZDR		
8:45		Welcome		Tram to IWS	
9:00		Möller Ion solid interactions	Schneider Basic processes in i(a)-PVD		
10:00			Coffee break		
10:30		Anders High density plasmas	Helmerson HiPIMS - Basics	Bilek Arcs - Basics	
11:15		Bradley Plasma diagnostics	Vlcek HiPIMS oxides/oxinitrides	Leson Industrial application of Arcs	
12:00		Posters flash I	Szyszka HiPIMS oxides	Final discussion	
12:45			Lunch		
14:00		Colligon IAD - basics	Hühne PLD - basics		
15:00			Coffee break	Visit IWS	
15:30		Rauschenbach IAD - Methods & Application	Prellier PLD application		
16:15		Ellmer IAD for oxides	Voevodin PLD hybrids		
17:00	Arrival at hotel and registration	Matias IBAD of buffer layers		Optional: Visit the Grünes Gewölbe Departure	
17:45		Posters flash II	Introduction to ion beam center		
18:15		Posters, drinks and sandwiches	Visit HZDR Bus transfer downtown		
20:00		Bus transfer to hotel	Conference dinner Poster Awards		
	Basics	IAD	HiPIMS	PLD	Arc

2 List of Talks

Wednesday, June 26

Basics

9:00-10:00	W. Möller	Ion-Surface Interactions in Thin Film Processing
10:30-11:15	A. Anders	
11:15-12:00	J. W. Bradley	Plasma Diagnostics in i-PVD

IAD

14:00-15:00	J. Colligon	Ion-assisted Deposition
15:30-16:15	B. Rauschenbach	Ion Beam Assisted Deposition
16:15-17:00	K. Ellmer	i(a)-PVD of functional oxide materials: magnetron sputtering of transparent conductive oxides
17:00-17:45	V. Matias	Ion-Beam Induced Crystalline Alignment during Film Growth

Thursday, June 27

Basics

9:00-10:00	J. M. Schneider	Basic processes in ionized-PVD
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HiPIMS

10:30-11:15	U. Helmersson	HiPIMS - Basics
11:15-12:00	J. Vlcek	High-rate reactive deposition of oxide and oxynitride films using high-power impulse magnetron sputtering
12:00-12:45	B. Szyszka	HiPIMS for ice free windshield applications

PLD

14:00-15:00	R. Hühne	Introduction to Pulsed Laser Deposition (PLD) as a versatile preparation method
15:30-16:15	W. Prellier	Combinatory epitaxy of oxides films made by laser ablation: from single crystals to polycrystalline substrates
16:15-17:00	A. A. Voevodin	Hybrids of Pulsed Laser Deposition with PVD methods for Nanocomposite Film Growth

Friday, June 28

Arc

10:30-11:15	M. MM Bilek	Cathodic Arcs
11:15-12:00	A. Leson	Vacuum Arc Deposition and its Applications

3 List of Posters

Poster flash I

June 26, 12:00 – 12:45

poster no.	presenter	title	abstr. p.
P01	B. Zimmermann	Hollow cathode arc enhancement in reactive PVD processes	85
P02	R. Würz	Influence of hollow cathode plasma activation on the growth of Cu(In, Ga)Se ₂ thin films	83
P03	S. Muhl	CHRAVA a more or less new thin film arc evaporation technique	72
P04	R. Bonet	Study of the performance of two macroparticle filter configurations implemented to an industrial PVD cathodic arc evaporation reactor.	55
P05	C. Vitelaru	Time resolved tunable diode laser spectroscopy in HiPIMS discharge for the spatio-temporal description of neutral species	81
P06	R. Feuerfeil	Position and Bias Dependent Optical Examination of a HiPIMS Plasma Discharge	5
P07	M. Hans	Energy-resolved mass spectrometry of an Al/Ar/O ₂ HPPMS plasma	64
P08	C. Wilde	Ion Energy Distributions in DC magnetron sputter deposition of Al-doped Zinc oxide	82
P09	T. Minea	2D PIC modelling of HiPIMS plasma. Application to spokes simulation by pseudo 3D-PIC	71
P10	O. Khvostikova	Applications of Monte Carlo simulation techniques at VON ARDENNE	67

poster no.	presenter	title	abstr. p.
P11	R. Franz	Angular dependency of ion energy distributions and NbO _x thin film growth in HiPIMS plasmas	59
P12	P. Barker	Ti and TiN: sputtering at increased deposition rate using chopped HiPIMS.	53
P13	I. Shchelkanov	High Current Impulse Magnetron Discharge. Influence of the single pulse power on a deposition rate.	77
P14	R.-K. Yadav	Growth of carbon-tungsten nanocomposites by high power impulse magnetron sputtering from compound targets	84
P15	L. Gao	Magnetron-sputtered Tungsten-Nitride Films as Model for Nitrogen-implanted Tungsten Surfaces	59
P16	G. Abromavicius	Properties of thin HfO ₂ , Nb ₂ O ₅ , Ta ₂ O ₅ films and HR coatings deposited by ion-assisted deposition	52
P17	P.J. Jobst	Polishable silicon coatings for the manufacturing of ultra-precise optical components	66
P18	T. Tolenis	Investigation of TiO ₂ and Nb ₂ O ₅ materials produced by Ion-Assisted PVD	78
P19	R. Feder	Influence of process parameters on thin film properties of ion beam sputter deposited Ag	57
P20	P. Pahlke	Ion beam textured TiN as template for YBa ₂ Cu ₃ O _{7-x} coated conductors	74

Poster flash II

June 26, 17:45 – 18:15

poster no.	presenter	title	abstr. p.
P21	M. Kühn-Kauffeldt	Triggerless vacuum arc plasma deposition of titanium oxide coatings on polymer tubes for medical application	70
P22	I. Tsyganov	Development of novel titanium-based surfaces using plasma and ion beam technologies	79
P23	V. Vishnyakov	Influence of preparation conditions on evolution of Titania phases	80
P24	M. Neubert	Magnetron Sputtering of low resistivity TiO ₂ -based transparent conductive oxides and the role of energetic particles	74
P25	A.A. Mosquera	Surface plasmon absorption in Ag containing amorphous TiO ₂ films grown by pulsed cathodic arc	72
P26	M. Jerčinović	Self-organization of nickel nanoparticles in dielectric matrices	65
P27	M. Krause	Ion-guided microstructure evolution of carbon-nickel nanocomposite films during ion beam assisted deposition: 3D sculpting at the nanoscale	68
P28	E. Guillen	Optical Selectivity Enhancement of Carbon-based nanocomposites: Simulation and Experiments	62
P29	S. Potocký	Characterization of Microwave Surface Wave Plasma in Linear Configuration and Growth of Nano-Sized Carbon Allotropes	75
P30	G. Englberger	Study of plasma filtered DLC films produced on industrial scale	56
P31	A. Pardo	Sheath thickness and microstructure in amorphous carbon thin film	75

poster no.	presenter	title	abstr. p.
P32	H. Grüttner	Fundamental Studies on the Deposition of Nanocrystalline Diamond (n-D) Films by Means of Pulsed Laser Deposition (PLD)	61
P33	M. Günther	DLC coatings for Automotive Applications of the Bosch Group	63
P34	R. Bertram	Effects of Pulsed Laser Irradiation of As-Deposited c-BN-Films using Photons of 157 nm Wavelength and Multi layers of h-BN/c-BN Bilayers and their Properties	54
P35	E. Almandoz	PVD nanostructured systems with high resistance to mechanical fatigue for industrial applications	53
P36	M. Evaristo	Deposition of Alloyed Transition Metal Dichalcogenides by Magnetron Sputtering Using Different Approaches	57
P37	M. Krug	Al ₂ O ₃ protective coatings on carbon fiber-based 3D-textile preforms prepared by ALD for application in metallic composite materials	69
P38	F. Nahif	Effect of ion energy and deposition rate on the phase formation of Al ₂ O ₃ thin films grown by filtered cathodic arc	73
P39	C. Wüstefeld	Microstructure design of TiAlN based coatings via energetic particle bombardment during cathodic arc evaporation	82
P40	D. Grochla	Time- and space-resolved high-throughput characterization of stresses during sputtering and thermal processing of Al-Cr-N thin films	60
P41	L. Shang	Oxygen Incorporation in Cr ₂ AlC Investigated by Combinatorial Thin Film Synthesis and X-Ray Stress Analysis	77
P42	C. Mastail	Growth-induced defect generation and intrinsic stress in Ta sputtered films: a comparison between α -Ta and β -Ta phases	70

4 Abstracts of Talks

Wednesday, June 26

09:00 Ion-Surface Interactions in Thin Film Processing

Wolfhard Möller

Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany,

w.moeller@hzdr.de

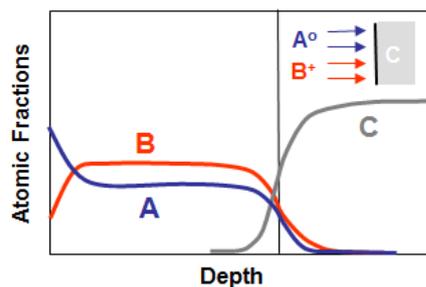


Figure 1: Compositional computer simulation of ion-assisted deposition of thin films using TRIDYN.

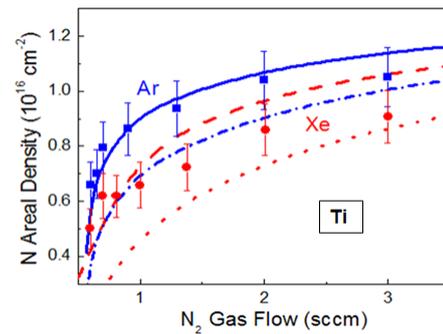


Figure 2: Modeling of target poisoning during reactive magnetron sputtering of TiN.

The lecture will address the interaction of fast atoms with solid surfaces with special emphasis on PVD surface processing. Initially, a short course on ion-surface interaction will address the basic processes of ion stopping and ranges, ion-induced damage, sputtering, ion mixing, and secondary electron production. Special emphasis will be directed to collisional computer simulation tools (TRIM, TRIDYN). Subsequently, common PVD variants will be characterized in terms of the involved irradiation conditions. The main parts of the lecture will then describe target interaction processes during magnetron sputtering and address general aspects of ion-assisted deposition, including the influence of ion bombardment on stoichiometry, structure and morphology of the growing film. A brief phenomenological display of self-organised multilayer formation will conclude the presentation.

Space for your notes

10:30 Generation and properties of highly ionized plasmas for thin film deposition

André Anders

Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94530, USA

Ionized and ion-assisted physical vapor deposition, which collectively shall be called i-PVD, is based on the supply of ions from a suitable plasma source. There are many options, with the selection of plasmas depending on the application. In this overview, popular choices will be discussed: sputtering with post-sputter ionization, high power impulse magnetron sputtering (HiPIMS), hollow cathodes, pulsed laser deposition, (filtered) cathodic arcs, and thermionic arc ion plating, to name the most important. Each of the methods delivers plasma with distinct properties and each has specific advantages and disadvantages in terms of area processed, uniformity, scalability, reproducibility, rate, and cost.

The field of research is quite active, with new discoveries and deeper understanding emerging, for example, in HiPIMS. Plasma diagnostics with high spatial and temporal resolution revealed the existence of traveling ionization zones (Fig. 1). They are critical for the operation of the discharge and for the production of the plasma utilized at a substrate. Ionization zones modify the local electric field over the target and produce plasma flares or jets leaving the target area in directions perpendicular as well as close to tangential relative to the target surface. Example measurements will be presented including high speed imaging and electrical probes.

Another example of research, and renewed interest in general, is the utilization of filtered cathodic arc plasma. Such plasma can deliver a high flux of ions with a favorable range of ion energies (several 10s of eV in kinetic and often > 10 eV in potential energy). Arc discharges are relatively easy to operate especially for reactive systems compared with reactive sputtering. This will be illustrated by the interesting case of doped zinc oxide, a transparent conductor.

Bibliography

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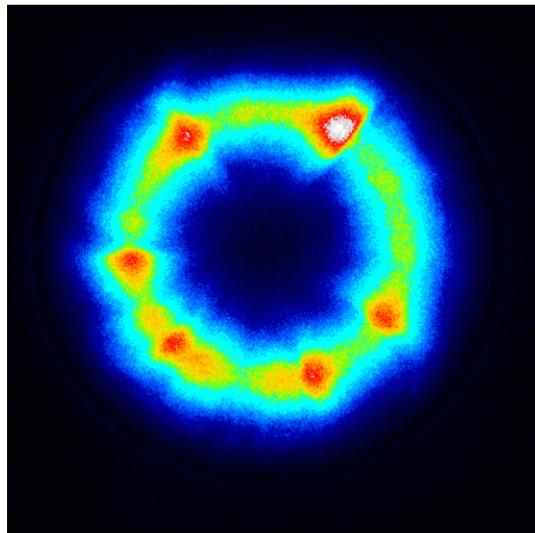


Figure 1: False color image of a niobium HiPIMS discharge in 0.3 PaKr, taken with an image exposure time of 10 ns; 5 cm diameter target, 150 A peak current, 138 A current at the moment of image taking, 50 μ s pulse, 200 Hz. The false color indicates intensity of emitted light, integrated over the visible spectrum [1].

Space for your notes

11:15 Plasma Diagnostics in i-PVD

James W. Bradley

Dept. of Electrical Engineering and Electronics, University of Liverpool, Liverpool, United Kingdom
j.w.bradley@liv.ac.uk

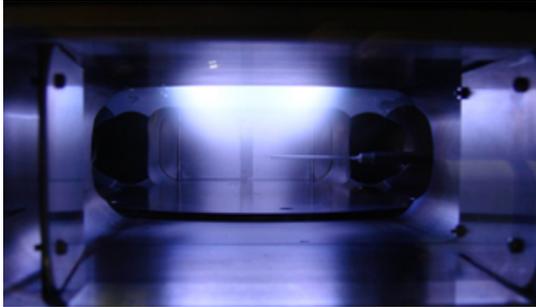


Figure 1: Photograph of a DC magnetron discharge operating in pure argon. The discharge is a typical purple-blue colour. A single Langmuir probe and stem can be seen in the plasma, used to obtain information on the plasma parameters.

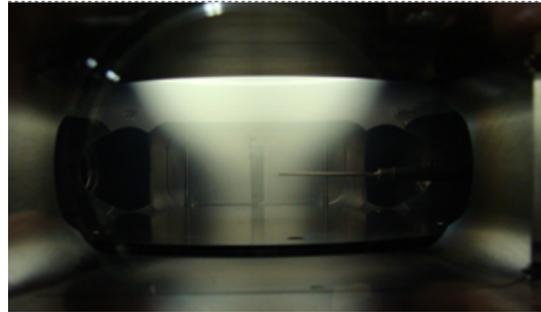


Figure 2: Photograph of a pulsed DC magnetron discharge operating in oxygen-argon mixtures. The discharge is a milky white. The plasma can be seen to have a different structure to that when operated in argon, with a greater axial extension.

Over the last 20 years, pulsed magnetron sputtering in the mid-frequency range (20 to 350 kHz) has become a valuable industrial technique for the deposition of engineering quality thin films and coatings, including dielectric materials. Recent developments in pulsed-magnetron technology include the exciting area of HIPIMS. These discharges operate at low frequency (50 to 500 Hz) but with ultra-high powers applied to the discharge.

In this presentation, the speaker will review many of the plasma diagnostic techniques (both electrical and optical) currently used to measure and monitor the plasma parameters in these pulse-modulated devices (including HIPIMS). The diagnostic techniques discussed will also be highly relevant to other low-pressure I-PVD systems.

In particular, the talk will review some of the basic underlying principles and theory of operation of intrusive (perturbing) electrical techniques to derive the temporal and spatial evolution of the plasma parameters (temperatures, densities, potentials, fluxes,

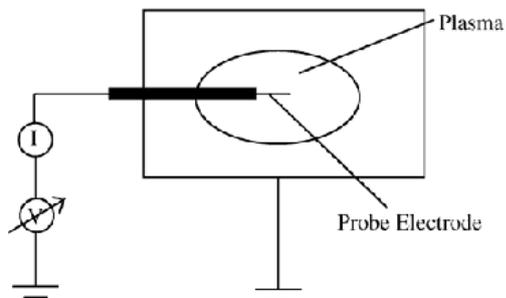


Figure 3: Typical Langmuir probe electrical arrangement.

etc.). These will include Langmuir probes, (single, double and triple configurations); emissive and heat flux probes; B-dot probes and energy-resolved mass spectrometry. Other techniques incorporating lasers such as photo-electron detachment will be discussed as a means to observe negative ion species in reactive configurations. In addition, the non-perturbing measurement techniques of optical emission spectroscopy and fast 2-D imaging will be introduced at a basic level. For each chosen diagnostic tool, it will be shown how that particular technique can yield interesting information on physical phenomena occurring in the plasma, such as hot electron creation, anomalous charged particle transport and existence moving structures. Some of the pitfalls and problems associated with electrical probes and analysers in pulsed discharges excited by rapidly changing voltages (and with therefore highly modulated plasma parameters) will be discussed.

Space for your notes

14:00 Ion-assisted Deposition

John Colligon

Dalton Research Institute, Manchester Metropolitan University, Manchester, UK, M1 5GD.

j.colligon@mmu.ac.uk

This abstract is intended to give a broad outline of the talk and the points identified will be covered in much greater detail in the oral presentation. Ion-assisted deposition of thin films (IAD) has been studied over many years. The term “ion-assist” implies “energy-assist” where a beam of energetic ions bombards the surface of a coating as the film grows. The material forming the coating is either evaporated or sputtered in the same vacuum chamber. The principal elements of the process are shown schematically in Fig. 1.

The additional energy provided by the ions is the key to many of the modern coating methods. These include, in order of increasing fraction of ionised species reaching the substrate, unbalanced magnetron sputtering (UBMS), closed-field UBMS, High Power Impulse Magnetron Sputtering HiPIMS) and Steered Arc Ion Sputtering. The effect of the additional energy, usually of order 30 to 100 eV per atom, brought to a surface by the ions is an increase in surface movement of the deposited atoms allowing these to locate to better sites. The collisional energy can also knock in atoms and densify the material. For higher ion-assist energies a rapid-quenching process can occur which can allow formation of phases normally associated with much higher temperatures. For example Averbach et al [1] calculated that 5 keV Cu ions bombarding a Cu sample create a 2 nm dia region containing atoms which move at an effective temperature of 5000 K only 0.25 ps after the impact. This region then rapidly cools at rates equivalent to 1014 K per second and can have a dramatic effect on the microstructure and phase of the bombarded material. This changes the whole nature of a surface coating when compared with standard room temperature deposition. The morphology of coatings formed using the non-ion-assisted method were shown to be related to the ratio T_s/T_m (substrate temperature and coating material melting temperature, respectively) by Movchan and Demchisin [2]. This guideline is simply based on the fact that for $T_s > T_m$ the coating material is able to migrate and form more stable bonds. During the initial stages of ion-assistance some substrate atoms (which would otherwise be ejected as sputtered atoms) move into the coating material and some film atoms are driven into the substrate to form an ion beam mixed layer, thereby improving the adhesion of the coating.

An example of the effect of IAD on microstructure, taken from the author’s own work, is the structure of a Titanium coating deposited with, or without Ar ion-assistance (Fig. 2). The columnar growth, typical of conventional PVD coatings is completely absent even with a low degree of ion-assistance of 1 Argon ion for every 2 Titanium atoms.

The densification of the deposited material by IAD is well predicted by computer models. Muller [3] showed that knock-on collisions can account for some of this densification process owing to the pervading inwardly-directed momentum of atoms which displace previously deposited atoms situated above vacancies into the open voids. A practical demonstration of this densification was provided by Martin et al [4] for O₂ ion-assisted deposition of Zr which was shown to be 14% more dense than Zr films formed without

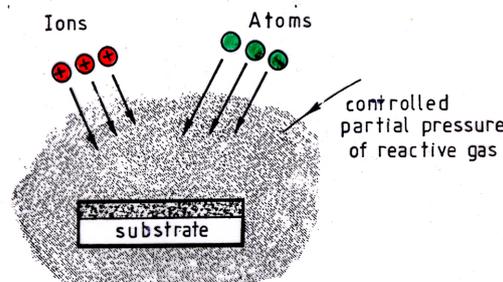


Figure 1: Main parameters for IAD of reactive coatings.

IAD.

Some of the earliest ideas on energy-assisted coating were developed by Berghaus in 1938 who filed a patent in the UK on “Improvements in and relating to the coating of articles by means of thermally vaporised material” [5]. In this development an electron beam was used to evaporate the coating material. This also served to promote ion formation so that the coated substrate was bombarded by ions during film growth. The main thrust for industrial application of this process was however led by Mattox in the 1960’s [6] with significant improvements following in terms of adhesion and performance of coated products compared with the earlier evaporation systems. The non-earthed substrate in the ion-plating plasma, as in all plasmas, develops a small negative voltage of order 30 eV. Kaufman and colleagues realised that an ion thruster source developed for steering space vehicles would have great potential for controlled studies of IAD [7] in which ion energy, ion to atom arrival ratio and ion species could be varied to find optimum IAD conditions.

This studies of IAD parameters began with these, and similar, ion sources. Harper et al [8] gathered together sets of reported data on IAD

and produced a graph of ion/atom ratio against energy. This showed that almost all reported property changes (stress reduction, adhesion, step-coverage) occurred in a region where the added energy per depositing atom had a value between 1 to 100 eV. Martinu et al [9] have extended this data with new data from microwave and RF systems used to form oxide coatings. These oxide coatings were found to require just below 100 eV per atom and it was seen that, for optical coatings, lower ion energies were needed.

This means that there is a further restriction on the choice of parameters to be used for IAD. This is not only limited to the magnitude of the specific added energy per atom, but also, to the maximum ion energy. This is clear from simple models of ion and damage ranges in materials. A 1 keV ion will penetrate several nanometres and create many atomic displacements leaving a damaged material with properties and performance quite different from the pure undamaged material. Adibi et al [10] showed this effect for deposition of TiAlN by applying the same energy per atom during deposition but different combinations of number of bombarding Nitrogen ions and ion energy. For 20 eV ion energy and varying ion/atom ratio the N content in the coating remained almost constant, whereas, for fixed ion/atom ratio and varying ion energy to 100 eV, the N level in the coating increased. Structural and lattice parameter changes in the coating were also reported. These types of changes are important, particularly for optical coatings.

Dark field TEM image, samples are grown at 473 K

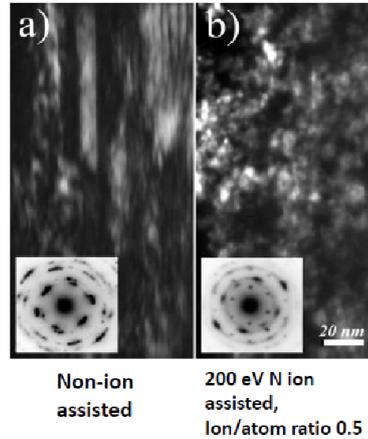


Figure 2: Showing the cross-sectional microstructure for TiN coatings deposited without and with ion-assistance.

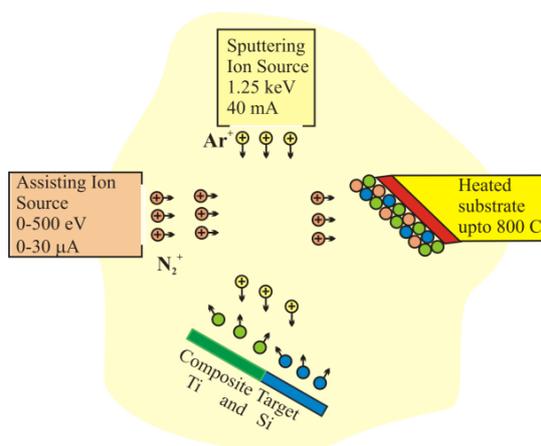


Figure 3: Dual ion beam system used for production of nanocomposite TiSiN hard coatings.

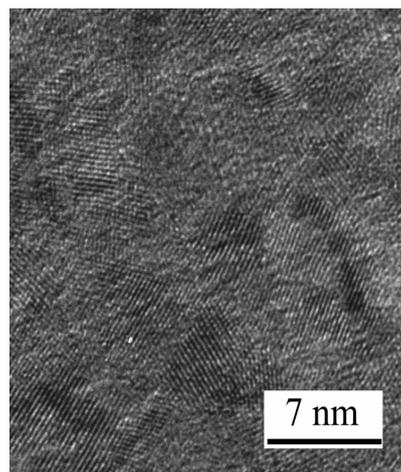


Figure 4: HRTEM of Ti-Si-N films with 9at.% Si formed using IAD with 400 eV N_2 ions; ion/atom ratio = 1. Crystalline regions of TiN are seen.

The variable nature of the resultant coating as a function of deposition parameters can however be used to advantage. For example the present author has applied a dual ion beam system, shown in Fig. 3, to promote the formation of hard nanocomposite Ti-Si-N films [11]. Under optimum IAD conditions and elemental composition the coating structure develops to form regions of $TiSi_2$ within a thin tissue lattice of Si_3N_4 (see Fig. 4) and this coating then has an increased micro-hardness of order 40 GPa.

Using a similar system so-called MAX phase coatings of Cr_2AlC have been formed which are layered materials where the Cr-C components are separated by Al.

In 1976 Weissmantel [12], working in Chemnitz (then Karl-Marx-Stadt) not far from Dresden, extended the IAD studies to look at reactive deposition where deposited Si atoms were bombarded by nitrogen ions to form Silicon Nitride. In this study the Nitrogen ions bombarded a growing Silicon film and it was shown that stoichiometric Si_3N_4 was formed. However this stoichiometric layer was only produced if the energy of the Nitrogen ions was low enough (N_2 ions at 680 eV were used which have an equivalent energy per arriving N of 340 eV)

This reactive deposition method has been developed in recent years as a means to form nanometer-sized components. For example, Mitsui et al [13] has used a 30 keV liquid metal Ga ion source to form ions which bombard a surface over which a jet of aromatic hydrocarbon gas flows. The ion bombardment breaks the C-H bonds and the carbon is deposited. With suitable manipulation of the substrate a solid structure can be built up to form 3D objects, such as a miniature bellows or spring.

Conclusion

The talk will attempt to cover the current status of IAD of surface coatings in more detail. It will also highlight some additional interesting ion-surface radiation effects which are not strictly related to deposition but, nevertheless, use ion energy to modify a material. One of these is Ion Beam Mixing which is well reviewed by Liu [14]. In this process ions of energy of order a few 100 keV are fired through thin multilayer stacks of materials A-B-A-B... and, by collisions, mix the materials to form alloys or compounds. The present author used this method to form Ni and Co silicides by bombarding a single layer of Ni

(or Co) on silicon with Xe, Kr, Ar and Ne ions [15]. A clear correlation was seen between the number of displacements per atom (dpa) at the interface between the metal and the silicon substrate and the stoichiometry of the silicide formed; for example as the dpa increased the composition would become more Si-rich forming a sequence of compounds for the Ni case from Ni₂Si to NiSi to NiSi₂. For simple near-surface modification the author developed a method known as Dynamic Recoil Mixing (DRM) where a thin layer of material is maintained by balancing the re-sputtering of film material with the arrival rate [16]. This allows continuous intermixing between coating and substrate leading to exceptionally durable thin coatings on materials such as plastics.

Another potential area of interest is Ion Deposition, where an energetic beam from a particle accelerator is slowed down to a few eV and deposited on a substrate. Lawson et al [17] showed that a coating of lead could be formed on steel using ions from an isotope separator and a special retardation system with an electro-optical lens arrangement.

Acknowledgment

I take the opportunity to thank many colleagues who have worked with me over the years and who should take credit for all references to “author’s work” in this review. I also acknowledge funding support from EPSRC and STFC.

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Space for your notes

15:30 Ion Beam Assisted Deposition

Bernd Rauschenbach

Leibniz-Institut für Oberflächenmodifizierung (IOM) Leipzig, Permoserstr. 15, 04318 and

Institut für Experimentelle Physik II, Universität Leipzig, Linnéstr. 5, 04103 Leipzig,

bernd.rauschenbach@iom-leipzig.de

Ion beam assisted deposition is the process of simultaneous thin film deposition and directed ion beam bombardment. Aspects of thin film growth that are beneficially influenced by ion bombardment during film deposition including for example the nucleation density, control of stress, epitaxy and composition, improvement of the adhesion and the possibility of low temperature deposition.

This contribution briefly describes the status of ion beam assisted deposition, the experimental arrangement and the role of the ion energy. The effect of the additional ion bombardment on thin film growth will be discussed, followed by a short review of the compound formation, the interface properties and a consideration of the film growth kinetics under ion bombardment.

This latter point will be described by using a modified thin film standard rate theory.

The stress, texture and epitaxial growth in thin deposited films can be a strong function of the ion energy, temperature and the arrival rate. The influence of these parameters on the orientation of the crystals, the epitaxial growth and the stress development is discussed. The ion bombardment offers an excellent means of control these thin film properties.

The most important trends in the ion beam assisted deposition technique are

1. hyperthermal ion beam assisted deposition (ion energy < 50 eV)
2. pulsed ion beam assisted deposition (pulse frequency up to 25 kHz)
3. the mono-energetic and mass separated low-energy ion beam assisted deposition.

These trends are discussed in this contribution shortly.

Although the ion beam assisted deposition processing is attractive from the research point of view, it must be recognized that practical implication of this technology will find its way to the industrial practice. In the last part of this short review examples are demonstrated for a successful transfer of this technology from the IOM into the industry (photovoltaic and extreme ultra-violet lithography, X-ray microscopy, ultra-thin layers).

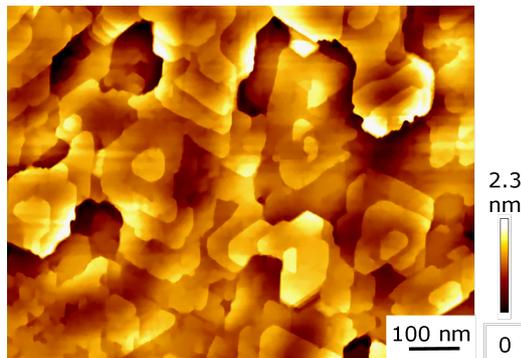


Figure 1: Topography of GaN on 6H-SiC substrates at the beginning of the deposition (film about 10 nm; 3D growth)

Space for your notes

16:15 i(a)-PVD of functional oxide materials: magnetron sputtering of transparent conductive oxides

Klaus Ellmer

Helmholtz-Zentrum für Materialien und Energie, dept. solar fuels, Hahn-Meitner-Platz 1, 14109 Berlin, Germany,

ellmer@helmholtz-berlin.de

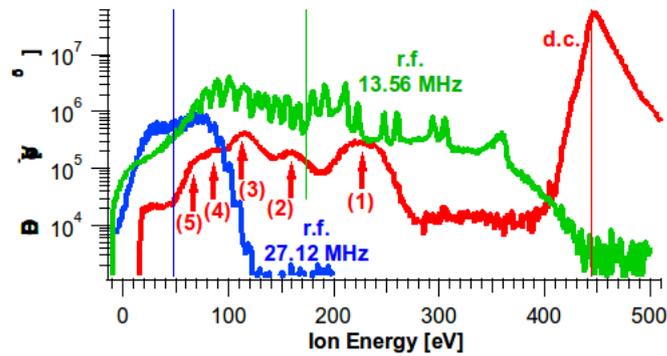


Figure 1: Ion energy distribution functions of O^- for a d.c. and two r.f. discharges (13.56 and 27.12 MHz). The bars represent the energy equivalent to the average target potentials ($-eV_{T0}$). Arrows mark the energetic positions of fragment peaks from larger molecules in the d.c. discharge. The parent molecules from which these O^- peaks result, are: (1) O_2^- , (2) AlO^- , (3) AlO_2^- , (4) ZnO^- , and (5) ZnO_2^- .

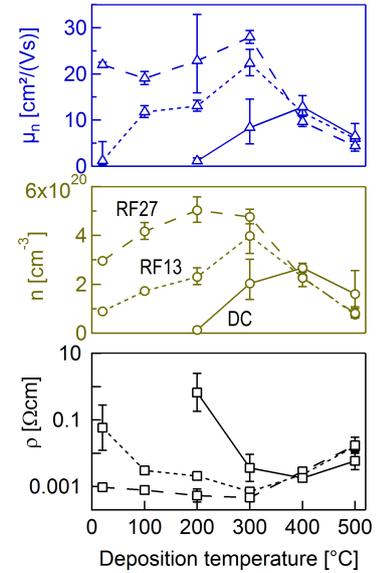


Figure 2: Resistivity, carrier concentration, and Hall mobility as a function of the deposition temperature for 3 different plasma excitation frequencies (solid line: DC, dotted line: RF 13.56 MHz, dashed line: RF 27.12 MHz).

Magnetron sputtering, invented by the renowned plasma physicist Penning already in 1939 [1], is today a widely used large-area, plasma-assisted deposition method for many industrial applications like

- architectural and low emissivity glass coatings,
- hard coatings,
- optical and protective films,
- magnetic layers for hard disk drives,
- transparent electrodes
- thin film solar cells [2],

to name only a few.

In this lecture the potential distribution and energetic species in a magnetron discharge are explained and related to electronic properties of Al-doped zinc oxide, a transparent conductive oxide (TCO), used for instance in thin film solar cells.

The energies of the species contributing and assisting the film growth are significantly higher compared to thermal or plasma-enhanced chemical vapour (PECVD) deposition processes. The sputtered species, forming the deposited film, exhibit energies in the range of some to tens of electron volts. Since in typical magnetron sputtering systems the discharge voltages can reach hundreds of volts, some species, especially negative ions (O-, S-, F- etc.), can even reach energies of hundreds of eV, see Fig. 1 (ref. [3]). This is one of the reasons, why magnetron sputtering is not yet used on an industrial scale for the deposition of active semiconducting films, for instance in thin film solar cells.

By using energy-resolved mass spectrometry we have shown that the detrimental high-energy flux of negative ions is strongly reduced when the discharge frequency is increased from d.c. up to 27 MHz. On the other hand, the often beneficial low-energy ion flux that the positive ions provide is enhanced for r.f. discharges. Thus, these quantitative ion energy and flux measurements explain the empirical fact, that for TCOs and other semiconductors often r.f. magnetron sputtering leads to better films.

This was demonstrated for ZnO:Al films, deposited as a function of the substrate temperature for 3 discharge frequencies: d.c., 13.56 and 27.12 MHz, see Fig. 2 (ref. [4]).

The electrical ZnO:Al film quality (resistivity, carrier concentration and Hall mobility) improves significantly with increasing excitation frequency, which can be attributed to the decreasing target voltage, i.e., a decreasing energy of the bombarding negative oxygen ions. The bowl-shaped dependence of the resistivity and the maxima of both carrier concentration as well as electron mobility can be explained by the ion energy dependent dynamic equilibrium between the formation of acceptor-like oxygen interstitials (Oi) compensating the extrinsic electron donors (AlZn) at lower substrate temperatures and the self-annealing of the interstitial defects at higher deposition temperatures. Higher discharge frequencies reduce the energy of the oxygen ions thus strongly reducing the effect of the oxygen interstitials.

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Space for your notes

17:00 Ion-Beam Induced Crystalline Alignment during Film Growth

Vladimir Matias

iBeam Materials, Inc., Santa Fe, NM 87501, USA,
vlado@ibeammaterials.com

We review ion-beam induced crystallographic texturing during thin film growth. The concept of ion-beam induced crystalline alignment is shown in Fig. 11. During film deposition an off-axis ion beam impinges on the film and induces in-plane crystalline alignment. The early research in this area was led by James Harper at IBM Research Labs in the early 1980's. The IBM Group showed texturing of thin metal films during ion beam assisted deposition (IBAD). The next big step in the field was at Fujikura Ltd. Labs in Japan in the early 1990's in the research group led by Yasuhiro Iijima. The researchers at Fujikura showed texturing of yttria-stabilized zirconia that was sufficiently good to be used as a template for epitaxial growth of cuprate superconductors with high critical currents. The third development, with even better texture, came out Stanford University in the mid-1990's led by Robert Hammond and it is now known as IBAD-MgO or ITaN (Ion Texturing at Nucleation). We discuss what is known for the phenomenology of these processes, focusing primarily on Stanford's and Los Alamos work on IBAD-MgO.

We examined details of crystalline-texture evolution during IBAD of MgO thin films. To perform these experiments we developed a unique experimental methodology based on linear combinatorics. This technique allows us to fabricate film-thickness wedges that maximize data collection and allow us to easily and systematically obtain texture evolution plots. MgO texture evolution can be separated into three different regions. During initial ion beam assisted deposition an amorphous layer is formed which is crucial for obtaining $\langle 100 \rangle$ out-of-plane grain alignment. Onset of texture appears in the first 1 to 2 nm of film deposit when MgO crystallizes. We separate out-of-plane $\langle 100 \rangle$ fiber texture that appears first, followed by in-plane grain alignment along the ion-beam assist direction. Texture improves with continued ion beam bombardment during deposition. Still further improvement is seen with growth of a homoepitaxial overlayer. We have studied texture evolution under different ion beam incidence angles and for combinations of different angles. We have developed an empirical quantification of the texture evolution in both IBAD and homoepitaxial layers. The best texture attained thus far in the MgO template layer on polished metal tape has a FWHM of about 1° . We discuss the use of these artificially crystal-aligned films as templates for epitaxial growth of functional

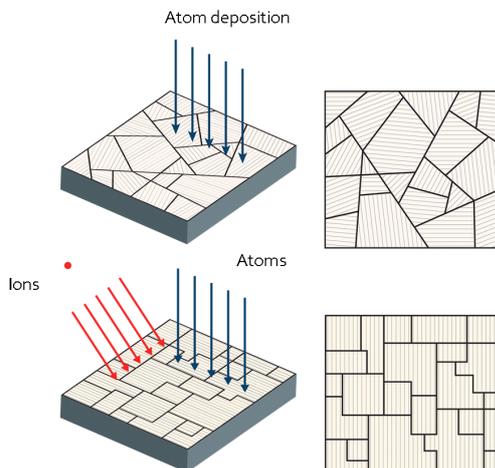


Figure 1: Typical film deposition on a polycrystalline substrate is shown schematically on top and ion induced grain alignment is shown on the bottom.

layers for power applications such as superconductors or photovoltaics.

This work was supported in part by the United States Department of Energy Office of Electricity Delivery & Energy Reliability.

Space for your notes

Thursday June 27

09:00 Basic processes in ionized-PVD

Jochen M. Schneider

Materials Chemistry, RWTH Aachen University,

jochen.m.schneider@googlemail.com

The effect of magnetic fields on the plasma composition for low pressure discharges is reviewed [1] and implications thereof for plasma processing and thin films growth in high vacuum are discussed [2]. The synthesis of protective as well as many multifunctional coatings in industry takes place in high vacuum growth systems. The residual gas in such systems is dominated by water.

Cathodic arc deposition and ionized magnetron sputtering are firmly established industrial synthesis techniques. The chemistry of cathodic arc plasmas is investigated by time-of-flight mass spectrometry as well as by energy resolved mass spectrometry. The hydrogen incorporation from residual gas during cathodic arc [2] and magnetron sputtering [3] is reported and the implications for the elastic and plastic properties of the coatings [4] are discussed. The temporal development of the plasma composition of a pulsed aluminium plasma stream in the presence of oxygen [5] is reported and the charge state resolved ion energy distributions of aluminium ions in a cathodic arc plasma are measured and analyzed [6]. Specifically the IEDFs of Al^+ , Al^{2+} and Al^{3+} were measured as a function of Ar pressure in the range from 5.7×10^{-5} to 2.13 Pa (0.01 to 256 *unitPa cm*).

A close to monoenergetic beam of Al^+ ions was obtained in an Ar/O₂ mixture at 128 Pa cm. Al₂O₃ films are deposited employing this monoenergetic Al^+ beam using a substrate bias potential to increase the ion energy. A critical Al^+ ion energy of 40 eV for the formation of the α – Al₂O₃ phase at a substrate temperature of 720 °C is determined [7]. This energy is used as input for classical molecular dynamics and Monte-Carlo based simulations of the growth process, as well as ab initio calculations [8]. The combination of theory and experiment indicates that in addition to surface diffusion the previously non considered subplantation is an important atomistic mechanism during ionized PVD of alumina [8]. Finally, the origin of O-ions during plasma processing is reviewed [9, 10] and the implications for thin film growth are discussed.

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Space for your notes

HiPIMS

10:30 HiPIMS - Basics

Ulf Helmersson

Dept. of Physics and Measurement Technology (IFM), Linköping University, SE-581 83 LINKÖPING, Sweden

ulfhe@ifm.liu.se

The high power impulse magnetron sputtering (HiPIMS) discharge is a recent addition to plasma based sputtering technology. In HiPIMS, high power is applied to the magnetron target in unipolar pulses at low duty cycle and low repetition frequency while keeping the average power about 2 orders of magnitude lower than the peak power. This results in a high plasma density, and high ionization fraction of the sputtered vapor, which allows better control of the film growth by controlling the energy and direction of the deposition species. This is a significant advantage over conventional dc magnetron sputtering where the sputtered vapor consists mainly of neutral species. The HiPIMS discharge is now an established ionized physical vapor deposition technique, which is easily scalable and has been successfully introduced into various industrial applications. The author give an overview of the development of the HiPIMS discharge, and the underlying mechanisms that dictate the discharge properties. First, an introduction to the magnetron sputtering discharge and its various configurations and modifications is given. Then the development and properties of the high power pulsed power supply are discussed, followed by an overview of the measured plasma parameters in the HiPIMS discharge, the electron energy and density, the ion energy, ion flux and plasma composition, and a discussion on the deposition rate. Finally, some applications of HiPIMS for film synthesis are illustrated

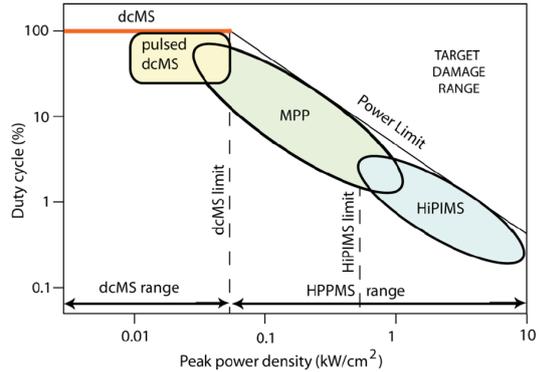


Figure 1: The total power, which is a function of peak power and duty factor, are limited by the target cooling efficiency. The approximative peak power ranges for different sputtering techniques are indicated in the figure [1].

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Space for your notes

11:15 High-rate reactive deposition of oxide and oxynitride films using high-power impulse magnetron sputtering

J. Vlcek and J. Rezek

Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Univerzitni 8, 306 14 Plzen, Czech Republic

vlcek@kfy.zcu.cz

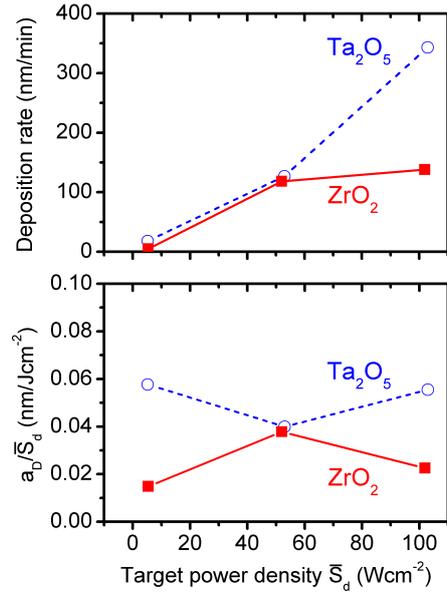


Figure 1: Figure shows deposition rates, a_D , and a_D/\bar{S}_d ratios, characterizing efficiency of the reactive magnetron sputtering, for the ZrO_2 and Ta_2O_5 films at a duty cycle of 10%.

In spite of successful applications of the high-power impulse magnetron sputtering (HiPIMS) to depositions of metallic and conducting compound films, it is still impossible to use the standard HiPIMS discharges with a typical voltage pulse length of 40 to 200 μs for reactive sputter depositions of dielectric films. The reason is arcing on the target surface during the deposition processes at high target power densities. It leads to inhomogeneity and defects in films and to instabilities of the deposition process.

To avoid these problems, we developed a pulsed reactive gas flow control (RGFC). It makes it possible to utilize exclusive benefits of the HiPIMS discharges, such as very intense sputtering, very high degrees of dissociation of RG molecules in the flux to the substrate, strong sputtering wind of the sputtered atoms, highly ionized fluxes of particles to the substrate and higher energies of the ions bombarding the growing films.

In the presentation, we report on details of deposition processes, including an energy-resolved mass spectrometry at the substrate position (energy distribution functions of positive and negative ions, and compositions of the integral fluxes of positive ions), and on films structure and properties. HiPIMS with the pulsed RGFC was used for high-rate reactive depositions of densified stoichiometric ZrO_2 and Ta_2O_5 films, and Ta-O-N films with tunable compositions onto floating substrates at low substrate temperatures (less than 250 $^\circ\text{C}$). The depositions were performed using a strongly unbalanced magnetron

with a planar zirconium or tantalum target (diameter of 100 mm) in argon-oxygen or argon-oxygen-nitrogen gas mixtures at a high average target power density in a period, , being up to 100 Wcm^{-2} . The repetition frequency of the pulsed dc power supply (HPM2/1, Huettinger Electronic) was 500 Hz at duty cycles ranging from 2.5 to 10 %. The total pressure of the gas mixtures was around 2 Pa.

Space for your notes

12:00 HiPIMS for ice free windshield applications

B. Szyszka^{1*}, V. Sittinger², S. Ulrich², M. Vergöhl²

¹Berlin Institute of Technology, Berlin, Germany

²Fraunhofer IST, Braunschweig, Germany

bernd.szyszka@tu-berlin.de

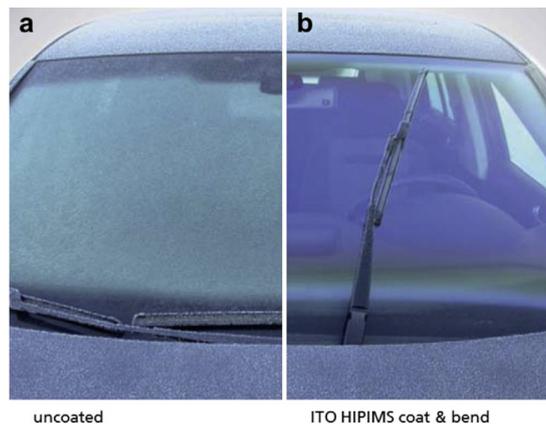


Figure 1: Comparison of frost formation on an uncoated windshield (a) with the frost preventing ITO HiPIMS outside Low-E coating (b) manufactured by coat and bend technology (b). The layer stack is glass / ITO (140 nm) / SiO_xN_y (40 nm).

The performance of glazings can be enhanced by means of functional coatings applied on the outside of the glazing (coating on position 1). This addresses for example the prevention of ice on automotive windshields, anti-reflection coatings and easy to clean coatings. Coating technologies for these applications must fulfill several demands: On the one hand side, the durability of the glass must not be hindered due to application of such coatings. On the other hand side, the coating technology must allow for cost efficient mass production, e. g. deposition on large area flat glass and glass processing after deposition, e. g. cutting, toughening and bending, is highly preferred.

This paper describes the development of the ITO HiPIMS coated ice free windshield which fulfills the demands outlined above where the deposition of very durable, bendable nc-ITO at room temperature has been achieved by means of HiPIMS under highly ionized conditions.

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Space for your notes

PLD

14:00 Introduction to Pulsed Laser Deposition (PLD) as a versatile preparation method

Ruben Hühne

IFW Dresden, Institute for Metallic Materials, Helmholtzstrasse 20, 01069 Dresden, Germany

r.huehne@ifw-dresden.de

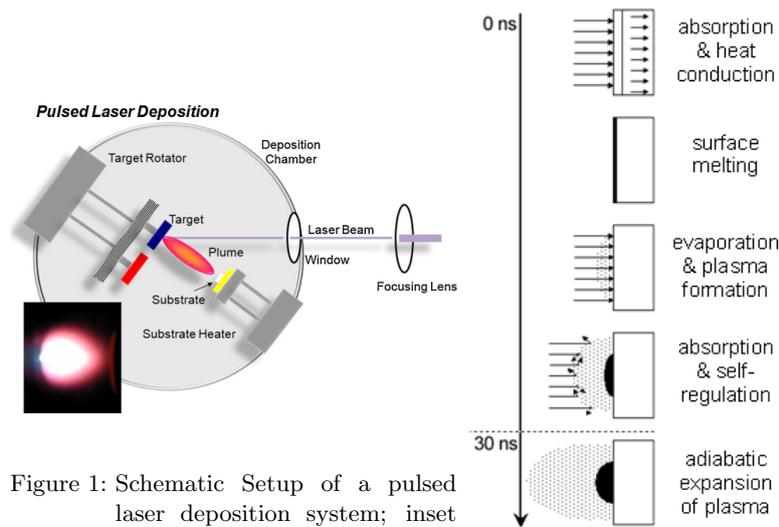


Figure 1: Schematic Setup of a pulsed laser deposition system; inset shows an optical image of a laser plume [19]

Figure 2: Basics steps during ablation process (after Holzapfel [20])

Pulsed Laser Deposition (PLD) is a versatile method for the growth of thin films. Whereas first experiments on this deposition method were already performed in the 1960s [1], it gained only limited interest in the following decades. A major breakthrough for this film growth technique was the successful preparation of epitaxial high temperature superconductors in the late 1980s [2, 3]. Since then PLD got widespread attention and is used now for the preparation of oxide, nitride, metallic, intermetallic or even organic layers.

The schematic setup of a PLD system is shown in Fig. 1. Typically, ns pulsed UV beams originating from excimer or frequency multiplied Nd:YAG lasers are directed to the surface of the target. The absorption of the high intensity laser beam leads to an ablation process of the upper layers of the target material and to the creation of a plasma plume. The plasma is ejected perpendicular from the target and provides the material flux for the film growth taking place on a substrate, which is often placed on a heater at the opposite side of the target.

This deposition technique has a number of advantages compared to other methods

[4, 5]. It provides under optimized growth conditions a stoichiometric material transfer from the target to the substrate even for complex materials and is compatible with a wide range of background pressures (starting from UHV conditions up to about 1 mbar). PLD is in general a clean process as the laser serves as an external energy source. The process has a high flexibility as almost any condensed matter materials can be ablated and a number of different target materials can be used sequentially by the application of a target carousel without breaking the vacuum. Finally, the energetic particles created within the plasma plume with energies up to a few hundred eV as well as the high instantaneous deposition rates can be used for the control of the film growth mode [6] or for the creation of metastable compounds.

Beside these advantages there are also a few drawbacks and challenges connected to the PLD process. The highly forward-directed nature of the plasma plume leads to strong variance of the thickness distribution of the grown films. Therefore, a sophisticated substrate movement is necessary to achieve homogeneous films on larger substrates. Secondly, the ablated material might contain macroscopic pieces (so-called laser droplets) with a size up to 10 μm . The occurrence of such particles is strongly dependent on the material, the target surface morphology and the energy density of the laser spot. Several methods were developed to avoid these droplets as for example the use of an off-axis geometry [7], the application of velocity filters [8] or shadow masks [9] as well as a cross-beam setup [10]. Finally, the bombardment of the film surface with high kinetic energy particles originating from the plasma plume might also create undesired crystallographic defects.

The ablation process itself can be described in several successive steps (Fig. 2)[4, 5]. At the beginning, the optical energy couples to the target material. Typically, the penetration and absorption depth of UV radiation is the nanometer range. The absorption of the laser energy in a short timescale of a few picoseconds leads to a rapid increase of the surface temperature of the target. The limited heat conduction results in a melting of the surface with a rapid propagation of the liquid-solid interface towards the target. Simultaneously, the uppermost layer vaporizes, if the energy density is sufficiently high. The typical vaporized thickness is about 1 to 10 nm, whereas the melt penetration depth might be up to 1 μm . The vaporized material is further heated by the continuing laser pulse creating a plasma, which is accelerated perpendicular from the target into the vacuum. The photon absorption in the plasma shields the target surface from further heating and produces plasma species with high kinetic energies. The plasma expands adiabatically with an angular distribution of the plume, which can be fitted to a $\cos^n(\Theta)$ function with values of n ranging from ≈ 4 to 30. It was demonstrated with time-resolved spectroscopy that ions, atoms or molecules have kinetic energies up to several 100 eV in the plasma. A background gas can be used to moderate these energies to significant lower values.

Due to the flexibility described above, PLD is widely used in research for the growth of thin films of functional materials [11]. Often an epitaxial growth on single crystalline substrates is desired to study the properties of these materials in detail or to tune the functionality for certain applications. Laser ablation might be used for reactive processes in an ambient gas atmosphere as applied for the growth of nitrides, carbides or oxides from elemental targets [5, 12, 13]. More recently, PLD was combined with an in-situ reflection high-energy electron diffraction (RHEED) control of the film surface allowing a precise layer-by-layer growth to realize multilayers and superlattices [14, 15, 16]. This approach is often termed as Laser MBE [17]. Finally, ion beam assisted PLD was successfully used to influence the texture of the growing film by the application of an additional ion gun on the substrate [12, 18].

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Space for your notes

15:30 Combinatory epitaxy of oxides films made by laser ablation: from single crystals to polycrystalline substrates

W. Prellier

Laboratoire CRISMAT, ENSICAEN, CNRS UMR 6508, 6 Bd Mal Juin, 14050 Caen Cedex, France

wilfrid.prellier@ensicaen.fr

Complex oxides represent a class of materials with several of exiting properties including magnetism, superconductivity or multiferroics. Thus, there are interesting for both fundamental research and applications. Using epitaxial strain, and tuning the parameters of the laser ablation growth, it is also possible in a thin film to modify the electronic properties as compare to bulk materials. While usually, the material is deposited on a single crystal to achieve the perfect epitaxy, I will show that using the appropriate conditions, it is also possible to synthesize the film on other type of substrate reaching a good local epitaxy. In the first case, the film can be also be made artificially using the superlattices approach. In this talk, I will show recent results on superconductor superlattices as well as our recent developed approach on functional oxides including thermoelectric films grown on a polycrystalline ceramic sample. At the end, it will provide insight into current perspectives and future trends of functional oxide thin films opening the route for the combinatory epitaxy. Partial support from ANR Labex, IDS Fun Mat and MEET projets are acknowledged.

Space for your notes

16:15 Hybrids of Pulsed Laser Deposition with PVD methods for Nanocomposite Film Growth

A. A. Voevodin

Nanoelectronic Materials Branch, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson Air Force Base, OH 45433-7750, USA

Andrey.Voevodin@wpafb.af.mil

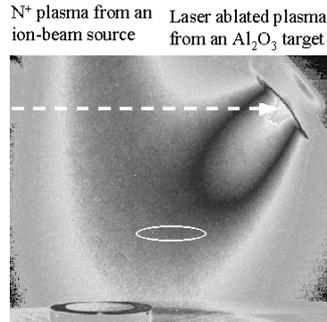


Figure 1: Photograph of the PLD and ion beam hybrid process, showing a plasma interaction channel between the ion-beam and laser ablation sources. The white circle indicates the substrate position, where AION films with increased nitrogen content were produced.

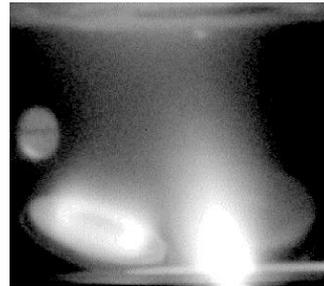


Figure 2: Photograph of MSPLD. Magnetron sputter round source (low left) provides W, Ti, Au and/or MoS_2 , WS_2 fluxes, while laser ablation (bottom) provides the carbon or oxide plasma plume.

Pulsed Laser Deposition (PLD) has a number of unique characteristics, which are not available when using other thin film methods. For example, it can be used to produce plasma plumes from high melting point target materials, such as graphite or metal oxides, carbides, nitrides, and borides. Plasma plumes produced by PLD are typically a few microseconds in duration, but very dense and provide conditions for the growth of correspondingly dense and impurity-free films [1]. The high kinetic energy of ablated atoms is used to produce coatings with crystalline structures at low substrate temperature. Such unique capability of PLD can be beneficially used to create nanocomposite and nanostructured materials, when PLD is combined with other physical vapor deposition (PVD) methods, such as ion beam growth, sputtering, and cathodic arc evaporation. The hybrids of PLD with other PVD methods are discussed.

A hybrid of PLD and ion beam deposition is found to provide unique short-lived interactions between pulsed laser ablated plasma and steady ion beam plasma flux [2]. These plasma interactions are explored in laser ablation of Al_2O_3 targets in the presence of a nitrogen ion beam to produce AION films (Fig. 1). The plasma channels between the two sources are observed during the short period of the ablated plume development and their spatial location is dependent on the nitrogen background pressure in the chamber. The plasma connection between the ion-beam and laser ablation sources results in an instantaneous 40-60% increase of the current extracted from the ion-beam source during laser plume development. Plasma spectroscopic analyses indicates the presence of

excited nitrogen oxide radicals during this short 5-10 μs interaction event. This synergistic effect of plasma enhancement is used to produce highly nitrogenated (20-30 at. % N) nanocrystalline AlON films at about 300 °C substrate temperature. A combination of magnetron sputtering and PLD (MSPLD) is a hybrid process which uses the high energy of the laser ablated plasma and relatively dense sputtering plasma stream to produce crystalline and composite films at reduced substrate temperatures and with a good growth rate [3, 4]. MSPLD process is shown in Fig. 2. A pulsed laser beam is used to generate a carbon or metal oxide plasma plumes, while one or two magnetrons are used to sputter metal and/or dichalcogenide materials in the direction of the substrate. Magnetron sputtering delivers a flux of metal and/or sulfur atoms to the condensation surface and thus provides a high growth rate. High energy plumes from the laser ablation of graphite or oxide targets (such as Al_2O_3 , ZrO_2 , etc.) are directed to the condensation surface, intersecting with the metal atom flux from magnetron sputtering. MSPLD is used for nanocomposite, multilayered, and gradient structures made of diamond-like carbon (DLC), carbides, oxides, dichalcogenides, and metals. Examples include TiC/DLC, WC/DLC/ WS_2 , ZrO_2/Au , $\text{Al}_2\text{O}_3/\text{MoS}_2$, $\text{ZrO}_2/\text{Au}/\text{MoS}_2/\text{DLC}$ and other nanocomposites with advanced mechanical characteristics [5, 6]. In pulsed MSPLD processes, the synchronization of PLD and pulsed sputtered plasma can be applied for additional ionization of r condensation fluxes and promotion of crystalline material growth. ZrO_2 -Mo films are produced with PLD and pulsed magnetron sputter synchronization [7]. Hybrid plasma imaging shows that under certain timing conditions between magnetron voltage pulse and laser pulse, the PLD plume can be additionally excited and this extends oxide plasma ionization. This process provides crystalline nanocomposite thin-films at 200 °C substrate temperatures that otherwise would not form.

A relatively less known variant of the MSPLD is a combination of matrix assisted pulsed laser evaporation (MAPLE) with magnetron sputtering. In the MAPLE process, a pulsed excimer laser is used to evaporate a frozen target consisting of organic or inorganic nanoscale sized particles and compounds dissolved in a volatile solvent matrix. Such particulates can include carbon nanoparticles, nanotubes, fullerenes, DNA structures, etc. The laser pulses vaporize the solvent and generate directed vapor stream to transport dissolved nanoparticles to the substrate surface, while the volatile solvent molecules are evacuated. Magnetron sputtering is used to embed these nanoparticles in metal or ceramic matrices. The advantage of this process is that it allows deposit films from delicate nanostructured materials, which are often stored as dispersion solutions to avoid agglomerations. The MAPLE process is very mild and its hybrid with magnetron sputtering is used to create novel hybrid materials for a wide range of applications, ranging from low friction coatings to sensors. In one example, a carbon nanoparticle-gold composite film is synthesized when using MAPLE for carbon nanoparticle evaporation and magnetron sputtering for gold deposition [8, 9].

The hybridization of the laser ablation and cathodic vacuum arc technology is also successfully applied. Such hybrid process is used for the production of hard wear protective coatings and multilayer functional materials, while achieving large area coverage and good production costs [10]. The process is pioneered by Fraunhofer-Institut für Werkstoff- und Strahltechnik, Dresden and is known under the name of Laser-ArcTM [11]. In this hybrid PVD process, the laser ablation is used for the initiation and then steering cathodic arc evaporation spots over the large area target materials. The arc operation in a pulsed regime is used to limit individual spot evaporation processes to between 20 and 100 μs time to avoid target overheating and reduce droplet emissions. The process provides a high degree of plasma ionization and allows for an efficient magnetic field filtering of the evaporated and ionized plasma fluxes. Such filtering prevents microparticle inclusion in the films. This hybrid technique is found to be especially beneficial for the growth of hard hydrogen-free tetragonal amorphous carbon films from graphite targets. It is applied on large substrate areas at the temperatures below 150 °C [12].

In summary, hybridizations of PLD with other PVD techniques use the benefits of the high energy and density of the pulsed laser ablated plasma to help produce crystalline and nanostructured materials at low substrate temperatures. In many cases, the synergetic efficiency of hybrid plasma processes enables a growth of nanocomposite materials which can be difficult to produce by other methods.

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Space for your notes

Arc

Friday, June 28

10:30 Cathodic Arcs

Marcela MM Bilek

School of Physics, A28, University of Sydney, NSW 2006, Australia

marcela.bilek@sydney.edu.au

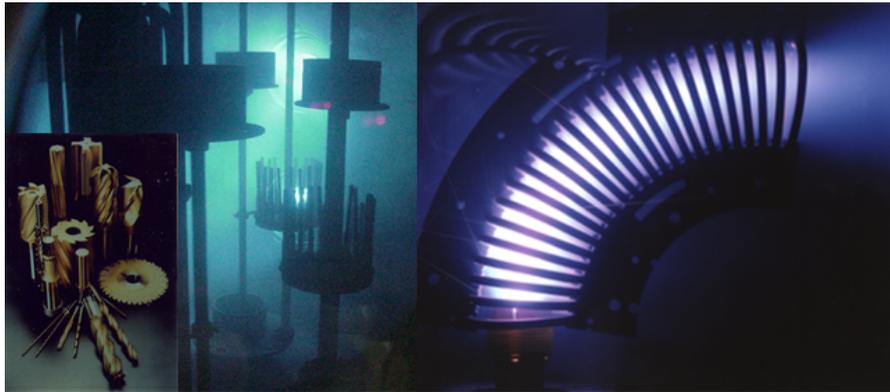


Figure 1: Photographs courtesy of Sutton Tools, Melbourne and Lawrence Berkeley National Laboratory, California.

Cathodic arcs provide a highly ionized plasma stream from a solid conducting target in the absence of background gas. They have found a number of applications in industry particularly for the production of protective coatings on tools and components. This presentation will introduce the physics of cathodic arc operation, describing plasma and macroparticle generation in cathode spots. Cathode spot dynamics at the cathode surface and the characteristics of the plasma stream in terms of ion charge states and energy distributions will be examined. Options for source design, both in pulsed and dc modes, will be reviewed and compared. The implications of macroparticle emission for various coating processes and magnetic filters enabling their removal from the plasma stream will be discussed. The physics of plasma transport through magnetic filters will be described and methods of optimizing filter throughput and shaping the plasma plume will be presented. The use of reactive gas and substrate bias in cathodic arc deposition to provide access to a broad range of coating compositions and microstructures will be briefly outlined and some issues related to such process augmentations will be highlighted.

Key Words: cathodic arc, cathode spot, highly ionized plasma, macroparticles, magnetic filters, ion charge states, influence of reactive gas, plasma immersion ion implantation

Space for your notes

11:15 Vacuum Arc Deposition and its Applications

Andreas Leson

Fraunhofer-Institut für Werkstoff- und Strahltechnik (IWS) Winterbergstr. 28, 01277 Dresden, Germany, www.iws.fraunhofer.de, +49 (351) 83391-3317

andreas.leson@iws.fraunhofer.de

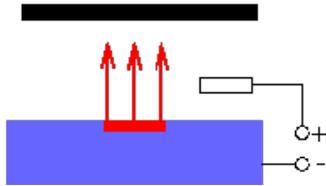


Figure 1: principle scheme of the arc process

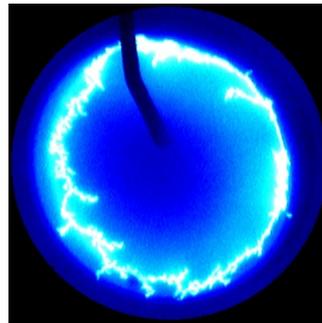


Figure 2: tracer of the cathodic arc spots

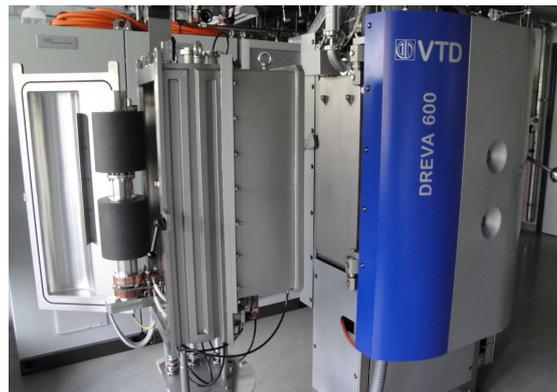


Figure 3: Deposition tool with a pulsed arc source for carbon coatings

Among the different thin film deposition methods the vacuum arc deposition process is one of the most established ones. The widespread use is due to the robustness and efficiency of the process. Moreover the arc process is characterized by a high degree of ionization, which leads to dense coatings with a high mechanical load capacity. On the other hand the arc process has the drawback to produce rather rough surfaces due to the emitted particles or droplets, which are typical for the process. The deposition of hard coatings on tools is a classical application of the arc process. Drills and cutting tools nowadays always use a hard coating of e. g. TiN or (Cr,Al)N in order to improve their lifetime and their performance. Diamond like carbon coatings (DLC) is another class of hard coatings which is widely used in industry. Most DLC coatings are deposited using

a PECVD process. However, arc deposited DLC coatings have certain advantages as compared to the ones made by PECVD. For instance their hardness usually is higher by a factor of 2 to 3. Moreover in combination with specific lubricants they show an extraordinary low friction resistance. These properties make them very attractive. Typical applications of these coatings are in the automotive sector. In addition they are used for instance as topcoats in hard disc drives. For the arc deposition of DLC coatings more sophisticated arc processes are necessary. In order to solve the mentioned droplet problem often an electromagnetic filter is used, which separates the droplets from the ion beam. Moreover, using a pulsed arc instead of a DC-arc also reduces the emission of droplets. The talk will present some characteristic arrangements for the arc deposition process. Representative commercial arc coating tools will be shown as well as typical examples of arc coated tools. Moreover details of the filtered arc process will be addressed and its usage in the deposition of smooth carbon coatings.

Space for your notes

5 Abstracts of Posters

Alphabetically ordered

P16 Properties of thin HfO_2 , Nb_2O_5 , Ta_2O_5 films and HR coatings deposited by ion-assisted deposition

Giedrius Abromavicius^{a*}, Alfridas Skrebutenas^a, Rytis Buzelis^b, Ramutis Drazdys^b, Andrius Melninkaitis^c, Darius Miksys^c, Valdas Sirutkaitis^c, R. Grigonis^c, T. Rakickas^c, R. Juskenas^d, A. Selskis^d

^aOptida Co., ^bCenter for Physical Sciences and Technology, ^cLaser Research Centre, Vilnius University, ^dInstitute of Chemistry
giedrius@optida.lt

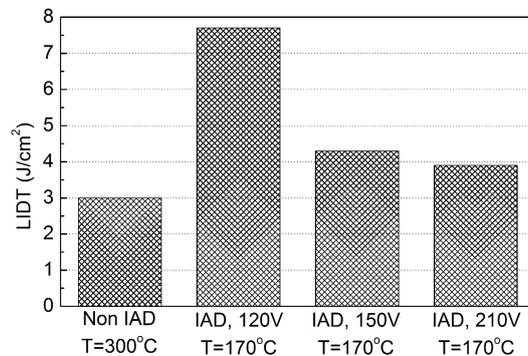


Figure 1: Laser-induced damage thresholds for HR @355 coatings deposited using IAD with different ion energies and e-beam deposition.

Results from several past collaborative investigations between Optida Co Ltd, Institute of Physics (currently Center for Physical Sciences and Technology), Laser Research Center (Vilnius University) and Institute of Chemistry are summarized and presented. Thin films of Nb_2O_5 and Ta_2O_5 were deposited using different ion source parameters - anode voltage and current of ion beam source (end hall, hot cathode type), as well, as other process parameters - substrate temperature, deposition rate. Refractive indices and absorption coefficients of the layers were determined. High reflective (HR) coatings ($\text{Nb}_2\text{O}_5/\text{SiO}_2$ and $\text{Ta}_2\text{O}_5/\text{SiO}_2$) for 1064 nm were deposited using three different sets of process parameters. LIDT values were measured according to ISO 11254-2 standard at first harmonic of Nd:YAG laser radiation ($\lambda = 1064$ nm, $\tau = 3.4$ ns). Lower anode voltage and higher current of IAD source resulted in higher LIDT value in $\text{Nb}_2\text{O}_5/\text{SiO}_2$ mirror case (5 J/cm²), and lower LIDT value in $\text{Ta}_2\text{O}_5/\text{SiO}_2$ mirror case (11.5 J/cm²). Thin films of HfO_2 layers using four different sets of anode voltage and current of IAD source were deposited and their optical (n,k), structural (XRD analysis) properties were determined. High reflective (HR) coatings for 355nm were deposited using three different IAD and one e-beam process. Spectral properties of these mirrors were measured, as well as LIDT (ISO 11254-2 standard, $\lambda = 355$ nm, $\tau = 4.6$ ns). All IAD deposited mirrors showed slightly higher resistance to laser pulses at 355 nm than non-IAD, and $U_a = 120$ V case gave the best result of 7.7 J/cm².

P35 PVD nanostructured systems with high resistance to mechanical fatigue for industrial applications

E. Almandoz*, S. Kulkarni, G.G. Fuentes, R.J. Rodríguez

AIN_tech, Asociación de la Industria Navarra, Cordovilla-Pamplona, Spain
ealmandoz@ain.es

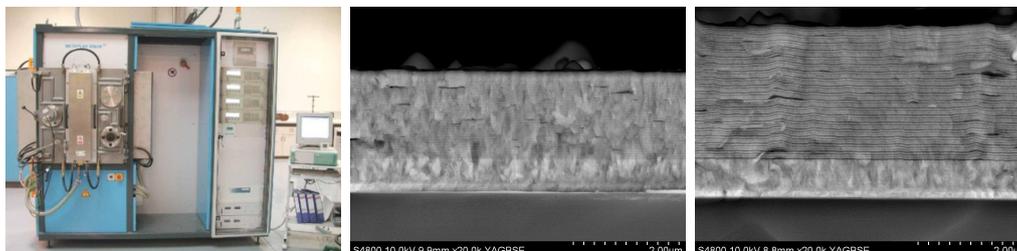


Figure 1: Metaplas IONON MZ323 semi-industrial PVD equipment (left), CrN/AlSiN multilayer coating, one rotation (centre), CrN/AlSiN multilayer coating, two rotations (right).

Traditional (monolithic) PVD coatings are known due to their high hardness and wear resistance, whereas not for a specially good toughness. Nevertheless several strategies exist for increasing toughness or fracture resistance of PVD deposited coatings, one of which is depositing multilayered coatings. This toughness increment is a requisite when trying to introduce PVD coatings on industrial machining, forming or movement transmission systems, due to the extremely hard mechanical requirements of such tools. Multilayered systems have been thoroughly developed at laboratory level and from a basic research point of view. In this sense, it exists a wide scientific literature that explains the improvements on properties such as hardness, Young modulus, fracture toughness,... obtained thanks to a design based on the construction of multilayered or nanomultilayered coatings. However, nowadays it is still a major challenge to scale up to industrial components these fine structures. This work compiles recent progresses of scaling up PVD nanomultilayer on industrial scale. Moreover a duplex treatment (nitriding + PVD coating) is also presented, which is completely conducted on a semi-industrial PVD equipment. TiN/CrN, CrN/AlSiN and TiN/AlSiN systems have been deposited on silicon and steel substrates with different bilayer periods controlling sample rotation. When using double rotation multilayer coatings with hexalayer periods are obtained. In general, the obtained multilayer coatings show increased properties compared with the ones of their respective monolayers as it was observed by nano-indentation and wear-tests.

P12 Ti and TiN: sputtering at increased deposition rate using chopped HiPIMS.

Paul Michael Barker*, Jörg Patscheider

Laboratory for Nanoscale Materials Science - Empa, Überlandstrasse 129, 8600 Dübendorf, Switzerland
Paul.Barker@empa.ch

Chopped HiPIMS, (c-HiPIMS), a modified version of high power impulse magnetron sputtering (HiPIMS) has been used to deposit titanium and titanium nitride films. Chopped HiPIMS is a variant of HiPIMS, where a single pulse is decomposed into several individual pulses and tailored through software control in the HiPIMS pulse generator to produce pulse sequences. The deposition rate, when using c-HiPIMS, depends upon the choice of c-HiPIMS pulse sequence with

systematic changes for both pulse-on and pulse-off times. For Ti, all choices of pulse-on and pulse-off times demonstrated deposition rates that were higher than for conventional HiPIMS (with an increase of up to 45 %) for similar repetition frequencies, total pulse-on times and time averaged powers. The trend for increased deposition rates when comparing c-HiPIMS to HiPIMS under similar conditions continued for TiN, with an increase of 50 % attained for TiN growth at comparable parameters. Whilst the c-HiPIMS deposition rates for Ti remain below those for direct current magnetron sputtering (DCMS), the gap has been markedly reduced allowing for reasonable deposition rates whilst producing film with structures that are significantly superior. Further, differences can also be seen between HiPIMS and c-HiPIMS films when analysed by SEM and XPS although films grown with varied c-HiPIMS parameters show no structural changes. Reactively grown, stoichiometric, TiN demonstrated that the deposition rates for c-HiPIMS and DCMS were comparable. Further, interesting current and voltage waveforms properties, whilst using c-HiPIMS, were observed under both reactive and non-reactive conditions. Differences in hysteresis behaviour were observed when comparing HiPIMS and c-HiPIMS. The increase in deposition rate is ascribed to a combination of reduced gas heating with increased heat dissipation, lowered self-sputtering and reduced ion trapping. Investigations to further understand the contributions of these factors are ongoing. However, that deposition rate can be improved under both reactive and non-reactive conditions not only demonstrates an improvement in HiPIMS utilization, but may also provides an insight into the mechanisms of HiPIMS as a PVD technique.

P34 Effects of Pulsed Laser Irradiation of As-Deposited c-BN-Films using Photons of 157 nm Wavelength and Multi layers of h-BN/ c-BN Bilayers and their Properties

René Bertram*, Steffen Weissmantel, René Boettcher

Hochschule Mittweida - University of Applied Sciences, Germany
bertram@hs-mittweida.de

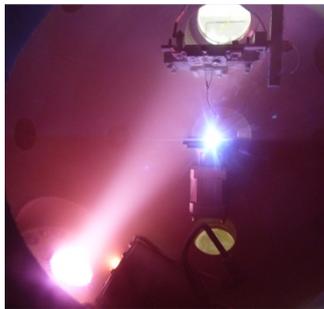


Figure 1: Photograph of i-PLD process.

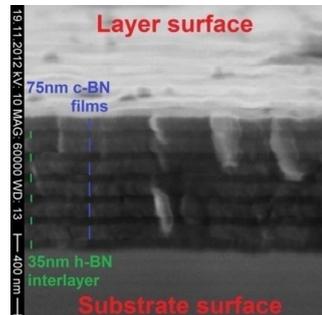


Figure 2: SEM image of multi layered hBN/ cBN film.

We present the effects of pulsed laser irradiation of as-deposited cubic boron nitride (c BN)-films using photons of 157 nm wavelength and 7.9 eV photon energy, respectively. The films are deposited by ion beam assisted pulsed laser deposition (i-PLD) using a KrF excimer laser of 248 nm wavelength and laser pulse fluencies up to 30 J/cm^2 on the pyrolytic hexagonal boron nitride target and applying an additional ion beam bombardment of the growing film using a mixture of nitrogen and argon ions produced in a r.f. ion source with 700 eV ion energy. The irradiation of such coatings with a fluorine laser was found to influence the number and size of sp^2 -bonded particulates and thus the further growth of the cubic BN phase as well as the $\text{sp}^3 / \text{sp}^2$ ratio.

So, alternating deposition and irradiation of sub-layers directly affects the quality of the entire c-BN films. Furthermore, calculations were done concerning the mean penetration depth of the photons in the c-BN films and, based on these evaluations of laser induced temperature fields, experiments have been carried out using proper sub-layer thickness. The influence of the irradiation of the films with photons on the intrinsic shear stresses, which limited the film thickness so far, was investigated and will be presented. Furthermore we will show first results of multi layered stacks consisting of alternating bilayers. These are assembled by hexagonal boron nitride (h BN) inter layers and subsequent cubic boron nitride layers in which the comparatively soft hexagonal phase is supposed to absorb mechanical stress induced by the cubic films and shall deflect the crack propagation as well as the failure dispersal into the film depth. This may result in higher fracture toughness and increased film thicknesses. For multi layers of some 2 μm each with an amount of cubic BN of some 1,2 μm measurements of the micro hardness showed up to 5000 in vickers hardness strongly depending on both the ratio of the h BN and the c BN sub layer thickness and a suitable minimum c BN sub layer thickness.

P04 Study of the performance of two macroparticle filter configurations implemented to an industrial PVD cathodic arc evaporation reactor.

R. Bonet*, J. Caro, M. Grané, J. Cardona, A. Pardo

Fundació CTM Centre Tecnològic. Av. Bases de Manresa, 1. 08242 Manresa, Spain
raul.bonet@ctm.com.es

Cathodic arc evaporation deposition technique offers unique characteristics for the development of PVD coatings. The high power density of the arc discharge on the surface of the cathode results in a high level of ionization, which in turns promotes an excellent coating adhesion. Nevertheless, the main drawback of this evaporation technique is the generation of a large amount of macroparticles (droplets) during the arc discharge. These micro-sized droplets are poorly adhered to the substrate and increase the surface roughness of the coating. Consequently, their presence is undesirable for many industrial applications where high mechanical performance, structural and chemical uniformity and good surface finishing of the coatings are required. Because the generated droplets are electrically quasi-neutral, the implementation of electric and magnetic fields can be used to separate them from the plasma to obtain droplet free coatings. In this work, the study of the performance, in terms of deposition rate and filtering efficiency (droplets density), of two magnetic filters coupled to an industrial PVD cathodic arc evaporation reactor is presented. The reactor is provided by two cathodic DC arc evaporation sources. The diameter of the cathodes is 80 mm, the typical discharge current is around 75 A, and the achieved deposition rate is 4 microns/hour. As a first stage, the equivalent circle diameter distribution of the droplets generated by these unfiltered sources has been studied by means of optical microscopy. In order to improve the surface quality of the coatings, two different configurations of curved magnetic filters have been designed and constructed:

- A quarter-torus duct filter bent at 90° (Aksenov-type).
- An out-of-plane double-bent filter (S-shape) formed by two ducts bent at 45° and 90° , respectively.

In both cases, the deposition rate and the macroparticle filtering efficiency have been optimized modifying the magnetic field intensity and the positive bias voltage applied to the filter duct. Whereas the S-shape filter offers an excellent performance in the elimination of the macroparticles, the experimental deposition rate obtained at the exit of the filter is very low (0.2 microns/hour). By the contrary, the quarter-torus filter configuration offers higher deposition rate to the detriment of macroparticle filtering performance. The obtained experimental results can be qualitatively explained by analyzing the distribution of the magnetic field lines along the duct filter which can be used as a guideline for the understanding of the plasma transport efficiency in both magnetic filter configurations. The 3D magnetic field distribution in these filters has been accurately studied by means of Finite Element Method (FEM) using ANSYS 14.0 software.

P30 Study of plasma filtered DLC films produced on industrial scale

Gregor Englberger

Fraunhofer IWS, Winterbergstraße 28, 01277 Dresden, Germany,
gregor.englberger@iws.fraunhofer.de

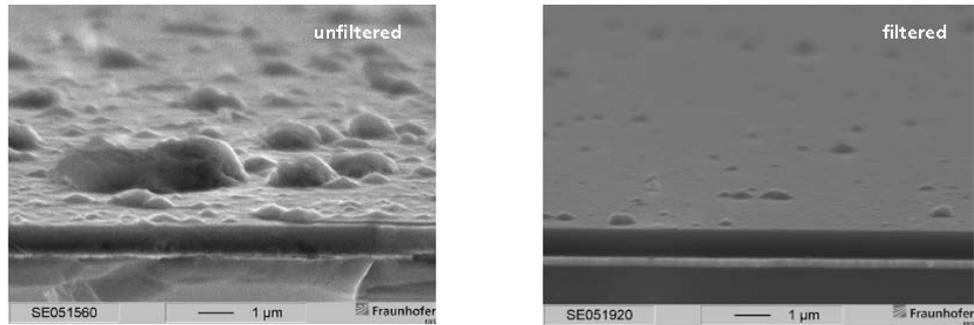


Figure 1: Deposited ta-C-films unfiltered (left) and with plasma filter unit (right)

DLC-films proved to have excellent properties for tribological coatings due to their high wear resistance and low coefficient of friction. Especially tetrahedral amorphous carbon represents a kind of DLC with outstanding tribological performance even under dry and mixed lubrication conditions. Up to now an efficient, industrial-suited ta-C production is only possible by arc-evaporation processes. Nevertheless, due to the unavoidable particle emission during the arc process, ta-C coatings have a high surface roughness and can often not be used without mechanical smoothening.

In spite of the very promising performance of ta-C films a comprehensive transfer on an industrial scale has not taken place yet. A missing technology for industrial scale production and high surface roughness, due to the unavoidable particle emission during the arc process, are accountable for that.

This work presents the development of an industrial-suited deposition system for ta-C films, basing on a laser-assisted arc combined with a plasma filtering unit.

The mode of operation of the plasma filtering unit will be in brief. First results of the plasma filtered ta-C-films and their tribological behaviour will be presented. The effect of the plasma filter technique with respect to the film topography has been demonstrated via roughness measurements and SEM pictures (Fig. 1). All results are compared and discussed to unfiltered ta-C-films.

P36 Deposition of Alloyed Transition Metal Dichalcogenides by Magnetron Sputtering Using Different Approaches

Manuel Evaristo* and Albano Cavaleiro

SEG-CEMUC Department of Mechanical Engineering, University of Coimbra, Rua Luis Reis Santos, 3030-788 Coimbra, Portugal
manuel.evaristo@dem.uc.pt

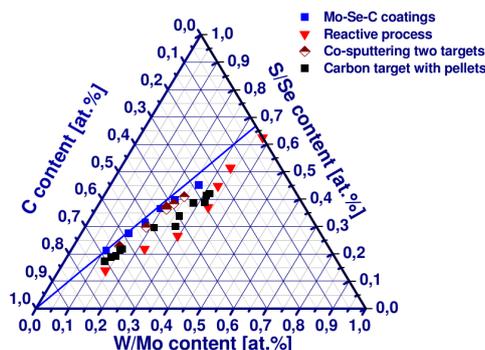


Figure 1: Composition of the coatings deposited using different methods for different systems.

Transition Metal Dichalcogenides (TMD) are known as solid lubricants, however the low load bearing capacity and the influence of the environmental conditions on the tribological performance makes them inappropriate for most of the tribological applications. The deposition of TMD by magnetron sputtering is one of the methods used to deposit in the form of thin films, since it allows the modification of the TMD properties. To improve the mechanical and tribological behaviour, different TMD (WS_2 , $MoSe_2$ and WSe_2) were alloyed with C, N and Ti. The depositions were done by PVD magnetron sputtering using different approaches. Coatings from the W-S-C system were deposited using 3 different methods co-sputtering from two targets WS_2 and graphite, sputtering from a composite target, graphite with WS_2 pellets and by a reactive process from a WS_2 target in a reactive atmosphere ($Ar + CH_4$). With a composite target, coatings from the system Mo-Se-C were also deposited.

P19 Influence of process parameters on thin film properties of ion beam sputter deposited Ag

Feder, R*; Neumann, H; Bundesmann, C; Rauschenbach, B

Leibniz-Institut für Oberflächenmodifizierung e.V., Permoserstr. 15, 04318 Leipzig, Germany
rene.feder@iom-leipzig.de

Ion beam sputter deposition (IBD) provides intrinsic features which influence the properties of the growing film, because ion properties and geometrical process conditions generate different energy and spatial distribution of the sputtered and scattered particles. A vacuum deposition chamber has been set up which allows ion beam sputtering of different targets under variation of geometrical parameters (incidence angle of primary ions and emission angle of secondary particles in respect to the target) and of ion beam parameters (ion species, ion energy) to make a systematic analysis of the correlation between the properties of the ion beam, the properties of the sputtered and scattered particles, and the properties of the deposited films. A set of samples with thin Silver films was prepared and characterized with respect to the film properties. The film thickness distribution was measured using step high profilometry as well as white light interferometry and

shows the expected, tilted cosine-like shape. Additionally the electrical resistivity was determined by 4 point probe measurements, showing a systematic influence from the used process parameter. The optical film properties were analyzed using a spectroscopic ellipsometer and revealed also a correlation between the ellipsometric parameter Ψ and the electrical resistivity measured before. Getting a correlation between the deposition parameters and the film properties, the energy distribution of the sputtered and scattered particles was measured using an energy-selective mass spectrometer. These measurements corroborate this correlation between the average energy of the film forming particles and the sputtering parameters (ion species, primary ion energy, incidence and emission angle). Among others, these experiments also revealed a high-energetic maximum for backscattered primary ions, which shifts with increasing emission angle to higher energy. Experimental data are compared with Monte Carlo simulations done with the well-known Transport and Range of Ions in Matter, Sputtering version (TRIM.SP) code [J.P. Biersack, W. Eckstein, Appl. Phys. A: Mater. Sci. Process. 34 (1984) 73]. The thicknesses of the films are in good agreement with those calculated from simulated particle fluxes. For the positions of the high-energetic maxima in the energy distribution of the backscattered primary ions, a deviation between simulated and measured data was found, most likely originating in a higher energy loss under experimental conditions than considered in the simulation. Financial support by DFG within project BU2625/1-1 is gratefully acknowledged.

P06 Position and Bias Dependent Optical Examination of a HiPIMS Plasma Discharge

Rainer Feuerfeil*, Tina Hirte

Robert Bosch GmbH
rainer.feuerfeil@de.bosch.com

Since the first experimental applications of the HiPIMS discharge it is of increasing interest in the fields of coating and surface pre-treatment and a number of promising applications are discussed in the literature. However, the vast field of parameters affecting the HiPIMS discharge still offers room for closer examination. Therefore, this publication deals with examination of plasma properties observed by optical emission spectroscopy in different positions in the coating chamber to determine and compare which species can be detected in front of the target and which arrive at the substrate surface. In both cases the optical fiber was installed parallel to the surface of the target or the substrate with a distance of approximately 15 mm and the measurements were performed without substrate rotation. Furthermore, the effect of synchronized substrate bias was investigated. The measurements were conducted with bias duty cycles of 9 or 14 %, being effective in time with the HiPIMS pulse or starting half a pulse-duration later. For the sake of comparison, discharges without bias and with DC bias were observed as well. The first experiments were focused on Cr and CrN coatings. First measurements show that distinct effects can indeed be observed in OES spectra at different positions in the plasma chamber. However, because of the differences in intensity, the values can only be compared in a qualitative way. The influence of the bias parameters on certain species is of special interest. The pulsed mode parameters used in the experiment seem to be especially attractive to the inert gas while the attraction of Cr is more effective in DC mode. Therefore, it can be concluded that plasma etching and coating deposition require different sets of bias parameters for maximum efficiency.

P11 Angular dependency of ion energy distributions and NbO_x thin film growth in HiPIMS plasmas

Robert Franz^{1,2*}, Cesar Clavero¹, Jonathan Kolbeck¹ and André Anders¹

¹Lawrence Berkeley National Laboratory, Berkeley, California, USA; ²Montanuniversität Leoben, Leoben, Austria
robert.franz@unileoben.ac.at

Recent studies of the plasma properties in high power impulse magnetron sputtering (HiPIMS) discharges have shown that self-organized plasma structures form in the vicinity of the target's erosion "racetrack." These structures comprise ionisation zones which are thought to be responsible for the high degree of ionization of sputtered atoms and gas atoms as well as for the high current levels observed in HiPIMS. Ionisation zones are related to the ExB drift of electrons yet they disrupt the close drift and cause electron jets and plasma flares, which in turn are thought to be responsible for ionization far from the target. In this way, ionization zones are of critical importance to the flux of ions arriving at the target. The situation is made even more complicated in reactive deposition where we need to take into account target poisoning and several different types of ion species, including negative ions. Traveling ionization zones and ejected electrons break the symmetry of magnetron discharges, with consequences for the properties of films deposited at different locations with respect to the magnetron. In particular, energetic (> 10 eV) and multiply charged (in the present case 2+) ions are ejected from the target at low angles with respect to the target surface. There is evidence that they move preferentially in the tangential-forward direction relative to an ionisation zone's motion. The motivation for the present work was therefore to study the influence of this spatially asymmetric ion distribution on the growth of thin films. As an interesting film material we picked Nb₂O₅, or more generally NbO_x, although we believe that the study is also applicable to other film systems. Substrates were placed in different angular positions relative to the magnetron (10, 50 and 90°) and the resulting NbO_x thin films were analysed as to their chemical composition, crystal structure, and other properties. A special factor in oxygen-containing magnetron plasmas are highly energetic negatively charged oxygen ions with energies between 500 and 600 eV in the present study. Since the electric field is distorted in the ionisation zones, special emphasis is given to the spatial distribution of negative oxygen ions and their influence on thin film growth. The results obtained contribute to the understanding of reactive HiPIMS plasmas and their applicability for synthesising thin oxide films. This work was supported by the Erwin Schrödinger Program (Project J3168-N20) of the Austrian Science Fund (FWF) and by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

P15 Magnetron-sputtered Tungsten-Nitride Films as Model for Nitrogen-implanted Tungsten Surfaces

L. Gao* , P. Wang and W. Jacob

Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstr.2, 85748 Garching, Germany
liang.gao@ipp.mpg.de

Nitrogen is foreseen as seeding gas for radiative cooling in the divertor of fusion devices such as ASDEX Upgrade and JET. With tungsten being used as plasma-facing material, the interaction of nitrogen and hydrogen isotopes with tungsten surfaces has attracted some attention. Laboratory experiments are hampered by the fact that WN_x layers formed by nitrogen implantation are very thin and therefore difficult to analyze by ion-beam methods. Therefore, magnetron-sputtered WN_x films (MS-WN_x) are introduced as a model system to study the interaction of N-implanted W surfaces with hydrogen plasmas. MS-WN_x films were deposited in Ar-N₂ mixtures with different N₂ partial pressures and in pure N₂ atmosphere with different substrate biasing during deposition. Ion beam analysis and XPS were applied for determining the absolute N content and the chemical composition. The results were compared with N-implanted W

films (Ni-Ws), which were implanted into W films on Si substrates from N₂ plasmas applying different substrate bias voltages. Different partial pressures during deposition lead to different deposition rates and produce films with different N concentrations and chemical bonding. For MS-WN_x films deposited without substrate bias, N concentration increases as the N₂ partial pressure increases. The highest N concentration appears in films deposited in pure N₂ gas. The W: N ratio of these films is 3:7. The stable WN phase with atomic ratio of 1:1 appears in the films deposited with 50% N₂ partial pressure. Also, the substrate biasing during the pure N₂ deposition has a large effect on the N concentration and the microstructures. By comparing the N concentration and the chemical compound from XPS spectra in both layer systems, MS-WN_x layers can now be used as a model system to further study the interaction of hydrogen plasmas with WN_x surfaces.

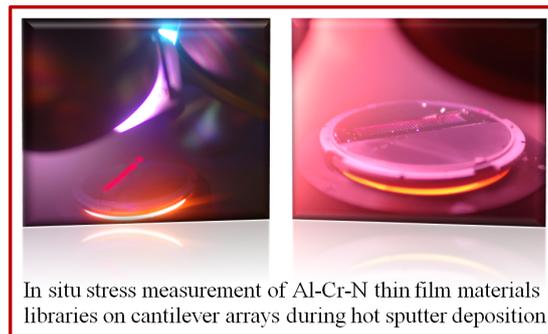
P40 Time- and space-resolved high-throughput characterization of stresses during sputtering and thermal processing of Al-Cr-N thin films

D. Grochla^{1*}, A. Siegel¹, S. Hamann¹, P.J.S. Buenconsejo¹, M. Kieschnick^{1,2}, H. Brunken¹, D. König¹ and A. Ludwig^{1,3}

¹Institute for Materials, Chair for MEMS materials, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany

²RUBION, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany

³Materials Research Department, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany
Dario.Grochla@rub.de



Mechanical stresses (extrinsic or intrinsic) are a crucial feature of thin films. The mechanical behaviour of thin film-substrate combinations are strongly affected by internal stresses, especially with respect to the adhesion, durability and tribological performance. Thus, gaining a better understanding of stress-inducing mechanisms and controlling the sign and amplitude of stresses in thin films is an important concern for surface engineering. Interfacial stress components due to lattice mismatch or different thermal expansion coefficients contribute to the overall film stress as well as dislocations, impurities, voids and grain boundaries. Several stress components are directly related to the film's microstructure. To gain closer insight into the mechanisms of stress development and relaxation, real-time measurements during film growth are necessary. Furthermore, it is of interest to correlate the stresses to the chemical composition and the corresponding microstructure. This is possible in composition spread type materials libraries, where thin films of different compositions are fabricated simultaneously and are therefore very well comparable to each other. In order to understand the stress development during sputtering and annealing as a function of composition, high-throughput measurement methods are needed which are both time-resolved and space-resolved. (Al_{100-x}Cr_x)N thin film materials libraries were fabricated on

micro-machined cantilever arrays, in order to simultaneously investigate the evolution of stresses during film growth as well as during thermal processing by analyzing the changes in cantilever curvature. The issue of the dependence of stress in the growing films on composition, at comparable film thicknesses, was investigated. Among the various experimental parameters studied, it was found that the applied substrate bias has the strongest influence on stress evolution and microstructure formation. The compositions of the films, as well as the applied substrate bias, have a pronounced effect on the lattice parameter and the coherence length. For example, applying a substrate bias in general leads to compressive residual stress, increases the lattice parameter and decreases the coherence length. Moreover, bias can change the film texture from [111] orientation to [200]. Further detailed analysis using X-ray diffraction and transmission electron microscopy clearly revealed the presence of a [111] highly textured fcc (B1 type) Al-Cr-N phase in the as deposited state as well as the coexistence of the hexagonal [110] textured Cr₂N phase, which forms in the Cr-rich region. These results show that the combinatorial approach provides insight into how stresses and compositions are related to phases and microstructures of different Al-Cr-N compositions fabricated in the form of materials libraries.

P32 Fundamental Studies on the Deposition of Nanocrystalline Diamond (n-D) Films by Means of Pulsed Laser Deposition (PLD)

Hagen Grüttner*, René Böttcher, Steffen Weißmantel

Hochschule Mittweida, University of Applied Sciences, Germany
h.gruettner@hs-mittweida.de

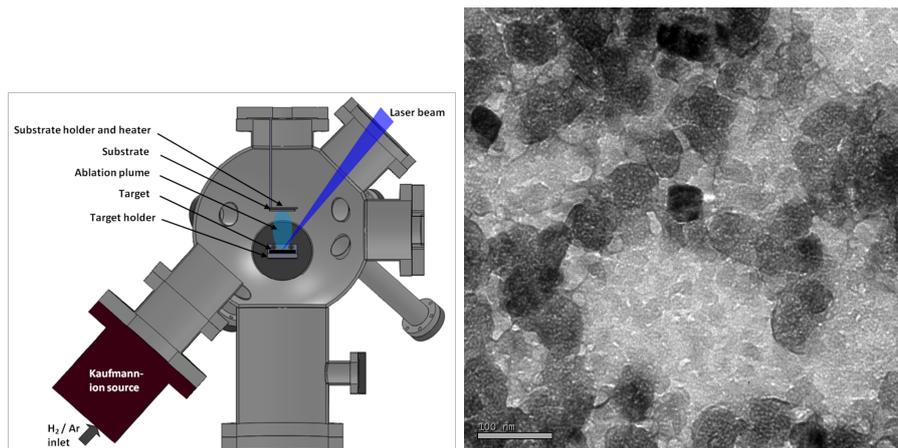


Figure 1: Experimental Setup (left); TEM- Image of a nanocrystalline diamond (n-D) film. (right)

The results of fundamental studies on the deposition of nanocrystalline diamond (n-D) films by means of pulsed laser deposition (PLD) will be presented. The n-D films were deposited on tungsten carbide substrates by pulsed laser ablation of a graphite target with a KrF excimer laser ($\lambda=248$ nm, max. pulse energy=500 mJ, repetition rate of 50 Hz) at elevated substrate temperatures and in hydrogen background gas. The laser pulse fluence was 12 J/cm² and the target to substrate distance was 4 cm. The variation of the microstructure of the films with temperature were investigated in the range of 400°C to 600°C and with hydrogen pressure in the range of 0.25 mbar to 7 mbar. The substrates were pretreated by wet chemical etching and with diamond suspension. The influence of the deposition parameters on the n-D growth was determined by Raman- spectroscopy, TEM, SEM and AFM. It will be shown that n-D films can be prepared by PLD using proper parameters.

P28 Optical Selectivity Enhancement of Carbon-based nanocomposites: Simulation and Experiments

Elena Guillén^{1*}, Irene Heras¹, Gintautas Abrasonis², Ainhoa Pardo³, Matthias Krause², Jose Luis Endrino¹

¹Abengoa Research, Sevilla (Spain)

²Helmholtz Zentrum Dresden Rossendorf, Dresden (Germany)

³Centre Tecnologic de Manresa, Manresa (Spain)

elena.guillen@research.abengoa.com

Carbon-based metal nanocomposites have been shown to be good material candidates for applications requiring optical selectivity. However their true potential usage largely depends on the optimization of their composition and microstructure. Diamond Like Carbon with different transition metals were grown on stainless steel and In-conel substrates using pulse filtered cathodic arc deposition from two repetitively pulsed cathodic arc sources with separate macroparticle filters. The influence of several transition metals (Ti, Zr, Cr, W, Mo, V and Nb) on their optical selectivity was investigated. Carbon metal-containing samples were prepared using two cathodic arc sources provided with a carbon cathode and a pure transition metal cathode. Different metal concentrations in the coatings were obtained by varying the average arc current of the metal pulsed cathodic arc source (Imetal). The volume fraction of metal was determined by combined Rutherford Backscattering Spectroscopy (RBS) and Nuclear Reaction Analysis (NRA) measurements. The structure of the deposited films was analyzed by Transmission Electron Microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy. In this study, the computer simulation program Coating Design (CODE) has been used to calculate optical properties of the different carbon-transition metal nanocomposites. The optical constants of various carbon-based nanocomposites were simulated using a physical model proposed by Bruggeman and Maxwell Garnett which averages the dielectric function of the components of the composite, which allows treating the composite system as an effective medium. The performed simulations allowed calculating the solar absorptance and thermal emittance of the nanocomposites. Varying the nanocomposite material configurations such as layer thickness, volume metal fraction, number of layers and multilayer stack resulted in new configurations that enhance the optical selectivity of these materials. Simulated reflectance was compared with spectrophotometry measurements of the deposited films with good agreement between them.

P33 DLC coatings for Automotive Applications of the Bosch Group

Marcus Günther*, Michael Fraune

Robert Bosch GmbH; Diesel Systems, Feuerbach Plant; Process Development Coating Technology (FeP/TEF14);
70442 Stuttgart; Germany
Marcus.Guenther2@de.bosch.com

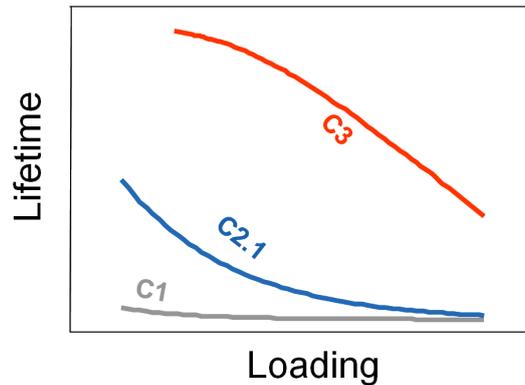


Figure 1: Oscillating wear test of three generations of Bosch carbon-based coatings

For many years the Bosch Group has put great effort into developing thin, wear resistant films. Those films were particularly developed for components of high pressure fuel injection systems, utilizing various plasma processes and thin-film technologies. Especially diamond-like carbon (DLC) coatings are of high importance for automotive applications - in particular Diesel injection systems - due to their unique tribological properties. In this presentation, the main automotive applications at the Bosch Group are discussed and classified. Current development trends towards better fuel efficiency and emission reduction are shown, including their implications on materials and production technology. State-of-the-art Diesel systems operate at pressures in the range of 2500 bar, further increases are expected. Higher combustion temperatures and multiple injections (pre-, main- and post-injections), and downsizing of motor systems with smaller and smaller contact areas pose additional challenges to the endurance of functional surfaces within pumps, valves and injectors. The current use of diverse fuel mixtures with various qualities in the global markets and the introduction of new fuel mixtures (e.g. bio-Diesel) necessitates the development of chemically inert coatings that are tolerant against chemical and particulate contaminations. To satisfy these permanently increasing requirements we developed three generations of DLC coatings at the Bosch Group. Corresponding to the various applications and load collectives, model wear and endurance tests were established to help fitting these coatings to the specific demands. Fig. 1 shows the increasing life time of three generations of Bosch carbon-based coating systems, tested with a simplified ball-on-disc wear test.

P07 Energy-resolved mass spectrometry of an Al/Ar/O₂ HPPMS plasma

M. Hans*, S. Mráz, J. M. Schneider

Materials Chemistry, RWTH Aachen University, D-52074 Aachen, Germany
hans@mch.rwth-aachen.de

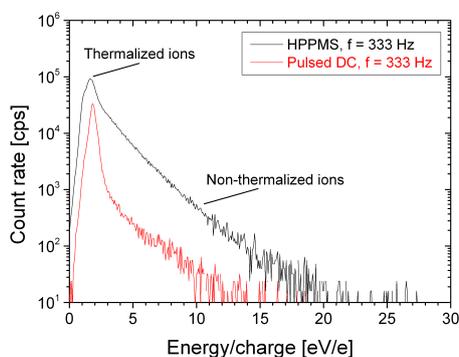


Figure 1

An Al target was sputtered in reactive Ar/O₂ atmosphere with a Zpulsor CyperiumTM power supply. Six micropulses with a frequency of 10 kHz, 5 μ s pulse on-time and 95 μ s pulse off-time were modulated by macropulses with 333 Hz, 0.6 ms on-time and 2.4 ms off-time, corresponding to an overall duty cycle of 1%. For comparison, a pulsed DC plasma generated with a Melec SIPP2000_10_500S power supply with 333 Hz frequency and 50% duty cycle and at identical time-averaged power as the HPPMS plasma was investigated. Plasma analysis was carried out with an energy-resolved mass spectrometer. The ion energy distribution functions (IEDF) of the Al⁺ ions for the HPPMS (black line) and pulsed DC (red line) plasma are shown in Fig. 1. It is evident that the Al⁺ IEDF in the HPPMS plasma is significantly wider than the one of the pulsed DC plasma. This may be attributed to the gas rarefaction effect as the transport of the sputtered atoms takes place at a locally lower pressure during HPPMS in comparison to the pulsed DC discharge.

P26 Self-organization of nickel nanoparticles in dielectric matrices

M. Jerčinović^{1*}, M. Buljan¹, N. Radić¹, P. Dubček¹, S. Bernstorff², J. Grenzer³, R. Hübner³, D. Pajić⁴, K. Zadro⁴

¹Ruder Bošković Institute - Zagreb (Croatia), ²Elettra Sincrotrone - Trieste (Italy), ³Helmholtz-Zentrum Dresden-Rossendorf (Germany), ⁴Faculty of Science - Zagreb (Croatia).
mjercin@irb.hr

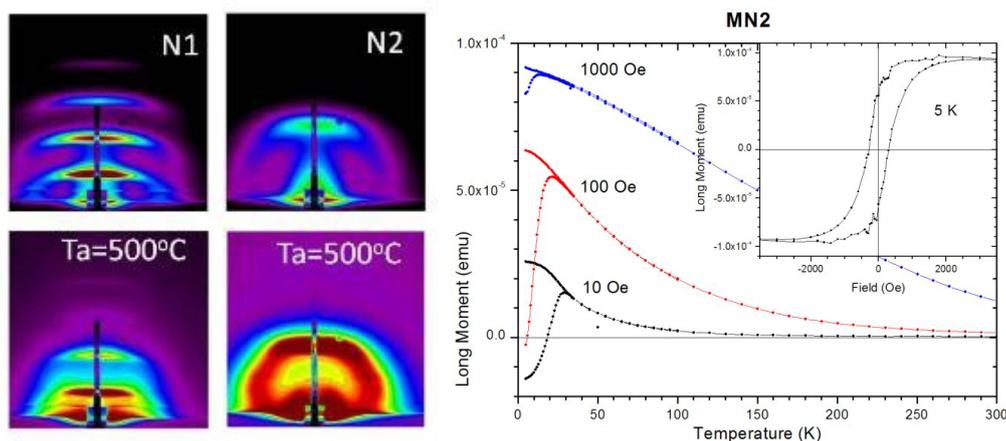


Figure 1: (left) GISAXS maps (first row = as grown; second row = annealed at 500°C). (right) Temperature dependence of the zero-field-cooled and field-cooled magnetization for sample N2 as grown (inset shows hysteresis at 5 K).

Ni nanoparticles (NPs) attract lot of interest as catalyst for carbon nanotube growth, as particles forming interacting or noninteracting ensembles, optoelectronic entities, etc. We have produced self-ordered Ni NPs either on surface or embedded into the alumina matrix starting from three types of nickel and alumina multilayered structures prepared by magnetron sputtering. The structure and morphology of the prepared materials have been examined by grazing-incidence small-angle X-ray scattering (GISAXS), grazing-incidence wide-angle X-ray scattering (GIWAXS), atomic force microscopy (AFM), and transmission electron microscopy (TEM), while magnetic properties were measured by SQUID magnetometer. Thin Ni films deposited onto dielectric's surface exhibit markedly different particle size distribution at room temperature and at elevated temperatures. The effect of temperature on NP formation has been employed for formation of 3-dim arrays of Ni NPs in dielectric matrix. Two types of precursor materials have been used: a) multilayers consisting of alternating pure Ni and pure alumina layers, and b) multilayers consisting of alternating mixed Ni+alumina and pure alumina layers. Both types of precursor material were deposited at room temperature and at elevated temperature, and subsequently annealed. The size of the Ni NPs and their average lateral distance was controlled by the amount of Ni in the Ni-containing layer, while their cross-layer interaction was governed by the thickness of intervening dielectric spacer. That way, the magnetic properties could be controlled, as well. An example of the effects of alumina dielectric spacer thickness (6 & 2 nm) and annealing temperature (RT & 500°C) upon Ni NPs sizes and spatial distribution is shown in composite GISAXS Fig. 1a. The size and spatial distributions of Ni NPs govern the supermagnetic properties of such an ensemble. An example of the blocking phenomena of superparamagnets is shown in Fig. 1b for sample N2.

P17 Polishable silicon coatings for the manufacturing of ultra-precise optical components

P.J. Jobst*, M. Schürmann, N. Kaiser

Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Albert-Einstein-Str. 7, 07745 Jena, Germany
Paul-Johannes.Jobst@iof.fraunhofer.de

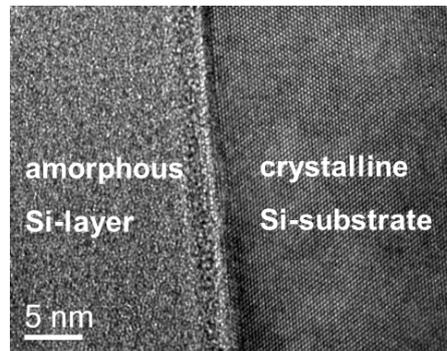


Figure 1: High-resolution TEM image of the interface between crystalline silicon substrate and amorphous silicon film

Introduction Common substrate materials for high-precision metal mirrors with excellent optical, mechanical and thermal properties are aluminum and aluminium-silicon-alloys. They are suitable for ultra-precise machining of complex optical shapes like aspheres and freeforms for mirrors of telescopes, spectrometers or scanners. Unfortunately, they cannot be polished to the required surface roughness.

Requirements and properties of polishable amorphous silicon layers Amorphous silicon layers can be deposited on such substrates and thus, they are an alternative to replace nickel-phosphorous layers which are currently used. Such silicon layers have to be thick enough to realise a subsequent polishing process, on the other hand they must not have too big layer stress which may cause delamination of the layer from the substrate. Furthermore they should have an amorphous layer structure to achieve a good polishability and the required surface roughness. Therewith they are enabling metal mirrors with minimised divergence loss from UV – to IR and are applicable for transmitting optics from NIR-IR spectral region.

Layer structure By using a modified magnetron sputtering technology amorphous-silicon layers with thicknesses up to 10 μm were deposited with an inline coating-system. Silicon layers which were deposited with this coating system by DC sputtering pulsed DC-sputtering and by MF-sputtering from dual magnetrons were analysed. The amorphous structure of deposited silicon layers was demonstrated by large angle X-ray diffraction measurements, high-resolution transmission electron microscopy (TEM, see Fig. 1) and by electron diffraction. The coating parameters were optimized regarding film thickness, homogeneity and porosity for deposition onto aluminum samples. The film stress was determined by the measurement of the deformation of coated silicon wafers.

Thin film stress For a durable coating the film stress should be as low as possible. Therefore the dependence of the stress of the sputtered silicon layers on the deposition parameters was

studied in detail. It was found that the application of a high process pressure could reduce the integrated compressive film stress at identical film thicknesses while an increase of the process power led to increased stress. As the application of high process power was desirable in order to achieve film thicknesses up to 10 μm , the possibility to interrupt the coating process and compose the film from several thinner single layers was investigated. In this case a considerable reduction of the film stress and a distinct reduction of the thermal load to the substrate during the coating process were observed.

Acknowledgement The authors are grateful to the German Federal Ministry of Education and Research (BMBF) for sponsoring their research in terms of the “Wachstums-kern Potential – Verbundprojekt: Ultrapräzise Silizium Optik”-grant under contract no. 03WKP11A.

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P10 Applications of Monte Carlo simulation techniques at VON ARDENNE

O. Khvostikova*, G. Haasemann, J. Neidhardt, U. Seyfert

VON ARDENNE Anlagentechnik GmbH, Plattleite 19/29, 01324 Dresden, Germany
Khvostikova.Olga@vonardenne.biz

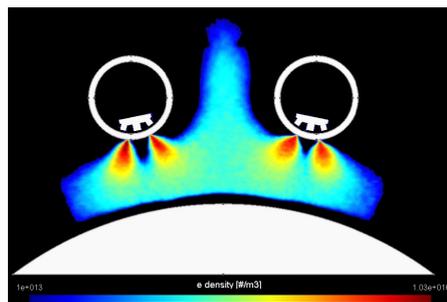


Figure 1: Distribution of electron density obtained from a plasma simulation

VON ARDENNE is a leading vacuum equipment manufacturer for architectural glass coating and advanced coating equipment for thin film solar applications as well as metal strip and web coating platforms for solar thermal and display applications, respectively. This coating equipment allows for manufacturing of technologically sophisticated products, which help to save resources and energy or open new ways to provide energy. VON ARDENNE develops and manufactures machines and equipment, with the help of which nanometer to micrometer thin functional layers are deposited on materials such as glass, metal strip or plastic web. This thin film technology based on sputtering deposition as well as electron beam evaporation has a wide range of applications such as architectural glass, smart phone displays, touchscreens, solar cells and heat protection foils for automotive glass. A methodical development and improvement of the sputtering technology requires an extended understanding of the process which is controlled by a wide range of parameters. Besides experimental investigations, the modeling and simulation of the process environment such as the gas particle distribution as well as the plasma discharge inside the process chamber provides a number of benefits. One advantage is the possibility of an in-depth analysis. Furthermore, modifications of process and design parameters can be

investigated prior to expensive real-life tests. At VON ARDENNE, a Monte Carlo simulation program developed at Fraunhofer IST Braunschweig is used to compute the gas flow and plasma discharge including the magnetic field inside vacuum chambers. An example of application concerns the improvement of the argon pressure homogeneity alongside a sputter target. This homogeneity is a prerequisite for meeting the uniformity requirements of less than $\pm 1.5\%$ for the up to 3.80 m long cathodes. Besides that, the plasma has a determining impact on the uniformity. Fig. 1 shows e.g. the electron density of a dual rotatable magnetron. The distribution of charge carriers obtained from plasma simulations can then be used to evaluate the equipment design and allows for conclusion regarding important technological parameters such as for example the erosion profile and, thus, the target utilization.

P27 Ion-guided microstructure evolution of carbon-nickel nanocomposite films during ion beam assisted deposition: 3D sculpting at the nanoscale

Matthias Krause^{1,2*}, Maja Buljan³, Thomas W. H. Oates⁴, Arndt Mücklich¹, Monika Fritzsche¹, Stefan Facsko¹, Matthias Zschornak¹, Sebastian Wintz¹, Jose L. Endrino⁵, Carsten Baetz^{1,6}, Artem Shalimov^{1,6}, Sibylle Gemming^{1,7}, Gintautas Abrasonis¹

¹Helmholtz-Zentrum Dresden-Rossendorf, PF-510119, 01314 Dresden, Germany

²Technische Universität Dresden, D-01062 Dresden, Germany

³Ruder Bošković Institute, 10000 Zagreb, Croatia

⁴Leibniz-Institut für Analytische Wissenschaft, ISAS e.V., Albert-Einstein-Str. 9, 12489 Berlin, Germany

⁵Abengoa Research, 41014 Sevilla, Spain

⁶Rossendorf Beamline, European Synchrotron Radiation Facility, F-38043 Grenoble, France

⁷Technische Universität Chemnitz, D-09107 Chemnitz, Germany

matthias.krause@hzdr.de

Ion assistance during film growth provides unique opportunities to influence the microstructure due to energy transfer and imposed directionality. For this study, the carbon:nickel system was chosen as model system. The growth of C:Ni nanocomposites without ion assistance is controlled by the phase separation under kinetic constraints of surface and volume diffusion and by the film growth rate. A systematic study of ion irradiation as a pure energy and momentum transfer agent in the context of surface diffusion assisted phase separations is, however, lacking. Here the influence of low energy (50-140 eV) assisting Ar⁺ ion irradiation on the morphology of C:Ni (5 at.% Ni to 50 at.% Ni) thin films will be reported. Two types of ordered nanostructures are identified and characterized: i) tilted columns and ii) compositionally modulated ripples, which are transferred into a periodic three-dimensional nanoparticle array. For i), the tilt angle and diameter of the nanocolumns are controlled by the deposition parameters. Complex secondary structures like chevrons with partially epitaxial junctions are grown by sequential deposition. For a given composition of the depositing flux, the transition from the columnar growth to the 3D pattern formation regime as a function of the assisting ion energy is demonstrated. The effects of the metal content and the assisting ion current on the self-organized 3D patterns and surface periodicity are studied. The observed microstructures evolution is explained by ion-induced effects.

Acknowledgement

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P37 Al₂O₃ protective coatings on carbon fiber-based 3D-textile preforms prepared by ALD for application in metallic composite materials

M. Krug^{1*}, A.Z. Abidin², M. Höhn¹, I. Endler¹, N. Sobczak³ and A. Michaelis²

¹Fraunhofer IKTS, Winterbergstraße 28, 01277 Dresden, Germany

²TU Dresden, Institute of Material Science, 01062 Dresden, Germany

³Foundry Research Institute, Zakopianska St. 73, 30418 Cracow, Poland
mario.krug@ikts.fraunhofer.de

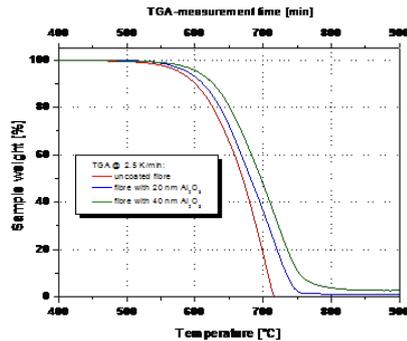
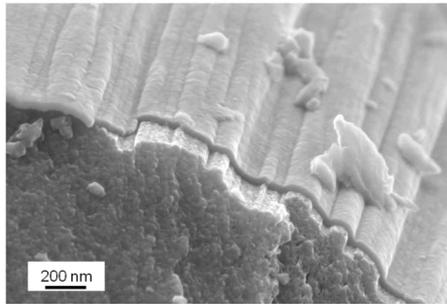


Figure 1: Conformal Al₂O₃-coating of a carbon fiber inside of a carbon fiber-based 3D-textile by atomic layer deposition

Figure 2: Oxidation resistance of a carbon fiber textile can be improved significantly by a thin ALD-Al₂O₃-layer

Carbon fiber-reinforced aluminum composites (Al/CF composites) offer favorable properties and high design flexibility for lightweight applications [1]. Nevertheless, poor wettability of carbon fibers by liquid aluminum alloys and high reactivity of carbon with liquid aluminum hinder a further development and limit the industrial application [2]. To overcome these limitations an alumina protective coating is applied by atomic layer deposition (ALD) on carbon fiber-based 3D-textile. The deposition is carried out at a substrate temperature of 220°C using the precursors trimethylaluminum (TMA) and ozone. SEM analysis revealed a conformal and uniform coating (30±5 nm) with good adhesion to the fibers (figure 1). Only a slight tensile strength reduction from 3.95 GPa to 3.25 GPa was observed due to coating. TGA demonstrated the significant improvement of oxidation resistance of carbon fibers by an alumina coating (figure 2). Alumina coated carbon fiber-based 3D-textile preforms are infiltrated with AlSiCu alloy.

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P21 Triggerless vacuum arc plasma deposition of titanium oxide coatings on polymer tubes for medical application

Marina Kühn-Kauffeldt*, Carmen Forster, Jochen Schein

Universität der Bundeswehr München, Germany
marina.kuehn-kauffeldt@unibw.de

Different kinds of artificial implants are widely used to maintain various body functions. The choice of the implant material is crucial for the implant functionality and compatibility with the organism. Polymer materials are interesting for medical applications involving blood contact due their properties, such as flexibility, gas permeability or chemical stability. Unfortunately those materials often have one drawback – their surface is not biocompatible. In order to change that a coating with certain cells could be used to prevent a reaction by the immune system but up to now such cells cannot attach a polymer surface. However it is known that titanium oxide has anti-inflammatory activity and its surface promotes grows of cells of different type. One possibility to improve surface properties of polymers interesting as an implant material is to coat their surface with titanium oxide and so to provide a surface more suitable for cell growth, without having to renounce the properties of the used polymer. Triggerless vacuum arc plasma deposition is an interesting technique for producing such coatings since vacuum arcs are known to deposit dense thin coatings with good adhesion properties. Moreover when using the pulsed deposition mode the thermal load can be kept low, which is crucial in order to avoid damaging the polymer substrates. Several investigations have shown that for example endothelial cells can grow on titanium oxide surfaces deposited by vacuum arcs on various substrates. In particular it was also shown that surface of plane polymer foils coated by titanium oxide using pulsed triggerless vacuum arc plasma deposition provides a suitable bedding for cell growth. In medical applications the geometry of the surface to be coated is often not plane but has a more complex structure. The advantage of the vacuum arc deposition is that the process can be adapted for coating of more complicated geometries, e. g. inner surface of tubes. The aim of this work is to modify the previously used deposition apparatus so that it is possible to deposit thin titanium oxide coatings on the surface of inner tubes using vacuum arcs. The main challenge here is to create a homogeneous coating while maintaining the quality of the coating as produced with the flat deposition setup. In order to achieve this goal different deposition geometries and deposition parameters are tested. To evaluate the quality of the obtained coating the coating distribution over the circumference of the tube is investigated. Moreover coating composition and structure are analyzed and compared to the coatings on the flat substrates.

P42 Growth-induced defect generation and intrinsic stress in Ta sputtered films: a comparison between α -Ta and β -Ta phases

C. Mastail*, J.J. Colin, A. Michel, C. Jaouen and G. Abadias

Institut P³, CNRS-Université de Poitiers, SP2MI-Téléport 2, Bd Marie et Pierre Curie, F-86962 Futuroscope-Chasseneuil, France
cedric.mastail@univ-poitiers.fr

The metastable tetragonal β -phase of Ta is commonly observed in tantalum sputtered films. This phase is characterized by a higher hardness and electric resistivity, compared to the equilibrium body centered cubic (bcc) α -phase allotrope. Despite its use in a variety of applications (resistor, capacitor, X-ray optic), the mechanical properties of the beta-phase are not well known. In the present work, we comparatively study the stress development during growth, and subsequent evolution during post-growth ion irradiation, in α and β -Ta sputtered films, by combining in situ wafer curvature and X-ray Diffraction (XRD). The influence of substrate bias voltage, in the [-200, 0] range, on the intrinsic stress and related lattice-expansion was investigated for both phases. Ion irradiation with 360 keV Kr ions, with low ion dose varying from 0.16 to 2 dpa, was used as an effective tool to study stress relaxation.

Alpha and beta Ta films were deposited by magnetron sputtering in Ar atmosphere on neutral

(a-Si) and crystalline bcc Mo (110) template layers, respectively. The elastic strain field in as-deposited and irradiated states was determined from XRD using the $\sin^2 \psi$ method, adapted for the case of textured layers, while the microstrain was obtained from a Williamson-Hall analysis of diffraction lines integral breadth.

β -Ta films were found to be more sensitive to the applied bias voltage, resulting in larger compressive stress (up to -2.4 GPa at -190 V) compared to α -Ta films (typically around -1.5 GPa). This different stress behavior is explained by a higher propensity to point-defect creation during growth, and their subsequent instability under ion irradiation, in the metastable beta-Ta lattice compared to equilibrium α -Ta.

P09 2D PIC modelling of HIPIMS plasma. Application to spokes simulation by pseudo 3D-PIC

T. Minea*¹, A. Revel¹, C. Costin² and L. Caillault¹

¹ Laboratoire de Physique des Gaz et des Plasmas-LPGP, UMR 8578, CNRS - Université Paris-Sud, 91405 Orsay, France

² Alexandru Ioan Cuza University, Faculty of Physics, Bd. Carol I nr. 11, Iasi, 700506, Romania
tiberiu.minea@u-psud.fr

Since 2000, the HiPIMS discharges have focused the attentions of the scientists and industrial companies due to their capability to highly ionize the sputtered material from the target opening new ways for PVD process control as well for tailored thin film materials. In spite of the important research effort made to better understand the HiPIMS, only a few works were devoted to plasma modeling and no one addresses the plasma 2D or 3D evolution during the pulse. In the last years we have developed a 2D Particle-in-Cell code – called OHIPIC (Orsay High density Particle in Cell) – simulating plasma behaviour including a simplified kinetics of Argon species treated by Monte Carlo [1]. The pulse was chosen very short ($\sim 5 \mu\text{s}$) and a weak plasma is assumed already present (corresponding to the dc case) in the discharge volume corresponding to pre-ionization power supply. Hence, it is possible to obtain very fast variation of the voltage ($\sim 1 \mu\text{s}$), but leading to important increase of the plasma density, more than two orders of magnitude. Moreover, the very narrow sheath (< 0.5 mm), the gyrofrequency and the stability criteria require the use of very small time-steps. In spite of all these constraints, OHIPIC can give a complete picture of the 2D (x, z) plasma parameter evolution at microscopic scale (e.g. *eedf*) and local macroscopic scale (potential, density, etc). The first address of the spokes phenomena via numerical modelling was performed using a posteriori 3D Monte Carlo technique [2], since spokes are intrinsically 3D. Using the knowledge acquired from OHIPIC, we have recently developed a pseudo-3D PIC model solving Poisson's equation not only in the plane perpendicular to the target (x, z), but also azimuthally, in (y, x) and (y, z). This is possible because the PIC particle trajectories are 3D calculated. In 2D OHIPIC, they are projected on the (x, z) plane. In pseudo-3D we use the projection of the same particles on two other planes (y, x) and (y, z), the latter one corresponding to the race-track. This highly reduces the computation time and produces good qualitative results. Numerical simulations shows that the velocity drift $\mathbf{E} \times \mathbf{B}/B^2$ combined with the space charge repulsion lead to a non uniformity of the magnetron plasma along the azimuthal direction (Oy) resulting in the creation of spokes [2]. The results obtained, such as ion and electron 3D density maps and their projection along the azimuthal direction will be presented and discussed, as well as the effect of the ion mass.

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P25 Surface plasmon absorption in Ag containing amorphous TiO₂ films grown by pulsed cathodic arc

A. Mosquera^{*1}, D. Horwat², E. Roman¹, S.Migot², S.Weber², J.M. Albella¹ and J. L Endrino³

¹ Instituto de Ciencia de Materiales de Madrid, CSIC, E-28049 Madrid, Spain.

² Institut Jean Lamour, Ecole des Mines de Nancy, Parc de Saurupt, 54042 Nancy, France.

³ Abengoa Research S.L, C/ Energía Solar 1, Palmas Altas 41014, Sevilla, Spain.

aamosquera@icmm.csic.es

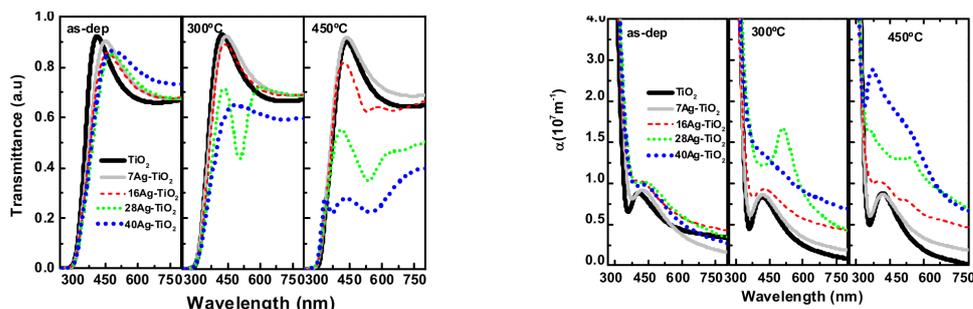


Figure 1: Optical properties of the Ag contained TiO₂ (a) before and after (b) and (c), the annealing at different temperatures. The SPR absorption band is observed for the films with highest silver concentration.

An unfiltered deposition system provided with a miniature cathodic arc (“minigun”) has been used to grow Ag containing TiO₂ films in a rich oxygen atmosphere. This technique is able to produce high ionized plasmas, allowing the control of the film morphology. By controlling the pulse ratio of the three cathodes minigun, it was possible to obtain films with different silver concentration and high adhesion to the substrate. The structural and optical properties of Ag containing TiO₂ films have been investigated. As-deposited samples show that silver is incorporated in the Ag⁺² and Ag⁺¹ state, coexisting with the amorphous TiO₂ structure in the films, with no evidence of surface plasmon resonance (SPR) effects. However, annealing the samples with (Ag/Ag + Ti) ratio concentration above 16.0% at 300 °C produces the evolution of the Ag oxides to metallic silver (Ag⁰), with the formation of nanoparticles that diffuse to the surface of TiO₂, resulting in an absorption band around 500 nm, associated to SPR effects. Higher annealing temperatures above 300 °C gives rise to a redshift in the surface plasmon absorption band, determined by the size of the Ag nanoparticles.

Furthermore, samples with Ag concentration higher than 28%, annealed at 450 °C show a delay in the crystallization temperature of the TiO₂ from the amorphous to the anatase phase.

P03 CHRAVA a more or less new thin film arc evaporation technique

S. Muhl^{*1}, S.E. Rodil¹, I. Camps¹ and E. Camps²

¹ Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, D.F. México.

² Instituto Nacional de Investigaciones Nucleares, Edo. de México, México

muhl@unam.mx

We present the work of the PlasNaMat group on the development of a new plasma assisted deposition method. This method is a cylindrical version of the Hot Refractory Anode Vacuum Arc (HRAVA) system developed by R.L. Boxman of Tel Aviv University, Israel. In our system, the electrodes rather than being parallel plates, consists of a water cooled cylindrical cathode and

a concentric graphite anode rod (CHRAVA). A solenoid surrounding the cathode can provide a variable magnetic field along the cathode axis. When a cathode arc is triggered, the magnetic field can be used to move the cathode spot in a circular path around the inside of the cathode. The anode is rapidly heated to around 2000 °C such that the deposited on the anode from the cathode arc is thermally evaporated and an anodic plasma (thermionic emission of electrons) plus the cathode plasma is generated. The advantage of the present arrangement is that a beam of emitted material is directed along the axis of the cylindrical cathode. Deposition rates can be ≥ 5 nm/s, with a degree of ionization up to 100 %. Additionally, the system can be used with a reactive atmosphere to produce compound deposits. We have studied the optical and electrical characteristics of the plasma as a function of the applied electrical power, gas pressure and the magnetic field. Thin films of aluminum, aluminum oxide and nitride thin films have been produced as a function of the experimental parameters.

P38 Effect of ion energy and deposition rate on the phase formation of Al_2O_3 thin films grown by filtered cathodic arc

*F. Nahif, S. Mraz, D. Music and J.M. Schneider

Materials Chemistry, RWTH Aachen University, 52074 Aachen, Germany
nahif@mch.rwth-aachen.de

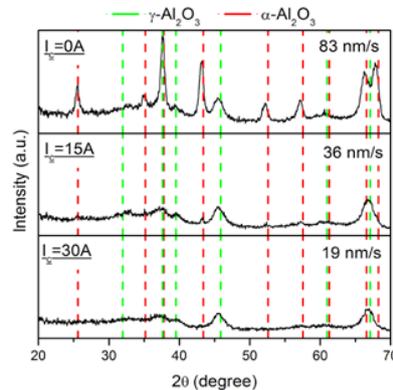


Figure 1: Phase evolution of Al_2O_3 thin films deposited at an Al^+ ion energy of 40 eV as function of reduced deposition rate. I_c indicates the different coil currents of the magnetic plasma defocussing coils.

The effect of ion energy on the phase formation of Al_2O_3 thin films is investigated by employing a monoenergetic Al^+ beam generated by using filtered cathodic arc technique. Ion energies in the range of 2 to 40 eV are probed by applying a substrate bias potential. The formation of the $\alpha\text{-Al}_2\text{O}_3$ phase at a substrate temperature of 720 °C is observed at a critical Al^+ ion energy of 40 eV [1]. Ab initio MD simulations suggest that subplantation is the atomic scale mechanism enabling the growth of the alpha phase at this energy [2]. The effect of the deposition rate on the phase formation is hence investigated at the critical Al^+ ion energy of 40 eV. The deposition rate was affected by defocussing the Al^+ ion beam. With decreasing deposition rate a transition from mainly $\alpha\text{-Al}_2\text{O}_3$ and traces of $\gamma\text{-Al}_2\text{O}_3$ to mainly $\gamma\text{-Al}_2\text{O}_3$ is observed.

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P24 Magnetron Sputtering of low resistivity TiO₂-based transparent conductive oxides and the role of energetic particles

M. Neubert^{*1}, T. Gebel², H. Liepack², A. Kolitsch^{1,3} and M. Vinnichenko¹

¹ Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, P.O. Box 510119, 01314 Dresden, Germany

² DTF Technology GmbH, 01108 Dresden, Germany

³ HZDR Innovation GmbH, 01328 Dresden, Germany
m.neubert@hzdr.de

TiO₂-based transparent conductive oxides (TCOs) are considered as a cost-efficient, environmentally friendly and chemically inert alternative to conventional TCOs. The Nb or Ta doped TiO₂ (TNO, TTO) films epitaxially grown on crystalline substrates show electrical and optical properties which are comparable to those of conventional TCOs. However, it is still a challenge to achieve low electrical resistivity polycrystalline TiO₂ films as required for the most applications. Furthermore, it is not possible to get low resistivity in polycrystalline films by direct growth at elevated substrate temperature. Only the two-step process involving the growth of amorphous TNO and TTO films on glass and their post-deposition annealing provides films with electrical resistivity in the range of 10 to 3 Ωcm. The major challenge to achieve low electrical resistivity films is the desired anatase growth due to the larger effective mass of rutile. It is known that the crystallization is strongly affected by the Ti/O ratio in the as-deposited films. However, there is still a contradiction which structural properties lead to rutile and anatase, respectively. In order to address this problem we prepared TTO films using direct current magnetron sputtering (DC-MS) followed by annealing in vacuum at 420 °C. During the DC-MS, amorphous films were grown on glass by using electrically conducting TiO₂-x:Ta targets. We applied a closed-loop feedback system based on a plasma emission monitor to fine-tune the oxygen partial pressure. The x-ray amorphous films convert into films with dramatically different structure during annealing depending on the oxygen partial pressure and total pressure used during the deposition. We show that it is possible to prevent the formation of rutile at higher total pressure in order to achieve desired anatase growth. We consider the energy of neutral and ionized particles as an important factor to form structural changes in the as-deposited films. The as-deposited films were systematically investigated using XRD, TEM, RBS and XANAS in order to find structural differences responsible for the phase formation.

P20 Ion beam textured TiN as template for YBa₂Cu₃O_{7-x} coated conductors

*P. Pahlke, J. Hänisch, L. Schultz, B. Holzapfel and R. Hühne

IFW Dresden, P.O. Box: 270116, 01171 Dresden, Germany

High temperature superconducting cuprates as YBa₂Cu₃O_{7-x} (YBCO) are promising materials for power applications at liquid nitrogen temperature. However, a strong biaxial texture is required in these compounds to achieve high current densities due to the detrimental effect of high angle grain boundaries. Ion Beam Assisted Deposition (IBAD) is one of the major approaches to realise biaxially textured templates, which are used afterwards for the growth of epitaxial YBCO layers to form a so-called coated conductor. The ion beam directed towards the substrate under an off-normal angle leads to an oriented nucleation of grains on amorphous or nanocrystalline surfaces. IBAD-TiN reveals a strong cube texture at a thickness of less than 10 nm, similar to the IBAD-MgO process. Recently, we started to study the influence of the deposition method on the texture formation during nucleation in IBAD-TiN. Therefore, we equipped our ion beam assisted pulsed laser deposition system with an additional electron beam evaporator. In all cases, a reactive deposition process was used for the growth of the TiN layer. The texture formation during nucleation was studied using in-situ reflection high energy electron diffraction. The influence of the different deposition conditions on the creation of a sharp cube texture in TiN will be discussed.

P31 Sheath thickness and microstructure in amorphous carbon thin film

*A. Pardo, R. Bonet, J. Caro

Fundació Centre Tecnològic Manresa
ainhoa.pardo@ctm.com.es

Cathodic arc physical vapor deposition is a widely used technique in the thin film growth of hard amorphous carbon (a-C). The plasma formed is mainly characterized by a high ionization degree ($\sim 100\%$) and by elevated ion energies (20 to 200 eV), responsible of the high densities and hardness achieved in the films. The ion energy at the growing surface is a determinant factor in the growth process (energetic condensation) and thereby on the formed microstructure. The energy and trajectory of the evaporated ions can be controlled by the application of electrical and magnetic fields. The application of negative bias to the substrate immersed in the plasma leads to the plasma sheath formation. In particular, the kinetic energy may be modified by collisions within the plasma sheath. The key factor to produce high hardness in a-C films is related to the promotion of sp^3 bonding. Therefore, assuming a collisional sheath, the microstructure of the film may be governed by the sheath thickness formed on the substrate surface.

This study explores the differences in microstructure and properties of hard amorphous carbon films grown on stainless steel substrates as function of the effective bias on the growing surface, i.e. as function of the ion energy of the incoming ions. The a-C films were deposited using a pulsed cathodic-arc plasma source combined with a 90° magnetic macroparticle filter applying a pulsed bias voltage to the substrate. As a strategy to reduce the plasma sheath thickness and therefore increasing the ion energy at the growing surface, one of the substrates was electrically isolated. The resultant microstructure has been studied by Raman and X-ray photoelectron spectroscopies, revealing a higher content of sp^3 hybridization in the electrically isolated substrate as compared to the biased one (47 to 63%). The tribological and mechanical properties of the films have been studied by Rockwell adhesion tests, nanoindentation and micro-scratch tests. Significant differences have been obtained in the adhesion, hardness (27 to 52 GPa), coefficient of friction (0.15 to 0.2) and micro-scratch critical load (1.06 to 1.33 N).

P29 Characterization of Microwave Surface Wave Plasma in Linear Configuration and Growth of Nano-Sized Carbon Allotropes

*Š. Potocký, M. Čada, O. Babchenko, T. Ižák, M. Davydova, B. Rezek and A. Kromka

Institute of Physics AS CR, v.v.i., Cukrovarnická 10, 162 00 Praha 6, Czech Republic
potocky@fzu.cz

Recently, design and optimization of the microwave plasma CVD techniques has reached matured state. Design and optimization of microwave plasma reactors is dominated by high pressure systems (10 to 100 kPa). However, such high pressure microwave plasma, also labeled as “hot plasma”, is limited in the plasma volume which is in a form of ball or ellipsoid in a typical diameter up to 7 cm. Instead of such systems, microwave surface wave (MW-SW) plasma utilizing linear antenna(s) or slot window(s) become an attractive CVD method for growth of carbon allotropes over large areas ($> 100\text{ cm}^2$) [1, 2, 3].

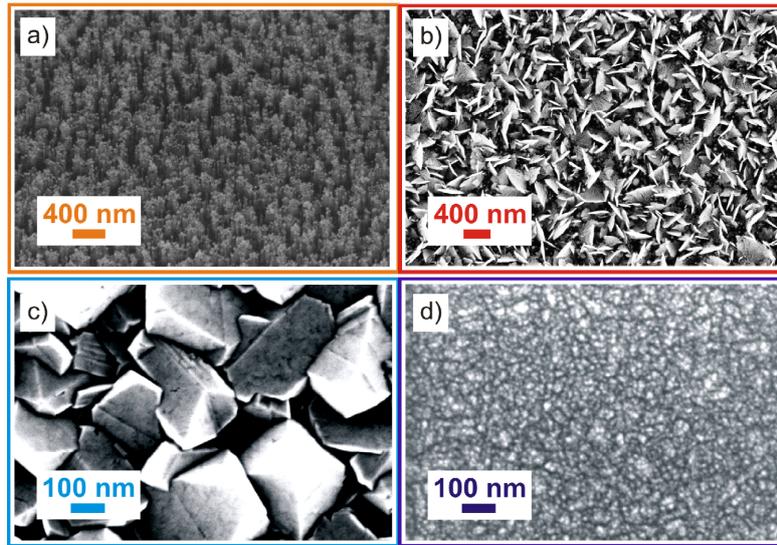


Figure 1: SEM morphology of the grown carbon nanostructures: a) CNT growth with RF bias, b) carbon nano-sheets growth with DC bias, c) large and lateral growth of diamond crystals grown at 6 Pa, and d) ultra small diamond crystals grown at 200 Pa in the microwave surface wave plasma reactor with linear antennas.

In this work we use a MW-SW plasma assisted CVD process to grow different carbon forms as carbon nanotubes, carbon nano-walls/sheets, diamond or even graphene (see Fig. 1). A complex correlation between process parameters, plasma characteristics and the deposit is presented. Spatially resolved Langmuir probe measurements were done to calculate plasma temperature, density of species, plasma potentials, etc. For the diamond thin film growth, i.e. all carbon atoms are in sp^3 hybridization, we found that transformation from poly- to nano-crystalline character is significantly influenced by plasma temperature and density, especially for process pressures lower than 50 Pa. On the other hand, the growth of sp^2 hybridized carbon forms (CNT and nano-walls/sheets) is a correlative of biased substrate. Decreasing of process pressure from 10 down to 6 Pa was required to grow perpendicularly oriented carbon structures over large areas. Applying dc or rf substrate bias is found as a crucial technological parameter for growth of sp^2 carbon allotropes by MW-SW plasma in the linear antenna configuration.

Finally, we will show that MW-SW plasma is also a promising way for surface treatment of carbon nanotubes or diamond thin films, and thus tailoring of their wetting properties (hydrophobic vs. hydrophilic).

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P41 Oxygen Incorporation in Cr₂AlC Investigated by Combinatorial Thin Film Synthesis and X-Ray Stress Analysis

*L. Shang, M. to Baben, J. Emmerlich, J.M. Schneider

Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, 52074 Aachen, Germany
shang@mch.rwth-aachen.de

The oxygen incorporation in Cr₂AlC was studied by combinatorial thin film synthesis. Thin films with chemical concentration gradient were deposited by DC magnetron sputtering from elemental targets, and oxygen was intentionally introduced. Ab initio calculation results indicate that oxygen is incorporated interstitially in the Al layer of Cr₂AlC, even for carbon-deficient Cr₂AlC. Two phase-regions of Cr₂AlC and Cr₂Al were investigated in order to study oxygen incorporation in carbon-deficient Cr₂AlC. X-ray stress analysis data indicate that the a and c lattice parameters increase with increasing oxygen content. These trends are in good agreement with the change in lattice parameters predicted by ab initio calculations and therefore corroborate the notion of interstitial oxygen incorporation in Cr₂AlC. A metastable solubility limit for oxygen of 3.5 at.% was determined. This is the first report on interstitial oxygen incorporation in MAX phases and may be of relevance to the initial stages of oxidation.

P13 High Current Impulse Magnetron Discharge. Influence of the single pulse power on a deposition rate.

*I.A. Shchelkanov and G.V. Khodachenko

National Research Nuclear University (MEPhI), Moscow, Russian Federation
shchelkanov.ivan@gmail.com

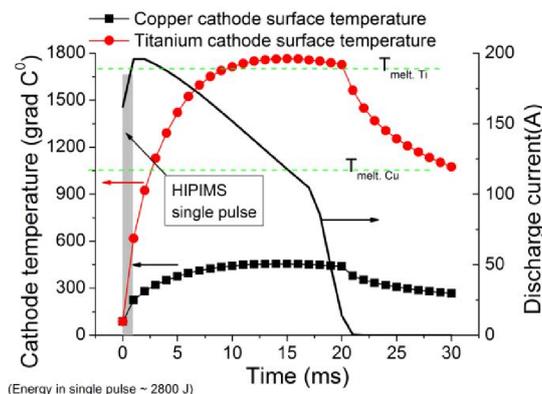


Figure 1: The time evolution of the titanium and copper cathode surface during a single impulse of the high current impulse magnetron discharge.

In early publications made by Mozgrin [1] et. al. an impulse deposition rate up to 80 $\mu\text{m/s}$ was reported for High Current Impulse Magnetron Discharge (HCIMD) with copper target and up to 6 $\mu\text{m/s}$ for titanium target.

This discharge operates in similar conditions as a well known HiPIMS discharge, but apart from the HiPIMS the HCIMD has a quasistationary phase with a high current up to 200 A with high voltage up to 1500 V and it operates with low frequencies from 0.01 to 10 Hz. The quasistationary phase of the discharge can be as long as 20 ms and single pulse energy can be as high as 2800 J. Such a high impulse power provides a very intensive heating of the cathode, this leads

to the evaporation of the target is started during the single pulse, hence the high deposition rate. Previously, there weren't any explanations of such a high deposition rate.

A mathematical model was built to investigate the evolution of the cathode surface temperature during the single pulse of the HCIMD. This model was verified by direct measurements of the cathode temperature. Assumptions: only eroded cathode area is heated with an incoming ion flux and the cathode as a whole is heated with current. The optic emission, thermal electron emission, secondary ion-electron emission, sputtering and evaporation are involved in cathode cooling. The temperature distribution is calculated inside the whole disk shaped cathode 2 mm thickness and 90 mm diameter. The magnetic system is slightly unbalanced that and cathode erosion zone is about 12 cm². The time step in the model is automatically adjusted to provide the temperature increase less than 2 ° per time step. The cathode has a perfect thermal contact with the water cooled body of the magnetron.

Due to the very low thermal conductivity of the titanium target a thin surface layer is heated up to the very high temperature, hence the sublimation and evaporation are started. The sublimation/evaporation provides a high deposition rate in the HCIMD. The theoretical model fully explains a metal coating high pulse deposition rate in the HCIMD.

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P18 Investigation of TiO₂ and Nb₂O₅ materials produced by Ion-Assisted PVD

T. Tolenis*, R. Drazdys and R. Juškėnas

Center for Physical Sciences and Technology, Savanoriu ave. 231, LT-02300 Vilnius, Lithuania
tomas.tolenis@ftmc.lt

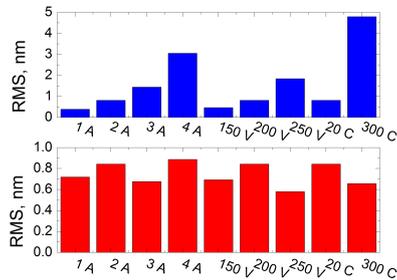


Figure 1: Surface roughness of TiO₂ (blue bars) and Nb₂O₅ (red bars) samples.

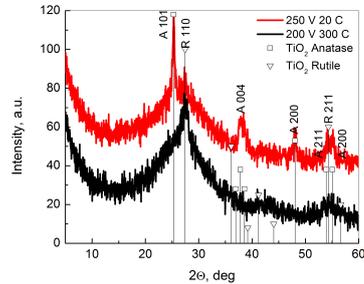


Figure 2: XRD measurements of TiO₂ samples produced with IBA voltage of 250 V and at 300 °C.

Optical and structural properties of high refractive index materials, produced by Physical Vapor Deposition (PVD) with Ion-Beam Assistance (IBA), was investigated. “Vera 1100” deposition machine with Kauffman type ion-beam source “IBS 120” was used to coat monolayers of TiO₂ and Nb₂O₅ materials. Different IBA regimes were used to deposit each sample. For optical properties of thin films, spectrophotometric measurements were obtained and dispersions of

refractive index and extinction coefficient were modeled. For structural properties of thin films, surface roughness were measured with atomic force microscope and for TiO_2 samples molecular structure was analyzed by X-Ray Diffraction (XRD) technique.

Standard IBA regimes was held to be 2 A current and 200 V voltage for anode, 0.45 A current for solenoid and temperature of 20 °C in the chamber. By changing one of the process parameter, the others were held standard. Thicknesses of the monolayers varied in the range 380 to 430 nm for Nb_2O_5 and 520 to 600 nm for TiO_2 .

For low particles energies (150 V) and density (1 A) of IBA, refractive indices were found to be low for both Nb_2O_5 and TiO_2 . By increasing the energy or the density of the particles, refractive index increased in both cases. The increase for TiO_2 (13 %) was observed to be bigger than for Nb_2O_5 (4 %). Dispersions of extinction coefficients continuously shifted to the blue side of the spectrum, when the energy or the density of IBA particles was decreasing. Increased temperature, was observed to have little influence on refractive index or extinction coefficient dispersions.

The surface roughness of the Nb_2O_5 thin films appeared to be independent of the process regimes (Fig. 1). In all cases the value of Root Mean Square (RMS) was below 1 nm. That agreed with the bare substrate measurements. For TiO_2 samples, RMS was increasing in every case: increasing IBA particles energy or density and by increasing the temperature of the substrates. Biggest roughness was obtained evaporating on the heated substrates. This fact was explained by measuring the molecular structure of TiO_2 films. Samples produced at 250 V of IBA and at 300 °C were polycrystalline. The dominated structure was Anatase and Rutile respectively (Fig. 2). The other films of TiO_2 were found to be amorphous.

P22 Development of novel titanium-based surfaces using plasma and ion beam technologies

I. Tsyganov

Department of Physical Metallurgy, Lipetsk State Technical University, Moskovskaya 30, 398600 Lipetsk, Russia
zyganov@daad-alumni.de

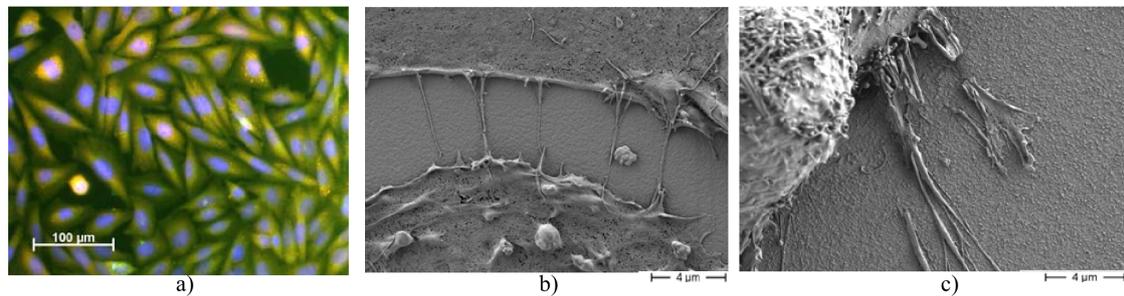


Figure 1: Cell attachment (a) and spreading (b) on bare $\text{TiN}_{0.4}\text{O}_{1.6}$ and on HA-coated $\text{TiN}_{0.4}\text{O}_{1.6}$ (c) 24 h after seeding.

Plasma and ion beam technologies have been proved to be effective approaches for modification of surface properties of different materials. In the present work, structure, phase composition, hydrophilicity and microhardness of titanium oxynitride TiN_xO_y , pure and phosphorus ions implanted TiO_2 coatings produced by metal plasma immersion ion implantation and deposition (MePIIID) were investigated.

The phase composition and correspondingly surface properties of the layers were strongly dependent on the partial pressure of the working gases in the vacuum chamber. The best wettability as well as maximal microhardness between investigated Ti-based films have been found for

the titanium oxynitride coating with average atomic composition $\text{TiN}_{0.4}\text{O}_{1.6}$, consisting mainly of amorphous Ti oxide with nitrogen substitution. These parameters for slightly amorphised P-implanted TiO_2 layer are between the corresponding values for $\text{TiN}_{0.4}\text{O}_{1.6}$ and rutile-type TiO_2 .

To evaluate the correlation between the structure of the layers and their cytocompatibility, the influence of the surfaces on the behavior of human osteoblast-like SaOS-2 cells was studied in vitro. The cells were cultured on the three Ti-based coatings, both on the bare surfaces as well as on the surfaces biomineralised from simulated body fluid (SBF). Fig. 1 shows exemplarily the typical cell attachment and spreading on the bare $\text{TiN}_{0.4}\text{O}_{1.6}$ surface as well HA-coated 24 h after seeding.

No statistically significant differences were observed for cell adhesion to all bare Ti-based surfaces. Cell proliferation and differentiation were surface sensitive and showed an opposite effect: cell differentiation on the P-implanted TiO_2 and TiN_xO_y surfaces was reduced whereas the proliferation increased in comparison to TiO_2 . The reason for this behaviour may be that phosphorus, nitrogen and their compounds in the surface act as biochemical functional groups with beneficial effects.

Biomimetalisation of the Ti-based layers from SBF affects adversely the cell behaviour on the surfaces in vitro. A possible explanation for this negative influence may be the uptake of calcium ions by hydroxyapatite phases formed in SBF.

In general, the good mechanical properties and biocompatibility of titanium oxynitride $\text{TiN}_{0.4}\text{O}_{1.6}$ and P-implanted titanium oxide TiO_2 without any toxic and/or expensive elements make these Ti-based layers interesting candidates for long-term studies in vivo.

P23 Influence of preparation conditions on evolution of Titania phases

V.Vishnyakov and J.Colligon

Dalton Research Institute, Manchester Metropolitan University, Manchester, M1 5GD, UK
v.vishnyakov@mmu.ac.uk

Titania (TiO_2) can exist in a few different phases amongst which anatase and rutile are the most widely known and the latter one is ubiquitous. However the former one, anatase, has lately attracted most attention due to its photocatalytical activity and ability to clean the environment from polluting substances. While bulk, liquid-based synthesis, of anatase has been developed and is widely used, the thin film route has only been industrially achieved by Chemical Vapour Deposition and a direct Physical Vapour Deposition (PVD) approach at low temperatures is but a daydream. In the majority of cases low temperature as-deposited PVD Titania films are amorphous and require additional post-deposition heating to transfer to the anatase phase.

In the present study Titania films were deposited onto Si and glass substrates at temperatures up to 4500 °C in a dual Ion Beam deposition system where one ion beam sputters the Titanium target and the other provides additional energy to control the nucleation and growth of the film. The composition of the film was monitored by X-Ray spectroscopy and the phase structure determined by micro-Raman. It was show that, by using ion bombardment, it is possible to prepare mixed phase anatase-rutile mixtures with the best possible catalytic activity at temperatures as low as 2500 °C. It was also found that the amount of oxygen content in the film needs to be closely monitored as an over-stoichiometric level of oxygen significantly suppresses formation of anatase and shifts the transition from amorphous to anatase phase to higher temperature.

P05 Time resolved tunable diode laser spectroscopy in HiPIMS discharge for the spatio-temporal description of neutral species

C. Vitelaru^{1,2*}, T.Minea¹, G. Popa³

¹ Laboratoire de Physique des Gaz et Plasmas, UMR 8578 CNRS, Université Paris Sud-XI, 91405 Orsay Cedex, France

² National Institute for Optoelectronics, POB – MG 05, Ro-77125, Magurele-Bucharest, Romania

³ Faculty of Physics, Al I Cuza University, Bd. Carol No 11, Iasi, 700506, Romania
catalin.vitelaru@inoe.ro

Magnetron sputtering is already a well-established technique widely used for thin film deposition and plasma processing [1]. Nevertheless, the recent development of pulsed power supplies [2] has launched new challenges in both fields of thin film deposition and plasma diagnostics. The time scale of relevant processes spans over several orders of magnitude: seconds for surface involving phenomena, milliseconds for the repetition rate and the transport of sputtered species, tens of microseconds for the phase ignition and stable state of the high power pulse, sub-microsecond for electron driven processes such as excitation, de-excitation, etc. Therefore, in the description of the rich physics involved in HiPIMS (High Power Impulse Magnetron Sputtering) process there is an acute need of time resolved diagnostic tools. Laser spectroscopy is one of the most suitable diagnostic techniques when it comes to the investigation of neutral or charged species in gas phase, having the advantages of being non-intrusive, offering local information and good spectral resolution. Among the different types of laser sources, the diode lasers are favored especially in the applications where the spectral resolution is critical, offering a line width of the measuring tool on the order of 1 to 10 MHz. These laser sources have been used for measuring particle density and temperature [3] or velocity distribution function [4, 5]. In the last years we have developed time resolved techniques suitable for the spatio-temporal description of particle density and temperature, both during the high power pulse [6] and in the afterglow phase [7]. This contribution offers an overview of these techniques, emphasizing the experimental procedures that have been used for different applications. There will be three main subjects of interest, which will be illustrated by typical results:

1. dynamics of neutral metal atoms (Ti) in the after-glow phase, involving transport to the substrate and thermalization
2. dynamics of gas (Ar) metastable atoms during the high power pulse, involving electron related processes, transport processes and gas rarefaction
3. kinetics of reactive gas (O) metastable atoms, both during the high power pulse and the after-glow phase, showing a temporal and spatial separation of volume and surface processes

in the reactive environment.

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P08 Ion Energy Distributions in DC magnetron sputter deposition of Al-doped Zinc oxide

Christian Wilde

Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion-Beam Physics and Materials Research, Bautzner Landstraße 400, 01328 Dresden, Germany and
Technical University of Dresden, Helmholtzstraße 10, 01069 Dresden, Germany
c.wilde@hzdr.de

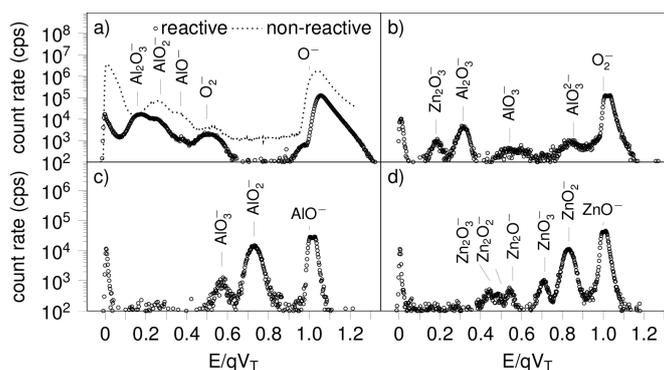


Figure 1: Energy distribution of different negative ions including the origin of fragments. All graphs were obtained at 450 and 1 Pa, which is in the transition mode in case of the reactive process in a)

The energy of ion in any PVD technique and its distribution (IEDF) is of decisive importance for film growth. On the one hand, low energetic ions increase the ad-atom mobility and lead to an improvement of film properties. On the other hand, higher energy incident ions induce atomic displacement, which in some cases leads to a disturbed growth and deterioration of film quality. However, the influence of the assisting ion irradiation for different energies is not completely understood. Here, we investigate ion distributions in the reactive and non-reactive magnetron sputter deposition of Aluminum-doped Zinc Oxide (AZO) in DC mode. We are comparing mass spectra, lateral distributions and different sputter regimes in reactive sputtering. Additionally, fitting approaches to high energetic ion distributions will be shown, including information about binding energies. Some attempts to explain the origin of ion and ion energy distribution will be made, leading to general conclusions about fundamental differences between reactive and non-reactive deposition of transparent AZO.

P39 Microstructure design of TiAlN based coatings via energetic particle bombardment during cathodic arc evaporation

Christina Wüstefeld^{1*}, David Rafaja¹, Mykhaylo Motylenko¹, Dietrich Heger¹, Claude Michotte², Christoph Czettl³, Martin Kathrein^{3,4}

¹ Institute of Materials Science, TU Bergakademie Freiberg, D-09599 Freiberg, Germany

² Ceratizit Luxembourg S.à.r.l., L-8201 Mamer, Luxembourg

³ Ceratizit Austria GmbH, A-6600 Reutte, Austria

⁴ Present address: PLANSEE SE, A-6600 Reutte, Austria

wuestefeld@ww.tu-freiberg.de

This study addresses the microstructure formation of TiAlN based coatings which were deposited by cathodic arc evaporation (CAE). For this purpose, TiAlN monolayers and TiAlN / AlTiRuN multilayers were deposited from powder metallurgical $Ti_{1-x}Al_x$ ($x = 0.40, 0.50, 0.60, 0.67$) targets and $Ti_{0.5}Al_{0.5} / Ti_{0.33-y}Al_{0.67}Ru_y$ ($y = 0, 0.01, 0.05$) targets, respectively. The CAE deposition

was done at different bias voltages between -20 V and -120 V in order to vary the energy of the impinging ions. The microstructure of the coatings was characterised by wavelength-dispersive electron probe microanalysis, X-ray diffraction, hardness measurements and analytical transmission electron microscopy using electron energy loss spectroscopy and X-ray energy dispersive spectroscopy. The microstructure analysis revealed the chemical and phase composition, the stress-free lattice parameter, preferred orientation of crystallites, crystallite size, microstrain and macroscopic lattice strain of the face centred cubic (fcc) (Ti,Al)N phase. It was found that the microstructure of the TiAlN based coatings can be designed by the applied bias voltage during deposition. With increasing bias voltage an increase of the microstrain and macroscopic lattice strain of the fcc (Ti,Al)N phase was observed which indicated a rising defect density and higher concentration fluctuations of Ti and Al within the fcc-phase at high bias voltages. The high defect density and the higher concentration fluctuations were accompanied by the formation of minor segregations of fcc-AlN or Al-rich fcc-(Ti,Al)N at high bias voltages leading to the reduction of the size of cubic crystallites. Furthermore, the application of a high bias voltage during deposition retarded the formation of wurtzitic AlN in the Al-rich coatings. The microstructure designed by the bias voltages influences the hardness of the as-deposited coatings on the one hand and the thermal stability of the coatings at elevated temperatures on the other hand.

P02 Influence of hollow cathode plasma activation on the growth of Cu(In,Ga)Se₂ thin films

R. Würz¹, F. Kessler¹, H. Morgner², S. Saager²

¹ Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden Württemberg (ZSW), Stuttgart

² Fraunhofer Institut für Elektronenstrahl- und Plasmatechnik (FEP), Dresden

roland.wuerz@zsw-bw.de

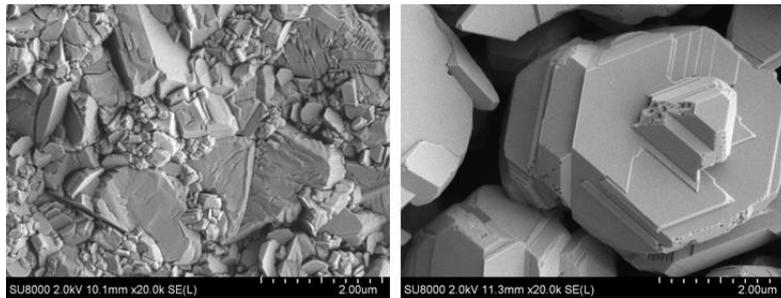


Figure 1: SEM top view on Cu:Se layers deposited without plasma (left) and with plasma activation (right).

When growing Cu(In,Ga)Se₂ (CIGS) absorber layers for CIGS thin-films solar cells on polyimide foil the maximum substrate temperature is limited to 450 °C to 500 °C compared to about 600 °C process temperature on glass substrates. Hence crystallization of CIGS grains needs to be optimized by e.g. prolonging the process time. That may be a possible option in the lab but not in industrial application. The activation of the CIGS-layer growth by plasma-activation is another way to enhance the crystallization process at low substrate temperatures.

Plasma-activation of vapor in thermal evaporation process results in additional excited and ionized particles. Ions gain additional energy by acceleration in the electric field of plasma sheath which covers the insulating substrate. The self-bias effect is employed for negative charging of the substrate surface. A special hollow cathode arc discharge source has been developed for CIGS plasma activation. Cathode and anode are arranged outside the vapor cloud. The plasma within the vapor is generated by directed electrons originate from the cathode of plasma source. The directed electrons are extracted through an aperture in the anode. An additional inhomogeneous magnetic field helps for thrusting plasma towards vapor cloud.

For qualification of plasma source, especially for modifying the source enabling long term operation in aggressive Se-atmosphere, experiments have been carried out with Cu:Se model system. Beside modification of plasma source the influence of plasma activation with variation of plasma parameters has been investigated using SEM- and EDS-analysis.

Fig. 1 shows the top view on layers deposited on Si-wafers at substrate temperature around 280 °C without plasma and with plasma activation. With plasma activation considerable changes in grain structure of deposited layers could be observed. Plasma activated deposition results in poly-crystalline structure with maximum grain size around 5 μm . The grain size of crystallites decreases with higher plasma dose.

EDS-investigations have revealed portions of copper from 65 to 67 at.% and of selenium from 35 to 33 at.% within the layers. It is assumed the deposited layers consist of a phase-mixture of $\beta\text{-Cu}_{2-x}\text{Se}$ (fcc-structure), Cu_3Se_2 (tetragonal structure) and $\beta\text{-CuSe}$ (hexagonal structure).

The hollow cathode plasma source as developed at FEP is inserted in a roll-to-roll CIGS inline process at ZSW to activate the CIGS growth. About the structural changes and other results will be reported.

P14 Growth of carbon-tungsten nanocomposites by high power impulse magnetron sputtering from compound targets

R.K. Yadav^{*1,2}, G. Abrasonis¹, F. Munnik¹, R. Heller¹, R. Hübner¹, W. Möller¹, J. Neidhardt³

¹ Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany.

² Institute of Plasma and Coating Physics, Linköping University, Sweden

³ VON ARDENNE Anlagentechnik GmbH, Dresden, Germany

er.rahul.y.1986@gmail.com

High-power impulse magnetron sputtering (HiPIMS, also known as high-power pulsed magnetron sputtering, HPPMS) is a method for physical vapour deposition of thin films which is based on magnetron sputter deposition. HiPIMS utilises extremely high power densities of the order of kWcm^{-2} in short pulses (impulses). A distinguishing feature of HiPIMS is its high degree of ionization of the sputtered metal and high rate of molecular gas dissociation. In this poster we present the study on the growth of C-W nanocomposite films grown in DC (MS) and HiPIMS modes. For deposition, we have used 3in C and C-W (90 to 10 at.%) substrates. In order to prevent arcing, the depositions were carried out with three-pulse sequence followed by a long off-time.

Film areal density was determined by Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA). Film microstructure was determined by Raman spectroscopy, X-Ray diffraction, and transmission electron microscopy. Film mechanical properties were studied by nanoindentation and scratch test. We got extensive arcing with pure carbon. In contrast, for the compound target we got stable plasma condition with duty cycle as low as 1 %. Deposited films consist of WC nanoparticles embedded in a carbon matrix. From NRA and RBS, the film areal density of tungsten shows a small decrease concomitantly with the duty cycle (transition from pulsed DC to HiPIMS). In contrast, the film areal density of carbon remains constant. This implies that in different sputtering modes like Ar^+ dominated in the pulsed DC mode or a mixture of Ar/W ions in the HiPIMS mode the average sputtering rate of carbon is not affected. A collisional computer simulation using TRIDYN was carried out to show a considerable sputter yield amplification of carbon when irradiated with a mixture of Ar/W ions. This is in-line with the observed stable carbon film areal density, which can be attributed to the compensation of the change in sputtering ion composition by sputter yield amplification due to W-enrichment of the target surface. Film characterization shows that there is no significant change between the films grown in DC and HiPIMS modes.

P01 Hollow cathode arc enhancement in reactive PVD processes

B. Zimmermann*, F. Fietzke, G. Mattausch

Fraunhofer-Institut für Elektronenstrahl- und Plasmatechnik FEP, Dresden, Germany
burkhard.zimmermann@fep.fraunhofer.de

Physical vapor deposition (PVD) processes generally suffer from the restriction that outstanding film quality excludes high rate film growth. Furthermore, in the case of reactive PVD, a sufficient activation of the reactive gas is desirable in order to enhance its reactivity. Hereby, plasma activation of the vapor as well as of the reactive gas is a powerful – and often necessary – tool. The atoms and molecules are dissociated, excited, or ionized in the plasma leading to enhanced particle energy; moreover, their impact energy at the substrate can be tailored by application of substrate bias, e.g. to fulfill optimal crystallization conditions. At FEP, a high-power plasma source based on the hollow cathode arc discharge has been developed for assisting high rate PVD processes [1]. Due to magnetic field stabilization, the working gas flow rate through the hollow cathode tube can be strongly reduced leading to remarkably increased discharge impedance and fed-in power up to 30 kW. Spatially resolved Langmuir probe measurements in argon atmosphere revealed plasma densities of 10^{10} to 10^{12} cm^{-3} in large vessel volumes of several hundred liters.

In this paper, the effect of hollow cathode plasma activation on reactive PVD will be shown comparatively in two processes. First, during reactive magnetron sputtering of chromium nitride, the hollow cathode plasma has been used for dissociation of nitrogen and additional ion bombardment of the substrate. Energy-resolved mass spectrometry measurements will be presented revealing enhanced ionization and dissociation of nitrogen as well as elevated energies of the generated plasma ions [2]. Furthermore, the pulsed bias current is strongly enhanced during the deposition process. Whereas the layer hardness is marginally increased from 23 to 26 GPa, the nitrogen incorporation is enhanced from 25 to 40 %, and SEM pictures (see Fig. 1: left without, right with plasma activation) show a remarkably denser microstructure as well as a smoother film surface. The deposition rate is 80 nm/min.

In the field of high-rate evaporation, the hollow cathode plasma source is an established standard tool for plasma activation due to the high achievable ionization rate. In this paper, plasma activation in the directed vapor deposition (DVD) process is presented as a second example [3]. An electron beam (70 kV, up to 10 kW) is used for evaporation of zirconium. The crucible is embedded into a nozzle providing a supersonic helium jet of typically 5 slm focusing the vapor and transporting it towards the substrate. Hence, the sideward vapor loss is reduced and a very high deposition rate up to 10 $\mu\text{m}/\text{min}$ is achieved. Oxygen is added into the jet for reactive deposition of zirconia. Due to the fast growth and the high gas pressure of about 10 Pa as a consequence of the high helium jet flow rate, the layers are amorphous and exhibit columnar structure. Application of the hollow cathode plasma in combination with substrate bias leads to dense crystalline structure of the zirconia layer, which has been characterized by X-ray diffraction.

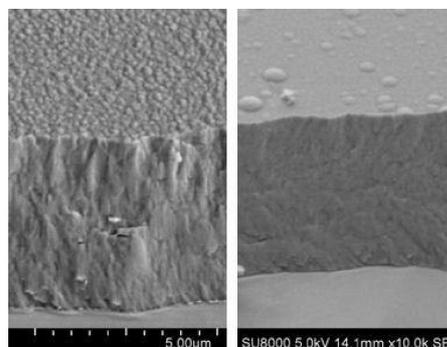


Figure 1

Due to magnetic field stabilization, the working gas flow rate through the hollow cathode tube can be strongly reduced leading to remarkably increased discharge impedance and fed-in power up to 30 kW. Spatially resolved Langmuir probe measurements in argon atmosphere revealed plasma densities of 10^{10} to 10^{12} cm^{-3} in large vessel volumes of several hundred liters.

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6 Other participants

Future study of PVD process of high powered magnetron sputtering and its usage in thin layer deposition

Peter Klein

Masaryk University, Faculty of Science, Department of Physical Electronics, Kotlarska 2, Brno 611 37, Czech Republic
pklein@mail.muni.cz

This abstract describes aims and future goals of author's PhD thesis, which is dedicated to study of PVD process of High Powered Magnetron Sputtering (HiPIMS) and its usage in thin layer deposition. Magnetron sputtering research has fairly long tradition at Masaryk University and HiPIMS research should make a new addition to it. With a support of the Grant Agency of Czech Republic the Melec SIPP 2000 HiPIMS generator was bought to be implemented on Alcatel SCM 650 industrial planar magnetron. This generator has two output channels, both can be operated in different modes which allows wide range of applications. For example it can be used for combine HiPIMS-DC process, as it is well known that thin layers made by HiPIMS have much better ratio between hardness and Young's modulus compared to conventionally deposited layers, but also have much slower deposition rate than DC deposited thin films. This makes HiPIMS form of sputtering uninteresting for industry. But if clever combination of conventional DC sputtering and HiPIMS is used, deposition rate should be close to DC and thin layer should have properties close to HiPIMS. The aim is to experimentally attempt this method obtaining coatings with wide range of properties, and if there will be positive results, share them with our long term industry partner. On the other hand the HiPIMS process itself is not fully understood, so another goal is purely scientific, to help better understanding of the processes accompanying high pulsed magnetron discharge. As an example in early experiments conducted in our laboratory it was observed that HiPIMS discharge of titanium tends to have two modes based on voltage limiting the discharge. In first mode discharge current tended to slowly distinguish itself after initial rapid rise during the pulse. This mode was very stable. Second mode could be characterized by continuous increase of current over time and it is extremely unstable, the slope of the current is rapidly changing. This behavior was also observed by Anders et al.[1] and was described as self sputtering phase thanks to multiply charged ions. This hypothesis could be tested by means of plasma diagnostics one of which is optical emission spectroscopy. It is planned to make time resolved optical spectra of HiPIMS discharge in different modes. Another point of research is reactive sputtering. The literature is disunited whether the reactive HiPIMS process has the hysteresis behavior, but majority of authors declares it has. From experiences with DC reactive magnetron sputtering, it could be said that it is hard to make quality coatings with high reproducibility. Thanks to earlier study at our laboratory using feedback system Speedflo® it is possible to deposit thin layers using DC reactive magnetron sputtering with high reproducibility. Next frontier is to make it possible with HiPIMS as well.

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Investigation and characterization of edge related effects and coatings on tools

Tim Krülle

Fraunhofer IWS Dresden; TU Dresden Institut für Werkstoffwissenschaft
tim.kruelle@iws.fraunhofer.de

During the coating of tools with e. g. TiN and CrN for different application the cutting edges of these tools lost their sharpness and the edge radius increase significantly. Beside this the homogeneity and the performance of these tools are not as good as it is necessary for an application with reduction of wear. Therefore a new coating technology has to be developed with a reduction of unwanted edge effects. Also the edges should keep their sharpness and edge radius or even decrease it.

Sequential processing and electro-optical characterization of CIGS solar cells with varied absorber compositions

A. Kusch*, M. Oertel, U. Reislöhner and C. Ronning

Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena Helmholtzweg 3, 07743 Jena, Germany
alexander.kusch@uni-jena.de

We investigate Cu(In, Ga)Se₂ solar cells produced in our own sequential processing line. The first step in the production of the cells is the deposition of a molybdenum back contact on soda lime glass, followed by the deposition of a metallic CIG precursor. Typically the precursor is a system of about 20 alternating layers of Cu₃Ga and In. Both the multi-layer system and the back contact are deposited by DC-magnetron sputtering.

The metallic CIG precursor is reactively annealed in two steps in a selenium vapour atmosphere where it is converted to an about 2 μm thick CIGSe absorber layer. The solar cell is completed by applying a buffer layer of CdS via chemical bath deposition, followed by ZnO and AZO window layers both deposited by means of RF-magnetron sputtering. The last step is the application of a Mo-Cu-Mo front grid via DC-magnetron sputtering.

Previous works show that the morphology and conductivity of the back contact depends on the deposition parameters. An impact on the quality of the electrical and mechanical contact to gallium free absorbers was showed and further adjustments need to be done when using CIGS.

Above all, the solar performance strongly depends on preparation details and the composition of the absorber. Electro-optical measurements show that the efficiency of gallium free cells can vary by up to 20 % as a function of the [Cu] : [In] ratios in the range of $0.75 < [\text{Cu}] : [\text{In}] < 0.95$. Also the incorporation of gallium is a big challenge on the way to higher efficiencies especially when utilizing a sequential process. Record CIGS cells have an integral gallium ratio in the range of $0.3 < [\text{Ga}] : [\text{Ga} + \text{In}] < 0.4$. Besides that, simulations show that the distribution of gallium throughout the absorber has an severe impact on solar performance. First results indicate that - contrary to co-evaporated CIGS - this distribution is for the most part dominated by the reaction kinetics during the selenization (which typically lead to a gallium grading towards the back contact). Different ways to influence the gallium grading and further improve solar performance beyond 13 % are under investigation.

PVD-processing of Novel Oxide Coatings for Metal Cutting

L. Landälv*^{1,2}, P. Eklund¹, L. Hultman¹ and B. Alling¹

¹ Linköping University,

² Sandvik Coromant AB
ludla@ifm.liu.se

This PhD work is performed in the Thin Film Physics Division at Linköping University in collaboration with Sandvik Coromant AB in Stockholm. It will be focused on the manufacturing and characterization of Al-Cr-O coatings in various crystal structures. The work is based upon earlier studies conducted at Linköping University [1] as well as other groups active in the field [2, 3, 4]. Specific topics that may be treated include seeking better understanding of our recently discovered vacancy stabilized fcc-(Al_{1-x}Cr_x)₂O₃ polymorph [5]. We use state-of-the-art PVD processing for these ternary oxides to control ion-surface interactions for film growth. Also we employ analytical electron microscopy and XPS to characterize the film microstructure evolution and chemical bonding state. The experimental results will be strengthened by first principles calculations [6] as well as cutting tests [7].

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Plasma induced in-situ nitrogen incorporation in CdTe-layers for solar cell applications

M. Salge*, C. Heisler, U. Reislöhner and C. Ronning

Institut für Festkörperphysik, Physikalisch-Astronomische Fakultät, Friedrich-Schiller-Universität Jena, Helmholtzweg 3, 07743 Jena, Germany

CdTe is a promising absorber material for solar cells considering its direct band gap of 1.5 eV. CdTe solar cells feature low production costs per watt and reach efficiencies of about 17% on a laboratory scale. The intrinsic p-type doping level of CdTe used for solar cell application is typically 10¹⁴ cm⁻³. However, the efficiency can be increased further by raising the doping level by several orders of magnitude [1]. Using group-V-elements as a dopant on tellurium lattice sites is one possibility to achieve an increase in carrier concentration. Thereby, nitrogen is a promising material because in CdTe it creates doping energy levels within the band gap close to the valence band edge.

The CdTe/CdS heterojunctions are deposited on FTO coated glass substrates. For the CdS layer close space sublimation is used, the CdTe layer is deposited by physical vapour deposition. During the PVD of the CdTe layer the incorporation of nitrogen is achieved by using an N-plasma source, the energy of incoming ions can be varied with an acceleration grid. Afterwards the substrates are cut into smaller pieces and activated with a CdCl₂-solution at 350 °C for 20 minutes. The solar cells are completed with the deposition of Cu-Au back contacts by thermal evaporation.

The solar cell characteristics like j-V-curve, efficiency and fill factor are determined by using an AM1.5 spectrum at room temperature. Additionally we use C-V-measurements to investigate the carrier concentration.

Previous experiments have shown a drastic decrease of efficiency and carrier concentration with increasing ion energy and no significant dependency in respect to nitrogen flux. The challenge is to incorporate nitrogen into the CdTe absorber layer in such a way that it creates shallow energy levels and thereby increase the carrier density.

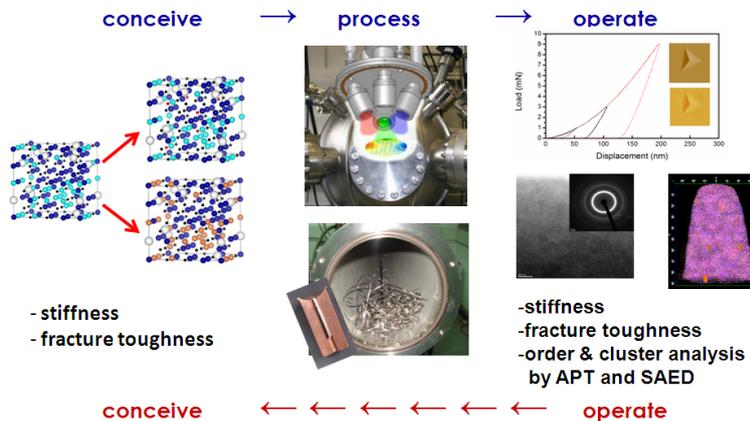
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Quantum mechanically guided design of ultra strong glasses

V. Schnabel

Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, D-52074 Aachen, Germany, schnabel@mch.rwth-aachen.de



Co based metallic glasses exhibit high strength above 5000 MPa as well as high stiffness. It is proposed to systematically explore the influence of the chemical composition of Co-based metallic glasses on the electronic structure, topology, stiffness and fracture toughness thereof. Material selection for the experiments is based on our ab initio MD data. For efficient investigation a physical vapour deposition combinatorial approach will be applied. Selected metallic glass compositions will be grown in the bulk form to further characterize relevant mechanical properties, such as fracture toughness. Topological and chemical ordering is analysed by atom probe tomography, selected area electron diffraction with a transmission electron microscope and high energy XRD techniques. It is envisioned that based on this research strategy the basic physical and chemical design principles required to realize future knowledge-based design of metallic glasses with high strength and stiffness as well as toughness can be identified.

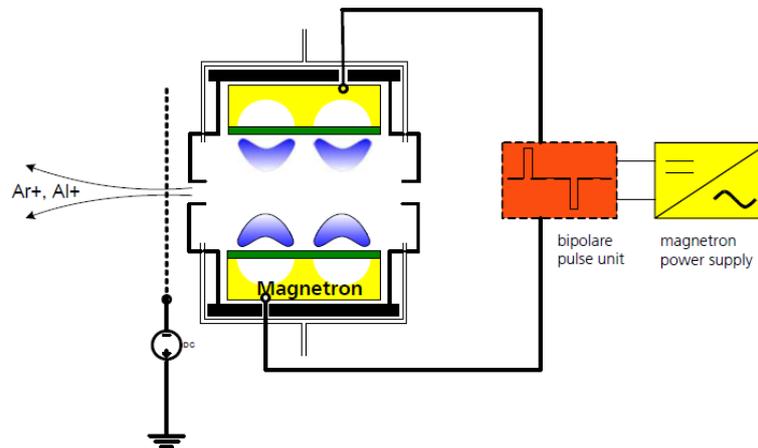
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A Magnetron Sputtering Broad-Beam Ion Source

T. Weichsel

Fraunhofer Institute for Electron Beam and Plasma Technology FEP
tim.weichsel@fep.fraunhofer.de



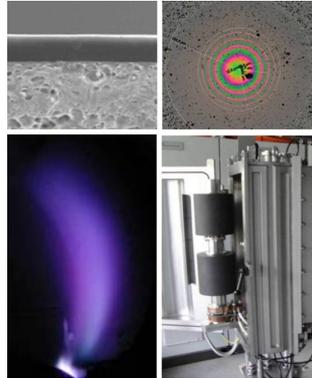
A demonstrator of a broad-beam ion source consisting of a face-to-face magnetron arrangement is going to be developed at the Fraunhofer Institute for Electron Beam and Plasma Technology FEP1. Utilizing High Power Impulse Magnetron Sputtering (HIPIMS) guarantees the formation of a highly ionized plasma for the extraction of ions by a suitable grid system. The PhD thesis is dealing with the characterization of the HIPIMS plasma by optical emission spectroscopy and Langmuir probe measurements. The Wilhelm and Else Heraeus seminar is a very good possibility to improve the understanding of the physical mechanisms in i-PVD processes and to get together with scientists for exchanges and discussions on similar issues.

This project is funded by the European Regional Development Fund under grant number 100101961.

High-rate ta-C deposition by Laser-Arc-Evaporation

Dr. Volker Weihnacht

Fraunhofer Institut für Werkstoff- und Strahltechnik (IWS) Winterbergstr. 28, 01277 Dresden, Germany
volker.weihnacht@iws.fraunhofer.de



Dr. Volker Weihnacht has studied materials science and metallurgy at Technical University Bergakademie Freiberg. Afterwards he joined the Leibniz Institute for Solid State and Materials Research Dresden for PhD work. He changed to Fraunhofer Institute Werkstoff- und Strahltechnik Dresden (IWS) in the department of PVD- and Nanotechnology. From 2007 he has been responsible for the carbon coating group and his work focusses on ta-C based coating systems for various tribological applications.

7 List of Participants

Speaker	mail	page no.
Anders, A.	aanders@lbl.gov	12
Bilek, Marcela	marcela.bilek@sydney.edu.au	48
Bradley, James	J.W.Bradley@liverpool.ac.uk	14
Colligon, John	J.Colligon@mmu.ac.uk	16
Ellmer, Klaus	ellmer@helmholtz-berlin.de	24
Helmersson, Ulf	ulfhe@ifm.liu.se	32
Hühne, Ruben	R.Huehne@ifw-dresden.de	38
Leson, Andreas	Andreas.Leson@iws.fraunhofer.de	50
Matias, Vladimir	vlado@ibeammaterials.com	28
Möller, Wolfhard	w.moeller@hzdr.de	10
Prellier, Wilfrid	wilfrid.prellier@ensicaen.fr	42
Rauschenbach, Bernd	bernd.rauschenbach@iom-leipzig.de	22
Schneider, Jochen	schneider@mch.rwth-aachen.de	30
Szyszkka, Bernd	bernd.szyszkka@tu-berlin.de	36
Vlcek, Jaroslav	vlcek@kfy.zcu.cz	34
Voevodin, Andrey	Andrey.Voevodin@wpafb.af.mil	44

Participant	mail	Presentation	p.
Abromavicius, Giedrius	giedrius@optida.lt	Poster P16	52
Almandoz, Eluxka	ealmandoz@ain.es	Poster P35	53
Barker, Paul	Paul.Barker@empa.ch	Poster P12	53
Bertram, René	bertram@hs-mittweida.de	Poster P34	54
Bonet, Raúl	raul.bonet@ctm.com.es	Poster P04	55
Englberger, Gregor	gregor.englberger@iws.fraunhofer.de	Poster P30	56
Evaristo, Manuel	manuel.evaristo@dem.uc.pt	Poster P36	57
Feder, René	rene.feder@iom-leipzig.de	Poster P19	57
Feuerfeil, Rainer	Rainer.Feuerfeil@de.Bosch.com	Poster P06	58
Franz, Robert	rfranz@lbl.gov	Poster P11	59
Fraune, Michael	michael.fraune@de.bosch.com	Participant	63
Gao, Liang	liang.gao@ipp.mpg.de	Poster P15	59
Grochla, Dario	Dario.Grochla@rub.de	Poster P40	60
Grüttner, Hagen	gruettne@hs-mittweida.de	Poster P32	61
Guillen, Elena	elena.guillen@research.abengoa.com	Poster P28	62
Günther, Marcus	marcus.guenther2@de.bosch.com	Poster P33	63
Hans, Marcus	hans@mch.rwth-aachen.de	Poster P07	64
Jerčinović, Marko	mjercin@irb.hr	Poster P26	65
Jobst, Paul Johannes	Paul-Johannes.Jobst@iof.fraunhofer.de	Poster P17	66
Khvostikova, Olga	Khvostikova.Olga@vonardenne.biz	Poster P10	67
Klein, Peter	pklein@mail.muni.cz	Participant	86
Krause, Matthias	matthias.krause@hzdr.de	Poster P27	68
Kruelle, Tim	tim.kruelle@iws.fraunhofer.de	Participant	87
Krug, Mario	Mario.Krug@ikts.fraunhofer.de	Poster P37	69
Kühn-Kauffeldt, Marina	marina.kuehn-kauffeldt@unibw.de	Poster P21	70
Kusch, Alexander	alexander.kusch@uni-jena.de	Participant	87
Landälv, Ludvig	ludla@ifm.liu.se	Participant	88
Mastail, Cedric	cedric.mastail@univ-poitiers.fr	Poster P42	70
Minea, Tiberiu	tiberiu.minea@u-psud.fr	Poster P09	71
Mosquera, Adolfo	aamosquera@icmm.csic.es	Poster P25	72
Muhl, Stephen	muhl@unam.mx	Poster P03	72
Nahif, Farwah	nahif@mch.rwth-aachen.de	Poster P38	73
Neubert, Marcel	m.neubert@hzdr.de	Poster P24	74
Pahlke, Patrick	p.pahlke@ifw-dresden.de	Poster P20	74
Pardo, Ainhoa	ainhoa.pardo@ctm.com.es	Poster P31	75
Potocký, Štěpán	potocky@fzu.cz	Poster P29	75
Saager, Stefan	Stefan.Saager@fep.fraunhofer.de	Participant	83
Salge, Martin	martin.salge@uni-jena.de	Participant	88
Schnabel, Volker	schnabel@mch.rwth-aachen.de	Participant	89
Shang, Lin	shang@mch.rwth-aachen.de	Poster P41	77
Shchelkanov, Ivan	shchelkanov.ivan@gmail.com	Poster P13	77
Tolenis, Tomas	tomas.tolenis@ftmc.lt	Poster P18	78
Tsyganov, Igor	zyganov@daad-alumni.de	Poster P22	79
Vishnyakov, Vladimir	v.vishnyakov@mmu.ac.uk	Poster P23	80
Vitelaru, Catalin	catalin.vitelaru@inoe.ro	Poster P05	81
Weichsel, Tim	Tim.Weichsel@fep.fraunhofer.de	Participant	90
Weihnacht, Volker	volker.weihnacht@iws.fraunhofer.de	Participant	91
Wilde, Christian	c.wilde@hzdr.de	Poster P08	82
Würz, Roland	roland.wuerz@zsw-bw.de	Poster P02	83
Wüstefeld, Christina	wuestefeld@ww.tu-freiberg.de	Poster P39	82
Yadav, Rahul Kumar	er.rahul.y.1986@gmail.com	Poster P14	84
Zimmermann, Burkhard	burkhard.zimmermann@fep.fraunhofer.de	Poster P01	85

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