Surface phenomena related to degradation of EUV mirrors

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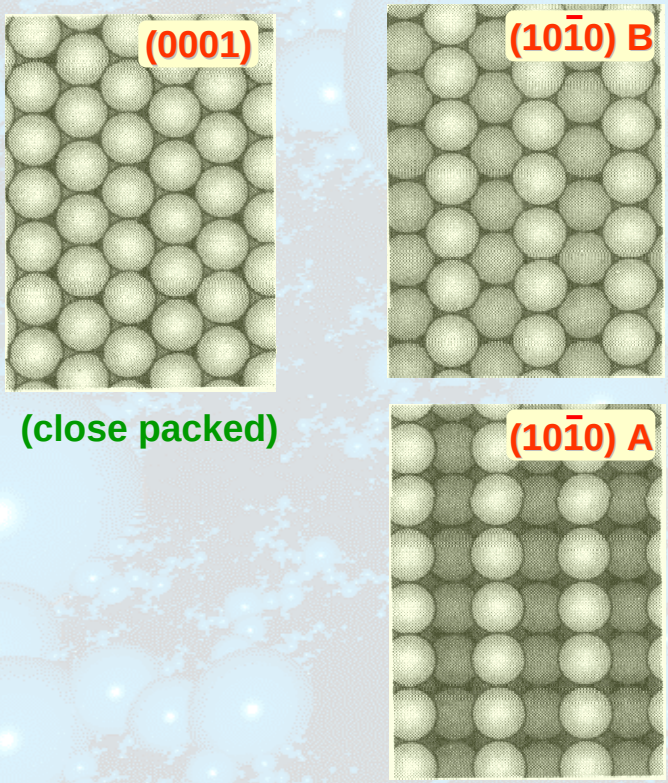
Topics

Atomic structure of Ru surfaces in some capping layers



(close packed)

(atomically rough)

The (0001) and (10$\bar{1}$0) faces of an ideal *hcp* crystal – possible surfaces in capping layers

- **Interaction of H_2O, O_2 with surfaces**
  focus on H_2O , O_2/Ru adsorption, desorption, reaction
- **Electron- and photon-stimulated surface processes**
  desorption, dissociation, oxidation
- **Plans, new results**
  different Ru surfaces, e-beam effects

Adsorption, desorption, dissociation of H_2O on metal surfaces

Thermochemical predictions:

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

← *Dissociation*

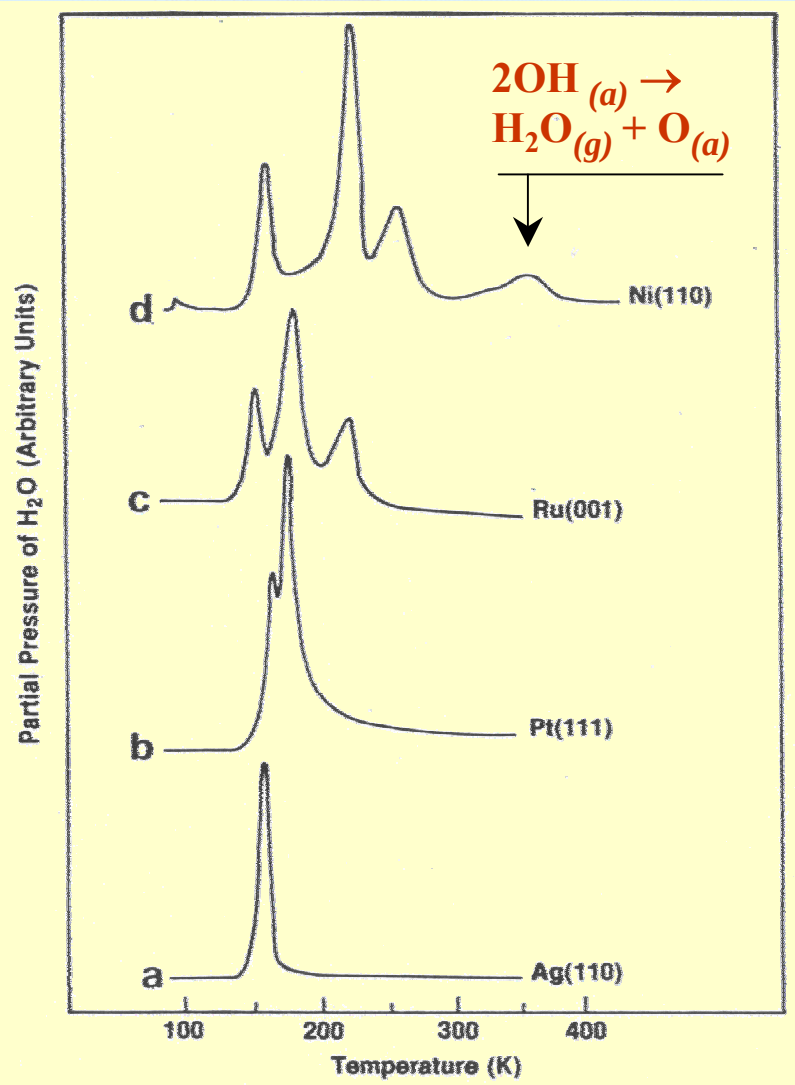
← *Borderline case*

← *Molecular adsorption*

Predictions:

Complete dissociation means

$$H_2O_{(a)} \rightarrow 2H_{(a)} + O_{(a)}$$



Thermal desorption spectra of water adsorbed on (a) Ag(110), ε = 3.0 L; (b) Pt(111), ε = 3.8 L; (c) Ru(0001), ε = 2.0 L; (d) Ni(111)

P.A.Thiel and T.E.Madey,
Surf. Sci. Rpts. 7 (1987) 211-385

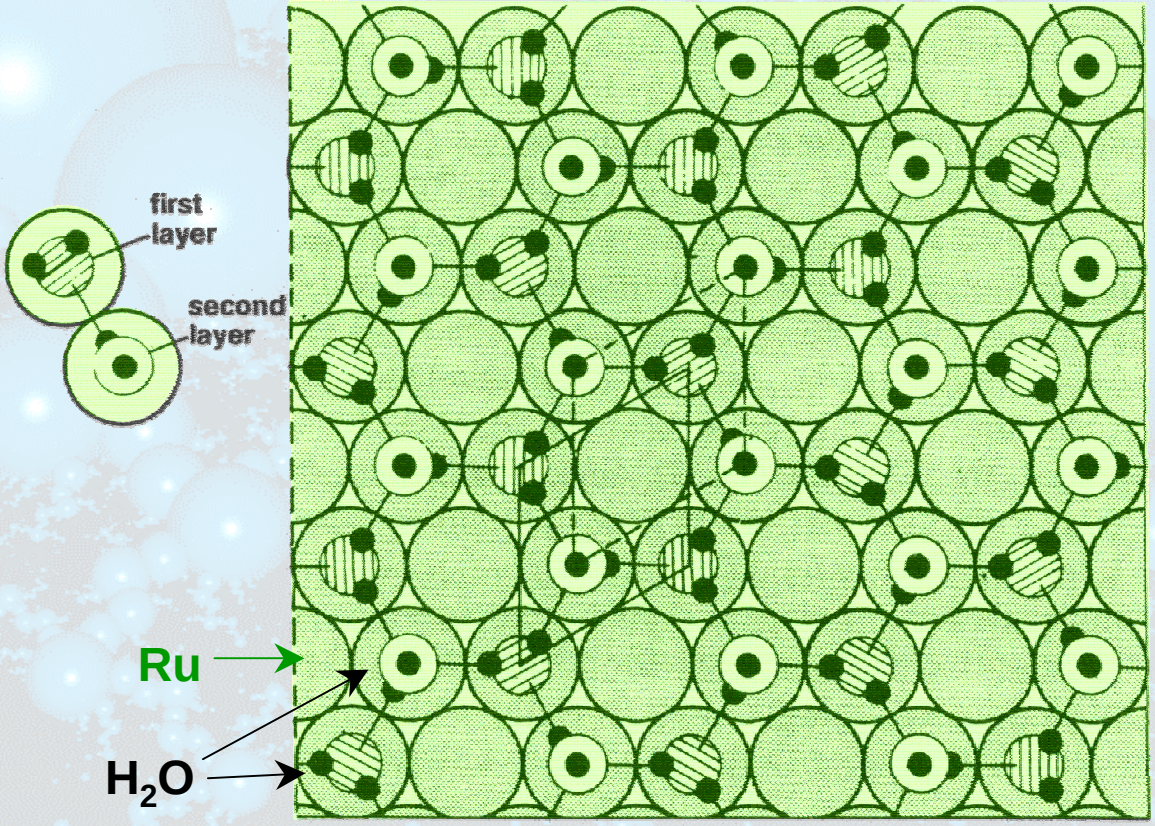
Bilayer structure of molecular water on Ru(0001)

– a subject of great current interest (molecular vs. partial dissociation)

$\tau \cong \tau_o \cdot \exp(E / RT)$

At steady state,
T = 300K, E ≅ 60 kJ/mol,
p ≅ 5×10^{-6} Torr H_2O,

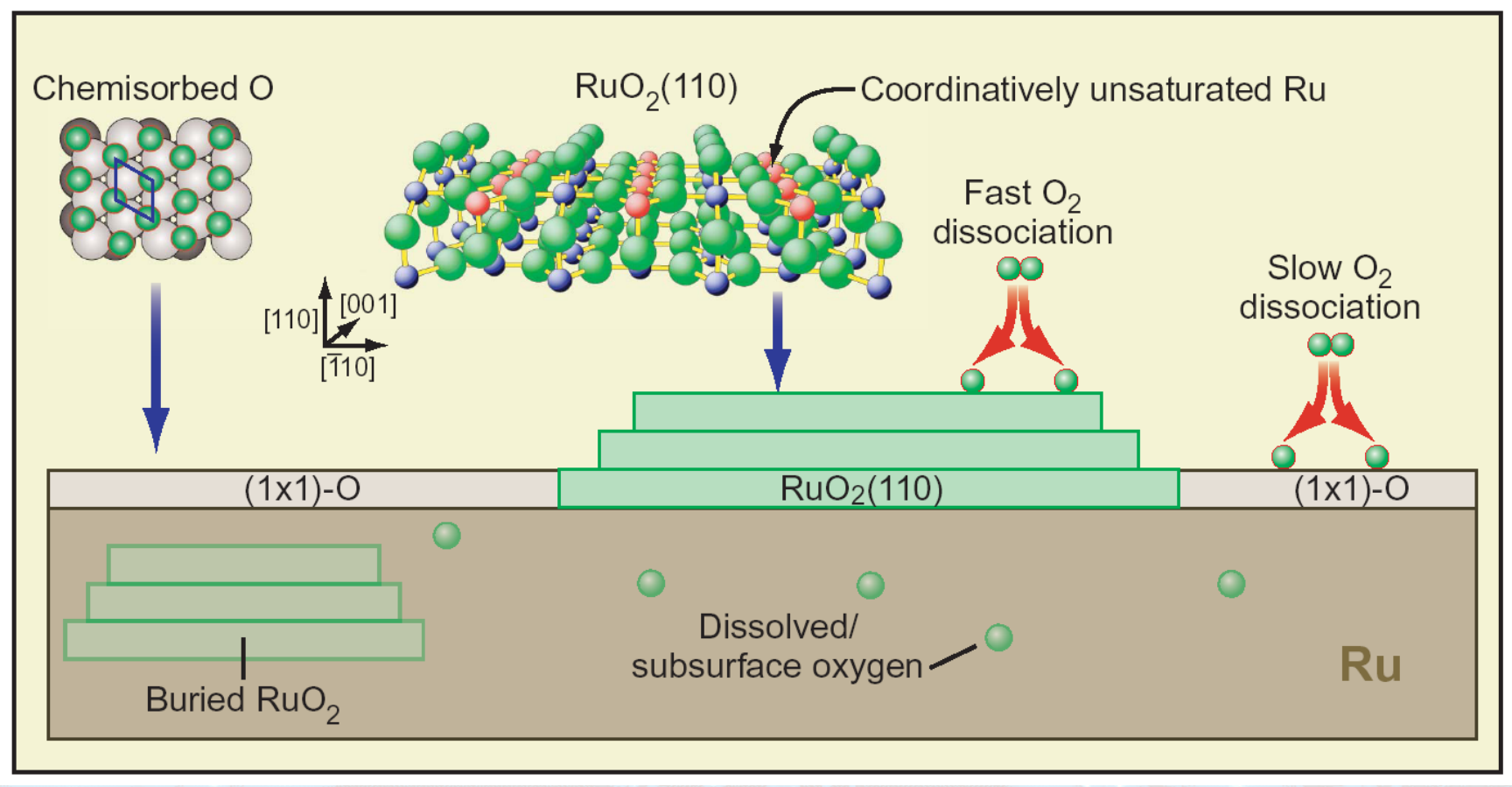
Coverage
$\theta = S \cdot F \cdot \tau \cong 0.01$ **ML**



Water monolayer on Ru(0001)

D.L. Doering and T.E Madey, Surf. Sci. 123 (1982) 305; P. J. Feibelman, SCIENCE 295 (2002)99

The rich oxygen chemistry of Ru(0001)

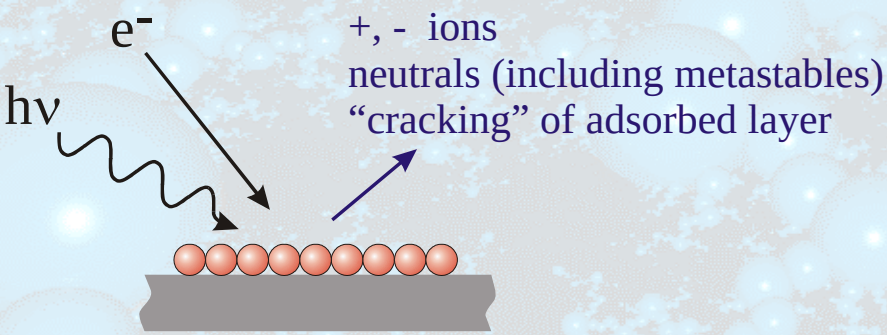


Chemisorbed oxygen, **surface oxide**, **buried oxides**, and **subsurface oxygen** may **coexist in the near-surface region**. This complexity is characteristic of the oxygen chemistry of many transition metal surfaces.

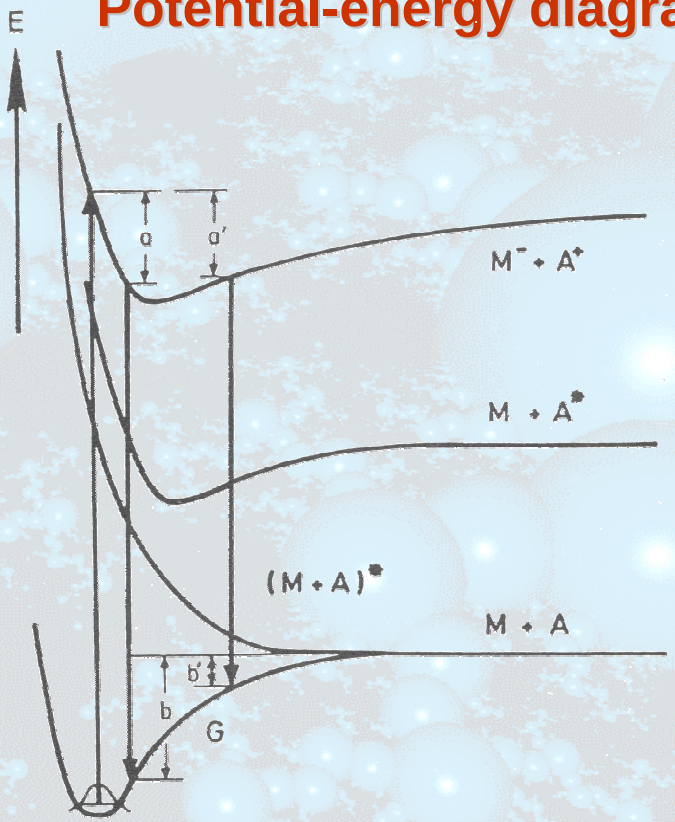
H. Over et al., Science 297 (2002) 2003-2005

Electron- and photon- stimulated desorption and dissociation

Desorption and dissociation of surface species



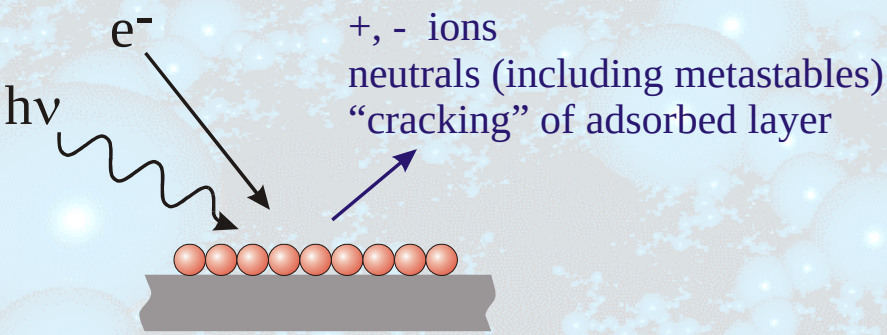
Potential-energy diagram



- electronic excitation;
- rearrangement to a repulsive electronic state
- conversion of repulsive energy to nuclear motion

Electron- and photon- stimulated desorption and dissociation

Desorption and dissociation of surface species



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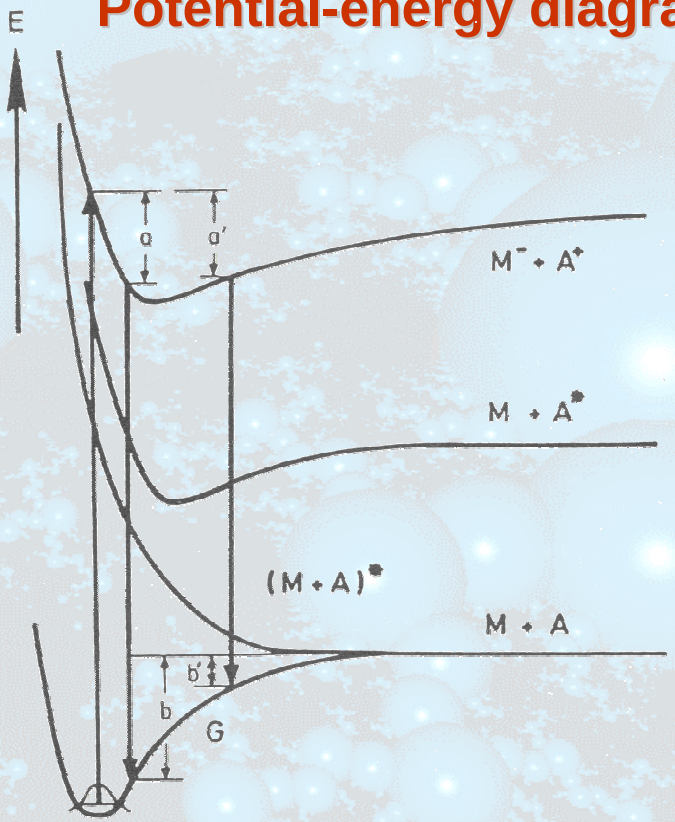


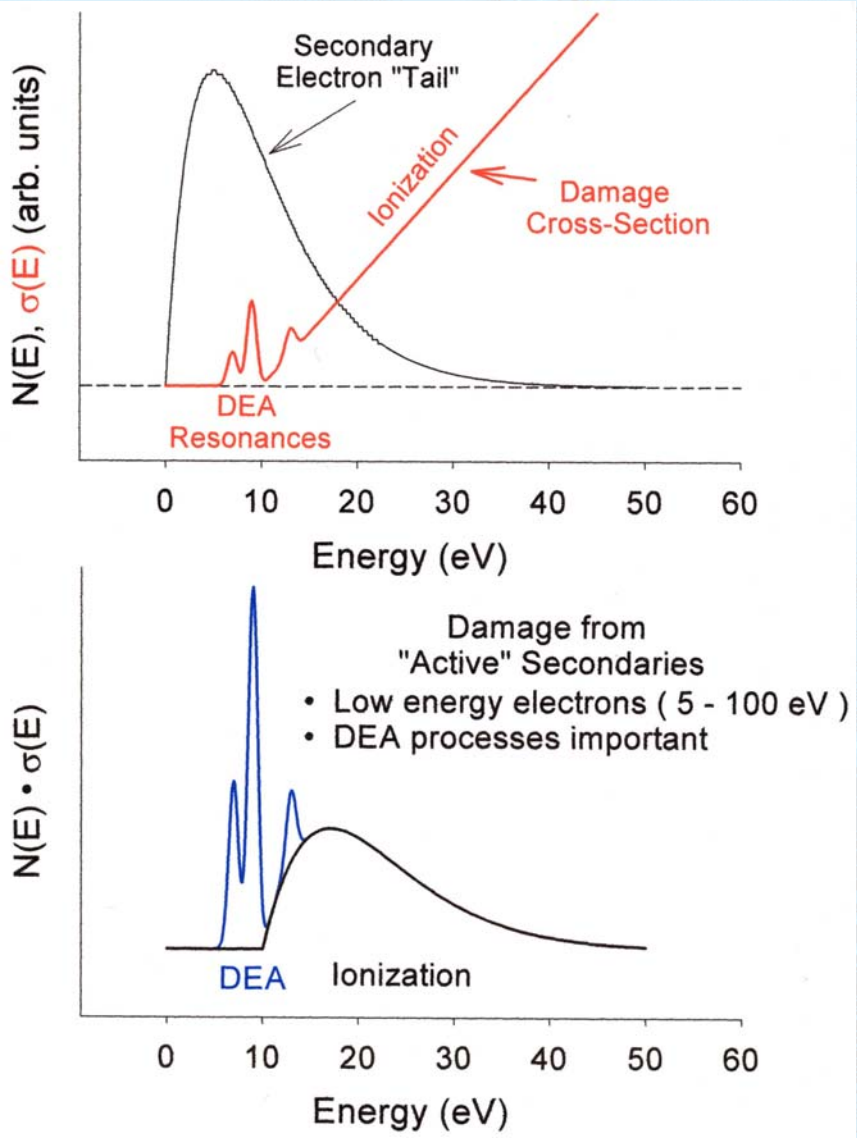
Break bonds via

- **direct process:** **hν (or e-beam) excitation of molecules**
- **indirect process:** **low energy secondary electrons**

The importance of low energy "secondary" electrons

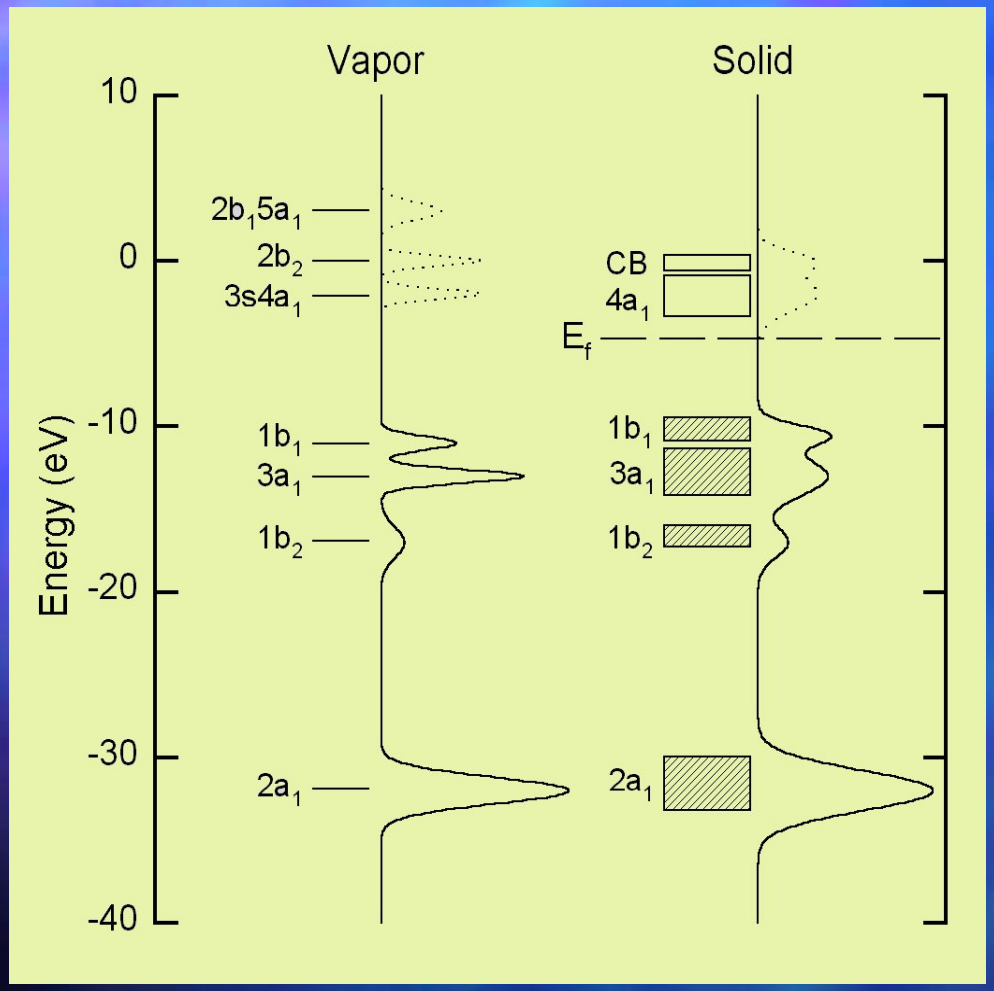
- **Low-energy processes are particularly important, but not well-understood.**

- **Pathways include ionization, dissociative electron attachment (DEA) resonances, and excited state (exciton) formation.**

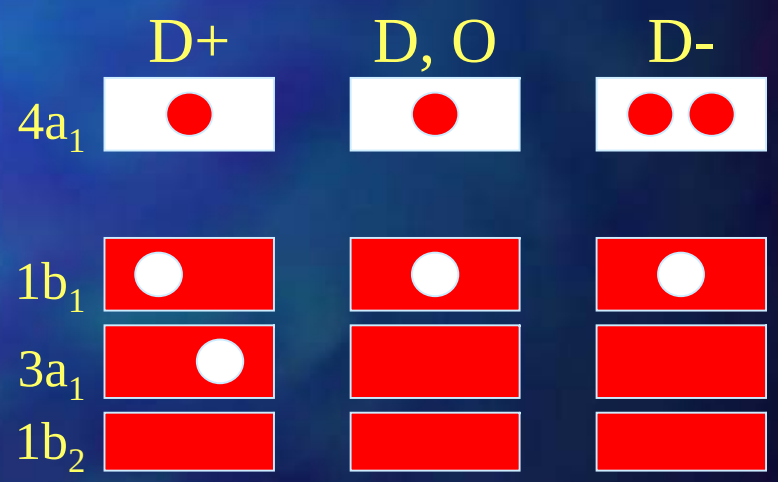


T. M. Orlando and D. Meisel, Chapter 17, 2001, ACS Symp. Series 778

The electronic structure of water and ice



- $4a_1$ is an anti-bonding orbital, excitonic in nature.
- Some dissociative electronic excitations of water:

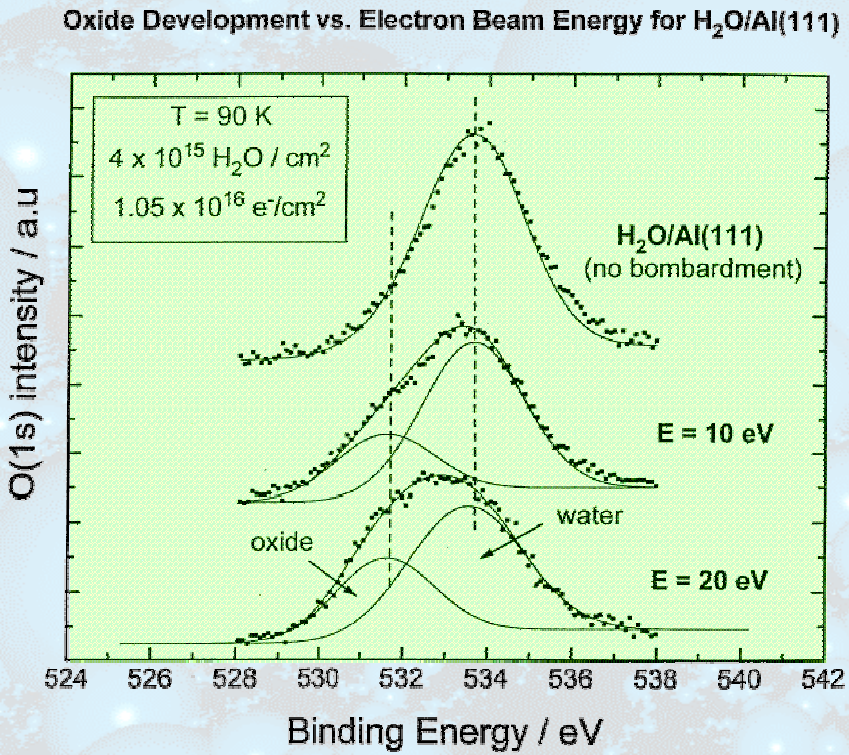


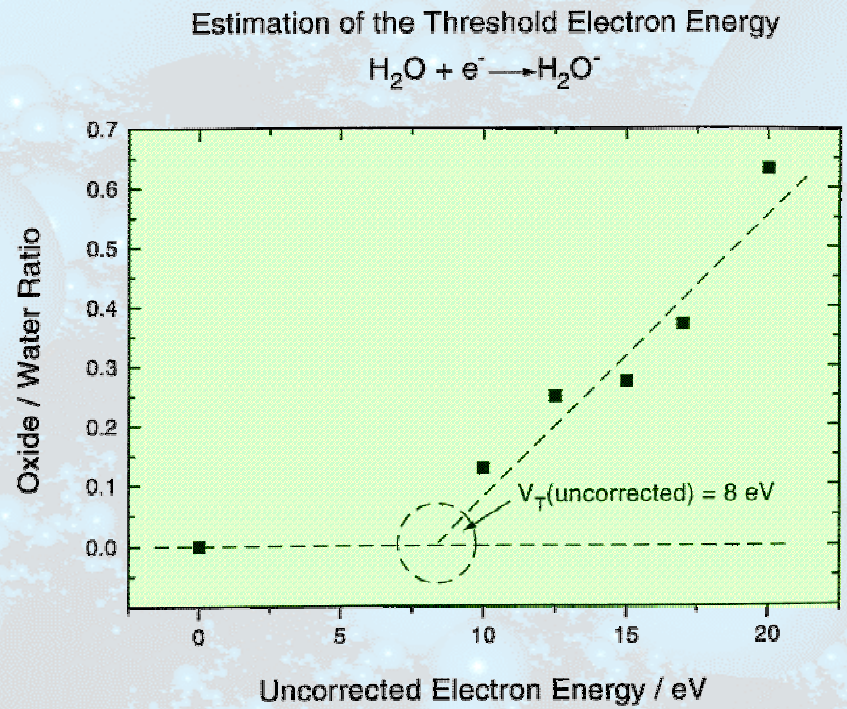
Narrowing of states produces increase in lifetime and therefore dissociation

T.M.Orlando et al.

Electron-induced oxidation of Al: electron bombardment of ultrathin ice film (~4 ML) on Al at 90K

H.D. Ebinger, J.T. Yates, Jr / Surface Science 412/413 (1998) 1–11



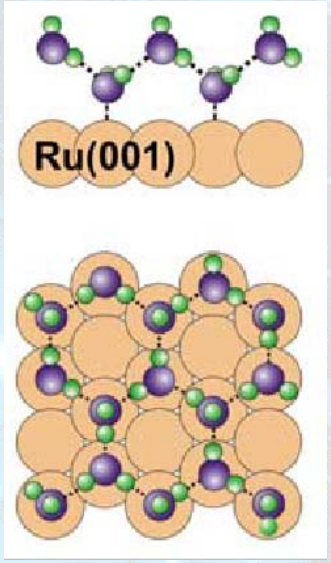


XPS after e-bombardment of the H_2O-covered surface at 90 K with various electron E at a constant electron fluence:
- The **upper spectrum - after 4×10^{15} H_2O cm^{-2} water deposition**.
- The two **lower spectra - the result of 10 and 20 eV electron bombardment** (the same electron fluence and water coverage).

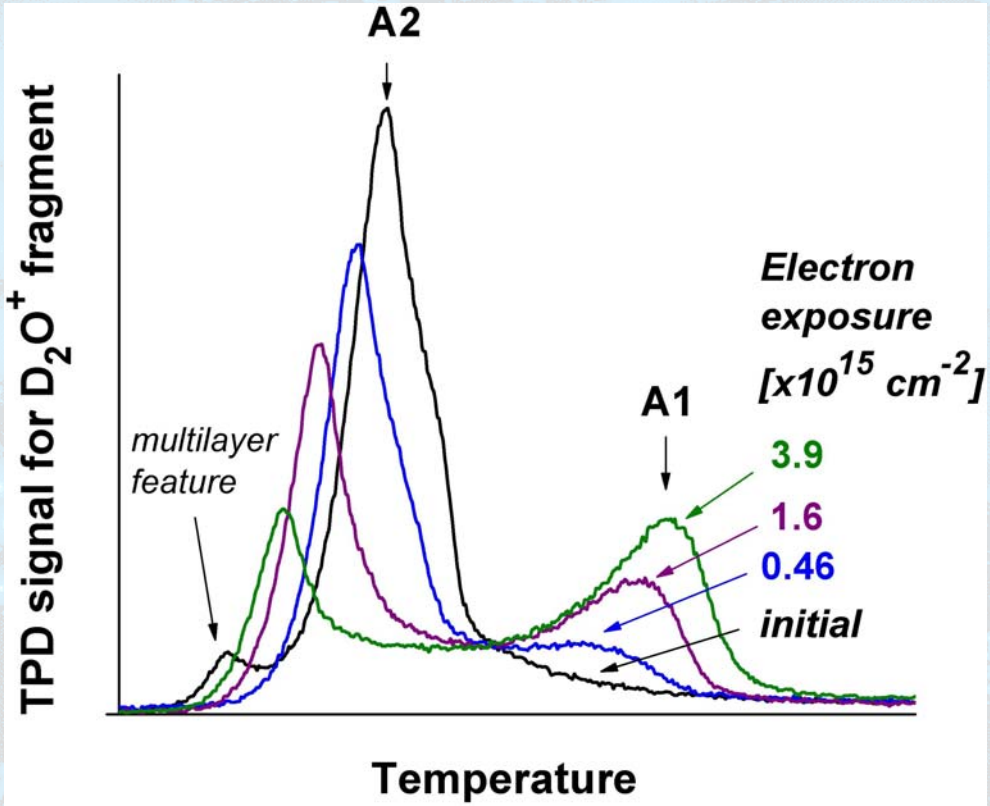
Peak area **ratio of oxide and water** O 1s component as obtained from XPS curve fitting **as a function of E**. The kinetic energy of the electrons is not corrected for the work function difference between sample and electron gun. From extrapolation, an **uncorrected threshold** electron energy for the water conversion process is of about **8 eV**. A **threshold corrected** for work function differences is of **6±1 eV**.

Electron-induced dissociation of water on Ru(0001)

Bilayer structure of D_2O on Ru(0001)



Modification of TPD spectra during irradiation of 1ML D_2O on Ru(0001) by 90 eV electrons

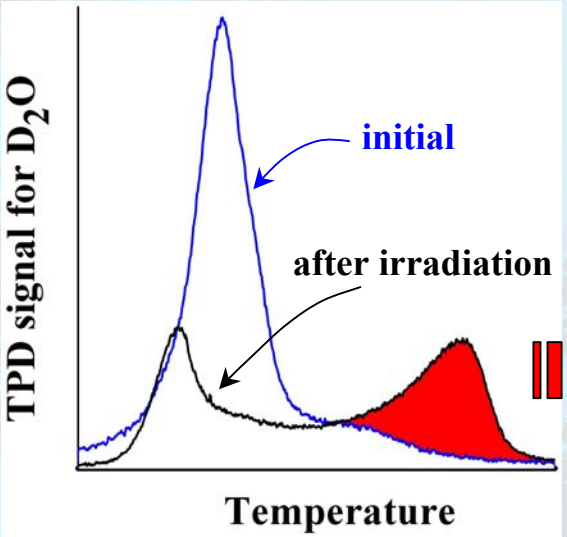


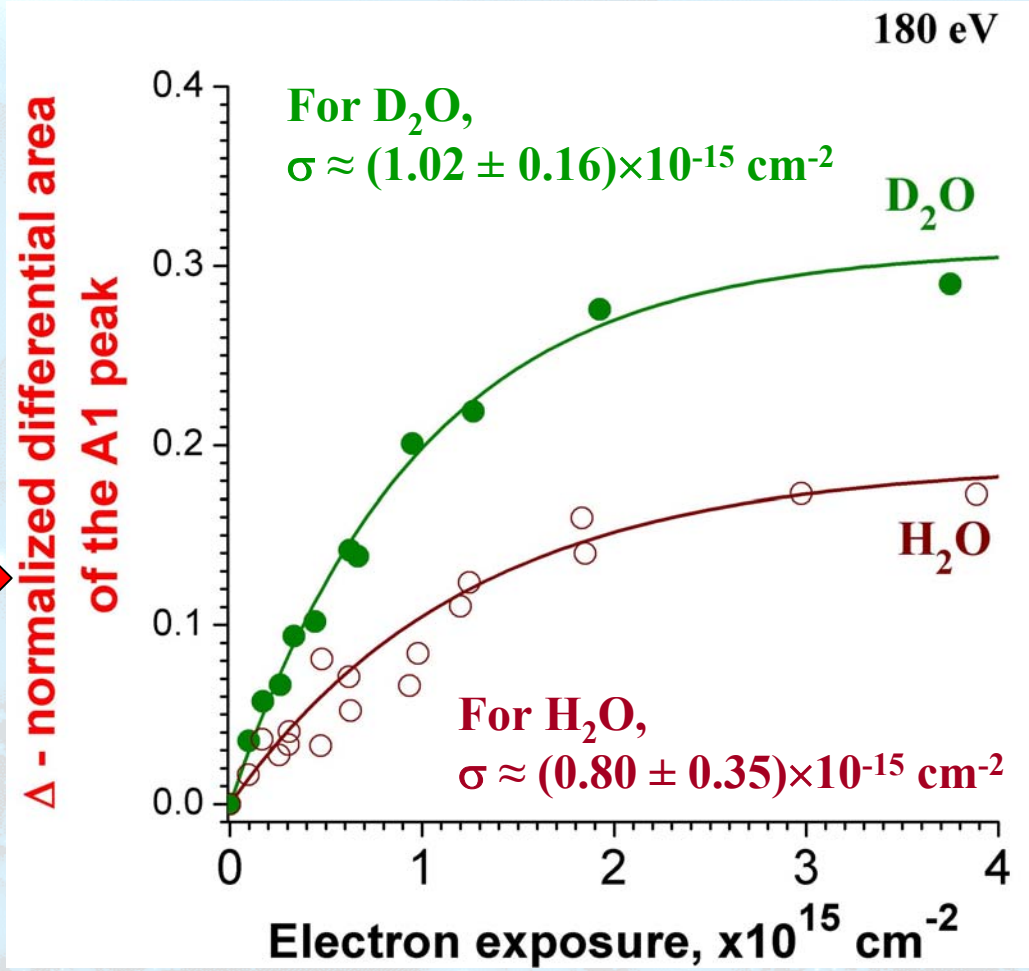
Appearance of A1 peak indicates water dissociation

N. Faradzhev, D. Menzel and T. E. Madey, in preparation

Electron-induced dissociation of water on Ru(0001)

How effectively does water dissociate?

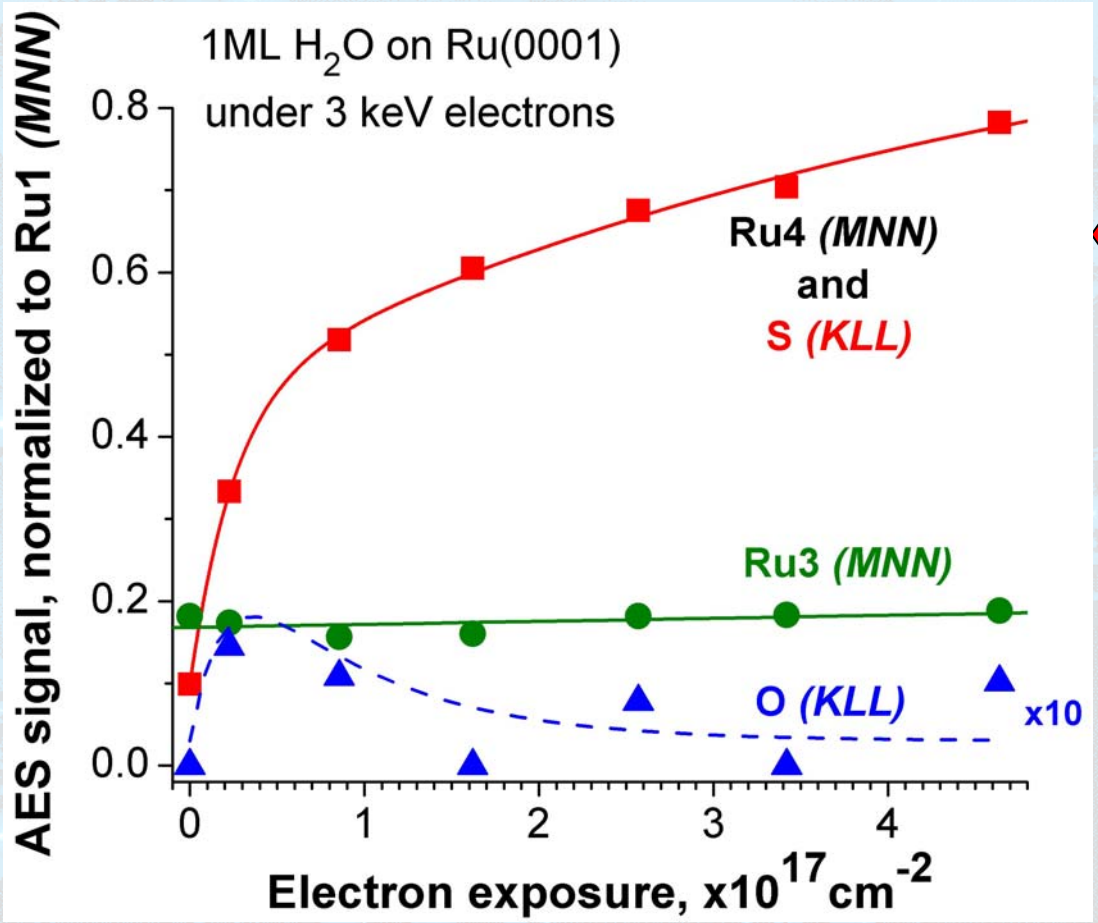


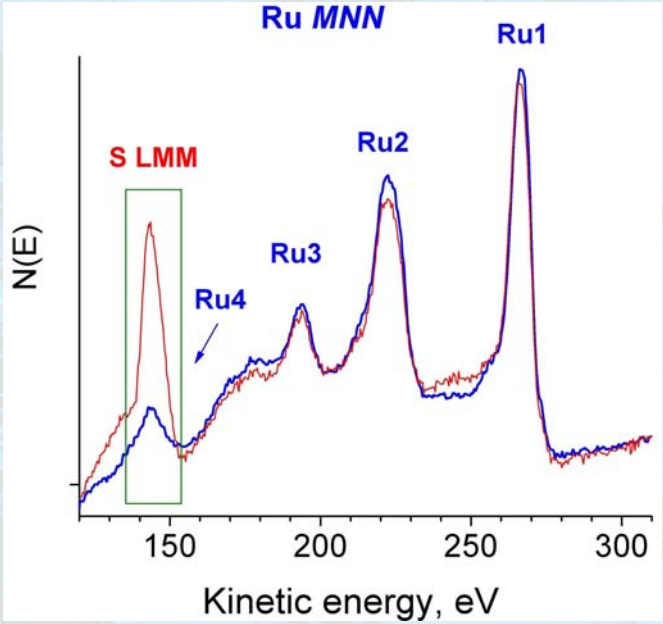


- **One H_2O molecule dissociates to H+OH for every electron bombarding the surface!**
- **Cross section σ for $e^- + OH \rightarrow O + H$ is ~ 50× smaller**
- **Steady state coverage of H_2O at 300K is ~ 0.01ML**

Traces of S-containing gases can block oxidation by e-beam

Initially p ~ 8×10^{-11} Torr
Introduce H_2O at p ≈ 2×10^{-6} Torr, e-beam





Surface contamination under e-beam depends on "History" of vacuum chamber; Traces of S-containing gas can block e-beam oxidation

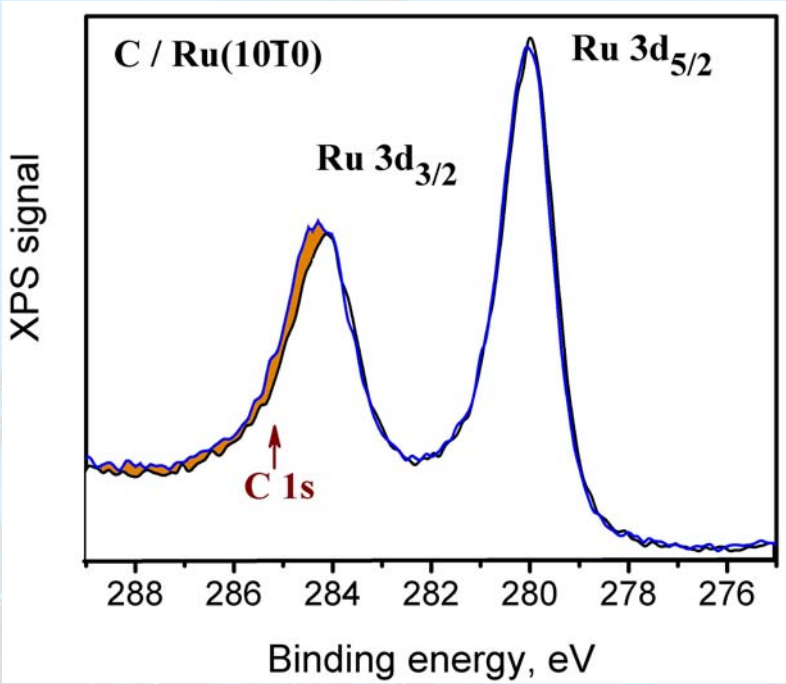
$E = (I \bullet t) / (q \bullet A)$

$I=1.2\ \mu A$; $A=13\ mm^2$; $q=1.6\times10^{-19}$ C

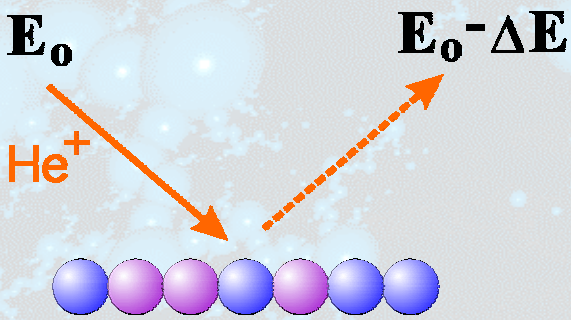
t=60 min => E≈2.5×10^{17} e/cm^2

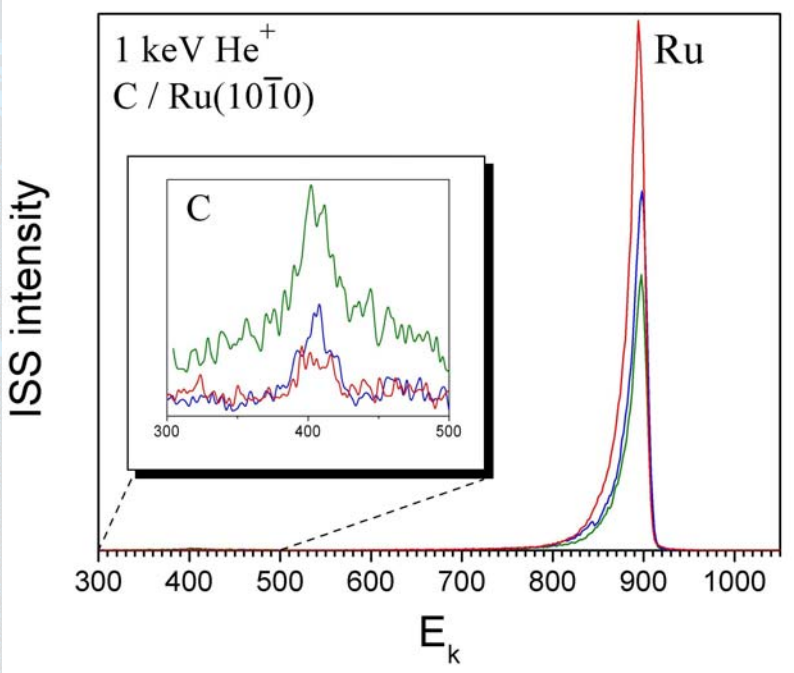
Detection of Carbon on Ru

Carbon growth may inhibit oxidation – but a carbon monolayer on Ru is hard to detect in XPS



To measure onset of C reactions, a sensitive spectrometry is needed: low energy ion scattering (LEIS)





Summary of H_2O, O on Ru

- **H_2O adsorbs, desorbs mainly in molecular form**

  Little adsorption on Ru at 300K (ca. 0.01 ML)
  Impurity O(ads) increases H_2O binding energy

- **Electron- and photon-stimulated surface processes**

  dissociation of H_2O by low-energy electrons
  electron-stimulated O incorporation expected
  (absorbed O, oxide)

- **Inhibition or remediation of oxides may be possible**

  role of S, C in trace background gases

- **The future – how do kinetics of adsorption, reaction, oxidation depend on atomic structure?**