4th – 6th DECEMBER 2017

Plzeň, Czech Republic

UNIVERSITY OF WEST BOHEMIA

RSD 2017

16th International Conference on Reactive Sputter Deposition

▸ PROGRAM

▸ ABSTRACTS

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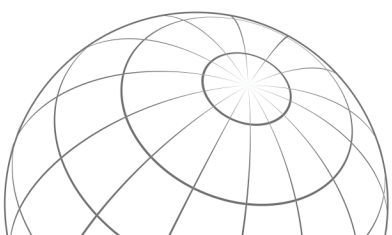

16th International Conference on Reactive Sputter Deposition

RSD 2017

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Plzeň, Czech Republic

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TRUMPF

Chairs

Jaroslav Vlček, *University of West Bohemia, Czech Republic*

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Welcome to RSD 2017

We are very pleased to welcome you to the 16th International Conference on Reactive Sputter Deposition held on 4th – 6th December, 2017 at the Angelo Hotel, Plzeň, Czech Republic. The conference is organized by the University of West Bohemia in cooperation with the Union of Czech Mathematicians and Physicists.

The International Conference on Reactive Sputter Deposition (RSD) was established by the DRAFT research group at the Ghent University in 2000. Since the beginning the conference has provided a platform among leading international scientists, engineers and students for a discussion of recent achievements in reactive sputter deposition. The conference has developed over time to an annual tradition, steadily growing without losing its focus on reactive sputtering and its fundamental aspects.

The 16th International Conference on Reactive Sputter Deposition is focused on the following topics related to reactive sputter deposition:

A. Plasma processes, plasma–surface interactions and thin film growth;

B. Films with controlled microstructure and functional properties;

C. Advanced protective coatings;

D. Applied research and industrial applications.

We gratefully thank all invited speakers and presenters for their contributions, and all sponsors and exhibitors for their financial support. We wish all the participants a stimulating and productive 16th International Conference on Reactive Sputter Deposition.

Jaroslav Vlček and Petr Zeman
Conference Chairs

Conference timetable

4th December (Monday)			
7:30	8:50	**Registration**	
8:50	9:00	**Conference opening**	
9:00	9:15	**MI1**	**J.M. Schneider**
9:15	9:30		
9:30	9:45	**MR1**	S. Konstantinidis
9:45	10:00	**MR2**	J.-F. Pierson
10:00	10:15	**MR3**	V. Gervilla
10:15	10:45	**Coffee break**	
10:45	11:00	**MI2**	**I. Petrov**
11:00	11:15		
11:15	11:30	**MR4**	M. Mikula
11:30	11:45	**MR5**	R. Dedoncker
11:45	12:00	**MR6**	B. Grančič
12:00	13:00	**Lunch**	
13:00	13:15	**MI3**	**L. Martinu**
13:15	13:30		
13:30	13:45	**MR7**	D. Kolenatý
13:45	14:00	**MR8**	V. Straňák
14:00	14:15	**MR9**	M. Fischer
14:15	14:45	**Coffee break**	
14:15	15:50	**Transfer to the university**	
15:50	16:00	**Welcome at the university**	
16:00	16:15	**MI4**	**J.E. Greene**
16:15	16:30		
16:30	16:45	**MR10**	S. Lucas
16:45	17:00	**MR11**	C. Bundesmann
17:00	17:15	**MR12**	O. Zindulka
17:15	17:45	**Light refreshment**	
17:45	18:45	**Visit of the facilities**	
19:00	19:30	**Transfer to the hotel**	

5th December (Tuesday)			
8:30	8:45	**TI1**	**E. Kusano**
8:45	9:00		
9:00	9:15	**TR1**	P. Vašina
9:15	9:30	**TR2**	M. Heintze
9:30	9:45	**TR3**	M. Jaroš
9:45	10:00	**TR4**	P. Mareš
10:00	10:30	**Coffee break**	
10:30	10:45	**TI2**	**M. Bilek**
10:45	11:00		
11:00	11:15	**TR5**	A. Anders
11:15	11:30	**TR6**	W. Gajewski
11:30	11:45	**TR7**	J. Hnilica
11:45	12:00	**TR8**	I. Fernández-Martínez
12:00	13:00	**Lunch**	
13:00	13:15	**TI3**	**D. Lundin**
13:15	13:30		
13:30	13:45	**TR9**	T. Kozák
13:45	14:00	**TR10**	R. Schelfhout
14:00	14:15	**TR11**	M. Fahland
14:15	14:30	**TI4**	**K. Strijckmans**
14:30	14:45		
14:45	15:00	**Coffee break**	
15:00	15:15	**Posters**	
15:15	15:30		
15:30	15:45		
15:45	16:00		
17:00	22:00	**Pilsner Urquell Brewery – Excursion and Dinner**	

6th December (Wednesday)			
8:30	8:45	**WI1**	**C. Mitterer**
8:45	9:00		
9:00	9:15	**WR1**	P. Novák
9:15	9:30	**WR2**	R. Ganesan
9:30	9:45	**WR3**	D. Donaghy
9:45	10:00	**WR4**	V. van Karsbergen
10:00	10:30	**Coffee break**	
10:30	10:45	**WI2**	**J.-W. Lee**
10:45	11:00		
11:00	11:15	**WR5**	H. Rueß
11:15	11:30	**WR6**	Š. Meškinis
11:30	11:45	**WR7**	J. Kousal
11:45	12:00	**WR8**	A. Usoltseva
12:00	13:00	**Lunch**	
13:00	13:15	**WI3**	**J. Vyskočil**
13:15	13:30		
13:30	13:45	**WR9**	Ch. Schiffers
13:45	14:00	**WR10**	D. Gloess
14:00	14:15	**WR11**	E. Schüngel
14:15	14:45	**Coffee break**	
14:45	15:00	**WI4**	**H. Gerdes**
15:00	15:15		
15:15	15:30	**WR12**	P. Souček
15:30	15:45	**WR13**	Y.-J. Weng
15:45	15:55	**Conference closing**	

Monday morning, 4th December

7:30	**Registration**
8:50	**Conference opening**

ORAL PRESENTATIONS (9:00 – 10:15)

Chairman: J. Vlček, *University of West Bohemia, Czech Republic*

9:00 **MI1** *p. 18*

Invited talk

Quantum mechanically guided material design and experimentally guided quantum mechanical calculations

J.M. Schneider

Materials Chemistry, RWTH Aachen University, Aachen, Germany

9:30 **MR1** *p. 20*

Oxygen vacancy stabilized zirconia thin films: Synthesis and properties

S. Konstantinidis[1], M. Raza[1], D. Cornil[2], J. Cornil[2], S. Lucas[3], J.F. Pierson[4], P. Boulet[4], H. Rinnert[4], D. Horwat[4], L. dos Santos Gómez[5], V. Esposito[5], S. Sanna[5], R. Snyders[1]

[1]Laboratory of Plasma-Surface Interaction Chemistry, University of Mons, Mons, Belgium
[2]Service de Chimie des Matériaux Nouveaux, University of Mons, Mons, Belgium
[3]LARN, University of Namur, Namur, Belgium
[4]Institut Jean Lamour, CNRS, Université de Lorraine, Nancy, France
[5]Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark

9:45 **MR2** *p. 22*

Local epitaxial growth and self-assembled growth of vertically aligned columns in copper oxide thin films

J.F. Pierson[1], Y. Wang[1], J. Ghanbaja[1], S. Bruyère[1], F. Soldera[2], D. Horwat[1], F. Mücklich[2]

[1]Institut Jean Lamour (UMR CNRS 7198), Université de Lorraine, Nancy, France
[2]Department for Materials Science, Functional Materials, Saarland University, Saarbrücken, Germany

10:00 **MR3** *p. 24*

Formation and morphological evolution of 3D atomic islands on weakly-interacting substrates

V. Gervilla[1], B. Lü[1], G. Almyras[1], J.E. Greene[2,3], K. Sarakinos[1]

[1]Nanoscale Engineering Division, Department of Physics, Chemistry and Biology, Linköping University, Linköping, Sweden
[2]Thin Film Physics Division, Department of Physics, Chemistry and Biology, Linköping University, Linköping, Sweden
[3]Materials Science and Physics Departments, University of Illinois, Urbana, Illinois, USA

10:15 – 10:45 Coffee break

Monday morning, 4th December

ORAL PRESENTATIONS (10:45 – 12:00)

Chairman: J.E. Greene, *University of Illinois, USA*

10:45 ***Invited talk***

MI2

p. 26

Control of micro- and nanostructure in transition metal nitrides and borides: Recent advances

I. Petrov[1,2], G. Greczynski[2], J. Rosen[2], J. Birch[2], L. Hultman[2], J.E. Greene[1,2]

[1]Frederick Seitz Materials Research Laboratory and Materials Science Department, University of Illinois, Urbana, Illinois, USA
[2]Department of Physics (IFM), Linköping University, Linköping, Sweden

11:15

MR4

p. 28

Age hardening in hard and tough Ta–Al–N coatings

M. Mikula[1,2], D.G. Sangiovanni[3,4], D. Plašienka[1], T. Roch[1], M. Čaplovičová[5], M. Truchlý[1], L. Satrapinskyy[1], R. Bystrický[6], D. Tonhauzerová[1], D. Vlčková[1], P. Kúš[1]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia
[2]Institute of Materials and Machine Mechanics SAS, Bratislava, Slovakia
[3]ICAMS, Ruhr-Universität Bochum, Bochum, Germany
[4]Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden
[5]Slovak University of Technology in Bratislava, University Science Park Bratislava Centre, Bratislava, Slovakia
[6]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

11:30

MR5

p. 30

Reactive sputtering of high entropy alloys with nitrogen – Tuning the unit cell

R. Dedoncker, D. Depla

Department of Solid State Sciences, Ghent University, Ghent, Belgium

11:45

MR6

p. 32

Mechanical properties of ternary V–Mo–N and quaternary V–Mo–Al–N coatings

B. Grančič[1], S. Uzon[1], M. Mikula[1,2], D.G. Sangiovanni[3,4], T. Roch[1], M. Truchlý[1], L. Satrapinskyy[1], P. Kúš[1]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Bratislava, Slovakia
[2]Institute of Materials and Machine Mechanics SAS, Bratislava, Slovakia
[3]Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden
[4]ICAMS, Ruhr-Universität Bochum, Bochum, Germany

12:00 – 13:00 Lunch

Monday afternoon, 4th December

ORAL PRESENTATIONS (13:00 – 14:15)

Chairman: I. Petrov, *University of Illinois, USA*

13:00 ***Invited talk***

MI3

p. 34

Durable smart and multifunctional optical coatings for energy saving and anticounterfeiting – New opportunities for pulsed reactive plasmas

L. Martinu, B. Baloukas, F. Blanchard, S. Loquai

Functional Coating and Surface Engineering Laboratory, Department of Engineering Physics, Polytechnique Montreal, Quebec, Canada

13:30

MR7

p. 36

Controlled reactive HiPIMS – Effective technique for low-temperature (300 °C) synthesis of VO_2 films with semiconductor-to-metal transition

D. Kolenatý, J. Vlček, T. Kozák, J. Houška, R. Čerstvý

Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Plzeň, Czech Republic

13:45

MR8

p. 38

Tailoring optical and electrochemical properties of ITO films deposited by means of reactive magnetron sputtering

V. Stranak[1], P. Sezemsky[1], D. Burnat[2], J. Kratochvil[1], H. Wulff[3], Z. Hubicka[4], M. Cada[4], R. Bogdanowicz[5], M. Smietana[2]

[1]Institute of Physics, University of South Bohemia, Ceske Budejovice, Czech Republic
[2]Institute of Microelectronics and Optoelectronics, Warsaw University of Technology, Warsaw, Poland
[3]Institute of Physics, University of Greifswald, Greifswald, Germany
[4]Institute of Physics, Academy of Science of the Czech Republic, Prague, Czech Republic
[5]Faculty of Electronics, Telecom. and Informatics, Gdansk University of Technology, Gdansk, Poland

14:00

MR9

p. 40

Hard transparent Al–Si/O–N coatings

M. Fischer[1], M. Trant[1], D. Scopece[1], C. Pignedoli[1], D. Passerone[1], K. Thorwarth[1], J. Patscheider[1], H.J. Hug[1,2]

[1]Empa, Laboratory for Nanoscale Materials Science, Dübendorf, Switzerland
[2]University of Basel, Department of Physics, Basel, Switzerland

14:15 – 14:45 Coffee break

14:45 – 15:50 Transfer to the university

Monday afternoon, 4th December

15:50 – 16:00 Welcome at the university

ORAL PRESENTATIONS (16:00 – 17:15)

Chairman: J. Musil, *University of West Bohemia, Czech Republic*

16:00 **MI4** *p. 42*

Invited talk

Fundamental properties of TM nitrides: Materials design strategies for extreme properties

J.E. Greene[1,2,3]

[1]*Depts. of Materials Science and Physics, University of Illinois, Urbana, Illinois, USA*
[2]*Physics Department, Linköping University, Linköping, Sweden*
[3]*Mat. Sci. Dept, National Taiwan University of Science & Technology, Taipei, Taiwan*

16:30 **MR10** *p. 44*

Pulsed reactive sputtering of chromium nitride from 12.5 to 87.5% of duty cycle, at 62.5 to 5000 Hz

E. Haye, S. Lucas, J.-J. Pireaux

Research Centre for the Physics of Matter and Radiation (PMR), University of Namur, Namur, Belgium

16:45 **MR11** *p. 46*

Systematics in reactive ion beam sputter deposition of TiO_2

C. Bundesmann, T. Lautenschläger, D. Spemann, H. Neumann

Leibniz Institute of Surface Modification, Leipzig, Germany

17:00 **MR12** *p. 48*

B-based coatings prepared by magnetron sputtering and cathodic arc co-deposition

O. Zindulka, M. Jílek, V. Sochora, I. Fojtl

SHM, s.r.o., Šumperk, Czech Republic

17:15 – 17:45 Light refreshment

17:45 – 18:45 Visit of the facilities

19:00 Transfer to the hotel

Tuesday morning, 5th December

ORAL PRESENTATIONS (8:30 – 10:00)

Chairman: D. Depla, *Ghent University, Belgium*

8:30 **TI1** *p. 50*	***Invited talk*** **Model calculation and visualization of time-dependent reactive gas mass balance change in Ti–O_2 reactive sputtering** E. Kusano *Advanced Materials Center, Kanazawa Institute of Technology, Hakusan, Japan*
9:00 **TR1** *p. 52*	**Evolution of titanium atom and ion density in reactive HiPIMS – Impact on hysteresis curve shape** M. Fekete[1], K. Bernátová[1], P. Klein[1,2], J. Hnilica[1,2], P. Vašina[1,2] *[1]Department of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic* *[2]CEPLANT, R&D Centre for Low-Cost Plasma and Nanotechnology Surface Modifications, Faculty of Science, Masaryk University, Brno, Czech Republic*
9:15 **TR2** *p. 54*	**Transition mode sputtering of Al_2O_3 – Hysteresis and process stability of large Al targets** M. Heintze, I. Luciu *TRUMPF Hüttinger GmbH + Co. KG, Freiburg, Germany*
9:30 **TR3** *p. 56*	**Plasma and floating potentials in magnetron discharges** M. Jaroš, J. Musil *Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Plzeň, Czech Republic*
9:45 **TR4** *p. 58*	**Long-term stability and disappearing anode effects during reactive DC and pulsed bipolar magnetron sputtering of Al_2O_3** P. Mareš, S. Kadlec, A. Marek *HVM Plasma spol. s r.o., Praha, Czech Republic*

10:00 – 10:30 Coffee break

Tuesday morning, 5th December

ORAL PRESENTATIONS (10:30 – 12:00)

Chairman: L. Martinu, *Polytechnique Montreal, Canada*

10:30 ***Invited talk***
TI2
p. 60

Synchronised external magnetic fields applied in HiPIMS enhance plasma generation in the race track as well as plasma transport to the substrate

M. Bilek[1,2,3], R. Ganesan[1], B. Akhavan[1], H. Najafiashtiani[1], D.G McCulloch[4], D.R. McKenzie[1]

[1]*School of Physics, University of Sydney, Sydney, Australia*
[2]*School of Aerospace, Mechanical and Mechatronic Engineering, University of Sydney, Sydney, Australia*
[3]*Australian Institute of Nanoscale Science and Technology, University of Sydney, Sydney, Australia*
[4]*Microscopy and Microanalysis Facility, RMIT University, Melbourne, Australia*

11:00
TR5
p. 62

Ion energy distributions in magnetron sputtering: Questions remain even after detailed measurements of the plasma potential

A. Anders[1,2]

[1]*Lawrence Berkeley National Laboratory, Berkeley, USA*
[2]*Leibniz Institute of Surface Modification, Leipzig, Germany*

11:15
TR6
p. 64

Arcing in high power impulse magnetron sputtering: Review of physical background and arcing mitigation methods

W. Gajewski, A.W. Oniszczuk, P. Różański, P. Lesiuk, P. Ozimek

TRUMPF Huettinger, Zielonka, Poland

11:30
TR7
p. 66

Spokes occurrence in HiPIMS discharge at different magnetic field strengths

J. Hnilica, M. Šlapanská, P. Klein, M. Fekete, P. Vašina

Department of Physical Electronics, Masaryk University, Brno, Czech Republic

11:45
TR8
p. 68

The application of a short positive voltage reversal in reactive HIPIMS: Enhanced deposition rate and improved coating properties

I. Fernández-Martínez[1,6], V. Bellido-González[2], J.A. Santiago[3], L. Mendizábal[4], M. Monclús[3], R. González-Arrabal[5], J. Molina[3], A. Wennberg[1,6]

[1]*Nano4Energy SL, Madrid, Spain*
[2]*Gencoa Ltd, Liverpool, United Kingdom*
[3]*Imdea Materiales, Madrid, Spain*
[4]*Fundación Tekniker, Eibar, Spain*
[5]*Instituto Fusión Nuclear, Escuela de Industriales de la UPM, Madrid, Spain*
[6]*hip-V AB, Stocksund, Sweden*

12:00 – 13:00 Lunch

Tuesday afternoon, 5th December

ORAL PRESENTATIONS (13:00 – 14:45)

Chairman: E. Kusano, *Kanazawa Institute of Technology, Japan*

13:00 **TI3** *p. 70*

Invited talk

Key features of reactive high power impulse magnetron sputtering

D. Lundin[1], N. Brenning[1,2,3], J.T. Gudmundsson[1,2,4], M.A. Raadu[2], T.J. Petty[1], F. Cemin[1], T. Minea[1]

[1]Laboratoire de Physique des Gaz et Plasmas - LPGP, Université Paris–Sud, Université Paris–Saclay, Orsay, France
[2]Department of Space and Plasma Physics, School of Electrical Engineering, KTH - Royal Institute of Technology, Stockholm, Sweden
[3]Plasma and Coatings Physics Division, IFM-Materials Physics, Linköping University, Linköping, Sweden
[4]Science Institute, University of Iceland, Reykjavik, Iceland

13:30 **TR9** *p. 72*

Modelling the dynamics of processes in reactive HiPIMS deposition of oxide films

T. Kozák, J. Vlček

Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Plzeň, Czech Republic

13:45 **TR10** *p. 74*

Current dependency of the compound sputtering yield

R. Schelfhout, K. Strijckmans, D. Depla

Research group DRAFT, Department of Solid State Sciences, Ghent University, Ghent, Belgium

14:00 **TR11** *p. 76*

A novel method for the optimization of reactive sputtering processes

M. Fahland, T. Vogt

Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology, Dresden, Germany

14:15 **TI4** *p. 78*

Invited talk

Reactive HiPIMS through the eyes of a 'simple' model

K. Strijckmans, R. Schelfhout, F. Moens, D. Depla

DRAFT – Department of Solid State Sciences, Ghent University, Ghent, Belgium

14:45 – 15:00 Coffee break

15:00 – 16:00 Posters

17:00 – 22:00 Pilsner Urquell Brewery – Excursion and Dinner

Wednesday morning, 6th December

ORAL PRESENTATIONS (8:30 – 10:00)

Chairman: J.M. Schneider, *RWTH Aachen University, Germany*

8:30 **WI1** *p. 80*

Invited talk

Reactive and non-reactive sputter deposition of MoO_x thin films

J.M. Pachlhofer[1], R. Franz[1], A. Tarazaga Martín-Luengo[2], E. Franzke[3], A. Bonanni[2], H. Köstenbauer[3], J. Winkler[3], C. Mitterer[1]

[1]Department of Physical Metallurgy and Materials Testing, Montanuniversität, Leoben, Austria
[2]Institute of Semiconductor and Solid State Physics, Johannes Kepler University, Linz, Austria
[3]Business Unit Coating, PLANSEE SE, Reutte, Austria

9:00 **WR1** *p. 82*

The role of oxygen in sputtered AZO and ZnO films used for ZnO nanorod-based device

P. Novák[1], J. Briscoe[2], T. Kozák[3], M. Kolega[1], J. Savková[1]

[1]New Technologies – Research Centre, University of West Bohemia, Plzeň, Czech Republic
[2]Materials Research Institute, Queen Mary University of London, London, UK
[3]Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Plzeň, Czech Republic

9:15 **WR2** *p. 84*

Control of process pressure and Ar/O_2 ratio in reactive-HiPIMS to deposit high-stability and high-mobility zinc oxynitride films for thin-film transistor devices

R. Ganesan[1,2], M. Trant[1], K. Thorwarth[1], H.J. Hug[1], M.M.M. Bilek[2], D.R. McKenzie[2]

[1]EMPA Materials Science and Technology, Dübendorf, Switzerland
[2]The School of Physics, The University of Sydney, Sydney, Australia

9:30 **WR3** *p. 86*

Deposition of Nb doped TiO_2 thin films using a hybrid CVD/HiPIMS technique

D. Donaghy[1], J. Kulczyk-Malecka[2], P. Chalker[3], P.J. Kelly[2], J.W. Bradley[1]

[1]Department of Electrical and Electronic Engineering, University of Liverpool, Liverpool, UK
[2]Surface Engineering Group, Manchester Metropolitan University, Manchester, UK
[3]Department of Mechanical, Materials and Aerospace Engineering, University of Liverpool, Liverpool, UK

9:45 **WR4** *p. 88*

Nb_2O_{5-x} vs. Nb targets for DC reactive magnetron sputter PVD of thin optical films

V. van Karsbergen, N. Weinberger, G. Strauss

Material Center Tyrol, Institute for Material Technology, University of Innsbruck, Innsbruck, Austria

10:00 – 10:30 Coffee break

Wednesday morning, 6th December

ORAL PRESENTATIONS (10:30 – 12:00)

Chairman: C. Mitterer, *Montanuniversität Leoben, Austria*

10:30 **WI2** *p. 90*

Invited talk

Improvement of deposition rate of high power impulse magnetron sputtering system using hybrid and superimposition approaches

J.-W. Lee[1, 2, 3], Y.-W. Su[1], C.-Y. Lu[1], W. Diyatmika[1], B.-S. Lou[4]

[1]Department of Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan
[2]Center for Thin Films Technologies and Applications, Ming Chi University of Technology, New Taipei, Taiwan
[3]College of Engineering, Chang Gung University, Taoyuan, Taiwan
[4]Chemistry Division, Center of General Education, Chang Gung University, Taoyuan, Taiwan

11:00 **WR5** *p. 92*

HPPMS deposition from composite targets: Effect of two orders of magnitude target power density changes on the composition of sputtered Cr–Al–C thin films

H. Rueß[1], M. to Baben[1,2], S. Mráz[1], L. Shang[1], P. Polcik[3], S. Kolozsvari[3], M. Hans[1], D. Primetzhofer[4], J.M. Schneider[1,4]

[1]Materials Chemistry, RWTH Aachen University, Aachen, Germany
[2]GTT-Technologies, Herzogenrath, Germany
[3]Plansee Composite Materials GmbH, Lechbruck am See, Germany
[4]Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden

11:15 **WR6** *p. 94*

Study on giant negative piezoresistance effect in diamond like carbon films deposited by reactive magnetron sputtering of Ni target

Š. Meškinis, A. Vasiliauskas, S. Tamulevičius, R. Gudaitis

Kaunas University of Technology, Institute of Materials Science, Kaunas, Lithuania

11:30 **WR7** *p. 96*

Inside gas aggregation cluster source: In-operando study of Ti/TiO_x nanoparticles production

J. Kousal[1], A. Shelemin[1], A. Kolpaková[2], P. Kudrna[2], M. Tichý[2], H. Biederman[1]

[1]Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic
[2]Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

11:45 **WR8** *p. 98*

Plasma metal and metal oxides nanoparticles coatings for new functional properties

A. Usoltseva, C. Rigaux, C. Vandenabeele, S. Wallon, S. Matioudaki, S. Lucas

Namur University (LARN-PMR), Namur, Belgium

12:00 – 13:00 Lunch

Wednesday afternoon, 6th December

ORAL PRESENTATIONS (13:00 – 14:15)

Chairman: J.-W. Lee, ***Ming Chi University of Technology, Taiwan***

13:00 **WI3** *p. 100*

Invited talk

Industrial challenges and applications of reactively sputtered hard coatings

J. Vyskočil, S. Kadlec, P. Mareš, T. Mates

HVM Plasma spol. s r.o., Praha, Czech Republic

13:30 **WR9** *p. 102*

HiPIMS makes reactive sputtering the future technology for premium cutting tools

T. Leyendecker[1], L. Zima[2], C. Schiffers[1]

[1]CemeCon AG, Würselen, Germany
[2]CemeCon s.r.o., Ivančice, Czech Republic

13:45 **WR10** *p. 104*

Reactive sputter deposition of Al_2O_3 layers on large area substrates

D. Gloess[1], T. Goschurny[1], H. Nizard[1,2], A. Drescher[1], M. Gittner[1], H. Bartzsch[1], P. Frach[1]

[1]Fraunhofer-Institut für Organische Elektronik, Elektronenstrahl- und Plasmatechnik FEP, Dresden, Germany
[2]Technische Universität Dresden, Institut für Festkörperelektronik (IFE), Dresden, Germany

14:00 **WR11** *p. 106*

Plasma enhanced reactive sputter deposition processes in application

E. Schüngel, J. Weichart, S. Gees, S. Schwyn-Thöny

Evatec AG, Trübbach, Switzerland

14:15 – 14:45 Coffee break

Wednesday afternoon, 6th December

ORAL PRESENTATIONS (14:45 – 15:55)

Chairman: J. Vyskočil, *HVM Plasma spol. s r.o., Praha, Czech Republic*

14:45 **WI4** *p. 108*	***Invited talk*** **Reactive HIPIMS and process control on industrial scale coating systems** H. Gerdes, J. Rieke, R. Bandorf, M. Vergöhl, G. Bräuer *Fraunhofer IST, Braunschweig, Germany*
15:15 **WR12** *p. 110*	**Nanocomposite nc-TiC/a-C:H coatings: enhancement of coating properties by utilization of HiPIMS and Ni doping** P. Souček, J. Daniel, J. Hnilica, K. Bernátová, L. Zábranský, V. Buršíková, M. Stupavská, P. Vašina *Department of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic*
15:30 **WR13** *p. 112*	**Multilayered TiVN/TiSiN hard coatings – Mechanical properties and tribological performance** Y.-J. Weng, Y.-Y. Chang *Department of Mechanical and Computer-Aided Engineering, National Formosa University, Yunlin, Taiwan*

15:45 – 15:55 Conference closing

ABSTRACTS

ORAL PRESENTATIONS

MI1 Quantum mechanically guided material design and experimentally guided quantum mechanical calculations

J.M. Schneider

Materials Chemistry, RWTH Aachen University, Aachen, Germany

The combination of modern electronic structure calculations with the highly efficient combinatorial thin film composition-spread method constitutes an effective tool for knowledge based materials design of hard and wear resistant coatings as well as of thin film metallic glasses. Besides elastic properties and phase stability also the interaction of the coating with the ambient can be described based on quantum mechanics. In the talk predictions of the interaction of coated tool surfaces with gases contained in the atmosphere as well as materials to be formed are discussed. Mo_2BC, transition metal nitride and oxynitride as well as boride coatings used for forming operations of Al and Polymers are investigated and experimental data characterizing these interactions will be discussed. Furthermore, the implications of the presence of point defect for the thermal stability of TiAlN will be analyzed and the nm-scale structure and composition of Mo_2BC coatings is presented.

Notes:

MR1 Oxygen vacancy stabilized zirconia thin films: Synthesis and properties

S. Konstantinidis[1], M. Raza[1], D. Cornil[2], J. Cornil[2], S. Lucas[3], J.F. Pierson[4], P. Boulet[4], H. Rinnert[4], D. Horwat[4], L. dos Santos Gómez[5], V. Esposito[5], S. Sanna[5], R. Snyders[1]

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[2]*Service de Chimie des Matériaux Nouveaux, University of Mons, Mons, Belgium*
[3]*LARN, University of Namur, Namur, Belgium*
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[5]*Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark*

We investigated the phase formation and properties of oxygen vacancy stabilized zirconia thin films. Zirconia (ZrO_2) is a material which exists in three crystallographic phases. The monoclinic phase is stable up to 1205 °C, the tetragonal phase appears from 1205 °C to 2377 °C, and finally the cubic phase is thermodynamically stable from 2377 °C to 2710 °C.

Using quantum-chemistry based calculations, we first show that the cubic phase is the most stable phase if more than 3 at.% of oxygen vacancies are incorporated in the ZrO_2 lattice. Optimized reactive magnetron deposition experiments were carried out and allowed to control the amount of O vacancies incorporated inside the zirconia lattice. The X-ray diffractograms of these oxygen vacancy doped zirconia films are in remarkable agreement with theoretical predictions, hence emphasizing that the incorporation of oxygen vacancies is the sole responsible mechanism for the stabilization of the cubic phase, at room temperature.

The thermal stability of the oxygen deficient zirconia thin films was then addressed. Temperature-resolved X-ray Diffraction experiments, performed in the air, show that these films are stable up to 750 °C. The ionic conductivity was also measured as a function of temperature. These oxygen vacancy stabilized zirconia films are ion conductors and it was observed that the conductivity increased dramatically as film as thin as 10 – 20 nm were deposited. For such coatings, ion conductivity as high as 7.4 S/cm was measured, at 725 °C. Finally, photolumuninescence results highlight the presence of occupied energy states in the band gap. This finding is also supported by quantum chemistry calculation data.

Notes:

MR2 Local epitaxial growth and self-assembled growth of vertically aligned columns in copper oxide thin films

J.F. Pierson[1], Y. Wang[1], J. Ghanbaja[1], S. Bruyère[1], F. Soldera[2], D. Horwat[1], F. Mücklich[2]

[1]*Institut Jean Lamour (UMR CNRS 7198), Université de Lorraine, Nancy, France*
[2]*Department for Materials Science, Functional Materials, Saarland University, Saarbrücken, Germany*

The copper-oxygen binary system contains three oxides (Cu_2O, Cu_4O_3 and CuO) that are suitable for energy applications: electrodes in Li-ion batteries, absorbent layer in solar cells, p-type transparent conductive oxide… The reactive sputtering is a powerful method to synthesize these three materials as pure phases or as mixtures. Recently, the local epitaxial growth (LEG) has been evidenced in Cu_2O thin films [1]. The conditions to extend the LEG to other phases such as Cu_4O_3 or NiO will be discussed. Finally, the consequence of the local epitaxial growth on the microstructure of biphased copper oxide thin films will be explained. Within a given oxygen flow rate range, it is possible to grow self-assembled vertically aligned columnar $Cu_2O + Cu_4O_3$ nanocomposite thin films on glass and silicon substrates at room temperature. Microstructure analyses show that each phase in nanocomposite films has the columnar growth along the whole thickness, while each column exhibits the single phase characteristics. The LEG of Cu_2O is responsible for such an unusual microstructure. The intermediate oxygen flow rate between those required to synthesize single phase Cu_2O and Cu_4O_3 films produces some Cu_2O nuclei, and then the local epitaxial growth provides a strong driving force to promote Cu_2O nuclei to grow sequentially, giving rise to Cu_2O columns along the whole thickness. Low resistivity has been observed in such kind of nanocomposite thin films.

[1] Y. Wang et al., Acta Mater. 76 (2014) 207.

Notes:

MR3 Formation and morphological evolution of 3D atomic islands on weakly-interacting substrates

V. Gervilla[1], B. Lü[1], G. Almyras[1], J.E. Greene[2,3], K. Sarakinos[1]

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[3]*Materials Science and Physics Departments, University of Illinois, Urbana, Illinois, USA*

Vapor condensation on weakly-interacting substrates leads to the formation of three-dimensional (3D) atomic islands. While it is widely accepted that this process is driven by minimization of the total surface and interface energy of the film/substrate system, current film-growth theory cannot adequately explain, at the atomic scale, the mechanisms and pathways by which 3D island formation and morphological evolution occurs. In this work, we use simulations based on a kinetic Monte Carlo algorithm to study qualitatively the initial stages of formation and the shape evolution of 3D atomic Ag islands grown on weakly-interacting substrates in the temperature (T_s) range 100 to 500 K. Our simulations show that up to a T_s value of 250 K islands exhibit rough edges and grow predominantly in-plane. At T_s values above 250 K a dramatic change in the island shape evolution is observed; the islands become compact, exhibit a pronounced 3D shape and grow by maintaining a constant height-to-radius (h/r) aspect ratio which saturates at a value of ~ 2 for $T_s \geq 325$ K. Our results also reveal the following chain of atomic events that lead to compact 3D island shapes: 3D nuclei are first formed due to facile adatom ascent at single-layer island steps, followed by second-layer nucleation and the formation of nanofacets on the sidewalls of 3D islands, which in turn facilitates adatom upward diffusion, facet growth and formation of new atomic layers in the out-of-plane direction. Based on this atomistic pathway, we conclude that the rate limiting process for triggering transition from flat to 3D island shapes is adatom crossing from the side nanofacets to the island top layer, as this determines the density of adatoms available for nucleation and growth of new atomic layers along the island growth direction. The overall results provide insights into the directed growth of metal nanostructures with controlled shapes on weakly-interacting substrates, including two-dimensional crystals for use in catalytic and nanoelectronic applications.

Notes:

MI2 Control of micro- and nanostructure in transition metal nitrides and borides: Recent advances

I. Petrov[1,2], G. Greczynski[2], J. Rosen[2], J. Birch[2], L. Hultman[2], J.E. Greene[1,2]

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Polycrystalline TiN and related transition-metal nitride (TMN) thin films are typically deposited by reactive magnetron sputter deposition and employed as diffusion barriers in microelectronics as well as hard, wear-, and corrosion-resistant coatings in mechanical and optical applications. We will review the fundamental film growth processes – nucleation, coalescence, competitive growth, and recrystallization – and their role in thin film microstructure evolution as a function of substrate temperature. Special attention will paid to in-situ substrate treatment by ion-irradiation and its effect on film microstructure and adhesion. We will also review recent advances in the selective use of metal ions during HIPIMS co-sputtering to extend the attainable structures and properties in metastable TMN with examples of $Ti_{(1-x)}Al_xN$, $Ti_{(1-x)}Si_xN$, and $Ti_{(1-x)}Ta_xN$. We probe the effects of (i) metal versus rare-gas ion irradiation as well as (ii) the type of metal ion uses (Ti vs Me). We employ a metastable NaCl-structure $Ti_{0.39}Al_{0.61}N$ as a model system to demonstrate that switching from Ar^+- to Al^+-dominated bombardment eliminates phase separation, minimizes renucleation during growth, reduces the high concentration of residual point defects, and thus results in dense, single-phase, stress-free films.

With the TiTaN system we show that synchronized pulsed ion bombardment in the hybrid system with the heavy-metal ions (Ta) permits to grow dense, hard, smooth, and stress-free thin films at lowered substrate temperature, with no external heating.

Overall, we demonstrate that using synchronous bias to select the metal-rich portion of the ion flux opens new dimension for ion-assisted growth in which momentum can be tuned by selection of the metal ion in the hybrid/cosputtering configuration and stresses can be eliminated/reduced since the metal ion is a component of the film.

We begin to apply the same comprehensive approach to Transition Metal Diborides (TMB_2). TMB_2 have many desirable physical and mechanical properties such as a high melting point, good thermal and electrical conductivity, high hardness, high wear- and corrosion resistance, as well as excellent chemical stability at elevated temperatures. A common problem in sputter-deposited MiB_x layers is that the film contains excess boron with x ranging from 2.4 to 3.5. It is important to be able to control the B/TM ratio during film growth as a first step to synthesizing epitaxial single crystal films in order to investigate their fundamental properties. We use TiB_x as a model system and study the effect of the discharge pressure and plasma density on the B/Ti ratio during magnetron sputtering of a TiB_2 target. We present results from establishing control of the B/Ti ratio in magnetron sputter-deposited TiB_x thin film and to synthesize stoichiometric single crystalline TiB_2 layers.

Notes:

MR4 Age hardening in hard and tough Ta–Al–N coatings

M. Mikula[1,2], D.G. Sangiovanni[3,4], D. Plašienka[1], T. Roch[1], M. Čaplovičová[5], M. Truchlý[1], L. Satrapinskyy[1], R. Bystrický[6], D. Tonhauzerová[1], D. Vlčková[1], P. Kúš[1]

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[2]*Institute of Materials and Machine Mechanics SAS, Bratislava, Slovakia*
[3]*ICAMS, Ruhr-Universität Bochum, Bochum, Germany*
[4]*Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden*
[5]*Slovak University of Technology in Bratislava, University Science Park Bratislava Centre, Bratislava, Slovakia*
[6]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia*

Here, we combine experiments and *ab initio* density functional theory calculations to investigate the evolution in structural and mechanical properties of Ta–Al–N coatings as a function of the annealing temperature *T*.

Magnetron-sputtered $Ta_{0.55}Al_{0.45}N$ thin films exhibit a dual-phase columnar structure which is formed of cubic B1 TaAlN solid solutions with small nanometer-size wurtzite AlN-rich inclusions segregated at column boundaries. The hardness of as-deposited TaAlN coatings, 29 GPa, which increases monotonously with the annealing temperature, reaches its maximum, 35 GPa, at $T = 1000$ °C. Transmission electron microscopy reveals that age hardening is due to formation of incoherent wurtzite AlN-rich precipitates at boundary phases followed by spinodal decomposition of the cubic TaAlN solid solution into coherent cubic TaN- and AlN-rich domains. At higher annealing temperatures, an increased diffusivity of point defects leads to transformation of the cubic metastable phases into stable w-AlN and h-TaN_{1-x} coarse-grained phases, thus resulting in hardness decreases to 24 GPa.

Present results reveal that thermal exposure of TaAlN coatings to ~ 1000 °C yields an increase in hardness of 17%, that is, comparable with the values obtained for well-known $Ti_{0.34}Al_{0.66}N$ coatings as a function of the annealing temperature [1,2]. However, the fact that the Young's moduli *E* measured for Ta–Al–N, which vary from 305 to 445 GPa, remain significantly smaller than those of $Ti_{0.34}Al_{0.66}N$ (between 430 and 630 GPa [2]) at all temperatures indicates that Ta substitutions significantly enhance toughness by reducing the coating stiffness, that is, improve resilience and/or promote plasticity.

[1] P.H. Mayrhofer, A. Hörling, L. Karlsson, J. Sjölen, T. Larsson, C. Mitterer, L. Hultman, Appl. Phys. Lett. 83, (2003) 2049-2051.

[2] A. Hörling, L. Hultman, M. Oden, J. Sjölen, L. Karlsson, Surf. Coat. Technol. 191, (2005) 384-392.

Notes:

MR5 Reactive sputtering of high entropy alloys with nitrogen – Tuning the unit cell

R. Dedoncker, D. Depla

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High entropy alloys are a new class of materials with at least 5 different metals in near-equimolar concentrations with promising properties such as a high degree of corrosion resistance and mechanical strength. When deposited with magnetron sputtering, these alloys form solid solution thin films with a (111) out-of-plane fibre texture. In this present study, the effect of nitrogen addition on the growth of two different high entropy alloys, i.e. CoCrCuFeNi and CoCrFeMnNi is discussed. Thin layers were deposited from powder targets which were mounted on a two inch magnetron. Powder targets allow to design fast and in all desirable concentrations the high entropy alloy-thin films and derived compounds. The nitrogen uptake results in an enlargement of the unit cell. Gradually increasing the nitrogen/argon ratio produces a steady growth towards a stoichiometry nitride with the NaCl (B1)-structure. Other deposition parameters such as current discharge, target-substrate distance and pressure also have an influence on the arriving metal-to-nitrogen ratio and thus influence the size of the unit cell. The results can be summarized in a model for fine-tuning the unit cell of high entropy nitrides.

Notes:

MR6 Mechanical properties of ternary V–Mo–N and quaternary V–Mo–Al–N coatings

B. Grančič[1], S. Uzon[1], M. Mikula[1,2], D.G. Sangiovanni[3,4], T. Roch[1], M. Truchlý[1], L. Satrapinskyy[1], P. Kúš[1]

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The concept of a multicomponent alloying using transition metals from VB and VIB groups (V, Ta, Nb, Cr, Mo, W) represents a suitable way of the improvement of thermal stability and mechanical properties of nitride, carbide and boride binaries.

In our contribution, we discuss the mechanical properties of V–Mo–N coatings deposited by reactive DC magnetron sputtering. We show that changes in coating's stoichiometry from (VMo)N to (VMo)$N_{0.5}$ result in an increase of the hardness from 14 GPa to 28 GPa, respectively. In addition, the high content of nitrogen vacancies in the single phase fcc-lattice (rock-salt) has a potentially positive effect on the coating toughness, which is demonstrated by the low value of Young's elastic modulus ~ 230 GPa.

We further discuss the mechanical properties of V–Mo–Al–N coatings. The addition of Al was motivated by the expected increase of oxidation resistance and potential solid solution strengthening and age hardening. Higher content of aluminium in as-deposited V–Mo–Al–N coatings results in change of cubic (rock-salt) to hexagonal (wurtzite) structure with a corresponding change in mechanical properties.

Acknowledgements

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Notes:

MI3 Durable smart and multifunctional optical coatings for energy saving and anticounterfeiting – New opportunities for pulsed reactive plasmas

L. Martinu, B. Baloukas, F. Blanchard, S. Loquai

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Optical coating (OC) applications represent a multibillion dollar market worldwide. Their applications range from antireflective (AR) coatings found on most optical components, to narrowband optical interference filters used in telecommunication to low emissivity (low-e) coatings for buildings and automobiles. As the range of applications of OCs continuously broadens and the need for an increased performance and versatility increases, it is becoming increasingly important to develop thin film materials with novel nanostructures or based on unconventional materials and approaches to supply them with multifunctional properties.

In this context and for many years now, we have been exploring the characteristics of new smart thin film devices that integrate active materials in passive OC systems, specifically electrochromic (EC) WO_3 and thermochromic (TC) VO_2. Regarding VO_2, we have demonstrated the efficient use of new fabrication technologies such as Reactive High Power Impulse Magnetron Sputtering (R-HiPIMS) for low-temperature deposition of high performance coatings that have subsequently been deposited onto polymeric substrates allowing one to consider applications such as retrofitting existing windows. The R-HiPIMS process has also been shown to provide VO_2 films which are several times more durable under stringent high temperature and high humidity conditions (80 °C and ~ 100% RH) compared to films prepared under standard conditions.

Another issue with TC VO_2, aside from its high deposition temperature and durability, is its low visible transmittance. In this respect, we have recently explored the integration of VO_2 into a passive low-e type OC, such as dielectric|VO_2|Ag|dielectric systems, to obtain a multifunctional low-emissivity architecture with tunable characteristics. Specifically, the use of silver allows one to lower the VO_2's thickness while maintaining a respectable solar transmission variation (ΔT_{sol}) as a function of temperature, while a lower thickness (and thus absorption) consequently results in a high T_{lum}. Indeed, we have shown a T_{lum} of 58.2% with a ΔT_{sol} of 7.1%. The presence of a thin Ag film also procures low emissivity properties, and prototypes show values in the 0.1 range. This unique parameter combination thus brings such TC films closer to commercial implementation.

On the WO_3 side, we have developed new single material porous/dense WO_3 electrochromic interference filters where both EC as well as interference effects are combined into a single structure. In combination with an appropriate control of the surface reactions, this offers a possibility to tailor the transmittance and reflection spectra of such coatings with enhanced durability for various applications such as color shifting active security devices, variable AR coatings, and advanced glazings for architectural glass.

Notes:

MR7 Controlled reactive HiPIMS – Effective technique for low-temperature (300 °C) synthesis of VO_2 films with semiconductor-to-metal transition

D. Kolenatý, J. Vlček, T. Kozák, J. Houška, R. Čerstvý

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Reactive high-power impulse magnetron sputtering (HiPIMS) with a pulsed O_2 flow control and to-substrate O_2 injection into a high-density plasma in front of the sputtered vanadium target was used for low-temperature (300 °C) deposition of VO_2 films with a pronounced semiconductor-to-metal transition onto conventional soda-lime glass substrates without any substrate bias voltage and without any interlayer. The depositions were performed using an unbalanced magnetron with a planar target of 50.8 mm diameter in argon-oxygen gas mixtures at the argon pressure of 1 Pa. The deposition-averaged target power density was close to 13 Wcm^{-2} at a fixed duty cycle of 1% with a peak target power density up to 5 $kWcm^{-2}$ during voltage pulses ranged from 40 μs to 100 μs. A high modulation of the transmittance at 2500 nm (between 51% and 8% at the film thickness of 88 nm) and the electrical resistivity (changed 350 times) at the transition temperature of 56 – 57 °C was achieved for the VO_2 films synthesized using 50 μs voltage pulses when the crystallization of the thermochromic phase (VO_2(R) during the deposition and VO_2(M1) at the room temperature) was supported by the high-energy (up to 50 eV relative to ground potential) ions. Principles of this effective low-temperature deposition technique with a high application potential are presented.

Notes:

MR8 Tailoring optical and electrochemical properties of ITO films deposited by means of reactive magnetron sputtering

V. Stranak[1], P. Sezemsky[1], D. Burnat[2], J. Kratochvil[1], H. Wulff[3], Z. Hubicka[4], M. Cada[4], R. Bogdanowicz[5], M. Smietana[2]

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[3]*Institute of Physics, University of Greifswald, Greifswald, Germany*
[4]*Institute of Physics, Academy of Science of the Czech Republic, Prague, Czech Republic*
[5]*Faculty of Electronics, Telecom. and Informatics, Gdansk University of Technology, Gdansk, Poland*

The study is focused on development of multifunctional ITO films for lossy-mode resonance optical-fibre-based sensors [1]. Lossy-mode resonance (LMR) sensors appeared a few years ago and represent a hot topic in the field of fast, small and smart sensors. From a practical point of view, the LMR sensor is the optical fibre coated with a thin film overlay, where the specific wavelength of the incident light propagated in the high-refractive-index overlay is attenuated at the certain thickness deposited onto an optical fibre. This effect is caused by a coupling between waveguide modes, then a specific lossy-mode is propagated in the thin film [2]. Such sensors have been successfully used for detection of different bio-compounds [3].

The contribution reports controlled deposition of optically transparent and electrically conductive ITO films fabricated by a combination of rf (13.56 MHz) and High Power Impulse Magnetron Sputtering (HiPIMS) systems without any post-deposition thermal treatment/annealing. ITO films were deposited onto Si substrates as well as on the optical fibres. Our main aim represents tailoring the ITO film properties to achieve relevant optical and electrochemical properties. Optical properties and LMR sensitivity were evaluated utilizing the shift of the transmission spectra in media with different refractive index (RI), while the electrochemical performance was estimated by cyclic voltammetry with ferrocyanide redox couple. It was shown that (i) reactive admixture of N_2 gas to the deposition process and (ii) pressure in the deposition chamber enable to optimize optical properties of ITO films. Nitrogen admixture shows minor influence on the RI, while it leads to a substantial decrease in electrical resistivity and electrochemical performance. It was shown that ITO film resistivity could be tuned in range of an order of magnitude by nitrogen admixture. The variation of these ITO properties are attributed to transformation of crystalline structure induced by various deposition conditions and studies here by X-ray diffractometer.

Acknowledgements

This work was financially supported by Czech Science Foundation (GACR) through project 16-14024S, the National Science Centre (NCN), Poland as a part of 2014/14/E/ST7/00104 project, and research NATO Grant SPS G5147.

[1] I. Del. Villar, F.J. Arregui, C.R. Zamarreno, J.M. Corres et al., Sensors and Actuators B240, (2017), 174.

[2] N. Paliwal, J. John, Fiber Optics Sensors, Springer International Publishing Switzerland, (2017).

[3] M. Sobaszek, M. Dominik, D. Burnat, R. Bogdanowicz et al, Proc. of SPIE 10233, (2017).

Notes:

MR9 Hard transparent Al–Si/O–N coatings

M. Fischer[1], M. Trant[1], D. Scopece[1], C. Pignedoli[1], D. Passerone[1], K. Thorwarth[1], J. Patscheider[1], H.J. Hug[1,2]

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Aluminum oxynitride (Al–O–N) and aluminum silicon nitride (Al–Si–N) can be fabricated as fully transparent coatings by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS). In the case of Al–O–N, working with O_2 was required, and for that purpose a specially adapted sputter setup was used. Since both of the ternary materials provide high hardness and adaptability in physical parameters such as their refractive index, they are interesting for e.g. optical protection applications.

Adding increasing amounts of O or Si to polycrystalline wurtzite AlN leads to a gradual transformation of the material microstructure. First, a solid solution is formed in which the dopant O/Si atoms disperse in the crystallite. Second, upon transgressing a distinct solubility limit at 6 – 8 at.% O/Si, a nanocomposite develops in which the crystallites get enveloped in an amorphous matrix. Third, at yet higher O/Si contents, the coatings consist of an amorphous network.

Within the initial solid solution regime, O replaces N and Si replaces Al in the wurtzite crystal lattice. This leads to a continuous shrinkage in the *c* lattice parameter measurable by XRD. A potential explanation for that is the generation of Al vacancies. Since both dopant atom sorts contain one valence electron more than the atoms they replace, the resulting electron excess can be compensated by vacancies instead of electron donating Al atoms. This hypothesis was tested by ab initio DFT calculations. *C* lattice parameter changes upon introducing O/Si and accompanying Al vacancy defects were calculated. Comparison with experimental results showed good agreement, and confirming thermodynamic and kinetic explanations could be given.

Notes:

MI4 Fundamental properties of TM nitrides: Materials design strategies for extreme properties

J.E. Greene[1,2,3]

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[2]*Physics Department, Linköping University, Linköping, Sweden*
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Transition-metal (TM) nitrides exhibit an enormous range of properties and offer a smorgasbord of opportunities for materials scientists. Cubic TM nitrides have wide single-phase compound fields that can be exploited. We show results for vacancy hardening (not associated with film strain) in 3d Group-IV TiN_x(001) and Group-V VN_x(001); the hardness H (and resistivity ρ) of epitaxial layers increases, while the elastic modulus E and the relaxed lattice constant decrease linearly, as x is decreased from 1.0 to 0.67 and 0.80, respectively. In contrast, $H(x)$, $E(x)$, and $\rho(x)$ for 5d Group-V TaN_x(001) remain constant due primarily to the presence of isoelectronic antisites.

All Group-IV TM nitrides, TiN, ZrN, and HfN, are very good metallic conductors with room-temperature resistivities of 12 – 14 μΩ·cm. 3d Group-III ScN(001) is a transparent semiconductor with an indirect Γ-X gap of 1.3 eV and a direct X-point gap of 2.4 eV. Reflectivity measurements from $Sc_{1-x}Ti_xN$(001) layers show TiN is strongly reflecting up to the reflectance edge at $\hbar\omega_e = 2.3$ eV, while ScN is transparent, and $\omega_e \propto x^{0.5}$ for the alloy. ZrN is intermediate with $\hbar\omega_e = 3.04$ eV. Thus, hard decorative coatings can be obtained with a wide palette of colors.

Superconducting transitions T_c for the Group-IV TM nitrides range from 10.4 K for ZrN to 9.18 K for HfN to 5.35 K for TiN. For comparison, superconductivity is not observed for the Group-IV rare-earth (RE) nitride CeN. These results are consistent with electron/phonon coupling parameters of 1.11 (ZrN), 0.82 (HfN), 0.73 (TiN), and 0.44 (CeN). The acoustic phonon modes soften monotonically with increasing cation mass; optical mode energies remain approximately constant for the TM nitrides, but are significantly lower for the RE nitride due a lower interatomic force constant.

The extreme range of materials properties available in TM nitrides and related systems can be enhanced through the formation of self-organized superhard nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanopipes. Self-organization strategies include controlled phase separation, surface-induced spinodal decomposition, surface segregation-induced renucleation, strain-induced roughening, surface anisotropy, and dynamic resputter yield amplification.

An issue with hard ceramic films, however, is that they are typically brittle, leading to failure by crack formation and propagation. We show several approaches to obtaining TM nitride layers that are both hard *and* ductile (i.e., tough). IV-VI and V-VI alloys, e.g. $Ti_{1-x}W_xN$ and $V_{1-x}Mo_xN$, exhibit dramatic delocalization of electron density leading to a more ductile response to shear stress while exhibiting increased hardness under tensile and compressive loading. Vacancy-induced toughening is also observed in understoichiometric $(V,Mo)N_x$ alloys. Another example involves the design of TM nitride multilayers defined not by composition differences, but by bonding differences, in alternating layers of essentially the same composition.

Notes:

MR10 Pulsed reactive sputtering of chromium nitride from 12.5 to 87.5% of duty cycle, at 62.5 to 5000 Hz

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Chromium nitride is a reference material for the study of sputtering mechanism in new sputtering processes such as reactive-HiPIMS, bipolar sputtering or deep oscillation magnetron sputtering [1]. The published works mainly focused on the effect of the negative bias on the substrate [1–3] or of reactive nitrogen [3–5]. Some study reported the effect of duty cycle [1,6,7] or frequency [2,3,8], but mainly in a limited range. This work reports the chromium nitride bipolar pulse sputtering on a wide range of duty cycle and frequency (from 12.5 to 87.5% of duty cycle, at 62.5 up to 5000 Hz). Among the already cited studies [1–8], it is located in an unconventional large process window (Figure 1a and b), near HiPIMS process, to pulsed DC.

In-situ measurement have been performed such as optical emission spectroscopy, discharge characteristic measurements (peak power, voltage), or dissipated power. In addition, ex-situ measurements have been performed on the deposited films, in order to investigate the composition, the morphology, the structure and microstructure, the mechanical, electrical and optical properties of the deposited films. In every case, chromium nitride CrN is formed, but the properties change. We show that the frequency is more adapted parameter to tune the optical properties, while the duty cycle affects the mechanical properties of the CrN layers.

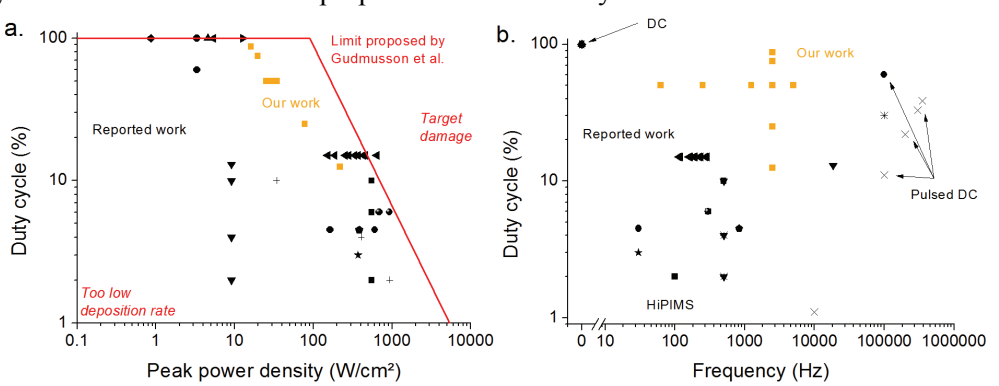

Figure 1 – Results from the present work, as compared to reported studies on CrN pulse reactive sputtering, in term of duty cycle vs. peak power density (a), and duty cycle vs. frequency (b)

[1] A. Anders, J. Appl. Phys. 121 (2017) 171101.

[2] G. Greczynski, J. Jensen, L. Hultman, IEEE Trans. Plasma Sci. 38 (2010) 3046–3056.

[3] G. Greczynski, J. Jensen, J. Böhlmark, L. Hultman, Surf. Coat. Technol. 205 (2010) 118–130.

[4] J. Lin, W.D. Sproul, J.J. Moore, S. Lee, S. Myers, Surf. Coat. Technol. 205 (2011) 3226–3234.

[5] Y.P. Purandare, A.P. Ehiasarian, P. Eh Hovsepian, J. Vac. Sci. Technol. Vac. Surf. Films. 34 (2016) 041502.

[6] W.-Y. Wu, B.-H. Hsiao, P.-H. Chen, W.-C. Chen, C.-T. Ho, C.-L. Chang, J. Vac. Sci. Technol. Vac. Surf. Films. 32 (2014) 02B115.

[7] K. Bobzin, N. Bagcivan, S. Theiß, J. Trieschmann, R.H. Brugnara, S. Preissing, A. Hecimovic, J. Vac. Sci. Technol. Vac. Surf. Films. 32 (2014) 021513.

[8] F. Ferreira, J.C. Oliveira, A. Cavaleiro, Surf. Coat. Technol. 291 (2016) 365–375.

Notes:

MR11 Systematics in reactive ion beam sputter deposition of TiO_2

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Ion beam sputter deposition (IBSD) is a physical vapour deposition (PVD) technique using a low-energy ion beam for sputtering a target. In contrast to other PVD techniques, for instance magnetron sputtering or evaporation techniques, IBSD offers more degrees of freedom for tailoring the properties of the secondary, film-forming particles and, hence, the properties of the films. Though widely used, the capabilities of IBSD have not been completely understood and utilized yet. The present paper focuses on closing this gap, i.e., it describes systematic investigations of the correlation between process parameters, properties of secondary particles, and film properties of TiO_2 deposited by reactive IBSD.

By changing ion beam parameters (ion energy, ion species), geometrical parameters (ion incidence angle, polar emission angle) and the target material (metallic or ceramic target), the angular and energy distribution of the sputtered target particles and scattered primary particles change systematically [1,2]. The energy distribution is predominantly affected by the scattering geometry and ion species. Ion energy, ion incidence angle and target material have only a small or negligible impact. Depending on the process parameters, the secondary particles can gain energies of up to several hundreds of eV caused by direct sputtering or scattering events. Basically, the average energy increases with decreasing scattering angle and increasing ion energy. Worthwhile to note, the contribution by high-energetic, scattered particles is stronger for sputtering with Ar ions than for sputtering with Xe ions.

The systematic changes in the particle properties have a direct impact on the properties of the TiO_2 films, namely, growth rate, composition, surface roughness, index of refraction, and mass density [3–5]. The growth rate increases with increasing ion energy and increasing ion incidence angle. Its angular distribution exhibits an over-cosine shape, which is assigned to anisotropy effects related to an incomplete evolution of the collision cascade. All films are amorphous and stoichiometric with a considerable amount of implanted primary particles. The atomic fraction of primary particles within the TiO_2 films decreases with increasing scattering angle. It is independent from ion energy, ion incidence angle, and target material, but it is larger for sputtering with Ar than for sputtering with Xe. The films are very smooth with a maximum root mean square roughness of about 0.22 nm. The root mean square roughness increases almost linearly with increasing scattering angle, and it is slightly smaller for the films grown by sputtering with Ar than for those grown by sputtering with Xe. Again, roughness is independent from ion energy, ion incidence angle, and target material. The index of refraction can vary strongly by up to 0.2, again, mainly influenced by scattering angle and ion species. The optical properties are strongly correlated with mass density data, i.e. the higher the mass density the higher the index of refraction. This observation is in agreement with reference data of TiO_2 films grown by various PVD techniques.

In summary, systematic correlation between process parameters, particle and film properties have been revealed. The most important parameters are the scattering geometry (scattering angle) and ion species. Ion energy and ion incidence angle have only a small or negligible influence. Interestingly, the greatest impact seems to be related to backscattered primary particles, a fact that has not been considered or at least underestimated so far. Previous investigations of the ion beam sputter deposition process of Ge, Ag or SiO_2 revealed similar correlations. We strongly believe that the results are of great technological interest because the knowledge of the systematics of the deposition process allows us to selectively tailor film properties.

[1] T. Lautenschläger et al., Nucl. Instrum. Methods Phys. Res., Sect. B, 385 (2016) 30.
[2] T. Lautenschläger and C. Bundesmann, J. Vac. Sci. Technol. A 35 (2017) 041001.
[3] C. Bundesmann et al., Nucl. Instrum. Methods Phys. Res., Sect. B, 395 (2017) 17.
[4] C. Bundesmann et al., Appl. Surf. Sci. 421 (2017) 331.
[5] C. Bundesmann et al., Eur. Phys. J. B, in press.

Notes:

MR12 B-based coatings prepared by magnetron sputtering and cathodic arc co-deposition

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Cubic boron nitride is clearly the most powerful/efficient material for machining of iron and its alloys. Cutting tools prepared by high-pressure synthesis are, however, costless. The motivation was to develop a technology for the preparation of PVD coatings with controlled content of B and with the possibility of modifying their microstructures.

The most common source of B for a PVD coating is magnetron sputtering from ceramic/composite targets. This method linked with low plasma ionization provides coatings with low thermal stability respectively hardness and, for the machining operations, a disadvantageous columnar microstructure. In addition, existing designs of magnetron targets do not allow the use of the needed industrial high power.

A practical solution is the possibility of magnetron sputtering (magnetron) and low-voltage arc (arc) co-deposition, where the magnetron provides the B and the arc additional ionization. A special cylindrical target patented in 2017 was designed for the magnetron. For transmission of the high loads this target uses deformations of thin Cu foils towards the target´s inner surface which results in a full-area contact to transfer the heat load and electric current. B_4C and TiB_2 targets with a diameter of 110 mm and a length of 550 mm can be thus loaded up to 20 kW. Along with the arc, coatings of any composition can be prepared. The effect of deposition parameters on the mechanical properties of TiN–BN, TiAlN–BN and CrAlN–BN systems depending on B content (0 – 70 at.%) and partial nitrogen pressure was studied. The method of co-deposition of magnetron sputtering and low voltage arc was also patented in 2017.

Notes:

TI1 Model calculation and visualization of time-dependent reactive gas mass balance change in Ti–O_2 reactive sputtering

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Reactive gas mass balance change in reactive sputtering has been an issue to be discussed from the viewpoints of process control and stabilization as well as theoretical interests. The mass balance change in reactive sputtering is time dependent for a constant reactive gas flow rate, and then after balancing of the reactive gas consumption to the introduction, a steady-state of the process is achieved [1]. The well-known hysteresis behaviors in reactive sputtering have been obtained for a steady-state mass balance during a series of reactive gas mass flow rate increase and decrease [2]. The time-dependent reactive gas mass balance changes have been shown by the following equation indicating the mass balance in a time increment (by modeling Ti–O_2 reactive sputtering);

$$Q_{introduced} + Q_{sputtered} = Q_{gettered} + Q_{oxidizing\_target} + Q_{pumped\_out} + Q_{residing}, \quad (1)$$

where $Q_{introduced}$ is the O_2 amount introduced into the chamber, $Q_{sputtered}$ *is* the O_2 amount suptter-etched from the oxide layer formed on the target surface, $Q_{gettered}$ is the O_2 amount gettered by depositing Ti, $Q_{oxidizing\_target}$ is the O_2 amount consumed for target surface oxidization, Q_{pumped_out} is the O_2 amount pumped out from the chamber by the vacuum-pump, and $Q_{residing}$ is the amount of O_2 gas residing in the chamber, resulting in the increase in the O_2 partial pressure to the next time increment (to induce the partial pressure diffrence between two time increments). During the time dependent process change, the target surface condition is changing until achieving a steady-state for a constant O_2 flow rate (F_{O2}), i.e., for a constant $Q_{introduced}$, causing changes in the balance among $Q_{gettered}$, Q_{pumped_out}, and $Q_{residing}$. At a steady-state, because $Q_{sputtered} = Q_{oxidizing\_target}$ *and* $Q_{residing} = 0$,

$$Q_{introduced} = Q_{gettered} + Q_{pumped\_out}. \quad (2)$$

In this paper, the O_2 mass balance change in Ti–O_2 reactive sputtering has been investigated based on a model of the time-dependent mass balance change [3, 4] to discuss the time-dependent O_2 mass balance change observed for a constant F_{O2} as a function time elapsed after the glow discharge ignition or after the set of a new value of F_{O2} from the value for a previous steady-state until the mass balance achieves to a steady-state for a given F_{O2} and other given conditions. As an example, time-dependent mass balance changes for target oxide layer formation starting from target coverage $\theta = 0$ and compound layer etching starting from $\theta = 1$ are calculated for various F_{O2}. In the calculation, discharge current and vacuum-pump pumping speed are given to be 2.0 A and 0.20 m^3/s, respectively, and sputtering yields from a metal target and from an oxide-layer-covered target are assumed to be 0.32 and 0.015, respectively. The time increment was set to be 1 s. At $F_{O2} \leq 7.0$ sccm ($Q_{introduced} \leq 0.12$ scc in a time increment), no avalanche-like target surface oxidization and subsequent decrease in $Q_{gettered}$ occurs in the time dependent change for a constant F_{O2}. At $F_{O2} = 7.0$ sccm, $Q_{gettered}$ shows avalanche-like decreases, as a result of the avalanche-like increase in target coverage to $\theta = 1$, in the time dependent change. After the avalanche-like change for $F_{O2} = 7.0$ sccm, most of O_2 introduced to the chamber is evacuated by vacuum pump, not consumed by gettering. For further increase in F_{O2}, no coverage change occurs, resulting in a constant $Q_{gettered}$. For the direction of the target oxide sputter-etching (the decrease in F_{O2}), at $F_{O2} \geq 5.0$ sccm ($Q_{introduced} \geq 0.083$ scc), no target-oxide-layer etching occurs, keeping a high O_2 partial pressure and a large Q_{pumped_out}. At $F_{O2} = 4.0$ sccm, the avalanche-like target-oxide-layer etching occurs, increasing $Q_{gettered}$ and decreasing Q_{pumped_out} as a result of the increase in Ti (metal) flux and decrease in O_2 partial pressure. These mass balance changes are all time-dependent, i.e., all mass balance changes are shown as a function of time elapsed for a constant F_{O2}. In addition, all of balance changes occur as a result of the target surface balance change. By graphing the time-dependent mass balance change as a function of time elapsed after the discharge ignition or after the change of F_{O2} from the value for a previous steady-state, it is possible to visualize the changes in $Q_{sputtered}$, $Q_{gettered}$, $Q_{oxidizing\_target}$, Q_{pumped_out}, and $Q_{residing}$ until achieving a steady-state for a constant F_{O2}. At the presentation, the time-dependent mass balance changes as well as a steady-state mass balance will be discussed based on results of experimental measurements and of the model calculations of the mass balance.

[1] E. Kusano, A. Kinbara, Time-dependent O_2 mass balance change and target surface oxidation during mode transition in Ti-O_2 reactive sputtering, J. Appl. Phys. 87 (2000) 2015-2019.

[2] E. Kusano, An investigation of hysteresis effects as a function of pumping speed, sputtering current, and O_2/Ar ratio, in Ti-O_2 reactive sputtering processes, J. Appl. Phys.70 (1991) 7089-7096.

[3] E. Kusano, Modeling of time-dependent process changes and hysteresis in Ti-O_2 reactive sputtering, J. Appl. Phys. 73 (1993) 8565-8574.

[4] E. Kusano, Model calculation of time-dependent changes in getter-pump pumping speed in reactive sputtering, 13th Intl. Symp. Sputtering and Plasma Processes, The Vacuum Society of Japan, July 9, 2015, Kyoto Research Park, Kyoto, Japan.

Notes:

TR1 Evolution of titanium atom and ion density in reactive HiPIMS – Impact on hysteresis curve shape

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Similar to the reactive dc or pulsed-dc sputtering, the R-HiPIMS is subject to hysteresis behaviour, however the hysteresis may be minimised or even suppressed by optimizing the R-HiPIMS process parameters. The exact mechanism behind the hysteresis suppression is still unknown and therefore this issue is yet highly disputed in the scientific community. Authors of [1] argue that the sputtering rate during pulses is greater than in dcMS, and the formation of a compound layer between HiPIMS pulses is reduced due to the gas rarefaction, which also includes rarefaction of the reactive gas. Authors of [2] claim that return of the target material ions leads to the reduced hysteresis behaviour in R-HiPIMS. Recently, the spectroscopic technique based on effective branching fractions was developed to determine the absolute ground state number densities of Ti atoms and Ti ions [3] and this technique was cross-validated by TD-LAS technique [4]. This technique is a powerful tool to reveal the processes taking place in the sputtering experiments including R-HiPIMS.

In this paper, we report the evolution of the sputtered Ti atom and ion ground state densities in R-HiPIMS for both oxygen and nitrogen gasses. The fast feedback system was employed to allow working in the transition region of the hysteresis curve in a well-controlled manner. For the discharge current density of ~1A/cm^2 and the pure metallic mode, the density of Ti atoms measured close to the target was 5.8×10^{16} m^{-3} and that of Ti ions was 2.0×10^{17} m^{-3} corresponding to ionized fraction of the sputtered species of 77%. As the reactive gas supply is increased, both densities decreases due to the lower sputtering rate of partially poisoned target. The ionized fraction of the sputtered species increases with the oxygen supply reaching 83% corresponding to the transition from the metallic to the compound mode. It continues to increase also in the transition regime reaching 88% for the oxygen supply corresponding to transition from compound to metallic mode. Increasing the oxygen supply in compound mode, the ionized fraction increases further. Very similar trends were observed also for the R-HiPIMS with nitrogen gas. It is assumed that the enhanced ionization of the sputtered titanium is caused by the combination of following effects: 1. enhanced residual time of the sputtered species in the magnetized plasma – lower amount of sputtered species causes lower gas rarefaction and thus the probability of the collision between sputtered species and residual gas increases 2. higher maximal current attained at the end of the pulse in transient and compound mode and thus higher plasma density 3. lower amount of sputtered species due to the target poisoning which may positively affect electron distribution function.

The shape of the hysteresis curve in R-HiPIMS was noticeable different from the one of dc magnetron sputtering operating at the same mean power – the transition from the metallic to compound mode and vice versa were shifted towards the lower reactive gas supply and the width of the hysteresis curve was reduced. The modified Berg model assuming that a part of the sputtered and ionized species are back-attracted to the target was developed. The flux of the titanium particles returning back to the target surface modifies the state of the sputtered target (it makes it more metallic) and also reduces the flux of the sputtered species to the substrate. The measured densities were included in the model and a quite good qualitative and quantitative agreement between measured and calculated hysteresis curves was obtained.

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[1] E. Wallin et al., Thin Solid Films 516, (2008) 6398.
[2] J. Čapek et al., J. Appl. Phys. 121, (2017) 171911.
[3] P. Vašina et al., Plasma Source Sci. Technol. 24(6), (2015) 065022.
[4] M. Fekete et al., J. Phys. D. Appl. Phys. 50, (2017) 365202.

Notes:

TR2 Transition mode sputtering of Al_2O_3 – Hysteresis and process stability of large Al targets

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In reactive sputtering of oxide films from Al targets, operation in the transition mode is highly desirable due to the high growth rates possible. Due to the hysteresis between metallic and oxidized target state, the process is not stable in transition mode and an external control loop for the reactive gas flow is needed to keep the process in transition mode. In this contribution we investigate the behavior of 3.75 m long Al targets as they are used in industrial coaters for architectural glass.

With planar targets, the transition mode is not readily accessible. Long term drifting of the operating point is observed as well as fast plasma instabilities in the time scale of a few milliseconds. With rotary targets, the transition mode is accessible by the established means, either by a gas flow control loop or by operating the power supply as a constant voltage source. A double hysteresis can be seen as reported in the literature [1]. The oxygen requirement for a set plasma voltage is different depending on whether the target was brought to the transition regime from the oxidized or the metallic state. However, process runs over several hours indicate that the double hysteresis may be only metastable.

A further challenge in large area coating is the maintenance of the lateral uniformity of the sputter rate. The plasma voltage alone does not reflect lateral non-uniformity of the target state, in fact, when entering the transition mode; one end of the target can become fully oxidized while the other is metallic. In consequence, voltage controlled operation is not sufficient and an additional external control loop of the lateral reactive gas distribution is needed.

[1] R. Schelfhout, K. Strijckmans, D. Depla, "The existence of a double S-shaped process curve during reactive magnetron sputtering", Appl. Phys. Lett. 109, 111605 (2016).

Notes:

TR3 Plasma and floating potentials in magnetron discharges

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This presentation shows great differences in values of the plasma U_p and floating U_{fl} potentials in sputtering discharges generated by single and dual magnetrons. It is shown that (i) the differences of U_p and U_{fl} result in strongly different properties of films sputtered by single and dual magnetrons at the same power delivered to the magnetron discharge, (ii) the values of U_p and U_{fl} strongly depend on the electric conductivity of the surface of grounded deposition chamber in the DC single and DC dual magnetron discharges, and (iii) the pulsed dual magnetron with closed magnetic field B and grounded pulse power supply is only one sputtering system which enables to sputter the films with fully reproducible properties [1].

[1] J. Musil, M. Jaroš, "Plasma and floating potentials in magnetron discharges", J. Vac. Sci. Technol. 35, 060605 (2017).

Notes:

TR4 Long-term stability and disappearing anode effects during reactive DC and pulsed bipolar magnetron sputtering of Al_2O_3

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Reactive magnetron sputtering from metal target is a well-established technique to deposit compound films at different composition by controlling the reactive gas flow. Target poisoning and resulting reduced sputtering rate influence the deposition process stability and give rise to hysteresis effects [1, 2]. Recently, a double S-shaped curve during reactive magnetron sputtering has been reported [3]. Using DC sputtering of Al target in the Ar + O_2 gas mixture, the authors found two S-shaped characteristic curves. One has been seen in moving from the metallic mode to the poisoned one and a different curve in moving the other way. This means two possible values of discharge voltage to maintain a defined value of oxygen partial pressure.

We have studied the long-term stability during Al_2O_3 sputtering in a Hauzer industrial load-lock deposition system with each chamber volume (load-lock and main chamber) over 1 m^3. Two rectangular Al alloy targets with size of 130 mm × 606 mm were powered either by a bipolar pulsed power supply PlasmaTec AC 12 kW (J. Schneider) with frequency of 43 kHz or by a DC power supply Pinnacle 6 kW (Advanced Energy) for sputtering from a single target. In both cases, hysteresis-free operation was maintained by a voltage control. Partial pressures of gases were measured by a quadrupole mass spectrometer Pfeiffer Vacuum SPM 220. Plasma composition was also analyzed by optical emission spectrometer AvaSpec 2048-3. The chamber was equipped by an external anode hidden behind a valve.

The long-term stability of the hysteresis behavior was measured by repeating cycles of increasing and decreasing of target voltage from 430 V to 530 V during single target DC sputtering and from 450 V to 700 V during bipolar sputtering. The cycle consists of four steps - decrease of voltage, holding at low voltage (close to poisoned mode at hysteresis curve), increase of voltage and holding at high voltage (close to metallic mode). The time period of each step of the cycle was held the same and we changed this period from 5 to 30 minutes.

During the single target DC sputtering, we could detect changes in the hysteresis S-shaped curve over time. In the first cycle, the target current is high at high voltage (close to metallic mode) and low at low voltage (close to poisoned mode). The target current follows different paths during the voltage increase and decrease steps of the cycle. This would be in perfect correlation with the double S-shaped process curve detection. But in the second cycle and the following ones, the decrease of current during high voltage step and increase of current during low voltage step can be detected. Both current paths during the voltage increase step and decrease step of the cycle are different again from each other but even from the previous two curves. The system develops to new stable states (metallic and poisoned) over several hours.

After a cycle or two, the whole chamber gets covered by an insulating Al_2O_3 film. The measured partial pressure of oxygen increases. The electrons can't reach the walls and plasma starts to glow intensively (confirmed by OES). When the external anode is opened, the system instantly reacts by moving closer to the metallic mode which means an increase of current at high voltage step of the cycle. At low voltage step of the cycle, a decrease of current is observed (also a proof of the more metallic state). All our observations indicate that the long-term behavior is caused by the effect of disappearing anode and corresponding effects on the plasma medium, resulting in higher necessary voltages for the same oxygen partial pressure and target condition.

Using bipolar sputtering, the effect of disappearing anode was not detected. This is understandable, as the anode in bipolar sputtering is the other target, which gets repeatedly cleaned during the opposite half-period of the bipolar cycle.

The experiments show a surprisingly long temporal evolution of the reactive sputtering system. Also, the origin of observed double S-curve should be more likely attributed to the anode and plasma effects than to the reactions on the target.

[1] S. Berg, J. Vac. Sci. Technol., A 5, 202 (1987).

[2] S. Kadlec, J. Musil and H. Vyskocil, J. Phys. D: Appl. Phys. 19, L187 (1986).

[3] R. Schelfhout, K. Strijckmans and D. Depla, Appl. Phys. Lett. 109, 111605 (2016).

Notes:

TI2 Synchronised external magnetic fields applied in HiPIMS enhance plasma generation in the race track as well as plasma transport to the substrate

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High Power Impulse Magnetron Sputtering (HiPIMS) has been shown to be an excellent technique for depositing dense, high quality thin films in both non-reactive and reactive modes. The high degree of ionisation of the depositing species allows fine-tuning of film properties and microstructures by the simple application of substrate bias. The main disadvantage of HiPIMS that has limited its translation to many commercial applications is its low deposition rate. Magnetic field guiding of the plasma from the racetrack where it is produced to the substrate where it participates in thin film deposition has been suggested as a way of enhancing the deposition rate.

Here we show the utility of externally applied pulsed fields synchronized with the HiPIMS pulse for the enhancement of deposition rate in both reactive and non-reactive HiPIMS. External magnetic fields were applied by a solenoidal coil that was placed above the magnetron target. In the case of a steady magnetic field in comparison to a pulse field, a higher voltage was required to initiate the HiPIMS discharge, a longer delay time was observed for current onset, and oxide films deposited in reactive HiPIMS became substoichiometric.

In contrast, for the pulsed magnetic field, film stoichiometry was maintained under all applied external magnetic field strengths. Higher target and substrate currents were observed when magnetic field pulses were synchronized with HiPIMS pulses. Varying the duration and delay times of the magnetic field after the application of the HiPIMS voltage pulse revealed that the afterglow of the plasma between HiPIMS pulses was quenched by the presence of the magnetic field. Therefore, the optimum operation with the highest plasma density was obtained by applying the external magnetic field only when the plasma was established and removing it at the end of the HiPIMS pulse.

We describe an approach to achieve maximum deposition rate while maintaining film stoichiometry and high film quality in reactive HiPIMS. Amorphous HfO_2 films with leakage current through the film of less than 5×10^{-5} A/cm^2 at 0.1 MV/cm were obtained at the maximum deposition rate. The refractive index, at a wavelength of 500 nm, of the film prepared with pulsed magnetic field was 2.05 with a low extinction coefficient of 8×10^{-5}. WO_3 multilayered electrochromic coatings with excellent properties were also deposited by taking advantage of the enhanced reactivity of species in the HiPIMS discharge.

In the non-reactive process, enhancement of the deposition rate by a factor of 3 was observed due to an expansion of the race track extent together with improved transport of ions to the substrate. A COMSOL simulation of the total magnetic field enables us to show that this behaviour can be attributed to enhancement in plasma generation, by broadening and intensification of the confining field at the racetrack, together with plasma collimation, by the establishment of a guiding field from the race track region to the substrate. A model to explain the findings is presented.

Notes:

TR5 Ion energy distributions in magnetron sputtering: Questions remain even after detailed measurements of the plasma potential

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It is well known that the energies of atoms and ions arriving on the surface of a growing film affect the film's microstructure. Therefore, much effort has been devoted to measure and understand atom and ion energy distribution functions. In magnetron sputtering, when neglecting collisions in the gas phase, atoms exhibit a Thompson distribution. The situation is more complicated for ions because their energy is changed by the local electric field above the target as well as by the electric field of the sheath above the substrate. The different contributions will be explained in light the local plasma potential distributions recently measured for the whole range from dc magnetron sputtering to high power impulse magnetron sputtering (HiPIMS) [1]. Both spoke and spoke-free modes are considered. The absolute values of plasma potential, as determined by emissive probes, and the ion energy distribution functions, as measured with an EQP300 plasma analyzer, still leave questions open that could be answered with ions "surfing" transient fields of plasma instabilities.

Acknowledgements

Contributions by Y. Yang and M. Panjan are gratefully acknowledged. This work was done at Lawrence Berkeley National Laboratory with support by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

[1] M. Panjan, A. Anders, J. Appl. Phys. 121 (2017) 063302.

Notes:

TR6 Arcing in high power impulse magnetron sputtering: Review of physical background and arcing mitigation methods

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High Power Impulse Magnetron Sputtering (HIPIMS) is the youngest Physical Vapor Deposition (PVD) technique available to the industry. The operation principle of HIPIMS is based on the delivery of power to the plasma discharge in short pulses with peak power of at least 500 W/cm^2 and peak current exceeding 1 A/cm^2. This results in a high ionization of the sputtered metal vapor used to improve the adhesion and properties of deposited coating. As the HIPIMS operates in the glow discharge regime it has been applied for different coating deposition where production of high quality, droplet-free coatings is strongly desired. As a consequence the HIPIMS-based processing is to replace some of industrial processes utilizing cathodic arc deposition where without application of electromagnetic filtering of the plasma flux, the droplets are incorporated into the coating. However, operation of HIPIMS discharge with high pulse power and current densities can also lead to formation of highly energetic arcs on the target surface, especially when used in reactive sputtering. Therefore, a precise and fast control of HIPIMS discharge parameters is required for successful mitigation of arc-induced damage of HIPIMS coatings.

The prime objective of this work is to review the basic knowledge about arc formation on the magnetron sputtering target operated in glow discharge mode. First, the physical mechanisms of glow and arc discharge will be compared, followed by analysis of electrical conditions typical for both discharges. Finally the influence of the reactive gas addition on arcing evolution on a poisoned target surface will be discussed.

Based on the theoretical consideration of arc formation the discussion will focus on second objective of the work which is the mitigation of arc-induced damage of coatings deposited by HIPIMS. The second part will be opened with the description of basic methods for detection of discharge shift from glow to arc type. The application of broad frequency range and regulated positive voltage pulse in Pulsed-DC sputtering of Indium Tin Oxide for photovoltaic cell production, will be used to illustrate basic industrial solutions used for arcing mitigation. As next, it will be showed that application of regulated quasi-rectangular HIPIMS voltage and current pulse shape does not lead to increased probability of arc formation. In contrary, using the experimental data of TiN coating deposition it will be demonstrated how the advanced pulse current control can be used for fast detection of arc formation. Furthermore, the efficiency of frequency and positive voltage pulse influence on arcing in HIPIMS sputtering will be compared with the Pulsed-DC sputtering results.

The discussion will be concluded with the analysis of new method for stabilization of reactive sputtering processes using a combined peak current value and average power control algorithm implemented in HIPIMS power supply.

Notes:

TR7 Spokes occurrence in HiPIMS discharge at different magnetic field strengths

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The non-reactive high power impulse magnetron sputtering (HiPIMS) discharge is not always homogeneously distributed over the target surface. Under certain conditions the plasma is concentrated in regions of higher local plasma density called spokes rotating above the erosion racetrack as was shown by high-speed camera imaging, optical emission spectroscopy and electrical probes [1,2,3].

The effect of magnetic field strength on spoke behavior was studied by high-speed camera imaging and optical emission spectroscopy (OES) in HiPIMS discharge using 3-inch titanium target. The spoke shape, number of spokes and spoke rotation velocity were observed by employed camera. The camera enabled us to record two successive images in the same pulse with time delay of 3μs between them. The time-resolved measurements of chosen Ti atom, Ti ion, Ar atom and Ar ion lines were made. The experimental conditions covered discharge current up to 350 A, pressure range of 0.15 – 5 Pa and magnetic fields strength of 37, 72 and 91 mT.

The plasma emission images captured by high-speed camera during HiPIMS pulses was divided into five groups: non-recognizable, stochastic, triangular, round and diffusive spokes. For the first time both diffusive and triangular shapes were observed for the titanium target. The maps of spoke occurrence were created for studied conditions. For the lowest magnetic field strength used in our experiment, only non-recognizable, stochastic and diffusive spoke were observed. For the magnetic field strength of 72 and 91 mT also round and triangular spoke were seen, while diffusive spokes were missing.

The number of spokes was determined for triangular and round spokes as they were easily countable for magnetic field strengths of 72 and 91 mT, where they were observed. Surprisingly, not only increase but also decrease of spoke number was observed with increasing discharge current. The decrease of the spoke number was observed for pressures higher than 1 Pa for the magnetic field strength of 72 mT, while for the stronger magnetic strength of 91 mT the decrease of spoke number was observed at pressures higher than 3 Pa. Until now either increase [1,4] or decrease [5,6] of the spoke number were reported. The spoke velocity increased with increasing discharge current for the magnetic field strength of 91 mT, while for 72 mT the spoke velocity was nearly constant. Increase of the pressure led to the decrease of the spoke velocity as was reported earlier [3, 4]. The spoke rotation velocity was independent on the magnetic field strength.

The optical emission spectroscopy was performed for the same experimental conditions as high-speed camera imaging. For all studied pressures, the chosen argon atom and titanium atom line intensities were most intensive at the beginning of the pulse. As the discharge current increased further during the pulse, the intensities of the both lines decreased. The titanium ion line intensity at the beginning of the pulse increased and then it saturated and even started to decrease despite the discharge current was still increasing. The argon ion line intensity increased similarly to the increasing trend of the discharge current during the pulse. The strongest argon ion line emission coincided with the appearance of the triangular spokes.

Acknowledgements

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[1] A.V. Kozyrev, N.S. Sochugov, K.V. Oskomov, A.N. Zakharov and A.N. Odivanova, Plasma Phys. Rep. 37, (2011) 621.
[2] A. Anders, P. Ni and A. Rauch, J. Appl. Phys. 111 (2012) 053304.
[3] A.P. Ehiasarian, A. Hecimovic, T. De Los Arcos, R. New, V. Schulz-von der Gathen, M. Böke and J. Winter, Appl. Phys. Lett. 100 (2012) 114101.
[4] P. Klein, J. Hnilica, Z. Hubička, M. Čada, M. Šlapanská, M. Zemánek and P. Vašina, Plasma Sources Sci. Technol. 26 (2017) 055015.
[5] J. Winter, A. Hecimovic, T. de los Arcos, M. Böke and V. Schulz-von der Gathen, J. Phys. D: Appl. Phys. 46 (2013) 084007.
[6] A. Hecimovic, V. Schulz-von der Gathen, M. Böke, A. von Keudell and J. Winter, Plasma Sources Sci. Technol. 24 (2015) 045005.

Notes:

TR8 The application of a short positive voltage reversal in reactive HIPIMS: Enhanced deposition rate and improved coating properties

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This paper demonstrates the implications of applying a short positive voltage reversal in reactive HIPIMS discharges. It is shown that not only the arc appearance is reduced, if not strong effects on the film ion assistance are observed. A 20% net increase in the deposition rate as well as an improvement in the film properties such as density or hardness are observed for two different coating systems: Tantalum Nitride and Titanium Nitride.

The benefits of using a positive reverse phase in a bipolar pulsed discharge has been already demonstrated in the past to be a relatively stable technology for reactive magnetron deposition of demanding processes such as sputtering of pure aluminum in the presence of reactive gases such as oxygen or nitrogen. The initial reason for using this asymmetric voltage polarity switch was the reduction of arc appearances by preventing charge build-up on target as electrons are attracted back to the target during the positive reverse phase [1,2]. Later, it has been observed that this operation mode also leads to higher plasma densities and electron temperature adjacent to the substrate, giving rise to the formation of high energy ions. In the case of HIPIMS, due to the high degree of ionization of the sputtered material, the implications of applying a short positive voltage reversal to the coating ion bombardment should be enormous.

This paper shows the differences on the voltage, peak current and floating potential evolution for different voltage reverse configurations. It is demonstrated that the floating potential can be shifted to positive values up to +650 V with respect to ground, thus creating highly energetic ions. A set of different TiN_x and TaN_x coatings were deposited with equal plasma power parameters during the negative pulse phase, but with and without positive voltage reverse. Differences in the coatings properties regarding deposition rate, elemental coating composition and mechanical properties are measured and correlated with the positive voltage reverse phase.

[1] J. Sellers "Asymmetric bipolar pulsed DC: the enabling technology for reactive PVD Surface and Coatings Technology" Surface and Coatings Technology, Volume 98, Issues 1–3, 1245–1250, (1998).

[2] J. H. Greiner and A. Halperin "First positive effects of the positive pulse (RF vs DC-P)" IBM Technical Disclosure Bulletin P. 2173, Vol. 17 No. 7 December 1974.

Notes:

TI3 Key features of reactive high power impulse magnetron sputtering

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This talk will address some of the challenges and possibilities of depositing compound coatings using high power impulse magnetron sputtering (HiPIMS). Both nitride and oxide systems will be covered during different modes of operation including metallic, transition, and compound modes. Key features in reactive HiPIMS, such as eliminated/reduced hysteresis, new types of process stabilization, stable high-rate deposition, and self-sputter recycling versus process gas recycling, will be addressed by using results from recent plasma modelling in combination with experimental plasma characterization. Furthermore, ionization of the material flux will be discussed in detail, since it enables effective surface modification via ion etching and self-ion assistance during film growth, as well as being a key feature in HiPIMS. This includes exploring the temporal evolution of the discharge plasma parameters, such as electron density and temperature, the neutral and ion composition, the ionization fraction of the sputtered vapor as well as of the reactive gas mixture, and the composition of the discharge current. The new insights gained from this analysis will be applied to a series of selected material systems, such as Al_2O_3, TiO_2, and HfN, in order to highlight the potential of reactive HiPIMS.

Notes:

TR9 Modelling the dynamics of processes in reactive HiPIMS deposition of oxide films

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Reactive high-power impulse magnetron sputtering (HiPIMS) is being used extensively to prepare various optically transparent dielectric oxide films with a high film density and index of refraction, and a low surface roughness (e.g. ZrO_2, Ta_2O_5 and HfO_2 films prepared by us using a pulsed reactive gas flow control and an optimized reactive gas inlet [1]). We have developed a time-dependent parametric model of the reactive HiPIMS deposition process [2] which helps us understand the relationships between the measured discharge and deposition characteristics. The model was applied to controlled reactive HiPIMS depositions of stoichiometric ZrO_2 films, carried out in our laboratories, (i) to clarify the complicated dynamics of the processes on the target and substrate surfaces during voltage pulses, and (ii) to corroborate the importance of the O_2 inlet configuration (position and direction) which strongly affects the O_2 dissociation in the discharge and the chemisorption flux of oxygen atoms and molecules onto the substrate. For the experimental conditions with the to-substrate O_2 inlets, the deposition-averaged target power density of 50 Wcm^{-2} and the oxygen partial pressure of 0.05 Pa (being close to the mean value during controlled depositions), our model predicts a low compound fraction, changing between 8% and 12%, in the target surface layer at an almost constant high compound fraction, changing between 92% and 93%, in the substrate surface layer during the pulse period (2000 μs). We show the importance of oxygen dissociation in the discharge plasma (enhanced by an optimized position and orientation of the oxygen inlet) to obtain stoichiometric films on the substrate while keeping a high deposition rate of films. The calculated deposition rate of 89 nm/min for these films is in good agreement with the measured value achieved for optically transparent stoichiometric ZrO_2 films prepared under these conditions.

[1] J. Vlcek, J. Rezek, J. Houska, T. Kozak, J. Kohout, "Benefits of the controlled reactive high-power impulse magnetron sputtering of dielectric oxide films", Vacuum 114, 131, 2015.

[2] T. Kozak, J. Vlcek, "A parametric model for reactive high-power impulse magnetron sputtering", J. Phys. D.: Appl. Phys. 49, 055202, 2016.

[3] T. Kozak, J. Vlcek, "Dynamics of processes during the deposition of ZrO_2 films by controlled reactive high-power impulse magnetron sputtering: A modelling study," J. Appl. Phys. 122, 043304, 2017.

Notes:

TR10 Current dependency of the compound sputtering yield

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The compound sputtering yield is a vital quantity during reactive magnetron sputter deposition. It largely influences the deposition rate, which is of prime industrial importance, but it also shapes the well-known hysteresis effect in the process curve. Several experimental methods to measure the sputtering yield of compounds by noble gas ion bombardment are discussed in literature. Although all methods determine the same quantity, large variations are found among them. The discrepancies cannot be explained by the difference in the measurement method (i.e. weight loss, etch rate, ratio of deposition rates, …). In contrast, a clear dependency of the compound sputtering yield on the source of the impinging ions, namely a magnetron discharge or an ion beam source, is noticed. Our study suggests however a more fundamental explanation. It is assumed that the compound sputtering yield depends on the current density of the bombarding ions. In order to vouch this statement, a novel method to determine the compound sputter yield during reactive magnetron sputtering based on reactive gas consumption is introduced. The method appears to be very fast as well as accurate, making it suitable for systematic studies of the compound sputtering yield. Such a comparative study is performed on aluminium oxide bombarded by 220 eV argon ions as a function of the ion current density. A decrease in sputtering yield with increasing ion current density is noticed. This behaviour can be divided into three clearly distinct regimes: the ion beam regime with a low current density, the magnetron regime with a high current density and the intermediate regime in between. The difference in sputtering yield between these regimes resembles the discrepancy of the compound sputtering yield in literature.

Notes:

TR11 A novel method for the optimization of reactive sputtering processes

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Reactive sputtering is a well-developed deposition technology. It has been proven in practice since several decades and has a comprehensive theoretical foundation. Nonetheless the scale up into the industrial environment is often hindered by the need of sophisticated operation or by concerns with respect to long term reliability.

The paper will present the usage of voltage transients for characterizing the reactive sputtering process. The proposed procedure can serve as a powerful complement to well established control parameters like impedance, plasma emission or oxygen partial pressure.

A double magnetron sputtering module was implemented into a roll-to roll-coating machine. The system comprised two planar magnetrons, each of them having 900 mm target length. The two magnetrons were powered in bipolar mode in the frequency range between 10 kHz and 50 kHz.

A reactive sputter process was set up for depositing aluminum oxide and zinc stannate layers onto polymer films. Metallic targets were used for both materials. A closed loop feedback control was set up for the oxygen inlet. Hysteresis curves were measured at different power levels. Maximum dynamic deposition rates of 25 nm·m/min and 90 nm·m/min were achieved for aluminum oxide and zinc stannate, respectively.

Extensive measurements of voltage transients will be presented. It is demonstrated how the shape of the voltage transient over the pulse length of several microseconds can be used for the determination of the exact working point on the hysteresis. Additional predictions can be made concerning the appropriate distribution of the oxygen flow and hence for achieving sufficient crossweb uniformity.

Notes:

TI4 Reactive HiPIMS through the eyes of a 'simple' model

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High power impulse magnetron sputtering (HiPIMS) showed to be the latest big revelation in the sputtering community over the last decade. It is already well established in several industrial applications where the higher ionization degree of the deposited species is exploited as one of the main advantages. Basically this PVD technique boils down to the concentration of the discharge power into short pulses. In maintaining similar average discharge power density compared to direct current magnetron sputtering (DCMS), sufficiently low duty cycles are applied. The high plasma density results in the high ionization degree of the sputtered species which can be back attracted to the target. This effect typically disadvantages the obtained deposition rate.

While the understanding of non-reactive HiPIMS is already quite broad, the transition to reactive HiPIMS (R-HiPIMS) is much younger. The addition of a reactive gas to the discharge complicates the story, similar as in reactive DCMS (R-DCMS). Non-linear behavior in the operation curves arises. These non-linearities manifest themselves most clearly in the so-called hysteresis of the operation curve. This means that process operation will not solely depend on the actual operation parameters, but will also depend on the operation history, or more specific on the target history. The basic mechanisms at the origin of the classical hysteresis effect arealready identified for a long time. Fundamentally, the same mechanisms play irrespective of the specific reactive sputtering technique like DCMS or HiPIMS. Nevertheless, moving to R-HiPIMS brought additionally effects into the picture. Those effects are implantation of sputtered species, gas rarefaction in front of the target, sputter cleaning of the target and recycling of out diffusing implanted gas. Notwithstanding that these effects are more prominent and as such more important in understanding hysteresis behavior for R-HiPIMS, they are not inherently connected to R-HiPIMS alone. In questioning the existence of hysteresis during R-HiPIMS, extensions to the RSD model have been applied [1]. This model is in continuous development aiming to grasp all the essential ingredients to fully understand the hysteresis behavior of reactive sputtering. As the RSD model [2] was initially developed for R-DCMS, its most recent advances start from R-DCMS. Potential key elements in explaining unraveled phenomena like the existence of a double hysteresis [3] are best first investigated for the 'simple' R-DCMS with the 'simple' RSD model, before moving to R-HiPIMS. This is motivated under the statement that "The reactive core aspects of reactive magnetron sputtering are technique independent".

[1] K. Strijckmans, F. Moens, and D. Depla, J. Appl. Phys. 121, (2017) 080901.

[2] K. Strijckmans and D. Depla, J. Phys. D: Appl. Phys. 47, (2014) 235302.

[3] R. Schelfhout, K. Strijckmans and D. Depla, Appl. Phys. Lett. 109, (2016) 111605.

Notes:

WI1 Reactive and non-reactive sputter deposition of MoO_x thin films

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Due to their unique optical, electrical and chemical properties, oxide-based thin film materials are widely used in industrial applications. In particular, depending on their oxidation state, molybdenum oxides (MoO_x) are characterized by a wide variation of electrical and optical properties, ranging from the non-transparent appearance with metal-like electrical conductivity of MoO_2 to the transparent and electrically insulating behaviour of MoO_3. Tuning chemical bond characteristics might thus enable to adjust their electrical and optical properties in a wide range, making them interesting candidates for optical and electronic applications.

Within this work, MoO_x thin films were synthesized by dc magnetron sputter deposition using three different approaches: (i) reactive sputtering from a Mo target in an Ar/O_2 atmosphere, where the partial pressure of oxygen was used to adjust the chemical composition of the films, (ii) non-reactive sputtering from MoO_x targets, and (iii) partial-reactive sputtering from MoO_x targets in an Ar/O_2 atmosphere. For reactive sputter deposition from Mo targets at moderate O_2 partial pressures, amorphous-like films dominated by MoO_2 bonds with electrical conductivity similar to metallic Mo and high optical absorbance of up to 70% were obtained. Exceeding a critical O_2 partial pressure results in formation of crystalline and highly transparent, but insulating MoO_3-dominated films [1,2]. Since such reactive deposition processes using high oxygen partial pressures are disadvantageous for large-scale synthesis of thin films due to process instabilities and target poisoning, in a second approach synthesis of MoO_x thin films by non-reactive dc magnetron sputter deposition using MoO_x targets was explored. The films obtained in the non-reactive mode exhibited an amorphous structure dominated by MoO_2 bonds with properties similar to those grown by the reactive process [3]. Small additions of O_2 to the process gas in a partial-reactive sputter process yielded the same transition in structure and properties of the films as in the reactive mode; however, at a significantly lower O_2 partial pressure. In general, the use of oxide targets in dc magnetron sputter deposition of MoO_x films offers an efficient and reliable alternative to films sputtered reactively from metal targets and might thus enable their use in a wide range of optical and electronic applications.

[1] J.M. Pachlhofer, C. Jachs, R. Franz, E. Franzke, H. Köstenbauer, J. Winkler, and C. Mitterer, Vacuum 131, (2016) 246.

[2] J.M. Pachlhofer, A. Tarazaga Martín-Luengo, R. Franz, E. Franzke, H. Köstenbauer, J. Winkler, A. Bonanni, and C. Mitterer, J. Vac. Sci. Technol. A 35, (2017) 021504.

[3] J.M. Pachlhofer, A. Tarazaga Martín-Luengo, R. Franz, E. Franzke, H. Köstenbauer, J. Winkler, A. Bonanni, and C. Mitterer, Surf. Coat. Technol, in press.

Notes:

WR1 The role of oxygen in sputtered AZO and ZnO films used for ZnO nanorod-based device

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ZnO nanorod-based devices such as piezoelectric nanogenerators, sensors and solar cells have been of increasing interest due to their potential applications in the field of flexible electronics. These devices usually contain Zinc oxide film as a seed layer for ZnO nanorods and indium thin oxide (ITO) film as transpared electrode. The main aim of the present work is a replacing of the preferably-used more expensive ITO in ZnO nanorod-based devices. The aluminium doped Zinc oxide (AZO) is an interesting candidate as a good transparency and a lowest resistivity in the range of $2-4\times10^{-4}$ Ωcm can be achieved. Nevertheless the resistivity of an AZO films strongly increases at low thickness and the optimal deposition temperature is about 300 °C. Thus the achieving suitable electrical properties of AZO films deposited on a flexible thermally sensitive substrates is still difficult.

In this study, all thin film depositions were performed by using BOC Edwards TF 600 deposition system equipped with two magnetrons linked to a radio-frequency (RF) and direct current (DC) power supply. The films were prepared by RF sputtering as well as co-sputtering from RF and DC magnetrons equipped by ceramic and metallic target, respectively. The substrate temperature was 100 °C, which is more attractive for some specific technologies such as flexible electronics. Electrical properties, namely sheet resistance, carrier concentration and mobility were determined by Hall measurement. The film structure and ZnO nanorods were investigated by the Scanning electron microscopy and X-Ray diffraction.

The relation between the observed film structure and the electrical properties was described by means of the one dimensional grain boundary model. The co-sputtering allowed gradual reduction of oxygen in the deposition process by increasing a DC power applied to metallic target. It was found that the lower amount of oxygen in the AZO film leads to the lower film resistivity due to activation of Al atoms, which act as donors [1]. The amount of oxygen also influences the resistivity of pure ZnO, which allows optimization of the seed layer for different types of ZnO nanorod-based devices.

[1] P. Novák, J. Briscoe, T. Kozák, M. Kormunda, M. Netrvalová, Š. Bachratá, Optimization of sputtered ZnO transparent conductive seed layer for flexible ZnO-nanorod-based devices, Thin Solid Films (2017).

Notes:

WR2 Control of process pressure and Ar/O_2 ratio in reactive-HiPIMS to deposit high-stability and high-mobility zinc oxynitride films for thin-film transistor devices

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In future displays, thin-film transistor (TFT) devices are required to switch on and switch off each pixel at unprecedentedly high rates owing to the enormously expanding prospect of display screens with ultra-high definition (4096 × 2160), large screen area (> 75 inches) and 3-D effects. Conventional amorphous Si:H-based TFTs suffer from low mobility. Amorphous oxide semiconductor materials such as In–Ga–Zn oxide-based TFTs, which has been tried as alternate exhibits less stability due to the Negative Bias Illumination (NBI) effects. TFTs based on amorphous-like ZnON films exhibit mobility > 100 $cm^2V^{-1}s^{-1}$ and excellent stability by its meager response to visible light illumination. Incorporation of nitrogen in depositing ZnON films and the migration of nitrogen atoms in the films after deposition are serious problems in the synthesis and utilization of ZnON films in TFTs, respectively. Here we demonstrated how the flow rate of reactive gases (O_2/N_2) in high power impulse magnetron sputtering (HiPIMS) can be used to achieve either crystalline or amorphous or the both phases. The nitrogen incorporation and electronic properties of ZnON films exhibit a strong dependence on the HiPIMS process conditions. At pressures > 3 mTorr, the formation of nanocrystalline structures provides robust compositional stability by reducing the reaction of oxygen with zinc. Films deposited at less O_2/Ar ratio and pressures ≤ 3 mTorr are all amorphous in nature and exhibit high electron mobility, negligible fast transient charging, little NBI and low noise characteristics. The chemical composition of the target surface and the energetic bombardment of negative oxygen ions on ZnON films have significant role in determining the crystallographic properties of the films. We showed that high mobility and high stability zinc oxynitride deposited by HiPIMS process can be applicable to a broad range of semiconductor and display devices.

Notes:

WR3 Deposition of Nb doped TiO_2 thin films using a hybrid CVD/HiPIMS technique

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Methods for the deposition of thin functional coatings, such as hybrid CVD/PVD technologies have the potential to become a means of overcoming the limitations of current processes, such as low deposition rates, or limited material/precursor choices, associated with CVD processes. Consequently, we have developed a hybrid system in which a single HiPIMS source is used to drive both the sputtering process and the CVD process for the production of doped-metal oxide coatings.

Unlike typical PVD/CVD hybrid systems, combining both processes in this way means that only one power supply is required. Thus, niobium-doped titania coatings were deposited on glass/Si substrates by this hybrid HiPIMS/CVD technique. The TiO_2 CVD coatings were deposited by the vapour drawn method. The HiPIMS process provided not only the source of Nb metal dopant in the film, but sustained the low temperature CVD process through a highly energetic plasma. As HiPIMS deposition rates are sensitive to magnetic field strength and the degree of unbalance, the film dopant content was adjusted via varying the magnetron magnetic field and not the applied target power.

The effect of processing parameters on generating a stable HiPIMS plasma across the process envelope has been studied in this work. The composition, microstructure/electrical properties of the deposited coatings have been investigated, in respect to variable process parameters, (e.g. substrate temperature and operating pressure) and through the use of energy resolved mass spectrometry.

Notes:

WR4 Nb_2O_{5-x} vs. Nb targets for DC reactive magnetron sputter PVD of thin optical films

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In this study an innovative process for depositing optically transparent niobiumoxide thin films by DC magnetron sputtering is investigated. Therefor substoichiometric Nb_2O_{5-x} target materials for several small values of *x*, powder metallurgically produced by hot isostatic pressing, are utilized. The films were deposited on various substrates, including quality glass and silicon waver, and the transparency and deposition rates have been correlated with different process parameters. I-V characteristics, Langmuir probe and optical emission spectroscopy were utilized to monitor the deposition processes. The results are compared with the conventional reactive sputtering practice of utilizing metallic sputter materials in combination with high values of partial oxygen gas pressure. As a part of this project, several methods for determining film thicknesses were explored and compared, i.a. SEM, AFM, IFM and UV-Vis-NIR Spectroscopy (Swanepoel Method). Crystallinity, index of refraction and transparency of the films were examined by XRD/HT-XRD, Prism Coupling (Refractometry) and UV-Vis-NIR Spectroscopy, respectively.

One could presume that additional oxygen is needed to fabricate stoichiometric layers with sub-stoichiometric targets. However, stoichiometric, highly transparent niobiumoxide thin films in the 0.1 to 2 µm thickness range were produced by DC magnetron sputtering utilizing sub-stoichiometric niobiumoxide targets of 71.6 mm in diameter at 250 W in an argon plasma at 0.6 Pa without any additional oxygen inlet gasflow. XRD and HT-XRD experiments on the films revealed that they are amorphous Nb_2O_5. Secondly, a negative trend of the transparency of the films with decreasing process pressure was found. No hysteresis effect was observed for various combinations of pressure, applied sputter power and additional oxygen gasflow. Higher deposition rates of transparent films were achieved as when a metallic niobium target in stable reactive mode was used. The findings are being interpreted as the physical mechanisms behind these phenomena are still to be understood; dependency of the sputter yield, angular sputter distribution and thermalization of sputtered particles in the process plasma on the process pressure, target surface composition and particle species, as well as technical conditions of the experimental setup, could play a major role.

Notes:

WI2 Improvement of deposition rate of high power impulse magnetron sputtering system using hybrid and superimposition approaches

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Among the physical vapor deposition techniques, the high power impulse magnetron sputtering (HiPIMS) technique has attracted lots of attention due to its extremely high peak power density for growing thin films with dense microstructure and excellent mechanical properties. However, the lower deposition rate of HiPIMS technique limits its application in industry. In this study, two methods using a hybrid HiPIMS and radio frequency (RF) power system, and a superimposed HiPIMS and mid-frequency (MF) power system were utilized to improve the deposition rate of pure HiPIMS. The TiCrSiN, TiN and CrTiBN hard coatings were grown by the hybrid HiPIMS-RF, and a superimposed HiPIMS-MF power system, respectively. For the hybrid HiPIMS-RF power system, the influence of RF power on the ion energy in the plasma, microstructure and mechanical properties of TiCrSiN coatings were discussed. For the superimposed HiPIMS-MF power system, the effects of duration ratios and the power ratios of MF/HiPIMS on the plasma characteristics, microstructure and mechanical properties of TiN and CrTiBN coatings were explored. We can conclude that the coating deposition rate increased greatly when the fabrication parameters of hybrid HiPIMS-RF and superimposed HiPIMS-MF power systems were properly adjusted. Meanwhile, the influences of target poisoning status on the structure and characteristics of the superimposed HiPIMS-MF grown TiN and CrTiBN coatings were also investigated.

Notes:

WR5 HPPMS deposition from composite targets: Effect of two orders of magnitude target power density changes on the composition of sputtered Cr–Al–C thin films

H. Rueß[1], M. to Baben[1,2], S. Mráz[1], L. Shang[1], P. Polcik[3], S. Kolozsvari[3], M. Hans[1], D. Primetzhofer[4], J.M. Schneider[1,4]

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Magnetron sputtering techniques are widely used to synthesize a large number of coatings either from elemental, compound or composite targets. Coatings synthesized by direct current magnetron sputtering (DCMS) from the latter two targets often exhibit a considerable compositional deviation from the target composition, in particular, for targets containing constituents with significant mass differences [1,2]. However, for high power pulse magnetron sputtering (HPPMS), where in contrast to DCMS, a large fraction of film forming species is ionized, the magnitude of compositional deviations has not been investigated.

Hence, the effect of target power density on the composition of sputtered thin films from a Cr–Al–C composite target, as Cr, Al and C exhibit significant mass differences, was studied by utilizing DCMS (2.3 W/cm²) and HPPMS (373 W/cm²) at various substrate bias potentials and temperatures. At floating potential, all Cr–Al–C thin films showed similar compositions, independently of the applied target power density. However, as substrate bias potential was increased to −400 V, aluminum deficiencies by a factor of up to 1.6 for DCMS and 4.1 for HPPMS were obtained. Based on the measured ion currents at the substrate, preferential re-sputtering of Al is suggested to cause the dramatic Al depletion. As the substrate temperature was increased to 560 °C, the Al concentration was reduced by a factor of up to 1.9 compared to the room temperature deposition. This additional reduction may be rationalized by thermally induced desorption being active in addition to re-sputtering.

[1] J. Neidhard, S. Mráz, J.M. Schneider, E. Strub, W. Bohne, B. Liedke, W. Möller, C. Mitterer, J. Appl. Phys. 104 (2008) 063304.

[2] S. Mráz, J. Emmerlich, F. Weyand, J. M. Schneider, J. Phys. D: Appl. Phys. 46 (2013) 135501.

Notes:

WR6 Study on giant negative piezoresistance effect in diamond like carbon films deposited by reactive magnetron sputtering of Ni target

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In present study hydrogenated diamond like carbon (DLC) and diamond like carbon based nickel nanocomposite (DLC:Ni) films were deposited by reactive magnetron sputtering of nickel (Ni) target. High power pulsed magnetron sputtering and direct current reactive magnetron sputtering was used for growth of the samples. Effects of the deposition condictions, chemical composition and structure on piezoresistive properties of DLC:Ni and DLC films were considered. In the case of DLC:Ni samples containing larger amounts of Ni, positive piezoresistive effect with the gauge factors in 1 – 4 range was observed. While for some samples containing few at.% Ni and samples containing no Ni, significant decrease of the resistance with the applied strain was found. In that case piezoresistive gauge factor values larger than −3000 were registered. Some correlation between the gauge factor values as well as sign of the piezoresistive effect and structure of the diamond like carbon matrix was found, too. Giant negative piezoresistive effect was explained by combination of two mechanisms. It is supposed that formation of the conglomerations of the sp^2 bonded carbon nanoclusters and/or areas with the decreased hydrogen content takes place. It is assumed that the applied tensile stress induces rearrangements of these conglomerations resulting in formation of the increased conductivity paths. At the same time, conductivity between the separate sp^2 bonded carbon nanoclusters is related to hopping and/or tunnelling of electrons.

Notes:

WR7 Inside gas aggregation cluster source: In-operando study of Ti/TiO_x nanoparticles production

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Gas aggregation clusters sources based on magnetron sputtering can produce a broad variety of nanoparticles – metals, oxides, plasma polymers or structured nanoparticles (e.g. core-shell). There is a broad range of literature on the characterization of the produced nanoparticles. However, there is still a considerable lack of experimental in-operando studies on the conditions inside the source during the formation of nanoparticles.

Recently, we focused on characterization of the composition of the gas and the plasma parameters during the production of the TiO_x nanoparticles [1]. We studied the role of oxygen admixture in the aggregation process and the influence of the presence of the particles on the plasma. The construction of the source allowed us to make a 2D map of the plasma parameters within the source.

The process of formation of Ti/TiO_x nanoparticles takes place in the reactive sputtering regime with slightly oxidized magnetron target with typically about 2% O_2 admixture in the working gas. We have monitored the correlation between the production of the nanoparticles, magnetron target oxidation and concentration of free O_2 in the system.

The presence of nanoparticles is expected to cause a drop in the plasma density. By mapping the plasma parameters using Langmuir probes, we have found that the presence of nanoparticles in the plasma causes more than one order of magnitude decrease of electron density and significant increase of the electron temperature. The strongest changes appear near the chamber axis, providing an indirect insight into the transport of nanoparticles inside the source.

Together, this information is expected to be useful for significant improvement in the models of the formation of nanoparticles in GAS that should take plasma-nanoparticle interactions into account.

Acknowledgements:

This work was supported by the grant GACR 13-09853S from the Czech Science Foundation and by the Charles University Grant Agency, grant No. 268115.

[1] J. Kousal, A. Kolpaková, A. Shelemin, P. Kudrna, M. Tichý, O. Kylián, J. Hanuš, A. Choukourov, H. Biederman, Plasma Sources Sci. Technol. 26 (2017) 105003.

Notes:

WR8 Plasma metal and metal oxides nanoparticles coatings for new functional properties

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Namur University (LARN-PMR), Namur, Belgium

Nanoparticles are now the object of the intense study due to their perspective properties and numerous possible applications. Some of these applications are facing with several limitations based on excessive reactivity or conversely low affinity of nanoparticles to some matrixes. Coating of nanoparticles can solve these problems creating protective layer or changing the chemical composition of their surface, which can improve nanoparticles incorporation and distribution in different matrixes.

Nanoparticles with different nature (Al, Al_2O_3, MgO, TiO_2 etc.) and morphology were coated via low pressure plasma polymerisation process of cyclopropylamine. Comparative study of coating deposition using three different plasma excitation setups (pulsed hollow cathode, inductive RF plasma and capacitive RF) was performed to reveal the technique which allows to create the most homogeneous and effective coating of nanoparticles. The composition and the morphology of the capping coating were characterized with using of complex of physical methods (XPS, TEM, TA).

Notes:

WI3 Industrial challenges and applications of reactively sputtered hard coatings

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HVM Plasma spol. s r.o., Praha, Czech Republic

Reactive magnetron sputtering is a well-established technique to deposit compound films. This overview deals with industrial challenges and applications of reactively sputtered hard coatings. The presentation concentrates on traditional applications of reactive sputtering for hard, tribological and decorative coatings but also on emerging applications such as galvanic Cr replacement, sensor and fuel cell applications.

Topics related to productivity of the deposition processes are covered, such as target power and related cooling design problems and challenges of target doping. The approaches to elimination of hysteresis effects and to process control are reviewed, especially those related to high-rate deposition in the transition mode close to the metallic one.

For such applications, enhanced ionization of both gas species and sputtered metal is important. Development of unbalanced magnetrons and closed-field arrangement has been followed by pulsed techniques (asymmetric bipolar pulsing, dual magnetron sputtering, reactive HiPIMS). Recently, an interesting hybrid technique of the mixed-mode HiPIMS with controlled transition to arc evaporation has been reported [1].

In case of dielectric coatings, the dual magnetron reactive sputtering has another advantage in eliminating the disappearing anode effect [2] and long-term reactive system development including the "double-S curve". Other problems of power balance between the pair of magnetrons, as well as the disappearing hysteresis in transition to reactive HiPIMS have been studied in the reactive dual magnetron sputtering [3,4]. An analytical model explains the disappearing effect based on the return of ionized sputtered metal during the HiPIMS pulses.

The quality of the coatings deposited by reactive magnetron sputtering in terms of growth defects is an important issue. Tribological films should be free of particles and large fast-growing grains. The dielectric coatings should be void-free. Examples of defects in films and their origin are presented in multilayers containing Cr and W-C:H layers[5].

[1] M.D.Tucker et al, J. Phys. D: Appl. Phys. 50 (2017) 145205.

[2] P. Mareš: „Long-term stability and disappearing anode effects during reactive DC and pulsed bipolar magnetron sputtering of Al_2O_3" (this conference).

[3] "Return of Target Material Ions Leads to a Reduced Hysteresis in Reactive High Power Impulse Magnetron Sputtering: Experiment" J. Appl. Phys. 121, 171911 (2017).

[4] "Return of Target Material Ions Leads to a Reduced Hysteresis in Reactive High Power Impulse Magnetron Sputtering: Model" J. Appl. Phys. 121, 171910 (2017).

[5] T. Mates: "Nanostructure of DLC layers for tribological applications" (Conference: 8th International Workshop on Polymer Metal Nanocomposite).

Notes:

WR9 HiPIMS makes reactive sputtering the future technology for premium cutting tools

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The change to e-mobility brings disruptive changes to car production. Today's power train manufacturing is heavily dominated by the machining of components for the combustion engine and the gear box. It's good news for the cutting tool industry that other areas such as the production of medical implants, aircraft industry and the 3C industry making cell phones, tables and other consumer gadgets are growing rapidly.

Common to these booming sectors is the need for an excellent surface quality of the workpiece after machining. Moreover these industries are mainly using stainless steel, non-ferrous alloys and they are the front runners of new materials such as titanium, Inconel® and heat resistant superalloys.

This paper will present how the benefits of reactive sputtering – smooth coatings, no droplets and a free choice in designing the film since almost any material can be sputtered – together with the ionization of the HiPIMS process turn into new industrial applications. Cases studies will include the correlation of indentation and machining data for Si-doped coating for stainless machining and for hard materials. The dense morphology of HiPIMS makes TiB_2 coatings a viable option for titanium alloys like TiAl6V which is very common in the aircraft industry. Micro indentation reveals hardness data above 40 GPa for a coating thickness up to 5 µm.

HiPIMS is a success story of transferring a new method within reactive sputtering into industry and thereby opening future business opportunities.

Notes:

WR10 Reactive sputter deposition of Al_2O_3 layers on large area substrates

D. Gloess[1], T. Goschurny[1], H. Nizard[1,2], A. Drescher[1], M. Gittner[1], H. Bartzsch[1], P. Frach[1]

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[2]Technische Universität Dresden, Institut für Festkörperelektronik (IFE), Dresden, Germany

In this paper, the breakdown field strength and resistivity of Al_2O_3 layers deposited in two different sputter coating machines using different variants of process control will be presented. Deposition runs were performed in a cluster sputter equipment for stationary coating of 8" substrates and in an inline sputter equipment with rectangular magnetrons (800 mm target size) for dynamic coating of substrates up to 650 × 750 mm².

Experiments in the inline coater using single-channel impedance control led to insufficient uniformity regarding layer stoichiometry and thickness distribution. This problem could be solved by combining the impedance control with a two channel optical plasma emission control. The interlaced control loops ensured deposition of stoichiometric Al_2O_3 over the coating area with a homogeneity better than ±3% on 500 mm. The achieved deposition rates were 2.5 nm/sec for stationary coating and 38 nm·m/min for dynamic coating with a single magnetron in the unipolar pulse mode, respectively. Insulation properties were measured on films with a thickness of 1µm on Si wafers. For Al_2O_3 films, a breakdown field strength of 5 to 6 MV/cm and a specific resistivity of 10^{16} to 10^{17} Ωcm was measured at room temperature.

Notes:

WR11 Plasma enhanced reactive sputter deposition processes in application

E. Schüngel, J. Weichart, S. Gees, S. Schwyn-Thöny

Evatec AG, Trübbach, Switzerland

The Evatec AG has developed a variety of evaporation, sputter and PECVD equipment and processes for the deposition of thin films and is a pioneer in industrial pulsed plasma and HIPIMS applications. Depending on the specific type of application, processes are custom tailored to ensure that the product meets the requirements in composition, optical properties, surface structure and stress. Especially reactively sputtered films in optical applications require extremely high quality, uniformity and reproducibility. One of the preferred solutions to control and optimize these processes is an additional plasma treatment of the growing film. In particular, the fundamental properties of thin films deposited in reactive sputter deposition processes are strongly altered when using an additional plasma treatment. Here, the effect of a superimposed capacitively coupled radio frequency plasma on both the deposition process and the thin film is investigated. Specifically, the sputter plasma and the plasma source are active at the same time in the same vacuum environment, allowing for an effective interaction. The substrates are placed on a rotating turn table and, hence, repeatedly exposed to both the sputter source and the plasma source. Depending on the conditions, the additional treatment by the plasma source may affect the deposition process physically by generating energetic ions, which bombard the surface, and chemically by generating reactive species such as atomic oxygen. A significant interaction between the DC pulsed sputter plasma, where the reactive gas flow is actively controlled to optimize the overall sputter conditions and the process rate, and the auxiliary RF plasma is observed. These effects are examined by various diagnostic approaches, such as voltage and ion energy measurements as well as optical emission spectroscopy. Moreover, the benefits in the surface roughness of the thin films grown in these processes with an additional plasma treatment and the according physical and chemical mechanisms are highlighted.

Notes:

WI4 Reactive HIPIMS and process control on industrial scale coating systems

H. Gerdes, J. Rieke, R. Bandorf, M. Vergöhl, G. Bräuer

Fraunhofer IST, Braunschweig, Germany

Reactive sputtering is a well-established technology for industrial sputtering. The process stabilization is carried out by varying the average power or the reactive gas flow. As input parameters the partial pressure of the reactive gas, the target voltage or the plasma emission is commonly used.

For reactive HIPIMS challenges regarding process control arise. For instance, the change of discharge voltage is strongly depending on the capacity of the used HIPIMS power supply. Even the plasma emission is lower in HIPIMS discharges (time-averaged) since the duty cycle is normally in the lower percentage range.

This talk will give an overview of different approaches for a reactive process control in combination with HIPIMS. The discussed feedback systems are based on plasma emission monitors either with optical filters for single emission lines or with a spectrometer. The controllers are regulating the oxygen flow by piezo-valves or mass flow controllers or by changing the off-time and therefore the average power. Furthermore, a possibility for controlling the ion to neutral ratio will be presented.

The different approaches will be presented for Alumina, Zirconia, and Titania on different sputtering plants equipped with planar magnetrons or even rotatables. The results include the voltage and current characteristics as well as the deposition rates and selected film properties.

Notes:

WR12 Nanocomposite nc-TiC/a-C:H coatings: Enhancement of coating properties by utilization of HiPIMS and Ni doping

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Nanocomposite coatings consisting of nanocrystallites embedded in an amorphous matrix (nc-TiC/a-C:H) can be tailored to exhibit unusual combination of properties such as high hardness and modulus combined with low friction and wear. These coatings are usually deposited utilizing direct current magnetron sputtering (DCMS) leading to low ionization of the sputtered titanium. High Power Impulse Magnetron Sputtering (HiPIMS) depositions generally leads to much higher ionization of the sputtered titanium which can alter the deposition process and in turn the properties of the deposited nc-TiC/a-C:H coatings [1].

It will be shown that using HiPIMS it was possible to make arc-free deposition of coatings with much higher carbon content (> 90 at.%) which was impossible for DCMS. When DCMS was employed black carbon layers were created on the target including the racetrack, whereas HiPIMS employment lead to a much cleaner target. This was due to significant ionization of sputtered titanium and its back attraction to the target in HiPIMS. This proved to be highly advantageous for deposition of coatings with high carbon content with regards to arc occurrence and moreover the deposition rate of carbon rich coatings was higher for HIPIMS compared to DCMS. Lower fraction of the a-C matrix phase was found to be created in HiPIMS deposited nanocomposite coatings with < 55 at.% of carbon as compared to DCMS deposited coatings. HiPIMS deposited coatings also exhibited better stoichiometry of the TiC grains. This shows that HiPIMS ensured carbon incorporation into TiC grains rather than forming of a-C matrix. Lower amount of a-C matrix corresponded with smaller mean grain separation distance of the TiC grains by the a-C matrix. This enhanced the nanocomposite grain boundary strengthening leading to overall higher hardness of HiPIMS deposited coatings compared to those deposited by DCMS. HiPIMS deposited coatings also exhibited lower lattice parameter. The crucial parameters for obtaining hardest coatings were found out to be the TiC grain stoichiometry and small mean grain separation by the a-C matrix corresponding to only a few monolayers of the matrix between the grains. HiPIMS utilization favored this structure enhancement making it a promising method of enhancement of mechanical properties of nc-TiC/a-C:H coatings.

Another way of improving nc-TiC/a-C:H coatings is to enhance their tribological properties. It has been proposed that doping of nc-TiC/a-C:H with weak carbide forming elements can lead to growth of a metastable phase with the weak carbide forming element being incorporated into the TiC crystallite [2]. Such a metastable grain would favor releasing of carbon if external energy is added e.g. via mechanical or thermal stresses. Therefore, a smart self-lubricating coating might be synthesized in this way. Nickel as the doping element was chosen for this study. It was found out that Ni doping led to Ni incorporation into the grains. The grain size as well as the mean grain separation was smaller, the surface features were refined [3]. Thus, doping by Ni was shown to alter the structure of nc-TiC/a-C:H coatings promising enhanced tribological performance.

Acknowledgements

This research has been supported by project LO1411 (NPU I) funded by Ministry of Education, Youth and Sports of Czech Republic.

[1] P. Souček, J. Daniel, J. Hnilica, K. Bernátová, L. Zábranský, V. Buršíková, M. Stupavská and P. Vašina, Surf. Coat. Technol. 311, (2017) 257.

[2] U. Jansson and E. Lewin, Thin Solid Films 536, (2013) 583.

[3] J. Daniel, P. Souček, K. Bernátová, L. Zábranský, M. Stupavská, V. Buršíková and P. Vašina, J. Nanomater. (2017) 6368927.

Notes:

WR13 Multilayered TiVN/TiSiN hard coatings – Mechanical properties and tribological performance

Y.-J. Weng, Y.-Y. Chang

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Ternary transition metal nitride hard coatings, such as TiSiN and TiVN, have been attracting great interest for industrial applications as protective coating materials because of their high hardness, and wear resistance. With respect to the potential nitride materials, innovative multilayered coatings with outstanding properties, as TiVN/TiSiN are synthesized. In this study, TiVN, TiSiN and multilayered TiVN/TiSiN coatings are deposited onto high-speed steels and tungsten carbide tools using cathodic-arc evaporation (CAE). To enhance adhesion strength between the coatings and substrates, TiN was deposited as an interlayer during the coating process of TiVN/TiSiN. The multilayered TiVN/TiSiN possessed different microstructures and mechanical properties by controlling the different negative bias voltages (30 ~ 180 V). By optimizing the bias condition of the deposition, the deposited TiVN/TiSiN coatings are anticipated to improve both the hardness and tribological performance. The field emission scanning electron microscope (FE-SEM) and the field emission gun high resolution transmission electron microscope (FEG-HRTEM) equipping with an energy-dispersive X-ray analysis spectrometer (EDS) are used to investigate the microstructure of the deposited coatings. Glancing angle X-ray diffraction is used to characterize the microstructure and phase identification of the films.

The adhesion strength of the coatings was evaluated by the Rockwell indentation and scratch adhesion tests. The hardness and elastic modulus of mechanical properties are measured. The fracture toughness (Kc) of the hard coatings, which is an important parameter in the reliability assessment of ceramic coatings, is determined by Vickers indentation to evaluate the resistance to crack growth. A ball-on-disc wear test is conducted to evaluate the tribological properties of the deposited coatings. Under high speed cutting environment, the wear behavior and cutting performance of carbide cutting tools are investigated by end milling of high strength aluminum alloys. The design of multilayered TiVN/TiSiN coatings is expected to possess the self-lubrication and wear resistance, and make the coating suitable for high speed cutting applications.

Notes:

Tuesday 15:00 – 16:00, 5th December

PO01 *p. 122*

Biological characteristics of tantalum oxide and zinc oxide coatings on titanium pretreated by plasma electrolytic oxidation

R.-A. Pan[1], Y.-Y. Chang[1], H.-L. Huang[2,3], M.-T. Tsai[4], J.-T. Hsu[2,3]

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PO02 *p. 124*

Dynamic impact resistance of nc-TiC/a-C:H coatings prepared by DCMS and HiPIMS

J. Daniel[1], J. Grossman[1], T. Fořt[1], P. Souček[2], K. Bernátová[2], L. Zábranský[2], V. Buršíková[2], P. Vašina[2], J. Sobota[1]

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PO03 *p. 126*

Niobium-doped DLC layers prepared by reactive HIPIMS

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PO04 *p. 128*

Advancements in the thickness prediction by numerical simulation in PVD on high shadowed complex 3D substrates in motion

M. Evrard, S. Lucas

Namur University (LARN-PMR), Namur, Belgium

PO05 *p. 130*

Impact of sputtered species ionization on hysteresis curve shape – Model and experiment

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PO06 *p. 132*

Duty cycle assisted modulation of morphology and composition of Vanadium oxide films grown by reactive HiPIMS for thermochromic applications

R. Ganesan[1,2], B. Akhavan[1], X. Dong[1], D.R. McKenzie[1], M.M.M. Bilek[1], M. Trant[2], K. Thorwarth[2], H.J. Hug[2]

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[2]EMPA Materials Science and Technology, Dübendorf, Switzerland

PO07 *p. 134*

Compact X-ray sources for non- destructive methods

A. Mozelev

Small Scale Research and Production Company RADICAL, Feldkirch, Austria

PO08 *p. 136*

Evolution of sputtered species densities in HiPIMS process with acetylene gas

K. Bernátová[1], M. Fekete[1], P. Klein[1,2], J. Hnilica[1,2], P. Vašina[1,2]

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PO09 *p. 138*

Optical and electrical properties of magnetron deposited $SnZnO_x$ coatings annealed at various temperatures

M. Kormunda[1], A. Hertwig[2], P. Ryšánek[1], S. Novák[1], L. Ivanov[3]

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PO10 *p. 140*

Magnetron sputtered Hf–B–Si–C–N films with controlled electrical conductivity and optical transparency, and with ultrahigh oxidation resistance

V. Šímová, J. Vlček, Š. Zuzjaková, R. Čerstvý, J. Houška

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PO11 *p. 142*

Targets fabrication for high-pressure planetology studies using reactive sputter deposition

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PO12 *p. 144*

Core-shell nanoparticles arising from plasma polymerization

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PO13 *p. 146*

Microstructure and mechanical properties of nanostructured W–B–C coatings prepared by magnetron sputtering

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Report on spoke rotation, merging and splitting in HiPIMS plasma

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Tribological properties of W–B–C protective coatings prepared by pulsed DC magnetron sputtering

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ABSTRACTS

POSTER PRESENTATIONS

PO01 Biological characteristics of tantalum oxide and zinc oxide coatings on titanium pretreated by plasma electrolytic oxidation

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It has been a challenge for many years that the surface modification of biomaterials with better antibacterial feature and biocompatibility. Plasma electrolytic oxidation (PEO) is a rising technology to improve the biocompatibility by producing porous surface for cell adhesion. In previous studies, thin films of tantalum oxide (Ta_2O_5) and zinc oxide (ZnO) have been found to show both biocompatibility in vitro and the antibacterial ability. In this study, a pre-treatment of surface modification on titanium (Ti) substrates has been made by PEO using a high power pulsed power supply. A porous oxide surface on Ti for cell adhesion is prepared. By using twin-gun high power impulse and RF magnetron sputtering, Ta_2O_5 and ZnO films are then deposited onto the porous surface of Ti substrates. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) are used to identify the surface morphology, crystal structure, and bonding state of the films. Staphylococcus aureus (S. A., Gram-positive bacteria) and Actinobacillus actinomycetemcomitans (A. A., Gram-negative bacteria) were tested to evaluate the antibacterial ability. S. A. and A. A. were tested by a fluorescence staining method (Syto9) and bacterial viability agar tests , and both of these two types of bacteria were the main origins of infection mostly occurred in clinical orthopedic/oral implants. The in vitro cytotoxicity was tested followed by the standard of ISO 10995-5:2009. Using the MTT assay, Cell viability and proliferation of human skin fibroblast cells and human osteosarcoma cell line (MG-63) cultured on these films were also studied. The result shows that an appropriate PEO pre-treated Ti with Ta_2O_5 and ZnO surface coatings improve both the antibacterial ability and biocompatibility in vitro.

Notes:

PO02 Dynamic impact resistance of nc-TiC/a-C:H coatings prepared by DCMS and HiPIMS

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Nanocomposite nc-TiC/a-C:H thin films consisting of titanium carbide crystallites embedded in hydrogenated amorphous carbon matrix exhibit unique combination of mechanical properties such as a high hardness and low friction [1]. The aim of the present work was to study dynamical wear resistance of the nc-TiC/a-C:H coatings deposited on a tungsten carbide (WC) substrates.

The nc-TiC/a-C:H coatings were deposited by hybrid PVD-PECVD process of sputtering titanium target in argon/acetylene atmosphere. Two series of coatings with different content of carbon were prepared utilizing both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS). Chemical composition, phase composition and microstructure of the nc-TiC/a-C:H coatings were determined using XRD, XPS and EDX analyses [2]. Nanoindentation test was used to determination of the nc-TiC/a-C:H coatings hardness and elastic modulus [2]. To evaluate impact resistance of the coatings in dynamic loading wear applications, an impact test was used. During testing, the coatings were cyclically loaded by a WC ball that impacts against the coating/substrate surface [3].

Shapes and dimensions of the impact imprints were measured and the mean volume of imprints was calculated. Dependencies of the imprints volume on the number of impacts were discussed in relation to the coatings composition and microstructure. The nc-TiC/a-C:H coatings under dynamic impact load exhibited strong influence on mechanical properties such as hardness and H^3/E^2 ratio. Differences in the impact wear resistance of the DCMS prepared and the HiPIMS prepared coatings are discussed with respect to the coatings microstructure and composition.

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[1] P. Souček, T. Schmidtová, L. Zábranský, et al.: On the control of deposition process for enhanced mechanical properties of nc-TiC/a-C:H coatings with DC magnetron sputtering at low or high ion flux, Surf. Coat. Technol. 255, pp. 8–14, 2014.

[2] P. Souček, J. Daniel, J. Hnilica, et al.: Superhard nanocomposite nc-TiC/a-C:H coatings: the effect of HiPIMS on coating microstructure and mechanical properties, Surf. Coat. Technol. 311, pp. 257–267, 2017.

[3] J. Sobota, J. Grossman, V. Buršíková, et al.: Evaluation of hardness, tribological behaviour and impact load of carbon-based hard composite coatings exposed to the influence of humidity, Diamond & Related Materials 20, pp. 596–599, 2011.

Notes:

PO03 Niobium-doped DLC layers prepared by reactive HIPIMS

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DLC (diamond-like-carbon) is widely used in technical applications for its wear resistance but also for its sensory properties. Depending on the process parameters, the properties of DLC can be varied in a wide range, from graphitic phases to more diamond-like phases. The method of deposition has a major impact on the properties of the resulting DLC layers. Furthermore, the addition of a certain metal ratio leads to significant changes in the morphology, as well as in electrical and mechanical properties. For example doping with metals like nickel is known to increase the electrical conductivity, decrease the thermal coefficient of electrical resistance (TCR), and enhance the strain sensitivity, i.e. the gauge factor of DLC layers.

In most cases DLC layers are prepared by a PECVD process in DC mode. In this work, the films were prepared in a reactive HIPIMS process using acetylene as hydrocarbon-precursor. A niobium target was used to add a certain metal ratio to the material. The influence of the preparation condition (sputtering mode, working pressure, gas compositon) on morphology (SEM), metal content, as well as on the electrical behavior is presented.

Notes:

PO04 Advancements in the thickness prediction by numerical simulation in PVD on high shadowed complex 3D substrates in motion

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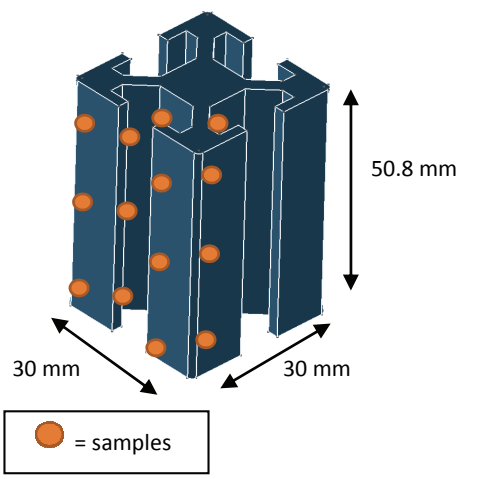
Today, plasma thin film (< 10 µm) deposition technology is used in lots of fields, in order to provide added value to substrates. Nevertheless, the deposition of films with uniform thickness on 3D complex shapes is still a challenge for various deposition systems. In the case of magnetron sputtering, concavities and different substrate orientations lead to macroscopic shadowing and affect the thickness uniformity. To predict these effects and adopt the best deposition geometry, algorithms are developed to simulate metal deposition on rotating complex 3D substrates within any coater geometries whatever the sputtered species. The obvious aim is to determine the optimal process deposition and sample rotation parameters to get the best film thickness uniformity. The modeling of complex shapes is performed by meshing objects with Delaunay-triangulation [1]. The deposition process is simulated in two steps: the angular and energy particles distributions are calculated at the cathodes surfaces by a simulation of sputtered metallic atoms by the gas atoms [2], the transport through the chamber and the deposition process is then performed by a Monte-Carlo code. To accelerate the deposition process, the algorithm is combined with a "cell-list-linked-like" method [3].

In this contribution, we will show the last developments and the benchmarking between simulation and experimental results for Cr deposition at various pressure and on rotating substrates as complex as the one described in the figure on the right.



[1] C. Geuzaine and J.-F. Remacle, "Gmsh: a three-dimensional finite element mesh generator with built-in pre- and post-processing facilities," International Journal for Numerical Methods in Engineering, pp. 1309-1331, 18 09 2009.

[2] J.F. Ziegles, J.P. Biersack and M.D. Ziegler, SRIM, The Stopping and Range of Ions in Matter, Annapolis, 2010.

[3] W. Mattson, B.M. Rice, "Near-neighbor calculations using a modified cell-linked list method", Computer Physics Communications, pp. 135-148, 119 1999.

Notes:

PO05 Impact of sputtered species ionization on hysteresis curve shape – Model and experiment

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During the last decade the HiPIMS has shown great promise in the field of reactive thin film deposition. In the reactive HiPIMS (R-HiPIMS) the discharge power is delimited within short energetic pulses, which in addition to an enhanced ionization of the sputtered species, also leads to enhanced dissociation of the reactive gas molecules. It results n the increase of gas reactivity with the surface, which is ultimately beneficial for the thin film formation [1]. Additionally, similar to the reactive dc or pulsed-dc sputtering, the R-HiPIMS system undergoes hysteresis behaviour, however the hysteresis curve shape significantly differs. Optimizing the R-HiPIMS process parameters, the hysteresis can be minimised or even suppressed. The exact mechanism behind the hysteresis suppression is still unknown and therefore this issue is yet highly disputed in the scientific community. Authors of [2] argue that the sputtering rate during pulses is greater than in dcMS, and the formation of a compound layer between HiPIMS pulses is reduced due to gas rarefaction, which also includes rarefaction of the reactive gas. Authors of [3] claim that return of the target material ions leads to the reduced hysteresis behaviour in R-HiPIMS.

To predict the general shape of processing curves for a wide variety of reactive sputtering processes operating in continuous wave regimes S. Berg developed his very famous and well accepted model [4]. In this model, the sputtered species flux is directed exclusively toward the substrate, however in R-HiPIMS, the sputtered species can be ionized and back-attracted to the target. The flux of the titanium particles returning back to the target surface modifies the state of the sputtering target (making it more metallic) and also reduces the flux of the sputtered species to the substrate. We have modified the original Berg model to allow a part of the sputtered species flux to return back towards the target surface. Absolute ground state number densities of Ti atoms and Ti ions measured at the target vicinity by the spectroscopic technique based on effective branching fractions [5,6] were included in the model as a part of the input data set and a quite good match between the measured and the calculated hysteresis curve was obtained for different experimental conditions. It proves that the return of the target material ions back to the target surface is very important phenomenon strongly influencing the hysteresis curve shape in R-HiPIMS.

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[1] S. Konstantinidis et al., J. Phys. D. Appl. Phys. 46, (2013) 205205.
[2] E. Wallin et al., Thin Solid Films 516, (2008) 6398.
[3] J. Čapek et al., J. Appl. Phys. 121, (2017) 171911.
[4] S. Berg et al., Thin Solid Films 476 (2005) 215.
[5] P. Vašina et al., Plasma Source Sci. Technol. 24(6), (2015) 065022.
[6] M. Fekete et al., J. Phys. D. Appl. Phys. 50, (2017) 365202.

Notes:

PO06 Duty cycle assisted modulation of morphology and composition of Vanadium oxide films grown by reactive HiPIMS for thermochromic applications

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The enhanced ionization of the sputtered target metals in the discharge plasma is one of the key advantages of High Power Impulse Magnetron Sputtering (HIPIMS) process, which allows modulating the morphology and composition of depositing films by the controlled energetic bombardment of target metal ions. The operation of HIPIMS with reactive gases O_2/N_2 leads to deposit films of various metal oxides and nitrides for the wide range of optical and electronic coatings with better quality than that of the coatings by direct current magnetron sputtering processes. In the past decades, vanadium oxides (VO_x) have attracted considerable attention, owing to their applications in batteries, super capacitors, switches, detectors and particularly in smart windows. The mixed oxidation states of vanadium with its oxygen and their different optical responses to the temperature make vanadium oxide as one of the most efficient thermochromic material. In this work, we demonstrated that by tuning the pulse characteristics in HiPIMS, dense stoichiometric VO_2 films can be deposited at the substrate temperatures < 270 °C. The deposited films exhibit maximum RMS surface roughness of 6 nm for the film thickness of 185 nm. Also, at the wavelength of 2.5 μm, the optimized films show an infrared modulation of about 42% at transition temperature of 57 °C. Apart from demonstrating the HiPIMS duty cycle dependent inherent characteristics of depositing vanadium oxide films, this work also optimize the parameters to synthesis desirable quality of vanadium oxide films for thermochromic applications.

Notes:

PO07 Compact X-ray sources for non- destructive methods

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The essential part of this set up is the source of artificial gamma radiation. A principal advantage of that kind of source for gamma logging is the possibility of remote handling excluding the danger in case of an accident. The souse consequences was designed for the most difficult application case – a deep borehole with a high temperatures and high pressure. Several variants of vacuum tubes were researched, the results are introduced. The up-to-date methods of researching radiations effects are usually based on the spectrometry of scattering irradiations exited by different radioisotopes sources. Now days, the ecological purity requirement for the geophysical devices with radioisotopes sources stimulates researches of other kinds of sources. In this connection, the sources of X-ray radiation represent an attractive alternative. Electron and ions acquire a high energy and produce X-rays with a relatively high efficiency by interaction with different materials. In this work, a principally new source using a radiation generator is proposed [1].

Preferable, the linear pulse electron accelerator comprises a capacitive energy storage connected to a high voltage charge unit, the output of the energy storage being connected to the primary coil of a Tesla transformer the secondary of which is connected to a cathode [2].The linear pulls electron accelerator preferably comprises a Tesla transformer for generating the high voltage pulses necessary for producing the gamma radiation. The primary coil of the Tesla transformer is connected to a capacitive energy storage and a discharger. The capacitive energy storages preferably connected to a high voltage charging unit. The high voltage output to the Tesla transformer is connected to an anode opposite which aheatable cathode is arranged along the longitudinal axis of the probe. The high voltage charging unit serves to charge the capacitive energy storage to a predetermined state before it is discharged to produce a high dI/dt in the primary coil of the Tesla transformer. The high voltage pulse thus generated by the Tesla transformer and applied between anode and cathode extracts electrons from the cathode and accelerates them to anode where they impact and by their deceleration generate a pulse of gamma radiation. Therefore, it is obvious the need of the minimum value C, which is equal to electronic gun capacitance in our case.

Several variants of vacuum tubes were researched, the results are cited. If we have diameter of vacuum tube $D = 90$ mm, the kinetic energy of electron $E = 1$ MeV; $D = 70$ mm, $E = 700$ keV; $D = 60$ mm, $E = 500$ keV; $D = 45$ mm, $E = 150$ keV. In the course of investigation a model generator was created. Carrying out researches with this model has also shown the expediency of subsequent investigations to confirm theoretical computations. As a result of the researches the following parameters have been received Diameter less than dot fill 70 mm Length less than dot fill 300 mm Weight less than dot fill 2 kg Electron source specification: Kinetic energy dot fill 500 keV Pulse duration dot fill 10 ns Impulse frequency dot fill 0.5 – 50 Hz.

[1] Mozelev A. High Voltage Discharge and Vacuum Insulation at the Minimising Volume, Int. Symp. Electrical Discharge and Vacuum Insulation. (ISDEIV1996) Berkeley, California, 1996.

[2] Mozelev A. et al. Probe for Radio logically Determine the Density of Rock In a Drilled Well, United States Paten Number 5,736,636. Date of Patent: Apr. 7, 1998.

Notes:

PO08 Evolution of sputtered species densities in HiPIMS process with acetylene gas

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High Power Impulse Magnetron Sputtering (HiPIMS) is a promising magnetron sputtering technique used for the deposition of thin films. The power in the HiPIMS is focused into the short energetic pulses which creates high flux of ionized sputtered particles towards the substrate [1]. Introducing a reactive gas in the HiPIMS process offers a possibility to grow compounds under highly non-equilibrium conditions. Similar to DC magnetron sputtering, the discharge properties including fluxes of the thin film forming species are strongly non-linearly dependent on the reactive gas supply. While using hydrocarbon as a reactive gas, it is possible to grow a nanocomposite protective coatings containing carbide grains embedded in carbon matrix or DLC coatings doped by a metal [2].

In this paper, we report the effect of increasing the mass flow rate of the acetylene ($Q_{\mathrm{acetylene}}$) gas on the sputtered Ti atom and ion ground state number densities using the spectroscopic method based on effective branching fractions [3]. Two main optical emission spectroscopy approaches are utilized. Firstly, time-resolved spectrometry of HiPIMS pulse (repetition rate of $f = 100$ Hz and pulse length of $\tau = 200$ μs) is conducted for $Q_{\mathrm{acetylene}}$ in range from 0 sccm to 6 sccm. We distinguish two main zones depending on the acetylene flow, where the Ti atom and Ti ion concentration differ while the temporal trends are similar. First zone at low acetylene flow, similar to a metallic regime of R-HiPIMS, is dominated by the rarefaction of buffer gas. Plasma contains primarily the sputtered species of titanium. The concentration of sputtered Ti atoms decreases in the second half of pulse length, while the concentration of sputtered Ti ions is increasing during the whole pulse. After increase of $Q_{\mathrm{acetylene}}$, dissociated hydrogen presumably remains in discharge and carbon-rich layer gradually covers the target surface. Second zone then represents the situation similar to the poisoned mode of reactive sputtering. The target surface is almost fully covered by the carbon-rich layer; thus, the overall concentration of sputtered titanium is significantly lower than that of the first zone and the argon gas rarefaction is less pronounced.

Consequently, the study of the optical emission spectroscopy time averaged over the whole pulse ($f = 120$ Hz, $\tau = 200$ μs) is conducted in the broad range of the acetylene flow rates. No hysteresis effect is observed neither for the R-HiPIMS nor for the R-DCMS process. Without acetylene flow supply, sputtered titanium atom density is 1.2×10^{17} m^{-3} and 0.7×10^{17} m^{-3} for R-DCMS and R-HiPIMS process, respectively. Additionally, the concentration of titanium ions for R-HiPIMS is determined to be 2.3×10^{17} m^{-3}, what is typically two orders of magnitude higher than for the DCMS process [4]. Increasing the acetylene flow the overall density of sputtered titanium atoms and ions decreases. However, the ionization fraction of the sputtered species in the R-HiPIMS remains constant at 80% for the whole studied acetylene flow range.

Acknowledgements

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[1] U. Helmersson, M. Lattemann, J. Bohlmark, A. P. Ehiasarian, J. T. Gudmundsson, Thin Solid Films 513 (2006) 1.

[2] J. Robertson, Diamond-like amorphous carbon.

[3] P. Vašina et al. Plasma Source Sci. Technol. 24(6), (2015) 065022.

[4] C. Christou, Z. H. Barber, Ionization of sputtered material in a planar magnetron discharge, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 18.6 (2000): 2897-2907.

Notes:

PO09 Optical and electrical properties of magnetron deposited $SnZnO_x$ coatings annealed at various temperatures

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The metal oxides have wide range of applications from transparent conductive films, gas sensors [1] up to spacecraft protection [2]. The wide range of materials and methods were already tested. The conductive transparent films are usually prepared with In although a lot of effort was made also on Al:ZnO.

Here presented coatings $ZnSnO_x$ were deposited by two 2in magnetron targets made from ZnO and SnO_2 connected to DC pulsed and RF power supplies, respectively. The nonreactive, pure Ar, and reactive gas mixture Ar/O_2 = 6/1 were used at constant total pressure of 0.2 Pa. Sputtering powers applied on the targets were varied in following manners. The DC pulsed power applied on ZnO target was kept constant 50 W, 50 kHz, 4 μs pulse on time duration and the RF power applied on SnO_2 target was set to values from 0 W (pure ZnO deposited) up to 150 W (up to 8 at.% of Sn in the coatings). The substrates were mounted on the holder at a floating potential at a room temperature. The deposited coatings were about 150 nm thick; we investigated them using a multiple methods strategy. The deposited films were investigated by XPS, XRD, 4point probe and spectroscopic ellipsometry as deposited at RT as well as after annealing at temperatures 200 °C and 450 °C for 10 minutes. The lower annealing temperature is still compatible with many of common polymeric substrates.

The amount of Sn in the films is proportional to applied RF power on SnO_2 target. But there is also significant influence of the post deposition annealing on the film compositions. The ratio Zn/Sn is reduced by the annealing process. Therefore the annealing is promoting the migration of Sn toward the surface and Zn to inside.

The plasma parameters during the deposition process shall be also investigated where different energies of species are expected from DC pulsed and RF powered plasma volumes. The expected higher energetic particles in the RF influenced plasma volume are delivering an additional energy to the growing film. Therefore, we observed systematic differences between refractive indexes in the films deposited with low RF powered SnO_2 magnetron at RT ($n \sim 1.7$) and post-annealed at 200 °C ($n \sim 1.87$) and practically no difference between RT and post-annealed film at higher RF power above 50 W ($n \sim 1.9$). The XRD results proved the transitions from an amorphous to more crystalline structure by post-annealing of the films.

The influence of the higher energy particles from RF magnetron plasma to growing film is interesting and it shall be further investigated.

[1] D. Fischer, A. Hertwig, U. Beck, D. Negendank, V. Lohse, M. Kormunda, N. Esser, Applied Surface Science 421 (2017) 480–486.

[2] W. Wang, C. Li, J. Zhang, X. Diao, Applied Surface Science 256 (2010) 4527–4532.

Notes:

PO10 Magnetron sputtered Hf–B–Si–C–N films with controlled electrical conductivity and optical transparency, and with ultrahigh oxidation resistance

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The present work focuses on the effect of nitrogen addition into hard and electrically conductive Hf–B–Si–C films in order to significantly improve their thermal stability in air at very high temperatures (above 1500 °C). Our motivation has been to develop new hard thin-film materials with a very low electrical and thermal conductivity, and high optical transparency or with a sufficiently high electrical conductivity for high-temperature protective coatings of electronic and optical elements, and for harsh-environment sensors.

Hf–B–Si–C–N films were deposited onto Si(100) and SiC substrates using pulsed magnetron co-sputtering of a single B_4C–Hf–Si target (at a fixed 15% Hf fraction and a 20% Si fraction in the target erosion area) in Ar + N_2 gas mixtures at the N_2 fraction ranging from 0% to 50%. A planar unbalanced magnetron (127 × 254 mm^2 target) was driven by a pulsed dc power supply operating at a repetition frequency of 10 kHz with an average target power of 500 W in a period and voltage pulse durations of 50 μs and 85 μs (duty cycles of 50% and 85%). The substrates were held at a floating potential and a temperature of 450 °C.

The as-deposited, optically non-transparent $Hf_7B_{23}Si_{22}C_6N_{40}$ film with 2 at.% of Ar possessing a hardness of 22 GPa and electrical resistivity of 4 Ωm, which was prepared with the 15% N_2 fraction in the gas mixture at the voltage pulse duration of 50 μs, and the as-deposited, highly optically transparent and electrically insulating $Hf_6B_{21}Si_{19}C_4N_{47}$ film with 3 at.% of Ar possessing a hardness of 20 GPa, which was prepared with the 25% N_2 fraction in the gas mixture and at the same voltage pulse duration, exhibited a very high oxidation resistance in air even up to 1600 °C.

Notes:

PO11 Targets fabrication for high-pressure planetology studies using reactive sputter deposition

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The ERC Planet Dive aims at providing experimental references for phase diagrams, equations of state and melting properties of planetary materials up to the TeraPascal pressure range (1 TPa = 10^{12} Pa = 10 Mbar). Two mains issues have been identified in order to complete successfully this task:

– A large range of sample with various chemical compositions (Fe, Si, Mg elements carbide and oxide alloys) and crystalline state is necessary for the planetary materials study.

– The multilayer targets fabrication needs to be perfectly control in order to monitor the compression evolution into the sample at such pressure and to obtain results repeatability.

To answer to this challenge, IMPMC has made the choice to develop thin films depositions and characterizations. Magnetron sputtering process allows reaching good stoichiometric control of the metalics alloys deposits. Moreover, reactive deposition mode allows to obtain oxydes or nitrides of metallic sample allows a huge diversity of deposition. Fe, FeO_x (figure 1), $FeSi_xC_y$, and $MgFe_xO_y$ depositions has been achieved with the reactive sputtering.

Main results of this work that will be presented are the FeO_x depositions, chemical analysis of the layer, crystalline structure obtained and temperature effects on the crystallinity and the compacity of the layer.

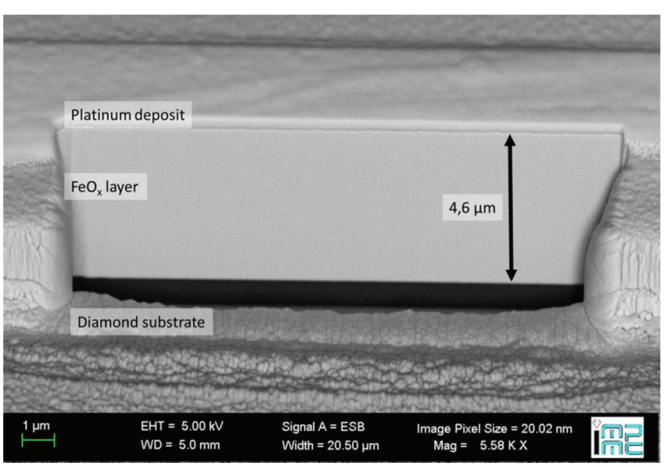

Figure 1: FIB preparation and SEM observation and of an FeO_x/diamond substrate sample.

Notes:

PO12 Core-shell nanoparticles arising from plasma polymerization

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Metal oxide nanoparticles are used in a wide range of applications including medicine, nanocomposites and optoelectronics [1]. The surface functionalization prior their exploitation is considered necessary and arises from the fact that the nanoparticles possess high surface area to volume ratio that leads to agglomeration [1,2]. Among different techniques for surface modification, plasma polymerization was chosen for the surface functionalization of ZnO, ZrO_2 and Al_2O_3 nanoparticles and was performed in a special, rotary homemade reactor [3], using cyclopropylamine as precursor monomer. Plasma polymerization has the ability to impart functionality in a wide range of materials included nanostructures [3–5], while preserving their bulk properties.

Chemical analysis of the functionalized nanoparticles obtained by X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) revealed that amino-based functionalities were grafted onto the nanoparticles surface, while morphological analysis that was carried out utilizing Transmission Electron Microscopy (TEM), showed that a homogeneous thin polymer film of approximately 5 nm is deposited onto the nanoparticles. The resulted material is characterized by a core shell structure.

Further analysis, regarding the nanoparticles' behavior in aqueous media, was examined by using the Hansen Solubility Parameters theory (HSP) [6]. The nanoparticles' dispersibility was tested prior and after the plasma functionalization in selected organic solvents and the results indicated a strong influence of the deposited polymer film. The additional amino functionalities tailored the nanoparticles' physicochemical affinity within selected organic media and led to a similar behavior for each kind of nanoparticles, regardless the core.

[1] S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, R. Kumar, Surface modification of inorganic nanoparticles for development of organic-inorganic nanocomposites – A review, Prog. Polym. Sci. 38 (2013) 1232–1261.

[2] M.Z. Rong, M.Q. Zhang, W.H. Ruan, Surface modification of nanoscale fillers for improving properties of polymer nanocomposites: a review, Mater. Sci. Technol. 22 (2006) 787–796.

[3] C. Rigaux, F. Tichelaar, P. Louette, J.L. Colaux, S. Lucas, First results of the surface modification of multiwall carbon nanotubes by a hollow cathode discharge, Surf. Coatings Technol. 205 (2011) 601–604.

[4] W. He, Z. Guo, Y. Pu, L. Yan, W. Si, Polymer coating on the surface of zirconia nanoparticles by inductively coupled plasma polymerization, Appl. Phys. Lett. 85 (2004) 896.

[5] S. Abou Rich, M. Yedji, J. Amadou, G. Terwagne, A. Felten, L. Avril, et al., Polymer coatings to functionalize carbon nanotubes, Phys. E Low-Dimensional Syst. Nanostructures. 44 (2012) 1012–1020.

[6] C.M. Hansen, Hansen Solubility Parameters-A User's Handbook, Second edi, CRC Press, Boca Raton FL, 2007.

Notes:

PO13 Microstructure and mechanical properties of nanostructured W–B–C coatings prepared by magnetron sputtering

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Nowadays, cutting tools are routinely coated by hard protective coatings to enhance their performance and lifetime. Such standard protective coatings are usually ceramic based. Although, they exhibit high hardness and high stiffness, they are also generally brittle. This can lead to facilitating of initiation and propagation of cracks reducing their performance and lifetime. Therefore, research and development of materials simultaneously exhibiting high hardness and moderate ductility is of high importance.

Recently a group of X_2BC nanolaminate materials (where X is transition metal) was calculated to simultaneously exhibit high stiffness and moderate ductility owing to alternating planes with strong and weaker bonds [1]. Mo_2BC has been the most studied material of the group. It was found out that high temperatures above 800 °C are needed to prepare hard crystalline Mo_2BC using DC magnetron sputtering system [1]. Lower temperature of ~ 400 °C was required when High Power Impulse Magnetron Sputtering was used [2].

The presented study is focused on the development of hard nanostructured W–B–C thin films in the X–B–C structure. Tungsten was chosen as the studied metallic element as it was calculated that W_2BC should exhibit the best mechanical properties of the group with B/G of 1.91 and Cauchy pressure of 71 GPa [3] indicating ductile behavior [4,5]. W–B–C coatings were synthesized using magnetron co-sputtering of W, B_4C and C targets. The C target was powered by mid-frequency pulsed DC to enhance the ion flux on the growing coating. Different surface analysis techniques including TEM, XPS, RBS, XRD, SEM and nanoindentation were used to analyze the deposited coatings. The carbon content of the coatings was kept constant and the influence of the B/W ratio on the microstructure and mechanical properties of deposited W–B–C coatings was studied. All the coatings exhibited good adhesion, high hardness and effective elastic modulus. The hardness of the coatings varied between 22.5 GPa to 25.7 GPa depending on the B/W ratio. The microstructure of the films was always columnar. The bond ratio was also studied. The contribution of W-B bonds to all the detected bonds increased from 34% to 58%, while W-W bond content decreased from 20% to 6%. Coatings with low B/W ratio exhibited lower fracture resistance compared to coatings with higher B/W ratios. The deposited coating system was found to possess promising properties for future generation of industrial protective coatings.

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[1] J. Emmerlich, D. Music, M. Braun, P. Fayek, F. Munnik and J. Schneider, J. Phys. D: Appl. Phys. 42, (2009) 185406.

[2] H. Bolvardi, J. Emmerlich, S. Mráz, M. Arndt, H. Rudigier, J.M. Schneider, Thin Solid Films 542, (2013) 5.

[3] H. Bolvardi, J. Emmerlich, M. to Baben., D. Music, J. von Appen, R. Dronskowski and J. M. Schneider. J. Phys. Condens. Matter. 25, (2013) 045501.

[4] S.F. Pugh, Phil. Mag. 45, (1954) 823.

[5] D.G. Pettifor, D.G., Mater. Sci. Technol. 8, (1992) 345.

Notes:

PO14 Tuning properties and behavior of magnetron sputtered Zr–Hf–Cu metallic glasses

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Metallic alloys are commonly fabricated as crystalline materials by a relatively slow-cooling casting of a melt. Magnetron sputter deposition as a non-equilibrium process with high cooling rates (higher than 10^6 K/s) is very suitable technique to prepare metallic alloys in an amorphous glassy state as thin-film materials. A short-range atomic ordering, based mainly on icosahedral clusters, in these materials gives rise to their exceptional physical and functional properties compared to their crystalline counterparts.

Recently, we have shown that Zr–Cu thin-film alloys can be prepared as metallic glasses in a very wide composition range (30 – 65 at.% Cu) by magnetron co-sputtering [1]. In the present study, we gradually substituted Hf for Zr and prepared two series of Zr–Hf–Cu thin films at approximately 46 and 59 at.% Cu. The films were deposited using three unbalanced magnetrons equipped with Zr, Hf and Cu targets in pure argon without an external heating. The magnetron with the Zr and Hf targets were operated in a dc regime while the Cu magnetron in a high-power impulse regime. The Zr, Hf and Cu contents in the films were controlled by adjusting the dc powers and the average target power in a period, respectively. The Zr–Hf–Cu thin films were investigated by X-ray diffraction, energy dispersive X-ray spectroscopy, differential scanning calorimetry, thermogravimetry, micro- and nanoindentation and atomic force microscopy.

Ternary Zr–Hf–Cu alloy films with an amorphous structure and glass-like behavior were prepared with a gradually increasing Hf/(Hf+Zr) ratio at 46 at.% Cu and 59 at.% Cu. A clear correlation among the evolution of the glass transition temperature, crystallization temperature, hardness and effective Young's modulus with increasing Hf/(Hf+Zr) ratio was observed. A linear increase of all these quantities can be attributed to an increase of average bond energy as Hf with more covalent character of bonds gradually substitutes Zr in the amorphous structure. The substitution of Hf for Zr also causes a shift of the onset of the oxidation to higher temperatures and enables to maintain the high oxidation resistance of the Zr–Hf–Cu thin-film metallic glasses even in the super-cooled liquid region. Tuning the elemental composition of the films allows us also to control the supercooled liquid region in a very wide temperature range from 405 °C to 533 °C. Annealing of the films to the supercooled liquid region results in a partial shape recovery of the films.

[1] P. Zeman, M. Zítek, Š. Zuzjaková and R. Čerstvý, J. Alloys Compd. 696, (2017) 1298.

Notes:

PO15 A kinetic Monte Carlo model for simulation of film growth deposited by reactive PVD

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In order to simulate the growth of oxides thin film by vacuum deposition methods, a model based on kinetic Monte Carlo (kMC) approach on a three-dimensional lattice has been developed. The model takes into account deposition of different species, metallic and reactive. Both metallic and reactive fluxes may consist of atoms as well as ions having their own energy and angular distributions.

The model includes two simulation parts, deposition and finding of equilibrium, which are performed in succession. During the simulation of deposition particles (Metal, O and their ions) are considered to be randomly thrown towards a substrate with the velocity according to given energy and incident angle distribution functions. Metallic atoms are supposed to be attached with the sticking probability equals to 1. Oxygen atoms or ions being deposited can diffuse for some time. They are supposed to be attached only if they find is a metal atom with a free bond while diffusing.

Effects of deposition of energetic particles are also taken into account. These effects are energy transfer from the projectiles to the film, sputtering of the film as well as re-deposition.

The presented model is able to predict the stoichiometry of the film as well as its morphology as a function of the parameters of metallic and reactive flows to the substrate and the relative amount of reactive gas in the deposition chamber.

In order to benchmark our modelling comparison with optical and morphological properties of the film will be performed.

Notes:

PO16 Nitride coatings by reactive ionized magnetron sputtering techniques for harsh environments

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In this work, ceramic coatings are designed to meet different technological issues of mechanical components employed for extreme conditions such as high temperature oxidative atmospheres, liquid metals, erosive-corrosive environments. Ta and Ti based binary and ternary nitride films were deposited by High Impulse Magnetron Sputtering (HiPIMS) or using a combination of HiPIMS and DC magnetron sputtering. High-density, adherent coatings, with reduced columnar structure and tailored residual stress were obtained, also on complex-shaped surfaces. Coatings were deposited on traditional and innovative substrates to improve their corrosion and wear resistance in critical environments. Mechanical and tribological properties were explored by nanoindentation, friction, wear and scratch tests. Oxidation and corrosion behavior were investigated too. [1,2] Morphology, composition, crystal structure and thickness were analyzed by SEM-EDS, XPS, XRD, calotest and optical microscopy.

[1] C. Badini, S.M. Deambrosis, E. Padovano, M. Fabrizio, O. Ostrovskaya, E. Miorin, G. D'Amico, F. Montagner, S. Biamino, V. Zin, Materials 9 (12) (2016) 961.

[2] C. Badini, S.M. Deambrosis, O. Ostrovskaya, V. Zin, E. Padovano, E. Miorin, M. Castellino, and S. Biamino, Ceramics International 43 (2017) 5417–5426.

Notes:

PO17 Transition from spokes into a homogeneous plasma in HiPIMS discharge

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In the past few years, the plasma inhomogeneities called ionization zones, bunches or spokes in high power impulse magnetron sputtering (HiPIMS) discharge got a lot of attention in magnetron comunity. For the first time, ionization zones were observed by Kozyrev et al. [1] in 2011. It was found that ionization zones rotate in **E**×**B** direction with velocity about 10 $km \cdot s^{-1}$ [1–5]. The plasma self-organization was studied in HiPIMS discharge depending on the gradually increasing current. It was observed that with the increasing current applied to the chromium target, homogeneous plasma self-organized into the localized ionization zones. Further increasing current the plasma became homogeneous again [6].

The transition from self-organized plasma into spokes to a homogeneous plasma was studied. In the experiment, the 51-mm-diameter chromium target was used. The transition was investigated by simple biased flat probe, mass spectrometry (MS) and optical emission spectroscopy (OES).

In the measurements by simple biased flat probe placed perpendicularly to the target edge, different plasma configurations were observed when varying the discharge current. At the discharge current of 49.6 A, the plasma was arranged into the spokes while at the current of 56.8 A, the plasma was homogeneous. For medium set current of 54.4 A, the plasma was in the transition region. In the measurements where flat probe was placed opposite to the target, the plasma seemed homogeneous for all studied discharge currents.

Mass spectrometry measurement was conducted in three distances (3 cm, 5 cm, 7 cm) from the target. For the same three current values, as before following ions and isotopes $^{52}Cr^{+}$, Cr^{2+}, Cr^{3+}, Cr^{4+}, Ar^{+}, Ar^{2+}, $^{54}Cr^{+}$ were measured. It was found, that increase of the discharge current by 13%, when the plasma transited from the spokes to the homogeneous plasma, a significant increase of ion flux (about 80%) was measured by a mass spectrometer.

OES measurements were carried out for the same discharge current values. Argon atom, chromium atom and ion lines were measured. OES measurements shown the low intensity of chromium ions at the beginning of pulse and high intensity at the end of pulse for all before mentioned conditions. Moreover, for homogenous plasma (56.8 A) a significant increase of chromium ions was observed, which corresponded with the results obtained from mass spectrometry.

Acknowledgements

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[1] A. Kozyrev, N. Sochugov, K. Oskomov, A. Zakharov and A. Odivanova, Plasma Phys. Rep. 37 (2011) 621.

[2] J. Winter, A. Hecimovic, T. de los Arcos, M. Böke and V. Schulz-von der Gathen, J. Phys. D: Appl. Phys. 46 (2013) 084007.

[3] A. Anders, P. Ni, and A. Rauch, J. Appl. Phys. 111 (2012) 053304.

[4] A. P. Ehiasarian, A. Hecimovic, T. de los Arcos, R. New, V. Schulz-von der Gathen, M. Böke, and J. Winter, Appl. Phys. Lett. 100 (2012) 114101.

[5] T. de los Arcos, R. Schröder, Y. A. Gonzalvo, V. Schulz-von der Gathen and J. Winter, Plasma Sources Sci. Technol. 23 (2014) 054008.

[6] W. Breilmann, A. Eitrich, C. Maszl, A. Hecimovic, V. Layes, J. Benedikt and A. von Keudell, J. Phys. D: Appl. Phys. 48 (2015) 295202.

Notes:

PO18 Reactive sputter deposition of VO_2 and V–W–O thin film libraries assisted by plasma emission monitor control

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The thermochromic material VO_2 shows potential in a variety of applications due to its insulator-to-metal phase transition. Reactive sputter deposition of VO_2 is a difficult process because of target poisoning and a narrow process window for single-phase VO_2. In our study, a plasma emission monitor (PEM) system was employed to monitor V plasma emission intensity, which was used as feedback signal to dynamically control the O_2 flow rate. As a series of setpoints of plasma intensity was adopted in the experiments, VO_x oxides evolve from V-rich phases to O-rich phases. In order to determine the optimal parameter for fabrication of pure VO_2 films, crystalline structures and temperature-dependent resistance of films were measured respectively by X-ray diffraction and four-point method.

To study element-doping effects on the transition properties of VO_2, a V–W–O thin film library was fabricated by reactive co-sputtering from the elemental targets V and W under PEM feedback control. High-throughput characterizations were performed to systematically study the composition spread, crystalline structure, temperature-dependent resistance and stress change of the transition along the library. The study indicates that as the concentration of W increases from 0.7 at.% to 4.4 at.%, the crystalline structure gradually shifts from VO_2 (M) phase to VO_2 (R) phase, accompanied by significant change in transition properties, e.g., transition temperature decreases from 58 °C to 14 °C, resistance change decreases from 3 orders of magnitude to 1 order of magnitude and the stress change across transition was weakened with increasing W amount.

Notes:

PO19 Predicting the main hydrocarbon chemistry pathways and deposition mechanisms in magnetron plasma enhanced chemical vapor deposition of amorphous hydrogenated carbon with a hybrid simulation approach

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Diamond-like carbon (DLC) coatings are well known for their exceptional properties such as low friction coefficient combined with high hardness and wear resistance, chemical inertness, optical transparency and adjustable electrical conductivity [1,2]. Complex substrate geometries and variable arrangements like those occurring in everyday DLC coating business are challenging in terms of film homogeneity, reproducibility of the same coating on numerous substrate parts and overall process stability. Therefore, every new substrate configuration requires experiments for adjusting optimal deposition conditions, which significantly limits the time and cost-efficiency of the coating production. Furthermore, some particular experimental set-up process could be difficult to transpose to others. This is why theoretical studies have to be conducted along with experimental ones to better understand the underlying processes and eventually propose ways to improve existing methods of deposition.

The aim of this study is to understand through simulation and experiments those underlying processes for a magnetron plasma assisted PECVD (Plasma Enhanced Chemical Vapor Deposition) depositing thin films of amorphous hydrogenated carbon. We base our model on an actual magnetron reactor with acetylene as the precursor gas. Our approach is to simulate the creation of radicals, their transport, the gas phase reactions and the surface interactions in an accurate 3D meshed model of our experimental reactor. For that, we use a hybrid simulation scheme [3], consisting of a fluid model of the plasma bulk giving us the ability to distinguish the leading constituents and reaction pathways, coupled with a highly parallelized DSMC code [4]. We use a well-known 2-terms Boltzmann equation solver [5] that can provide the reactions rates and the electron transport coefficient with our compiled database of relevant cross sections. We use a 0D fluid model to predict the evolution of the concentration of the different species. Particular attention is given to limit the number of considered reactions to the most contributing ones [6,7]. Surface chemical reactions and sticking coefficients [8] are included into the DSMC simulations, in order to model the carbon deposition, as well as a model for sputtering emission of the cathodes.

[1] J. Robertson, “Diamond-like amorphous carbon,” Mater. Sci. Eng. R Reports, vol. 37, no. 4–6, 129–281, 2002.

[2] J. Benedikt, “Plasma-chemical reactions: low pressure acetylene plasmas,” J. Phys. D. Appl. Phys., vol. 43, no. 4, 43001, 2010.

[3] M. Mao et al., “Computer modelling of the plasma chemistry and plasma-based growth mechanisms for nanostructured materials,” J. Phys. D Appl. Phys. J. Phys. D Appl. Phys, vol. 44, no. 44, 174030–16, 2011.

[4] A. Pflug, M. Siemers, T. Melzig, L. Schäfer, and G. Bräuer, “Simulation of linear magnetron discharges in 2D and 3D,” Surf. Coatings Technol., vol. 260, 411–416, 2014.

[5] G. J. M. Hagelaar and L. C. Pitchford, “Solving the Boltzmann equation to obtain electron transport coefficients and rate coefficients for fluid models,” Plasma Sources Sci. Technol., vol. 14, no. 4, 722–733, 2005.

[6] A. Hurlbatt et al., “Concepts, Capabilities, and Limitations of Global Models: A Review,” Plasma Process. Polym., vol. 14, no. 1–2, 1600138, Jan. 2017.

[7] M.M. Turner et al., “Uncertainty and sensitivity analysis in complex plasma chemistry models,” Plasma Sources Sci. Technol, vol. 25, 2016.

[8] E. Neyts, “Mathematical Simulation of the Deposition of Diamond-like carbon (DLC) Films Wiskundige Simulatie van de Depositie van Diamond-like carbon (DLC) Filmen,” no. Dlc, 2006.

Notes:

PO20 Tribological properties and oxidation resistance of WN_x thin films at high temperatures up to 500 °C

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The paper reports on the structure, microstructure, mechanical properties, friction coefficient μ, wear rate k and oxidation resistance of the WN_x films; here x = N/W is the stoichiometry of nitride films. The films were reactively sputtered from a W target of diameter of 100 mm on Si(100) and Steel 15330 substrates in a mixture of Ar + N_2 gases using an unbalanced magnetron powered by the AC pulsed power supply. The properties of sputtered WN_x films were characterized by (i) X-ray diffraction (XRD), (ii) Scanning Electron Microscope (SEM), (iii) micro-indentation testing, (iv) pin-on-disk tribometry in wide range of temperatures T from room temperature (RT) up to 500 °C and (v) ellipsometry. It was found that sputtered WN_x films are polycrystalline nanocomposites composed of either a mixture of low-T α-W and high-T β-W_2N phases at $x \leq 0.5$ or high-T β-W_2N and low-T δ-WN phases and exhibit: (1) high values of the hardness H, H/E^* ratio, elastic recovery W_e increasing with increasing x up to 34 GPa, 0.13 and 88%, respectively; here E^* is effective Young's modulus, (2) the friction with Al_2O_3 ball (i) increases from 0.3 ÷ 0.4 at RT to 0.8 ÷ 1.2 at 200 °C and (ii) decreases to 0.5 ÷ 0.6 at 400 °C and sliding distance of 1000 m, (3) the wear with Al_2O_3 ball increases from 10^{-8} mm^3/Nm at $T \leq 200$ °C up to ~2.5×10^{-6} mm^3/Nm at T ranging from 200 to 400 °C. The WN_x films are completely removed from the substrate at T = 500 °C already at sliding distances of about 350 to 600 m due to formation of the WO_x scale on the coating surface.

Notes:

PO21 Low-temperature growth of epitaxial ZrB_2/Al_2O_3 (1000)

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ZrB_2 is an ultra-high temperature ceramic with melting point above 3000 °C. In addition, ZrB_2 exhibits high hardness, corrosion-resistance and high thermal and electrical conductivities. Owing to aforementioned properties, ZrB_2 is suitable for e.g. cutting tools and aerospace applications. Growth of stoichiometric, epitaxial ZrB_2 films by DC magnetron sputtering was reported on 4H-SiC [2] and Al_2O_3 [1], and additionally a relationship between epitaxy and resistivity was established [2]. However, the growth temperature for epitaxial ZrB_2 films was 900 °C [2], thus excluding use of heat-sensitive substrates, such as steels and metals. Our work aims to elucidate whether the onset temperature for epitaxial ZrB_2 films can be reduced by increasing adatom mobility through ion-assisted growth. The incident ion flux during film growth was adjusted by adding a coil surrounding the growth setup, thus enhancing the outer pole of the unbalanced magnetron, as suggested by Petrov et al. [3]. The ion energy was controlled by applying a bias to the substrate. For different combinations of ion bombardment and ion energy, films were grown at temperatures ranging from 500 to 900 °C. Structural and electrical properties were investigated by X-ray diffraction ($\theta/2\theta$ and pole figures) and 4-point-probe resistivity measurements, respectively. Using a substrate bias of −30 V and coil current of 3 A at a growth temperature of 700 °C, it was found that the ZrB_2 (0001) peak intensity, normalized to the substrate Al_2O_3 (0006) peak intensity, matched that of coatings grown at 900 °C and floating substrate bias potential. The results indicate that using ion-enhanced growth with low ion energies could significantly decrease the onset temperature for highly textured coatings, which would allow to reduce the substrate temperature necessary when growing highly textured ZrB_2 films. This shows a route for enabling growth of highly oriented ZrB_2 films on temperature-sensitive substrate materials.

[1] L. Tengdelius, E. Broitman, J. Lu, F. Eriksson, J. Birch, T. Nyberg, L. Hultman, and H. Högberg, Acta Mater. 111, (2016) 166-172.

[2] L. Tengdelius, G. Greczynski, M. Chubarov, J. Lu, U. Forsberg, L. Hultman, E. Janzén, and H. Högberg, J. Cryst. Growth 430, (2015) 55-62.

[3] I. Petrov, F. Adibi, J. E. Greene, W. D. Sproul, and W.-D. Münz, J. Vac. Sci. Technol., A 10, (1992) 3283-3287.

Notes:

PO22 Properties of WBC coatings prepared by magnetron sputtering from industrial segmented target

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Machining tools are routinely coated with thin films to sustain required performance and durability. The most common coatings for tools are based on ceramic materials. Ceramics exhibit high hardness, however, they are also quite brittle, which facilitates formation and spreading of cracks. This leads to a premature degradation of the coated tool.

A solution would be to prepare coatings simultaneously exhibiting high hardness together with enhanced ductility. Such a combination of properties was predicted by ab-initio calculations in X_2BC systems (where X = W, Mo, Ta etc.). These systems should form an inherently nanolaminated structure due to their specific bonding structure. Therefore, ductile behavior of such coatings would hinder formation and spreading of cracks [1, 2].

W–B–C coatings in this study were synthesized using magnetron sputtering from a single segmented cylindrical target in an industrial configuration. Advanced segmented target was used to precise controlling chemical composition of coating. The target was composed of W, C, B_4C cylindrical segments with same radii but different heights. Highly-inhomogeneous coatings were deposited on various substrates to determine the influence of chemical composition on coatings properties afterwards. The depositions were carried out at 450 °C.

Chemical composition of the coatings was determined using energy dispersive X-ray spectroscopy (EDS/SEM) and Rutherford backscattering spectrometry (RBS). Strong correlation was observed between coating chemical composition and setup of the target. Mechanical properties and microstructure of the prepared coatings were also studied. Indentation techniques were used to determine the hardness and elastic modulus. Internal stress of coatings was determined by measuring the curvature of coatings on silicon strips. Grazing angle of incidence X-ray diffraction was used to characterize the microstructure of the coating.

A simulation of chemical composition was created to further support the experimental results. Two step approach was used: TRIM was used to simulate the target sputtering, specifically to acquire the sputter yield, energy and angular distribution of the sputtered species and SIMTRA code was used to simulate the transportation of sputtered particles in the chamber. In order to efficiently perform the simulations of complex segmented targets an in-house software tool was developed. This tool enables design of any segmented target and set deposition properties (pressure, temperature, sputtered particles distribution, etc.). Good agreement between the simulations and experiments was observed.

Acknowledgements

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[1] J. Emmerlich, D. Music, Journal of Physics D: Applied Physics, (2009) 42.

[2] H. Bolvardi, J. Emmerlich, M. to Baben, D. Music, J. von Appen, R. Dronskowski, J. M. Schneider, Journal of Physics. Condensed Matter : An Institute of Physics Journal, 25, (2013) 45501.

Notes:

PO23 Preparation of Ag/LiF nanocomposite films using simultaneous high pressure magnetron sputtering and thermal evaporation

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We present a preparation of Ag/LiF nanocomposite films by high-pressure magnetron sputtering. Localized surface plasmon resonance in metallic nanoparticles can induce significant enhancement of electromagnetic field in the nanoparticle's vicinity. The high-intensity electromagnetic field is essential for luminescence processes such as down-conversion or up-conversion. Energy transfer rates and photoemission rates can also be affected by SPR. For these reasons, this can be a promising method to fabricate efficient light conversion layers. Silver nanoclusters are created in an aggregation chamber exploiting gas condensation. The aggregation chamber with the magnetron head is separated from the main chamber by an orifice with the diameter of 4 mm. The pressure in the aggregation chamber is increased by an Ar flow. Silver nanoclusters are transported through the orifice into the main chamber. A tungsten evaporation boat in this chamber enables simultaneous deposition of silver nanoparticles and a fluoride matrix. Homogeneous Ag/LiF nanocomposite coatings can be prepared using this method. The concentration of nanoparticles is controlled by a deposition rate of evaporated fluoride. First, we studied deposition of silver nanoparticles. These nanoparticles were deposited on Si and glass substrates at various pressures and various magnetron-orifice distances. Their height and lateral size is estimated by Atomic Force Microscopy and Scanning Electron Microscopy. Optical properties are studied using spectrophotometry and spectral ellipsometry. Computer simulations were carried out using generalized Mie model of a multiparticle system. The calculated absorption efficiency is compared with the optical measurement.

Notes:

PO24 Wettability of DC-MS and HIPIMS TaN and TiB_2 coated AISI H13 steel by molten aluminum

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Wettability tests with molten Al and Al–Si–Cu were performed on PVD coated AISI H13 tool steel samples by means of a sessile drop method. Coatings tested include magnetron sputtered and HIPIMS TaN and TiB_2. Evolution of contact angle between the substrate and molten aluminum was measured for 2 h at 800 ºC for bare steel and all coatings. The influence of the composition, thickness, and microstructure of the coatings were investigated by means of XRD, SEM/EDS to elucidate the mechanism of the reactive wettability. Bare steel samples show a higher reactivity for both aluminum alloys than the coated samples. The thickness of the coating and the microstructure of the films have been proved to play a key role in the reactive wettability kinetics.

Notes:

PO25 Low-temperature deposition of thermochromic VO_2 films on glass and kapton using reactive deep oscillation magnetron sputtering

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A modified version of HiPIMS, called Deep Oscillation Magnetron Sputtering, with a pulsed O_2 flow control and to-substrate O_2 injection into a high-density plasma in front of the sputtered vanadium target was used for low-temperature (330 °C) deposition of thermochromic VO_2 films onto conventional soda-lime glass (1 mm thick) and flexible kapton polyimide foil (25 μm thick) substrates without any substrate bias voltage and without any interlayer.

The depositions were performed using a strongly unbalanced magnetron with a planar vanadium target of 100 mm diameter in argon-oxygen gas mixtures at the argon pressure of 0.5 Pa. Voltage macropulses, composed of 10 voltage micropulses (pulse-on time of 20 μs and pulse-off time of 30 μs), with a total length of 500 μs and repetition frequency of 640 Hz were used for all depositions with a maximum target power density of up to 735 Wcm^{-2} during pulses at a deposition-averaged target power density close to 20 Wcm^{-2}.

A high modulation of the transmittance at 2500 nm (even between 77% and 17% for VO_2 films on the kapton substrate) was achieved for the VO_2 films on the glass and kapton substrates at the transition temperatures of 57 – 64 °C.

This low-temperature magnetron sputter technique is of key importance for compatible fabrication of thermochromic VO_2-based multilayer coatings for smart windows and smart radiator devices (spacecrafts) applications requiring enhanced luminous transmittance and solar transmittance modulation at a decreased transition temperature.

Notes:

PO26 Design and optimization of metal–dielectric multilayer coatings for non-polarizing beam splitters

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Non-polarizing beam splitters (NPBs) are widely used for a variety of photonic applications ranging from interferometry and holography. Most of NPBs are multilayer coatings. Often, they are consisting of low and high refractive index layers such as metal oxides. Formation of these multilayer (> 20 layers) coatings could be very complicated; it requires high precision and process control. Moreover, optical properties of metal oxides may be additionally influenced by the preparation conditions [1]. Recently, it was reported that NPBs could be made with the use of ultrathin silver and metal oxide layers. In this work, we suggest to use ultrathin copper that is cheaper and have higher oxidation resistance.

In current research, for NPBs formation ultrathin copper and niobium oxide layers were used. Copper is known for using not only in microelectronics, but also as optical coating applications, for example, as telescope mirror layers. Niobium oxide films possess unique physical and chemical properties, such as high refractive index, excellent chemical stability and laser irradiation resistance, as well as low optical absorption in the visible and near infrared light spectrum [2,3]. This results in their wide implementation in optical interference filters, beam splitters, high-reflectivity and anti-reflective coatings, as well as other functional coatings applications.

Previously, in our laboratory Nb_2O_5 films were optimized. They were prepared by reactive magnetron sputtering using a feed-back optical emission monitoring [2]. Unique possibilities of the deposition process control lead to formation of films with high refractive index and low loss [1,2]. Present work is mostly concentrated on optimization of ultrathin copper layers. Moreover, we will show a design and preparation of complex ultrathin copper and niobium oxide multilayer coatings for NPBs.

[1] A. Belosludtsev, K. Juškevičius, L. Ceizaris, R. Samuilovas, S. Stanionytė, V. Jasulaitienė, S. Kičas, Appl. Surf. Sci. 427B (2018) 312-318.

[2] K. Juškevičius, M. Audronis. A. Subačius, S. Kičas, T. Tolenis, R. Buzelis, R. Drazdys, M. Gaspariūnas, V. Kovalevskij, A. Matthews and A. Leyland, Thin Solid Films 589 (2015) 95-104.

[3] G. Abromavicius, R. Buzelis, R. Drazdys, A. Melninkaitis, D. Miksys, V. Sirutkaitis, A. Skrebutenas, R. Juskenas and A. Selskis, Proc. SPIE, 6403 (2007) 640315.

Notes:

PO27 High power impulse magnetron sputtering Mo–N coatings deposition on temperature sensitive substrates

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In industrial field, advanced technological solutions to protect structural materials against oxidation and wear phenomena is increasingly demanded. Hard protective coatings represent a suitable resource to achieve these purposes. Physical Vapor Deposition techniques are extensively used to deposit transition metal nitride films. However, they usually require rather elevated deposition temperatures to accomplish desired performance, becoming incompatible with sensitive substrates like Al alloys (e.g. silicon cast alloys pistons for high-speed engines). High Power Impulse Magnetron Sputtering technology allowed obtaining high quality Mo–N coatings at low temperature on a soft Al–Si alloy, proving to be an enabling technology for coupling apparently incompatible materials. Produced films exhibited good adhesion, noteworthy mechanical characteristics (hardness ≥ 22 GPa) and notable tribological properties.

Notes:

PO28 Structure, vibration properties and *p*-type conductivity of the Zn–Ir–O thin films deposited by reactive DC magnetron sputtering

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Realization of transparent oxide *p*-type semiconductor thin films as components in the *pn* junctions is highly necessary for the transparent oxide electronics. ZnO thin films are widely studied as a transparent conducting oxide (TCO) material. However, *p*-type doping of the ZnO is extremely difficult due to the self-compensation effect from the native donor defects [1]. Polycrystalline thin films of $ZnIr_2O_4$ [2] and $ZnRh_2O_4$ [3] are shown as transparent *p*-type semiconductors and retain the electrical properties in the amorphous phase [4]. In this study, we report on local structure, vibration spectra and electrical properties of the Zn–Ir–O thin films deposited by reactive magnetron co-sputtering.

Zn–Ir–O thin films were deposited on glass, Si, Ti and polyimide substrates, by DC reactive magnetron co-sputtering from metallic Zn and Ir targets in an $Ar+O_2$ atmosphere. The Zn target was sputtered at a constant power mode. To vary the Zn to Ir ratio from 0 to 1 in the films, the sputtering power of the Ir target was varied.

The structure of the amorphous Zn-Ir-O films mostly consists of the ZnO_4 tetrahedra and IrO_6 octahedra. The valence state of Ir ions changes from 5+ to 4+ with the increase of the Ir concentration. Above 5.1 at.% of Ir, the film's structure changes significantly, with the nano-crystallites becoming smaller and the structural atomic network gradually becoming different from crystalline w-ZnO until the wurtzite phase becomes undetectable at 12.4 Ir at.%. An intense Raman band at approximately 720 cm^{-1} appears upon Ir incorporation and can be ascribed to O_2^{2-} ions. Measurable electrical conductivity appears together with a complete disappearance of the wurtzite-type ZnO phase. The conduction type undergoes a transition from *n*- to *p*-type in the Ir concentration range between 12.4 and 16.4 at.% [5].

[1] J. C. Fan et al., Progress in Materials Science 58 (6) (2013) 874-985.
[2] M. Dekkers et al., Appl. Phys.Lett. 90 (2) (2007) 21903-21903.
[3] H. Mizoguchi et al., Appl. Phys. Lett. 80 (7) (2002) 1207-1209.
[4] S. Narushima et al., Advanced Materials 15 (17) (2003) 1409-1413.
[5] M. Zubkins et al., Thin Solid Films 636 (2017) 694-701.

Notes:

PO29 Control-oriented modeling and stabilization of reactive sputter processes

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Reactive sputter processes are well established in the industry as well as in the scientific communities of thin solid film and vacuum science, but studies from a control engineering point of view are rare. As the requirements on the thin film properties rise, systematical methods are needed for the modeling of the process and the design of controllers. This presentation shall fill the gap between the physical modeling of reactive sputter processes with metal targets and reactive gases like oxygen and their systematical control for stable deposition processes.

First, the control-oriented modeling is discussed and the nonlinear process is analyzed with respect to its controllability, stability, equilibrium states and dominant dynamics. An important result is that the process behavior can be classified by an Abel differential equation with one manipulated variable and one controlled variable. Experiments for the validation demonstrate the usability of the proposed model and parameter identification approach [1].

Second, a design method for the control of the voltage or optical emission is presented. By Lyapunov's direct method intervals for the controller parameters can be calculated with respect to the parameters of the nonlinear process to achieve a stable feedback loop. The intervals allow the postulating of tuning rules and the systematically design of the controller on the basis of experiments without the need of an identified process [2]. If the process parameters are identified the corresponding control parameters can be also calculated directly without prior experiments, which enables the consideration of target aging in the control design [3].

In conclusion also the modeling and control of sputter processes with respect to multiple-input signals and multiple-controlled signals are shown. For the modeling, artificial neural networks are combined with ordinary differential equations to approximate the static nonlinearities and the dynamics [4]. The identified neural networks can be used for the multiple-input multiple-output control of the process [5]. The proposed modeling and control method is validated by experiments.

[1] C. Wölfel, P. Awakowicz, J. Lunze, IFAC World Congress, (2017) 14292-14298.

[2] C. Wölfel, P. Awakowicz, J. Lunze, International Conference on Process Control, (2017) 109-114.

[3] C. Wölfel, P. Awakowicz, J. Lunze, Conference on Control Technology and Applications, (2017) 25-30.

[4] C. Wölfel, S. Kockmann, P. Awakowicz, J. Lunze, To appear in International Conference on Control, Automation and Systems, (2017).

[5] C. Wölfel, S. Kockmann, P. Awakowicz, J. Lunze, Asian Control Conference, (2017) submitted.

Notes:

PO30 Hard (Zr,Ti) alloy films with small amount of oxygen resistant to cracking

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The poster reports on the effect of the addition of small amount of oxygen into Ar sputtering gas on the microstructure, mechanical properties and macrostress of the (Zr,Ti) alloy films prepared by DC magnetron sputtering. It was found that the addition of small amount of oxygen into Ar sputtering gas makes it possible to sputter nanocrystalline (Zr,Ti,O) alloy films with high hardness $H > 10$ GPa, high ratio $H/E^* \geq 0.1$, high elastic recovery $W_e \geq 60\%$ and enhanced resistance to cracking; here E^* is the effective Young's modulus. The main result of the presented investigation is the demonstration that the incorporation of a small amount of O into a (Zr,Ti) alloy film is a very effective way to form the flexible (Zr,Ti,O) alloy films with enhanced resistance to cracking. [1]

[1] J. Musil, S. Zenkin, R. Čerstvý, S. Haviar, Z. Čiperová: (Zr,Ti,O) alloy films with enhanced hardness and resistance to cracking prepared by magnetron sputtering, Surface and Coatings Technology 322 (2017), 86-91.

Notes:

PO31 Report on spoke rotation, merging and splitting in HiPIMS plasma

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Lately it was found that HiPIMS plasma is not always homogeneously distributed over the racetrack area of the target, but it undergoes self-organization into the ionization zones, called spokes [1]. Spokes are observed to rotate above the racetrack in the **E**×**B** direction with velocities around 10 km·s^{-1}. The appearance, amount and velocity of the spokes change with the change of experimental conditions [2]. Moreover, spoke spontaneous merging of the spokes during the pulse was revealed [3].

The presented spoke study was performed in both non-reactive as well as reactive nitrogen HiPIMS plasma using simultaneous broadband optical screening via ICCD camera (200 ns time scale) and strip probes embedded into the niobium target. Strip probes measured actual local current delivered to the target, thus when the spoke passed over the strip probe a distinct local current modulation was observed. Typically the current modulation might reach up to twice the average value, which matches well with the radially integrated optical emission intensities obtained by the ICCD camera.

The dual diagnostic system enabled the observation of a set of spokes as they rotated. Fast events of the spoke merging and splitting were recorded. The two spokes with similar sizes and intensities were observed to merge into one larger spoke, while the retaining the velocity of the trailing spoke. In the merged spoke both the plasma emission intensity and the current collected by the embedded probes was redistributed to have their maximum at a trailing edge. The reverse process, where one larger spoke was observed to split into two smaller spokes. Similar to spoke merging, the plasma in the created spokes redistributed so both the plasma emission intensity and the current collected by the embedded probes had their maximum at a trailing edge. Additionally, total charge collected by the embedded probes during the spoke splitting was conserved.

After the spoke merging or splitting events occurred, the new spoke configuration was not always stable in time. Often the large spoke split into two smaller spokes only to reform a short time later. However, for a given experimental conditions only a slight variation from the average number of spokes m was observed (typically a change of $\Delta m = 1$). In addition, a simple phenomenological model was developed to relate the number of spokes m with the spoke dimensions, spoke velocity and gas atom velocity.

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[1] A. V. Kozyrev, N. S. Sochugov, K. V. Oskomov, A. N. Zakharov and A. N. Odivanova, Plasma Phys. Rep. 37, (2011) 621.

[2] P. Klein, J. Hnilica, Z. Hubička, M. Čada, M. Šlapanská, M. Zemánek and P. Vašina, Plasma Sources Sci. Technol.26, (2017) 055015

[3] A. Hecimovic, V. Schulz-von der Gathen, M. Böke, A. von Keudell and J. Winter, Plasma Sources Sci. Technol. 24, (2015) 045005.

Notes:

PO32 Highly adhesive single-step room temperature carbon nitride coatings on medical quality steel without interlayer by reactive Ar/N_2 HiPIMS

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Carbon nitride films exhibit extremely low friction (friction coefficient < 0.15) making them attractive for applications in electronic, aerospace, mechanical and biomedical coating industries. Depositing carbon nitride (CN_x) at room temperature and achieving good adhesion without any interlayer is still a great challenge. In this work, we use mixed-mode technique (sputtering mixed with arc) of HiPIMS sputtering to deposit highly adhesive (HF1) single-step carbon nitride coatings directly on 316L medical quality steel substrates neither providing external heating nor depositing any interlayer. Operating High power impulse magnetron sputtering (HiPIMS) in this mode generates short-lived cathode spots in the magnetic racetrack which consequently produce large numbers of carbon and nitrogen ions. The interfacial steel-C-N layer typically grows beneath CN_x films by energetic ion impact during deposition, which is considered advantageous for film adhesion. The nitrogen composition in CN_x films and the gas temperature are governed by the HiPIMS pulse length and the N_2-to-Ar gas flow ratios. The mechanical and bio-compatible properties of the CN_x films show a correlation to the nitrogen composition and substrate bias. The physical and chemical properties of CN_x films are adjustable by HiPIMS pulse length and N_2-to-Ar gas flow ratio to achieve strikingly low thrombogenicity, and to improve the capability of coatings to covalently immobilize protein molecules directly from buffer solution.

Notes:

PO33 The effect of hydrogen on friction behavior of W/a-C:H coatings prepared by reactive high target utilization sputtering

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Carbon based coatings create an extended family of coatings with wide range of mechanical and tribological properties resulting from their structure and composition. When doped by metals, e.g. W, nanocomposite structure with controlled hardness and reduced residual stresses can be obtained. Their mechanical as well as friction properties are determined by the excess of lubricious carbon provided by hydrocarbon gases (usually C_2H_2 or CH_4) during reactive sputtering. The incorporation of hydrogen from hydrocarbons and/or intentionally added into the sputtering atmosphere offers additional way to influence friction behavior, especially in a humid air compared to dry air or vacuum. The work is devoted to the investigation of the effect of hydrogen on the hardness and friction behaviour of W/a-C:H coatings with different contents of hydrogen prepared by reactive High Target Utilization Sputtering (HiTUS). The content of hydrogen in the coatings was determined by Elastic Recoil Detection Analysis (ERDA) and the friction behaviour of the coatings was investigated in humid air, dry nitrogen and vacuum as a function of hydrogen content.

Notes:

PO34 Reactive sputter deposition of transparent and low refractive-index MgF_2 thin films by using a double-grid negative-ion retarding electrode

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MgF_2 thin films deposited by magnetron sputtering show optical absorption in the visible range because of the formation of F defects or Mg clusters by the incidence of energetic F^- ions to substrate [1, 2]. In addition, deposition rate of sputter deposited MgF_2 thin film is less than a few nm/s [1, 2], which is regarded as rather low compared to that of other compound thin films. In this study, effectiveness of negative bias voltage applied to a double-grid electrode set between the cathode and the substrate on increase in film deposition rate and suppression of optical adsorption has been examined in MgF_2 reactive sputter deposition using Ar–CF_4 mixture as discharge gas.

The sputtering apparatus used in the experiments was a batch-type system with the cathode of a Mg plate (76.2 mm dia., 99.99% in purity). The distance between the target and the substrate was 51 mm. A double-grid electrode with 120 mm by 120 mm squared was set between the target and substrate. The distance from the grounded grid to the target and between the two grids were 15 and 6 mm, respectively. The grid adjacent to the target was grounded and the other was biased. The pressure of discharge gas of Ar+CF_4 was kept at 0.8 Pa. The flow rates of Ar and CF_4 were 2.5 sccm, respectively. The cathode was driven by dc power supply (AE MDX 1.5K). The cathode power ranged 100 – 108 W for a constant discharge current of 0.3 A. The retarding voltage was changed from 0 to −500 V. Borosilicate glass plates ($80 \times 80 \times 0.9$ mm^3) were used as substrate. Thickness of thin films was measured by using a stylus profiler. Optical transmittance and reflectance were measured by a double-beam spectrophotometer.

The change in the retarding voltage affected both the film deposition rate and optical absorption. The MgF_2 thin film deposited without applying a retarding voltage to the driven grid showed the multiple-ring-shaped area with optical absorption. By applying a retarding voltage of −100 V, the ring-shape was disappeared and transparent MgF_2 thin films were deposited. The optical absorption coefficient of thin films was reduced to $< 2 \times 10^{-4}$ nm^{-1} in the visible range and the refractive index was < 1.40. Film deposition rate was increased to > 10 nm/min from < 1nm/min by applying a retarding voltage of −30 to −500 V. In addition, the film thickness uniformity distribution in the substrate was drastically improved due to the increase of the deposition rate in the area facing to the target erosion.

The reduction in optical absorption and the increase in film deposition rate in the area facing to the target erosion is judged to result from the suppression of negative ion incidence to substrate. It has been reported that, in the discharge containing CF_4 gas, the negative ion density becomes higher than the e^- density [3]. In addition, the distribution of negative ions showed the peaks at the position facing the target erosion [4]. These reported results well support the hypothesis that the bias voltage applied to the retarding electrode suppress the incidence of negative ions to the substrate. One of the interesting points obtained in this study is the fact that the suppression of optical absorption and the increase of film deposition rate were achieved by applying a low retarding voltage of < -50 V to the grid. The low-voltage suppression suggests that the most of the negative ions arriving to the retarding electrode are formed in the bulk of plasma and then accelerated during passing the plasma sheath in front of the grounded grid, which is upward from the plasma potential. The deposition of transparent and high index MgF_2 thin films by reactive sputtering is thought to be advantageous to the fabrication of large area optical devices.

[1] L. Martinů, et al., Thin films prepared by sputtering MgF_2 in an rf planar magnetron, Vacuum 35 (1985) 531, 1985.

[2] K.Iwahori, et al., Optical properties of fluoride thin films deposited by RF magnetron sputtering, Appl. Opt. 45 (2006) 4598-4602.

[3] M. Haverlag, et al., Measurements of negative ion densities in 13.56 MHz rf plasmas of CF_4, C_2F_6, CHF_3, and C_3F_8 using microwave resonance and the photodetachment effect, J. Appl. Phys. 70 (1991) 3472-3480.

[4] S. Mahieu, et al., Modeling the flux of high energy negative ions during reactive magnetron sputtering, J. Appl. Phys. 106 (2009) D93302.

Notes:

PO35 Post-annealing of Ta–O–N films prepared by reactive HiPIMS: A step towards effective water splitting

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The TaON material is a promising candidate for application as a visible-light-driven photocatalyst splitting water into H_2 and O_2 and thus converting solar energy into chemical energy. The photo-generated electron-hole pairs act here as the active water splitting species. In order to work as an effective water splitting photocatalyst, the material must satisfy certain conditions: (1) band gap of proper width (preferably corresponding to visible light absorption), (2) suitable alignment of the band gap with respect to the water splitting redox potentials [1] and (3) highly crystalline structure allowing effective electron and hole transport through the film.

To prepare the Ta–O–N films in this work, we used reactive HiPIMS with the reactive gases being introduced to a high-density plasma in front of the target. This approach made it possible to efficiently control the elemental composition and thus properties of the films by changing the nitrogen fraction in the reactive gas flow. We were able to tune the optical band gap for visible light absorption at preserved proper alignment. However, the as-deposited films exhibited amorphous structure. In order to enhance the electron transport through the films and possibly reduce the recombination rate of the photo-generated electron-hole pairs, the films were post-annealed at 900 °C in vacuum. After annealing, Ta–O–N films prepared at a proper oxygen to nitrogen ratio exhibited a pure TaON phase. The change in electron transport was investigated by measuring electrical resistivity, which decreased considerably after annealing. As a result, we obtained a thin-film material with a properly aligned band gap of ~ 2.6 eV (corresponding to visible light absorption) and enhanced electron mobility.

[1] A. Kudo, Y. Miseki, Chem. Soc. Rev. 38 (2009) 253.

Notes:

PO36 Tribological properties of W–B–C protective coatings prepared by pulsed DC magnetron sputtering

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One of the many applications of thin films is the protection of tools as appropriate coatings increase the tool's efficiency and lifetime. Hard ceramics such as TiN, TiAlN and c-BN are the most commonly used materials for this purpose. However, these materials exhibit brittle behaviour, which facilitates the formation and spreading of cracks in the coating. This leads to premature failure of the coating. A solution for this problem would be materials that are simultaneously hard and ductile. This seemingly contradictory combination of properties has been predicted in a group of materials consisting of a metal, boron and carbon [1]. These materials exhibit an inherently nanolaminated structure with alternating regions of high and low electron density. W–B–C has been predicted to have the highest toughness and ductility out of this group of materials and will therefore be the subject of this study.

Mid-frequency pulsed-DC magnetron sputtering was used to deposit W–B–C coatings in this study. The effect of coating composition and the deposition parameters on the structure, mechanical and tribological properties of the coatings was investigated. X-ray diffractometry has shown a low level of crystallinity due to high enthalpy of formation of crystalline W_2BC phase. Higher deposition temperature resulted in better crystallinity. Hardness of the coatings ranged from 21.5 to 27 GPa. Samples with a higher level of crystallinity exhibited higher hardness. Main emphasis was placed on the tribological properties of the coatings. Also, the influence of the measuring temperature on the tribological properties of the coatings was investigated. It was found that the deposition temperature and the measuring temperature had the greatest influence on the tribological properties of the coatings. Coatings prepared at elevated temperature of 500 °C showed significantly lower wear and better adhesion in tribological measurements. The coefficient of friction decreased with increasing temperature of the substrate during measurement. Coating composition measurements after high temperature tests have shown that this decrease was due to the formation of W–O Magnéli phases that acted as a solid-state lubricant.

[1] H. Bolvardi, J. Emmerlich, M. to Baben, D. Music, J. von Appen, R. Dronskowski, J. M. Schneider. J. Phys.: Condens. Matter 25 (2013) 045501 (6pp).

Notes:

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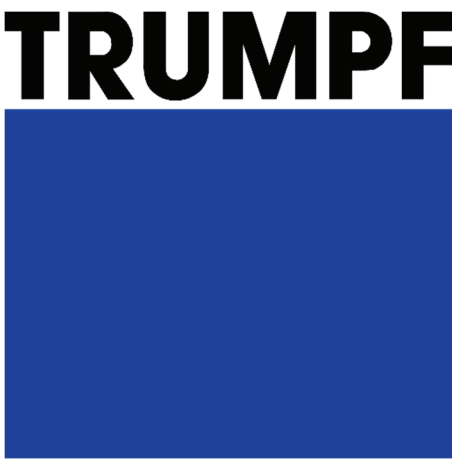

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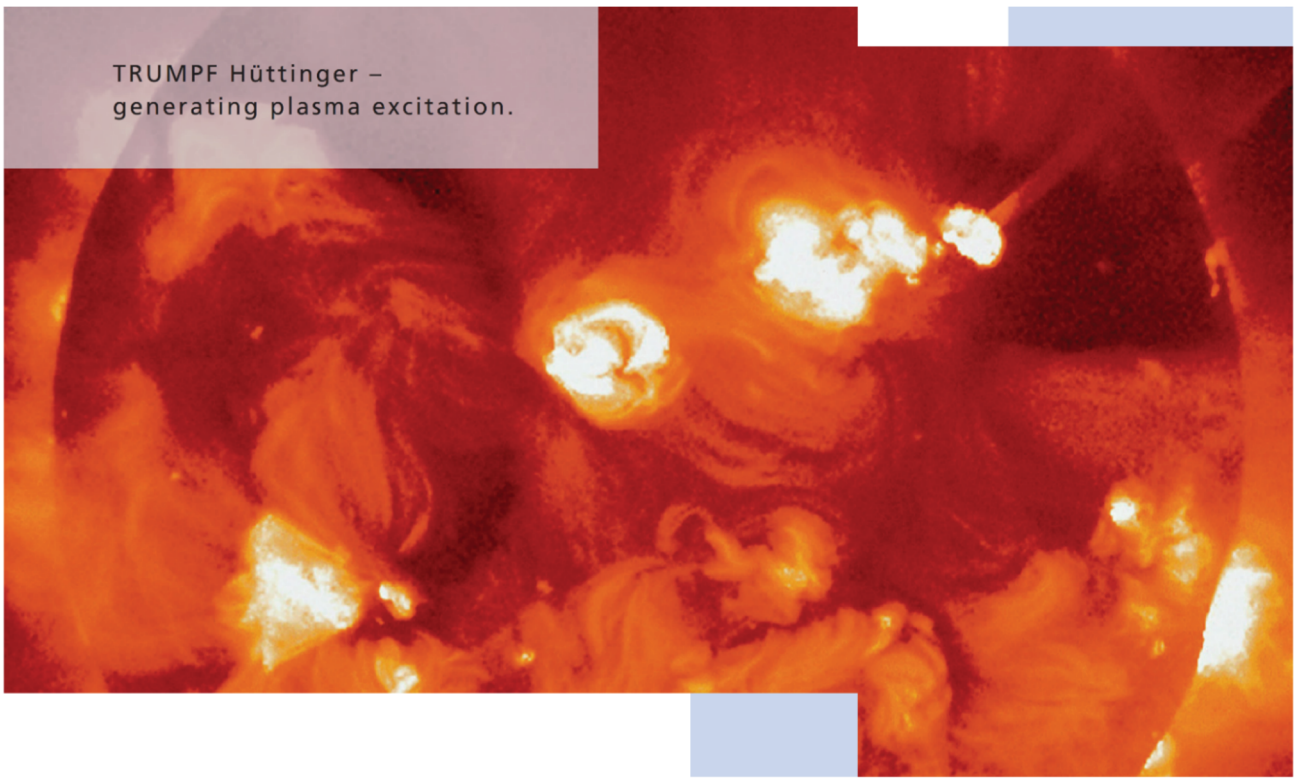

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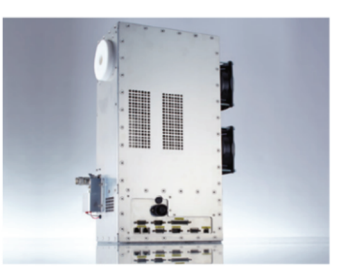

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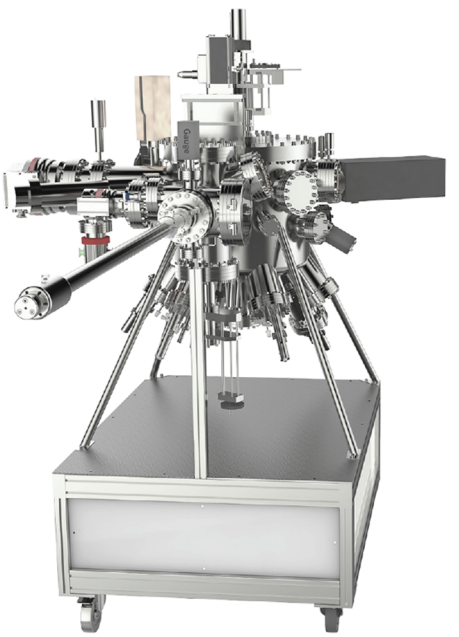

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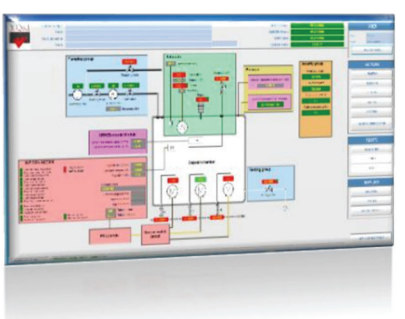

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