RUHR-UNIVERSITÄT BOCHUM



# Plasma-surface interactions: diagnostics

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#### Surface processes and reactive plasmas

Plasma controls surface processes: *deposition, etching, surface modification* 

Surface processes influence plasma properties:

 $Ar/O_2$  plasma cleaning of stainless steel reactor with hydrocarbon film on the wall:



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Plasma composition is determined by surface reactions!

#### Surface processes and hydrogen plasmas

Plasma controls surface processes: deposition, sputtering, surface modification

Surface processes influence plasma properties:

W impurity accumulation in the JET tokamak, UK



Nucl. Fusion 54 (2014) 083028

**Plasma composition is determined** by surface reactions Impurity accumulation plays a detrimental role on the performance

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JET tokamak wit the ITER-like wall (CCFE/JET)

 $P_{br} \propto Z^2 \qquad P_{line} \propto Z^4$ 

2

# How to address surface processes relevant to plasma deposition?

**Our goal** deposition of thin film or etching of wall material almost always a combination of deposition and etching



surface

Which plasma species arrive at the wall? Which energy do they have?

How do they react at the wall? How does the material form? plasma

How do they influence the plasma?



Which species leave the surface? What is their energy?

# **Key challenges**

- energy distributions (ions, fast neutrals)
- molecular radicals
- synergistic effects
- not well-defined surfaces
- heterogeneous surface reactions



#### The unreconstructed surface of nickel Scanning tunneling microscopy image





IBM Research, Almaden Research Center

surface

#### Cross-section of a-C:H film Molecular dynamics simulation



E. Neyts *et al.*, Diam. Rel. Mat. 13 (2004) 1873

#### Outline



Plasma-surface interactions – short summary

**Diagnostics of plasma surface processes** 

- ex-situ and in-situ plasma diagnostics
- beam experiments and growth models

#### Low energy particles at the surface



 $r + \gamma + s = 1$ 

Gas temperature in low pressure plasmas  $T_h \sim 300 - 2000 \text{ K}$ 

 $E_{k} \sim 0.026 - 0.17 \text{ eV}$ 

Lower than the binding energy between atoms in the material



Overall surface reaction probability:  $\beta = \gamma + s = 1 - r$ 

Surface reactions often depend on surface coverage

$$\theta = \frac{n_{surface,occupied}}{n_{surface,all}} \in \langle 0, 1 \rangle$$

# Interaction particle-substrate

**Physisorption** 

weak van der Waals dipole-dipole interaction

For metals:



interaction between particle and its virtual image



E. Zaremba, W. Kohn, Phys. Rev. B15, 1769 (1977) A. Zangwill, 'Physics at surfaces', Cambridge Univ. Press, Cambridge (1988)

#### Chemisorption

Electron exchange - chemical bond

By metals:

and

electron donated from conduction band

By insulators:

e.g. reaction at unpaired electron

 $\rightarrow$  radical site/dangling bond or radical insertion into existing bond

> Binding energy > 0.5 eV Minimum much closer to the surface



# When is a particle reflected and when captured at the surface?



# **Surface diffusion**



Surface diffusion can be promoted e.g. by ion bombardment.

# **Surface reactions**

Two basic mechanisms:

#### 1) Eley-Rideal



Direct reaction upon impact

- only barrier-less and exothermic reactions
- usually involves radicals

Reaction rate:  $R = k p_A \Theta_B$  f surface coverage pressure (~flux to the surface)

*T*prod > *T*substrate

Example:  $H(g) + H(s) \rightarrow H_2(g)$ hydrogen abstraction

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#### 2) Langmuir-Hinshelwood



Reaction of adsorbates at the surface

- most common surface reaction mechanism
- allows reactions between molecules

Reaction rate: 
$$R = k \Theta_A \Theta_B$$

Tprod~T substrate

Example: CO(s) + O(s) 
$$\rightarrow$$
 CO<sub>2</sub>

10

#### **Ion-surface interaction**

Typical ion energies in low pressure plasmas: eV - keV



Possible interaction at the surface:

- a) Reflection: used for surface diagnostic
   "Ion Scattering Spectroscopy" ISS
- b) Secondary electron emission important for a plasma ignition and operation:  $\gamma$ -coefficient
- c) Ion implantation: e.g. Plasma Immersion Ion Implantation (PIII);  $E_{ion} > 10 \text{ keV}$
- d) Structural changes in the material:
  enhanced cross-linking → ion assisted growth
- e) Sputtering of material

Dependent on ion energy

# Ion-surface interaction: stopping power

Ion interaction in the material:



#### **Ion-surface interaction: stopping power, example**



Stopping power: carbon on carbon



Data from: http://www.exphys.uni-linz.ac.at/stopping/ 13

## **Ion-surface interaction: binary collision cascade**



At the ion energy range of few eV to few keV: Binary Collision Approximation (BCA) can be used

TRIM code (TRansport of Ions in Matter)



Incoming ion

# Physical sputtering of target atoms



#### **Sputtering of graphite**



K. Krieger in 'lectures on plasma physics' Summer university for plasma physics (1993) TRIM is also valid for low energies ( $\sim E_{SB}$ ) but chemical effects can dominate the results.

Sputtering yield is dependent on M<sub>projectile</sub>

- more effective E transfer at higher M
- Drops at high energies
- energy deposited more into the volume
- Chemical reactions can enhance it
- chemical sputtering  $\rightarrow$  see later

#### E<sub>ion</sub> ~ 100–1000 eV: sputter yield can be estimated by Sigmund-formula (1969):

$$Y = \frac{\Gamma_{sputtered}}{\Gamma_{ions}} \sim \frac{E_{ion}}{E_{SB}} \frac{4m_im_t}{(m_i + m_t)^2} \frac{3\alpha}{4\pi^2}$$
$$\alpha = \alpha \left(\frac{m_t}{m_i}\right) \in (0.1 \div 2) \qquad \text{empirical factor}$$

16

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**Plasma-surface interactions – short summary** 

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- ex-situ and in-situ plasma diagnostic
- beam experiments and growth models

#### Surface reactivity $\beta$ : imaging of radicals interacting with surfaces (IRIS)







J. M. Stillahn *et al.*, Annu. Rev. Anal. Chem. 2008. 1:261–91 D. Liu *et al.*, Appl. Mater. Interfaces, 2009, 1 (4), pp 934–943

#### Surface reactivity $\beta$ : imaging of radicals interacting with surfaces (IRIS)

		Fxcited		Radiative	Dipole	Relative surface	
Species	Plasma sources	transition	$\lambda(nm)^a$	lifetime (ns)	(D)	reactivity <sup>b</sup>	Reference(s)
C <sub>2</sub>	C <sub>x</sub> H <sub>y</sub>	$A^1\Pi \leftarrow X^1\Sigma^+$	691	$1.85 \times 10^4$		_	143
$C_3$	C <sub>x</sub> H <sub>y</sub>	$A^1\Pi \leftarrow X^1\Sigma^+$	410	200	0.44	low/moderate	126, 139
CH	C <sub>x</sub> H <sub>y</sub> , CH <sub>3</sub> OH	$A^2 \Delta \leftarrow X^2 \Pi$	430	537	0.55	high	117, 139
CHF	CH <sub>x</sub> F <sub>4-x</sub>	$A^1A'' \leftarrow X^1A'$	571	$2.45 \times 10^{3}$	1.30	low/moderate	144
CF	$C_xF_y$	$A^2 \Sigma^+ \leftarrow X^2 \Pi$	224	26.7	0.64	low/moderate	65
$CF_2$	$C_xF_y$	$A^1B_1 \leftarrow X^1A_1$	226	61	0.44	low	65, 84
CCl	CCl <sub>4</sub> , CH <sub>4</sub> /Cl <sub>2</sub>	$A^2 \Delta \leftarrow X^2 \Pi$	279	105	_	_	145
CN	CH <sub>3</sub> CN, CH <sub>4</sub> /N <sub>2</sub>	$B^2 \Sigma^+ \leftarrow X^2 \Sigma^+$	387	65	0.50	high	140, 146
NH	NH3, N2/H2	$A^3\Pi \leftarrow X^3\Sigma^-$	336	440	1.39	low/moderate	130
$\mathrm{NH}_2$	NH3, N2/H2	$A^2A_1 \leftarrow X^2B_1$	598	$10 \times 10^3$	1.82	moderate	130
NO	NO, N <sub>2</sub> /O <sub>2</sub>	$A^2 \Delta \leftarrow X^2 \Pi$	226	205	0.16	_	147, 148
OH	${\rm H}_{2}{\rm O}, {\rm H}_{2}/{\rm O}_{2}$	$A^2\Delta \leftarrow X^2\Pi$	308	686	1.80	moderate	28, 149
SiCl	SiCl <sub>4</sub> , Cl <sub>2</sub> <sup>c</sup>	$B^2 \Sigma^+ \leftarrow X^2 \Pi$	297	10	_	—	150
SiCl <sub>2</sub>	SiCl <sub>4</sub> , Cl <sub>2</sub> <sup>c</sup>	$\mathrm{A}^1\mathrm{B}_1\!\leftarrow\!\!\mathrm{X}^1\mathrm{A}_1$	320	$4.5 \times 10^3$	1.46	low	135
SiF	SiF <sub>4</sub> , CF <sub>4</sub> <sup>c</sup> , SF <sub>6</sub> <sup>c</sup>	$A^2\Sigma \leftarrow X^2\Pi$	437	230	1.07	moderate	24, 101
$SiF_2$	SiF <sub>4</sub> , CF <sub>4</sub> <sup>c</sup> , SF <sub>6</sub> <sup>c</sup>	$\mathrm{A}^1\mathrm{B}_1\!\leftarrow\!\!\mathrm{X}^1\mathrm{A}_1$	225	6.2	1.23	low	24, 98
SiH	SiH4, Si <sub>2</sub> H <sub>6</sub>	$A^2 \Delta \leftarrow X^2 \Pi$	413	534	0.14	high	20, 107
$SiH_2$	SiH <sub>4</sub> , Si <sub>2</sub> H <sub>6</sub>	$\mathbf{A}^1\mathbf{B}_1\!\leftarrow\!\mathbf{X}^1\mathbf{A}_1$	580	111	0.16	moderate	109
SO	SO <sub>2</sub> , SF <sub>6</sub> /O <sub>2</sub>	$B^3\Sigma \leftarrow X^3\Sigma$	235	16.2	1.55	—	151
$SO_2$	SO <sub>2</sub> , SF <sub>6</sub> /O <sub>2</sub>	$\mathrm{A}^1\mathrm{B}_1\!\leftarrow\!\!\mathrm{X}^1\mathrm{A}_1$	300	$10 \times 10^3$	1.63	—	151

<sup>a</sup>Excitation wavelength for listed transition.

<sup>b</sup>Relative reactivity scale: low = < 0.1; low/moderate =  $\sim 0.1-0.3$ ; moderate =  $\sim 0.3-0.7$ ; high =  $\sim 0.7-1.0$ .

<sup>c</sup>Species of interest is produced during Si processing.

# Surface reactivity $\beta$ : well / cavity Experiments





C. Hopf, T. Schwarz-Selinger, W. Jacob, A. von Keudell, JAP 87, 2719 (2000)



# Measurement of $\beta$ in plasmas

Density of reactive species in front of a reactor wall

*Confinement time of a given species in the reactor* 



Flux lost at the surface

$$j_{lost} = \frac{1}{4} n_{wall} v \frac{\beta}{1 - \beta/2}$$

Special case (e.g. CH<sub>3</sub> radical)



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#### Effective diffusion length (empirical)



#### Determination of surface reactivity $\beta$ : decay in plasma afterglow

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A. von Keudell et al. unpublished

cps

Surface changes after switching off the plasma!

#### Determination of surface reactivity $\beta$ : decay in modulated plasmas

RUB

 $\rightarrow$  surface does not change significantly



#### Determination of surface reactivity $\beta$ : decay in modulated plasmas

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 $\mathrm{SiH}_{\!_{4}}$  partial pressure varied, total pressure constant

SiH<sub>4</sub> partial pressure constant, total pressure varied

Substrate temperature (°C)

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## Measurement of surface reactions: spinning wall experiment

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Donnelly et al., e.g.:

- P. F. Kurunczi et al., Phys. Rev. Lett. 96, 018306 (2006)
- L. Stafford et al., Pure Appl. Chem. 82, 1301 (2010)

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#### Measurement of surface reactions: spinning wall experiment

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Recombination of atomic oxygen:

L. Stafford et al., J. Vac. Sci. Technol. A 26 (2008) 455



Recombination of atomic chlorine:



Cl recombination depends on Cl₂ surface coverage → has to be considered in e.g plasma models

L. Stafford et al., J. Phys. D: Appl. Phys. 42 (2009) 055206



#### Measurement of surface reactions: spinning wall-effect of impurities

2 h

0.0

8.6

68.5

8.4

3.7

10.9

Spinning wall combined with Auger electron spectroscopy and evaporation sources.







L. Stafford et al., J. Vac. Sci. Technol. A 26 (2008) 455

Effect of controlled "contamination" on the surface on O atom recombination coefficient:



FIG. 6. Recombination coefficients,  $\gamma_0$ , of O-atoms on oxidized Si, measured before (cvcle 7) and after (cvcles 7-13) successive Cu doses of 1.4  $\times 10^{13}$ , 2.8  $\times 10^{13}$ , 5.6  $\times 10^{13}$ , 1.4  $\times 10^{14}$ , 8.4  $\times 10^{14}$ , and 3.4  $\times 10^{15}$  cm<sup>-2</sup>, respectively, and after the surface was recoated with sputtered Si for 2 h (cycle 14, open triangle) and 4 h (cycle 15, open square).

J. Guha et al., J. Appl. Phys. 105, 113309 (2009)

Small contamination can have large effect! The surface is not as clean as you think!

#### Outline



**Plasma-surface interactions – short summary** 

**Diagnostics of plasma surface processes** 

- ex-situ and in-situ plasma diagnostic
- beam experiments and growth models

#### Beam experiment to study surface reactions of "plasma" particles

Beam sources of radicals or ions are used to simulate in low pressure chamber the conditions in



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#### Beam experiments: CH<sub>3</sub>|H synergism, simple vs. extended model

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30

# Measurement of surface reactions: infrared absorption



M. Meier, A. von Keudell JAP 90, 3585 (2001)

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2600

2800

FTIR absorption spectra of an a-C:H film

sp<sup>3</sup>CH<sub>3</sub> asy

3000

3000

wavenumber (cm<sup>-1</sup>)

sp<sup>2</sup>CH, olef, sym

sp<sup>2</sup>CH olef

sp<sup>2</sup>CH aromat

sp<sup>2</sup>CH<sub>2</sub>

olef, asy

3100

**†**10<sup>-4</sup>

3200

Evolution of an FTIR spectrum after turning off the CH<sub>3</sub> radical source



FTIR can also be used in combination with isotopes (e.g. flux of D or  $D_2$ )

## "Simple" test of a growth mechanism

Analysis of a T-dependent growth of a-C:H films from electron cyclotron resonance  $CH_4$  discharge



in CH<sub>4</sub> plasma





#### → combination of constant deposition rate with T-dependent film erosion by hydrogen

#### **Beam experiments:** ion-assisted film growth: energy dependence of *s*(CH<sub>3</sub>| H<sub>2</sub><sup>+</sup>)



A. von Keudell, M. Meier, C. Hopf, Diamond and Related Materials 11, 969 (2002)

## Beam experiments: ion-assisted film growth: film properties



A. von Keudell, M. Meier, C. Hopf, Diamond and Related Materials 11, 969 (2002)

# Beam experiments in study of physical and chemical sputtering

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Sputtering of graphite



K. Krieger in 'lectures on plasma physics' Summer university for plasma physics MPI für Plasmaphysik (1993)

#### Beam experiments allow:

- measurements of absolute sputtering yields
- determination of angular dependence
- study of different chemistries

# Angular dependence of sputtering yield: physical sputtering





Ion incident angle (degree from normal)

Dependence of etching yield on ion incident angles Formation of "grass" due to micromasking

Lecture Notes on Principles of Plasma Processing F.F. Chen, J.P. Chang http://www.ee.ucla.edu/~ffchen/Publs/Chen208i.pdf

#### Angular dependence of physical sputtering yield: TRIM calculation



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# Angular dependence of sputtering yield: chemical sputtering





Lecture Notes on Principles of Plasma Processing F.F. Chen, J.P. Chang

#### Depends on material:

Cl can be easily implanted into poly-Si  $\rightarrow$  chem. sput. but not into SiO<sub>2</sub>  $\rightarrow$  physical sputtering

[1] J.P. Chang *et al.*, JVSTA15, 1853 (1997)

Proper angular dependence for each material has to be incorporated into profile simulators

#### Reactive sputtering: molecular dynamic simulation



Fig. 11. Sputtering yield of polysilicon by Cl<sup>+</sup> in the low energy regime, in comparison to molecular dynamic simulation results and low energy sputtering yield by Ar<sup>+</sup>.



Cl-rich surface layer – reduces the surface binding energy – lower threshold, higher yield...

#### **Beam experiments: chemical sputtering**



The famous plasma surface interaction experiment by Coburn and Winters JAP 50, 3189 (1979)



# Key features in the success of chemical sputtering

Anisotropy, selectivity, removal of etch products

*Chemical etching*: selective, fast, good removal of etch products, but no anisotropy Physical sputtering:

anisotropic, but not very selective, slow and problems with removal of etch products



# Conclusions

# Plasma is a unique tool for surface modification

- provides reactive radical species with high reactivity at the surface
- provides energetic ions  $\rightarrow$  essential for selective and anisotropic etching
- allows film growth at low substrate temperatures

# Surface processes are determined by

- the fluxes of incoming species (including their energy and angular distribution)
- the state of the surface (temperature, composition roughness, passivation...)
- synergistic mechanisms between different species at the surface

# Surface processes can be analyzed in

- particle beam experiments
- time resolved experiments (modulation of plasma, afterglow decay)
- time resolved measurement of surface properties (IR absorption, isotopic studies)
- spinning wall experiments, rotating substrate experiments
- well/cavity experiments
- molecular dynamic simulations, TRIM simulations

- ...

K. W. Kolasinski, Surface Science, John Wiley & Sons Ltd., 2002

A. Zangwill, 'Physics at surfaces', Cambridge Univ. Press, 1988

M. Nastasi, J.W. Mayer, J.K. Hirvonen, *Ion-solid interactions: Fundamental and applications*. Cambridge University Press,1996

F.F. Chen, J.P. Chang, *Lecture Notes on Principles of Plasma Processing* http://www.ee.ucla.edu/~ffchen/Publs/Chen208i.pdfc

W. Eckstein, *Computer Simulation of Ion Solid Interactions*. Springer Series in Materials Science, Berlin and Heidelberg, 1st edition, 1991.

P. Sigmund. Sputtering by ion bombardment: Theoretical concepts. In R. Behrisch, editor, *Sputtering by Particle Bombardment I*, pages 9-71. Springer, Berlin, 1981.

J.W. Coburn, H. Winters, JVSTA16, 391 (1979)