HIGH RATE PECVD OF A-C:H COATINGS IN A HOLLOW CATHODE ARC PLASMA



B. ZIMMERMANN¹, F. FIETZKE¹, H. KLOSTERMANN¹, J. LEHMANN², F. MUNNIK², W. MÖLLER²

¹⁾ FRAUNHOFER-INSTITUT FÜR ELEKTRONENSTRAHL- UND PLASMATECHNIK FEP, DRESDEN, GERMANY ²⁾ INSTITUT FÜR IONENSTRAHLPHYSIK UND MATERIALFORSCHUNG, HELMHOLTZ-ZENTRUM DRESDEN-ROSSENDORF, DRESDEN, GERMANY

INTRODUCTION

EXPERIMENTAL SETUP

ARC HOLLOW CATHODE »LAVOPLAS«

- large volume plasma source (plasma density of 10¹⁰ ... 10¹² cm⁻³ in a volume of several 100 l)
- magnetic field allows for reduced working gas flow \rightarrow strongly increased plasma density and range
- applications: plasma etching, plasma-assisted evaporation (e.g. Al) and reactive sputtering (e.g. CrN)







AMORPHOUS HYDROGENATED CARBON (A-C:H) FILMS

- 3 types of a-C:H: polymeric, graphitic, diamond-like carbon
- typical applications: tribological coating reducing wear or friction; biocompatible coating (implants)
- common deposition techniques: RF PECVD, (reactive) magnetron sputtering, arc evaporation

HOLLOW CATHODE ARC PECVD

- high rate PECVD: efficient activation of acetylene for a-C:H deposition with rates of up to 1 µm/min
- suitable for coating of large areas as well as 3D components



- sputter magnetron PPS 5 equipped with titanium target

PLASMA CHARACTERIZATION: ENERGY-RESOLVED MASS SPECTROMETRY

The reduction of the working gas flow rate (argon through the hollow cathode tube) leads to strongly increased acetylene (C₂H₂) dissociation. In the mass spectrum depicted below, signals recorded at three different values of working gas flow rate are shown. Signals of dissociation and polymerization as well as of hydrogenated residual gas and of working gas can be identified and the signal intensity increases with decreasing flow rate through the hollow cathode.

The ion energy distributions consist of a low energy peak (plasma potential: ions from the bulk plasma) and high energy tails (ions generated in the hollow cathode/anode vicinity at elevated potential). From the energy distribution shape of each single species (see depicted distribution functions), it can be derived that whereas dissociation is stimulated by high energy electrons near the hollow cathode orifice, polymerization predominantly takes place in the bulk plasma.



ratio mass number/elementary charge (amu)

-10 0 10 20 30 40 50 60 70 80 90 100

ion energy (eV)

ion energy (eV)

FEP

(discharge current 100 A, magnetic field 60 mT, constant argon/acetylene flow rates 100/200 sccm, 0.3 Pa)

(discharge current 100 A, magnetic field 60 mT, argon/acetylene flow rates 15/200 sccm, 0.1 Pa)

A-C:H FILM DEPOSITION AND ANALYSIS

- hollow cathode-based plasma pretreatment
- sputtering of 100 ... 200 nm titanium as sublayer
- arcPECVD of a-C:H (discharge current

The highest nanoindentation hardness has been reached in the case of substrate cooling and high substrate bias voltage (diamond-like a-C:H, substrate temperature up to 290°C). The content of hydrogen measured by elastic recoil detection analysis and Rutherford backscattering <u>spectrometry</u> (ERDA/RBS, with 1.7 MeV He⁺ ions) as well as of the sp³ sites obtained by Raman spectroscopy (see right figure) has been found to be medium. <u>Scanning electron microscopy</u> (small figure) reveals a dense microstructure and a smooth surface of the coatings.

Without substrate bias, soft **polymer-like films** have been produced with high hydrogen and sp³ contents, respectively, as the hydrogen atoms are predominantly bonded by sp³ sites to carbon atoms.

Without substrate cooling, high substrate temperatures of ca. 500°C were reached due to thermal load at high bias voltages resulting in graphitic film properties. The values of hardness, hydrogen and sp³ content are low in this case.

film character	thickness (nm)	hardness (GPa)	H content (at%)	sp ³ con- tent (%)	
polymeric	lymeric 250		42	40	
diamond-like	250	18.2	31	25	

100 A, magnetic field 60 mT, argon through hollow cathode tube 15 sccm)

and the second se	And Address of the Ad					and the second se	
	the second se						
of the Party of th	and the second se	Contract of the local division of the local	and the second se	and the second second second second	and the second s	and the second second second	

500nm SU8000 4.0kV 1.9mm x80.0k SE(U)

graphitic	500	6.1	18	20

CONCLUSIONS

REFERENCES

ArcPECVD has been found to be a versatile PECVD technique with very high deposition rates and simple technological assembly. Energy-resolved mass spectrometry reveals plenty of dissociation and polymerization products in the argon acetylene plasma; the energy distribution of the ions depends on the spatial distribution of their origin. A-C:H layers with a film hardness of up to 18.2 GPa have been deposited. First deposition experiments on small components treated as bulk good have been carried out successfully and will be published elsewhere. The presented results will be described in detail in a paper submitted to *Surface and Coatings Technology*.

F. Fietzke, H. Morgner, S. Günther, Plasma Process. Polym. 6 (2009) S242 B. Zimmermann, F. Fietzke, W. Möller, 54th SVC Ann. Tech. Conf. Proc. (2011) 337 B. Zimmermann, F. Fietzke, W. Möller, Surf. Coat. Technol. 205 (2011) S393 A. Buuron, F. Koch, M. Noethe, H. Bolt, Surf. Coat. Technol. 116-119 (1999) 755 J. Robertson, Mater. Sci. Eng. R 37 (2002) 129 C.A. Charitidis, Int. J. Refract. Mat. Hard Mater. 28 (2010) 51 A.C. Ferrari, J. Robertson, Phys. Rev. B 61 (2000) 14095

CONTACT

FRAUNHOFER-INSTITUT	ΡΗΟΝΕ	+49 351 2586-386
FÜR ELEKTRONENSTRAHL- UND PLASMATECHNIK FEP	FAX	+49 351 2586-55-386
BURKHARD ZIMMERMANN		
WINTERBERGSTRASSE 28	B U R K H A R D	.ZIMMERMANN@FEP.FRAUNHOFER.DE
01277 DRESDEN, GERMANY	WWW.FEP.	FRAUNHOFER.DE

ACKNOWLEDGEMENT

The authors gratefully acknowledge Bernd-Georg Krätzschmar for support in the technical realization of the experimental setup, Beate Leupolt from Fraunhofer-Institut für Werkstoff- und Strahltechnik Dresden for the Raman spectroscopy measurements, and Dr. Olaf Zywitzki and Dr. Thomas Modes for the nanoindentation measurements as well as the SEM analysis.