Photochemistry on Surfaces – Applications to EUV Mirror Cleanup

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Outline of Talk

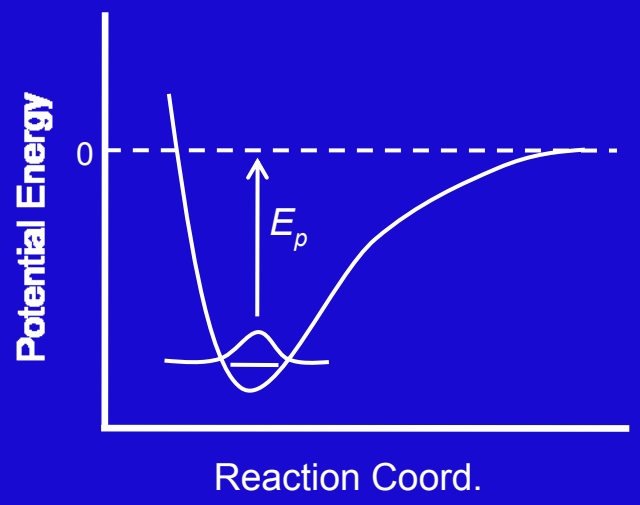
- Fundamentals of the Photoexcitation of Molecules on Surfaces

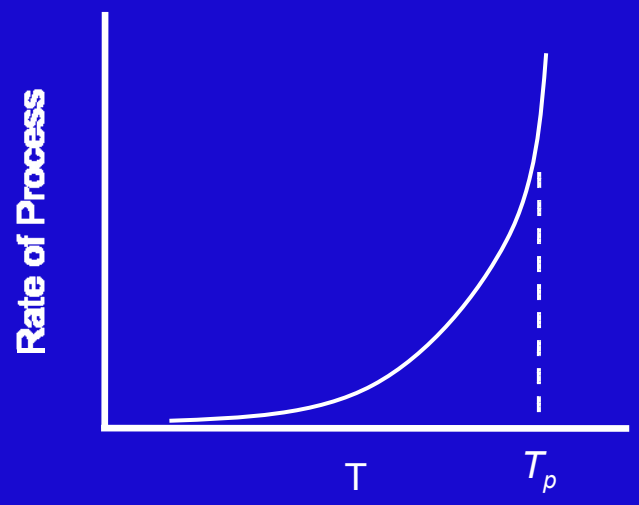
  -- Thermal and electronic excitation processes in adsorbed organic molecules.
  -- Charge transfer through molecules
  -- Secondary electrons from incident photons
  -- Chemistry induced by low energy electron attachment to molecules

- Photooxidation of Organics on TiO_2 Surfaces

  -- Electron-hole pair production
  -- Cleaning organic films by sunlight
  -- Kinetics of photoprocesses – role of electron-hole recombination
  -- Special sites for oxygen on TiO_2?

Thermal Excitation of a Process at a Surface

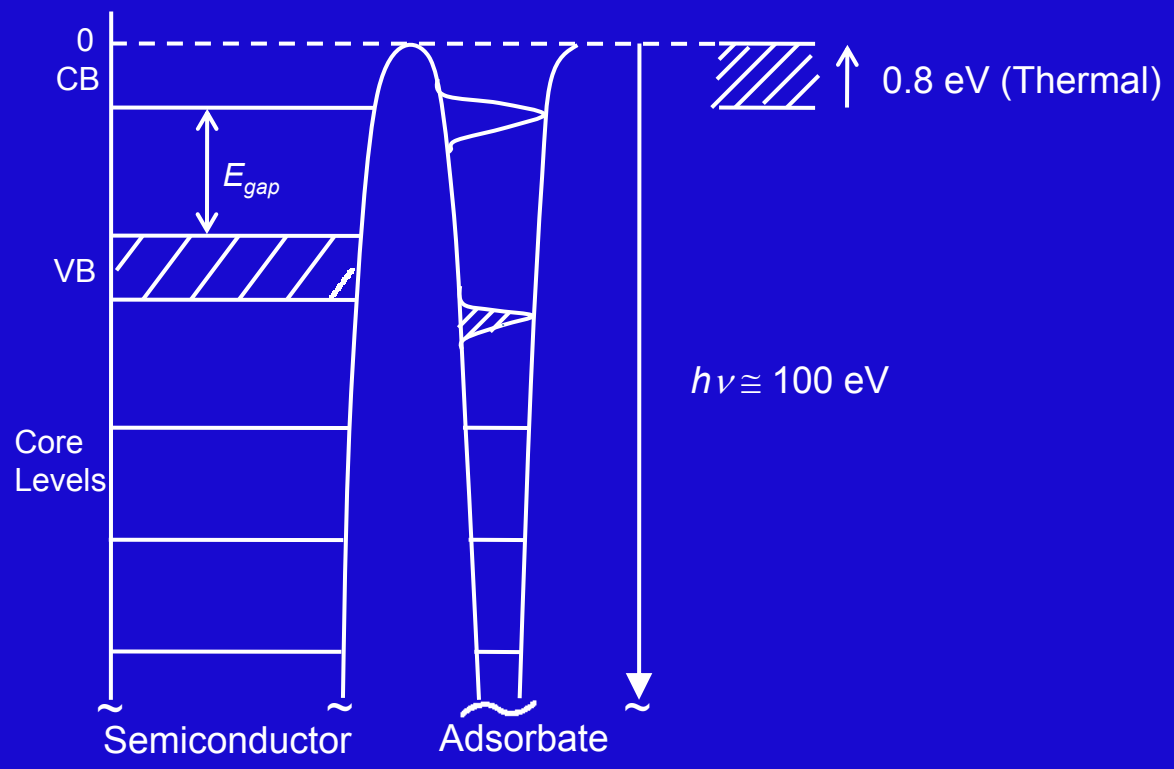




At T_p = 300 K, $E_d \cong$ 20 kcalmol^{-1} $\cong$ 0.8 eV

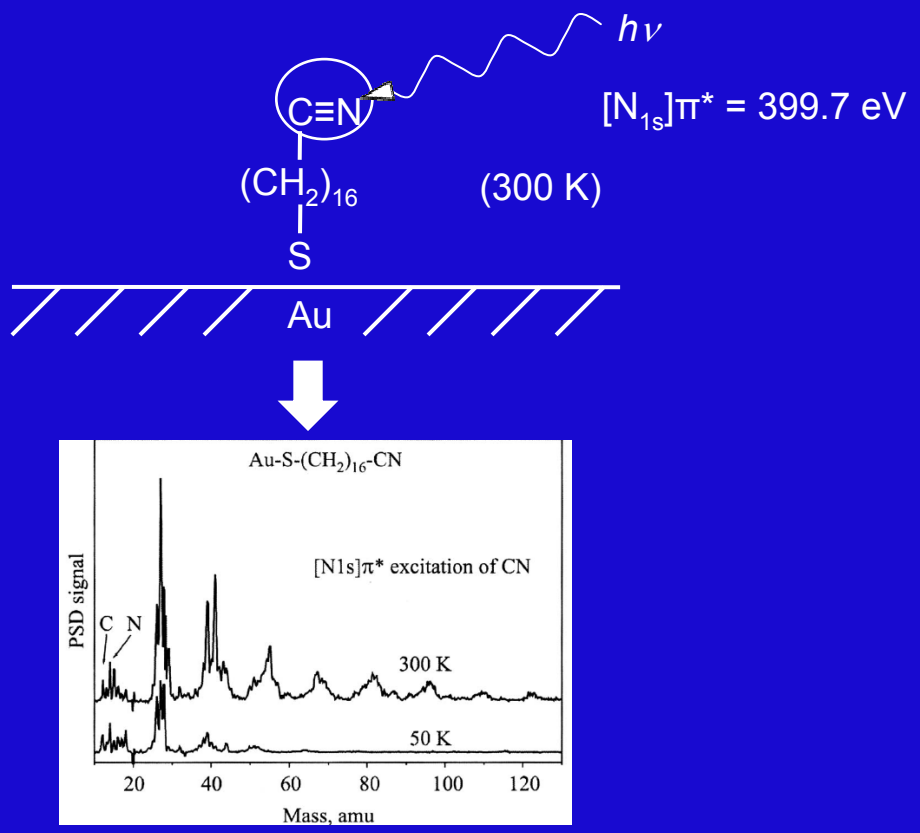
- This is the typical energy regime for thermally-activated surface CHEMISTRY near 300 K.

Electronic Excitation at a Semiconductor Surface



• For surface photo chemistry excited by deep excitation many processes can occur, in the solid and in the adsorbate electronic systems.

Localized Direct Excitation in an Adsorbed Molecule

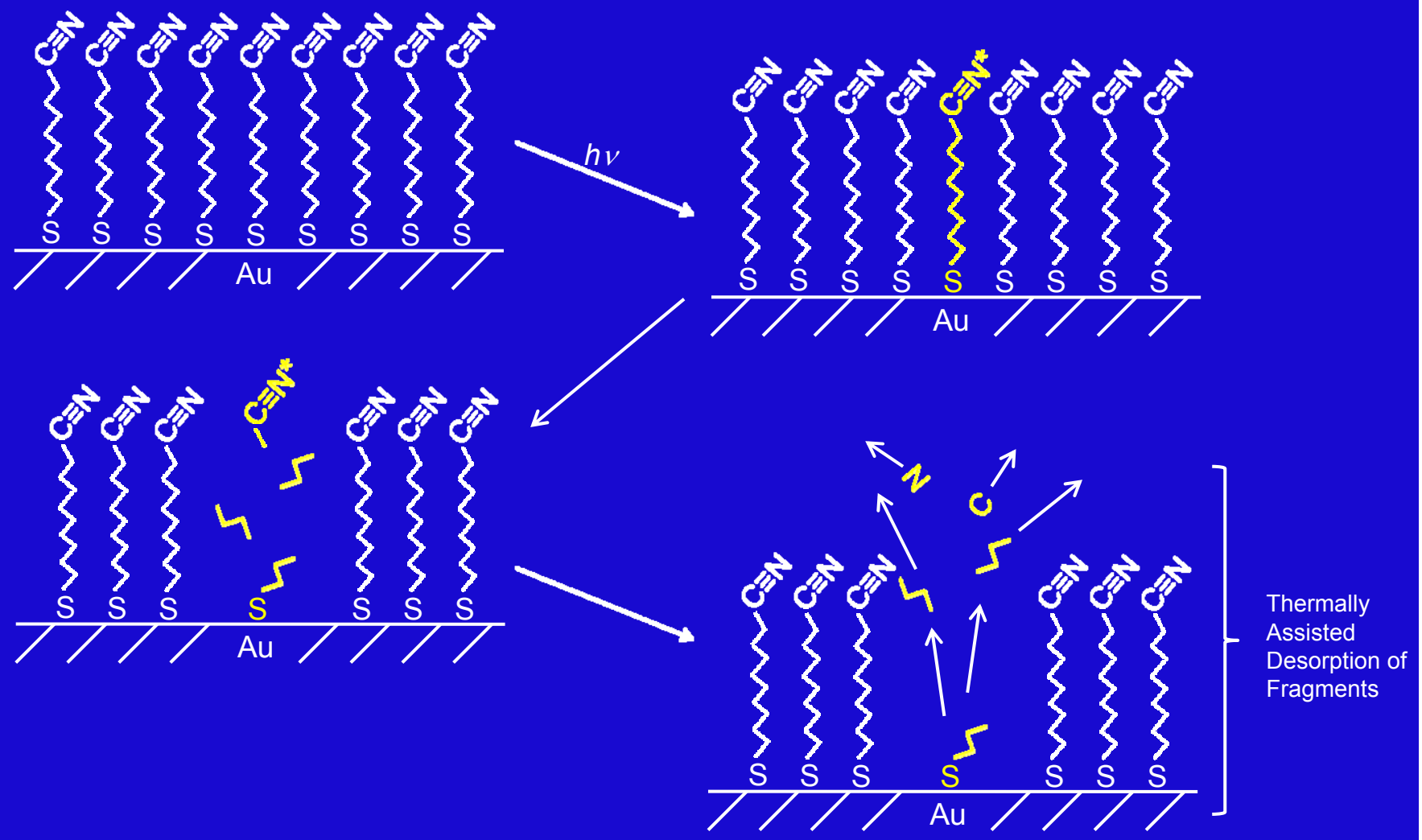


- Even though electronic excitation is localized in C≡N bond,
  - many neutral fragments are ejected
  - raising T from 50 K to 300 K enhances yield of fragments

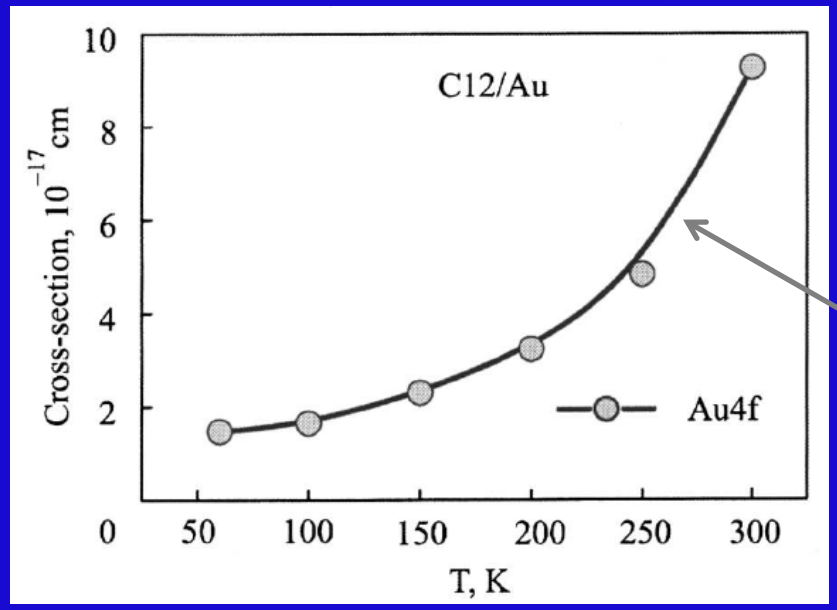
∴ thermal effects assist fragment desorption

Bauer *et al*. Low Temp. Phys. **33** (6-7), June-July 2007

Schematic of Bond Breaking Processes Coupled with Thermally Activated Diffusion



Large Cross Section for Organic Layer Desorption by $h\nu$ = 250 eV

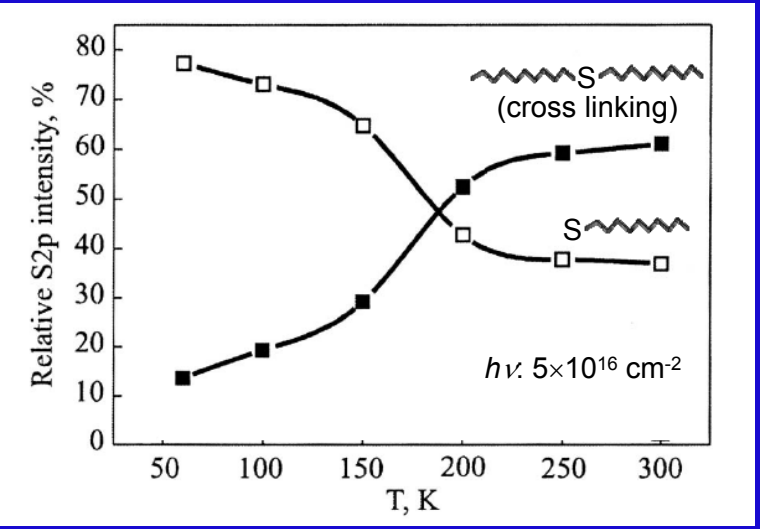


Thermal Effect Coupled to Electronic Excitation

Cross Section = 2-10 $\times$ 10^{-17} cm^2 (big)

Bauer *et al*. Low Temp. Phys. **33** (6-7), June-July 2007

Cross Linking Also Occurs as T is Increased

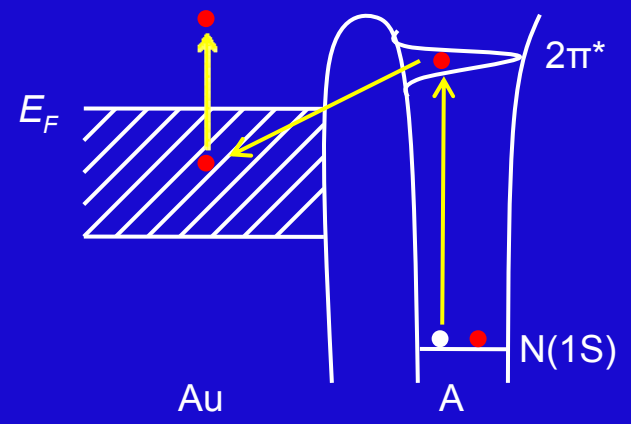


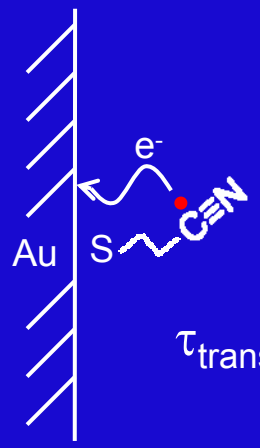
Quote: "… temperature is a parameter which steers electronically stimulated modification of all parts of thin organic films on surfaces,…"

Bauer *et al*. Low Temp. Phys. **33** (6-7), June-July 2007

Charge Transfer – Substrate/Molecule

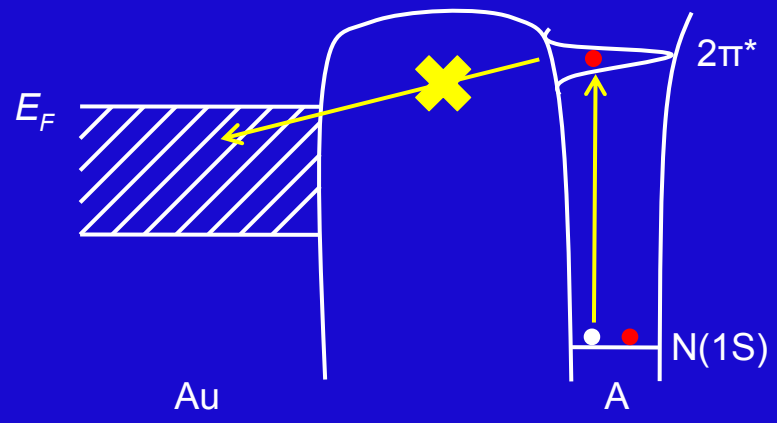
A→A*→A⁺ ➡ chemistry

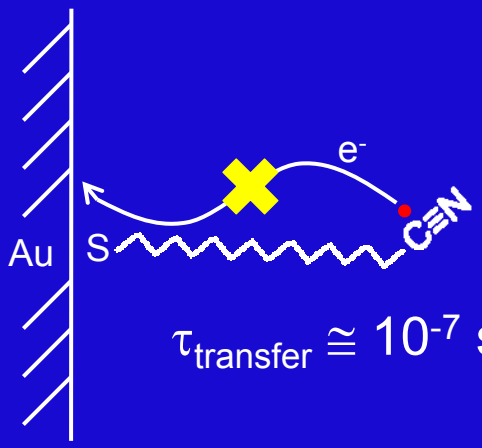




$\tau_{transfer} = 15 \pm 4 \times 10^{-15}$ s

A→A* ➡ chemistry





$\tau_{transfer} \cong 10^{-7}$ s

Charge Transfer Rate to Substrate ➡

$G(N)=G_0 e^{-\beta N}$

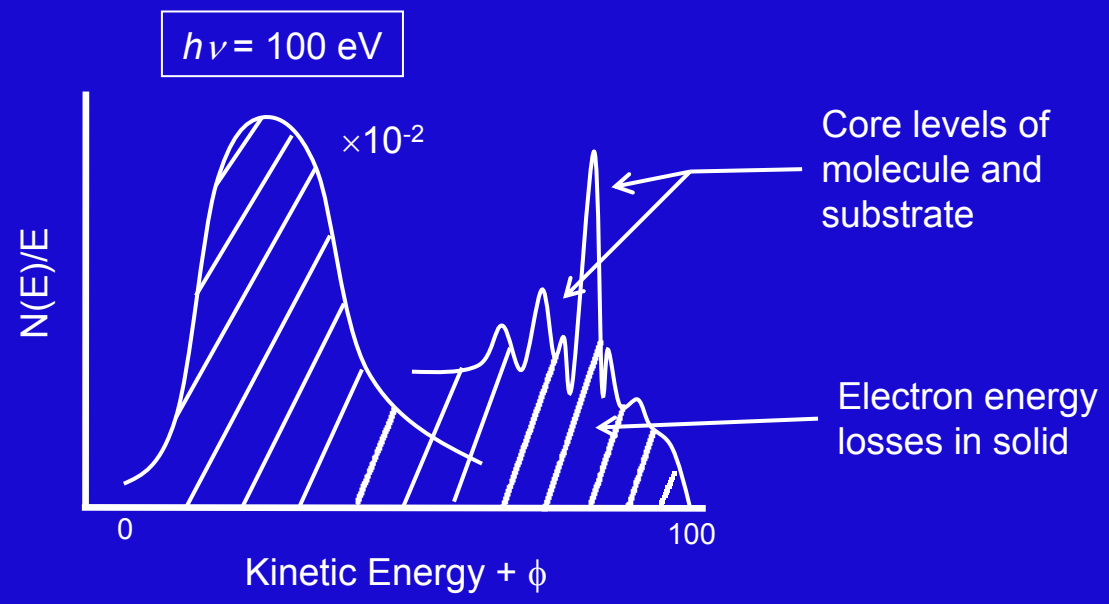
$G_0=2e^2/h$

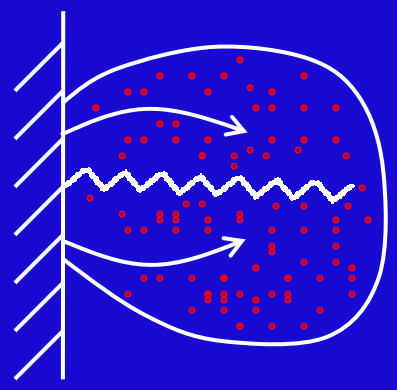
N=num. of CH_2 groups

$\beta \cong 1$

Neppl *et al*. Chemical Physics Letters 447 (2007) 227

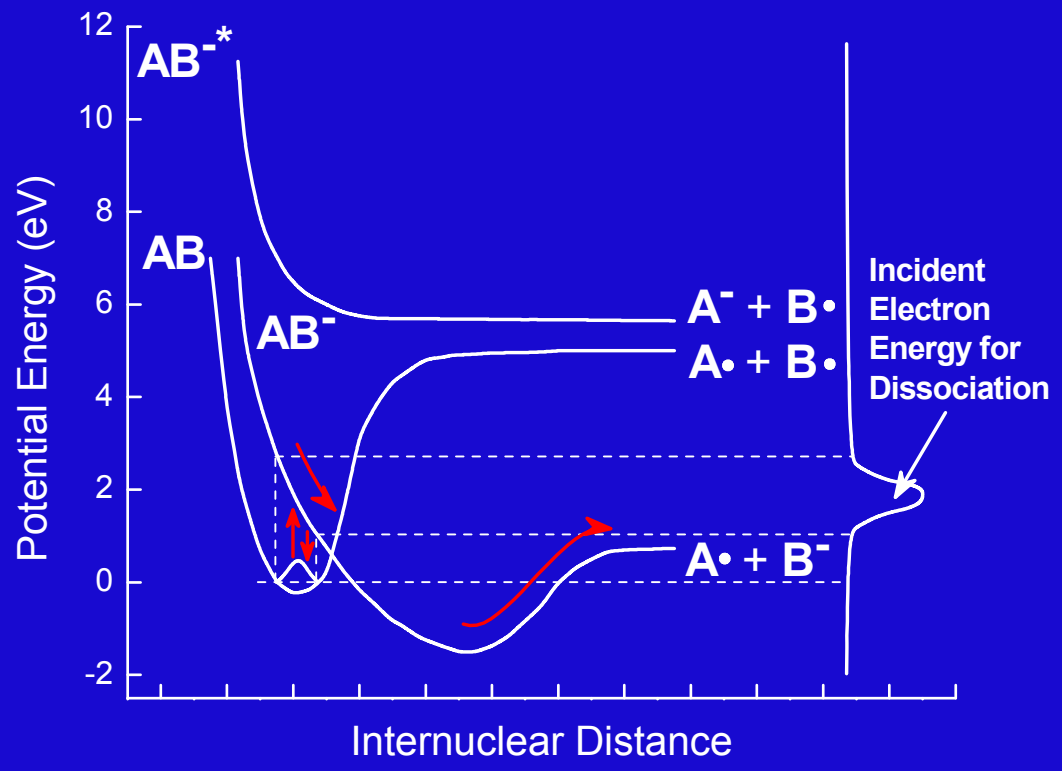
Production of Secondary Electrons in Substrate by $h\nu$ = 100 eV

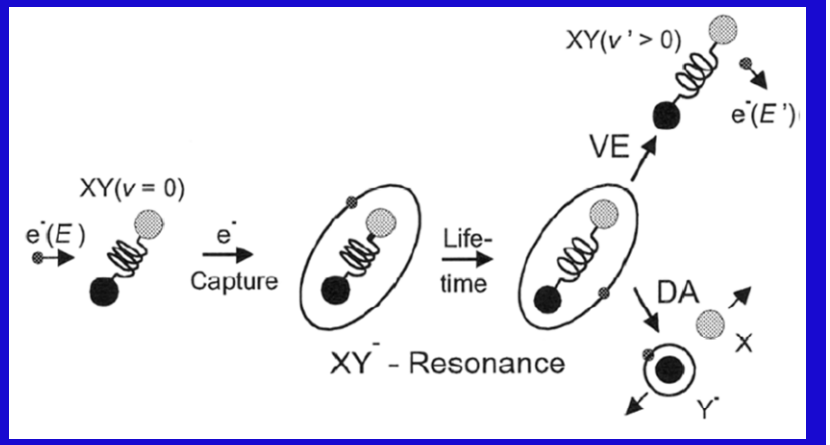




Molecule is bathed in secondary electrons.

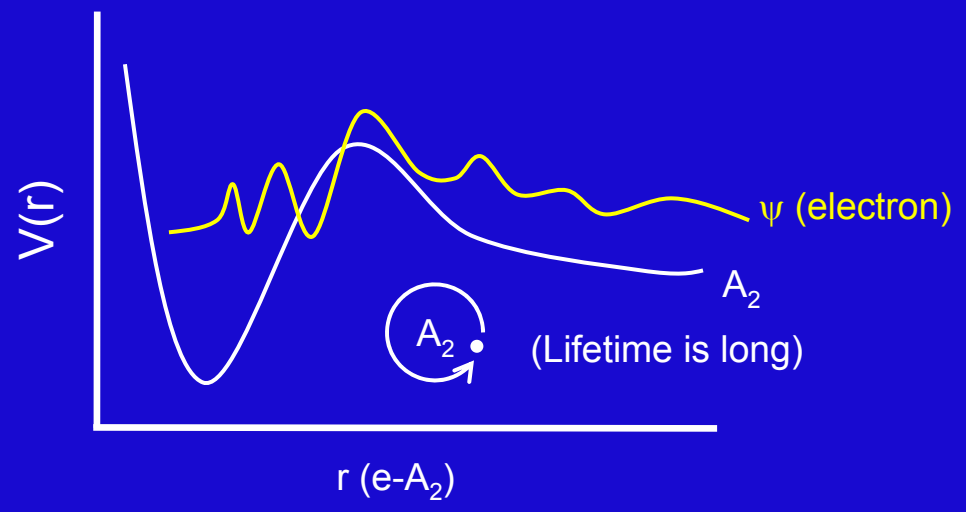
Dissociative Electron Attachment Processes



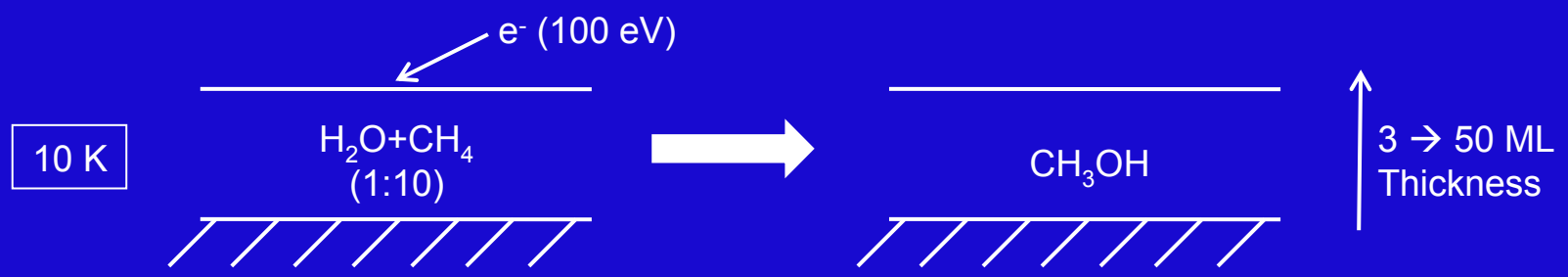


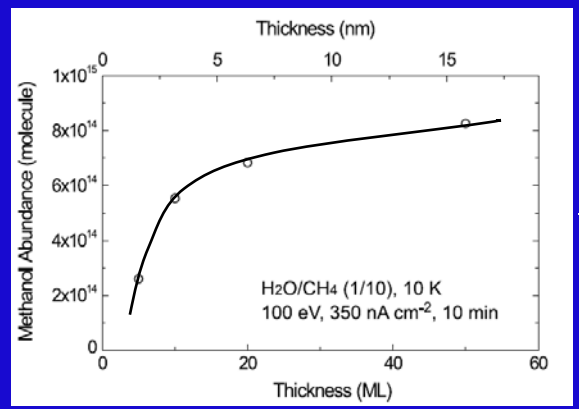
Arumainayagam *et al*. Surface Science Reports, submitted (2009)

Electron Trapping in Centrifugal Barrier – Lifetime Enhancement Promoting Dissociation



One Example of Reaction Induced by Low Energy Electrons





Caused by ~ 1 ML of 100 eV electrons

$H_2O + e^- \longrightarrow H\bullet + \bullet OH$

$CH_4 + e^- \longrightarrow \bullet CH_3 + \bullet H$

$\bullet CH_3 + \bullet OH \longrightarrow CH_3OH$

These reactions have a very high cross section.

Wada *et al*. The Astrophysical Journal, 644:300-306, 2006 June 10

Summary – Electronic Excitation of Reactions in Surface Layers

- Electronic and Thermal Excitation Coupled.
- Localized Core Excitations Spread through Molecule – Bond Breaking and Cross Linking Occur.
- Charge Transfer Effects To/From Substrate.
- Secondary Electrons → Dissociative Electron Attachment (DEA)
- DEA – High Cross Section

Photo Oxidation of Organics on TiO_2

- TiO_2 has served as an effective substrate for photoactivation of organic molecules for ~30 years.

1972: Water Splitting at n-TiO_2 Electrodes

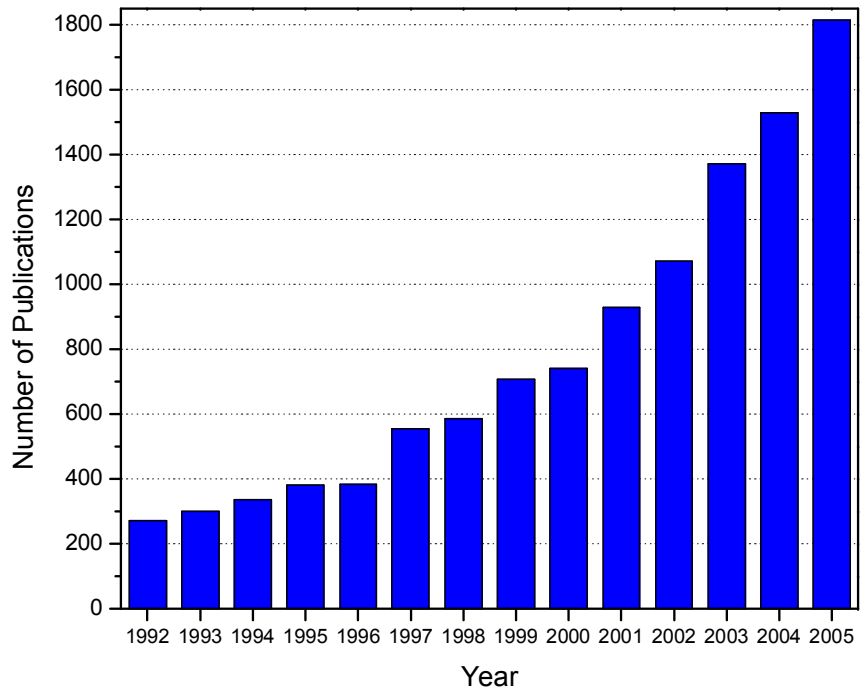
Electrochemical Photolysis of Water at a Semiconductor Electrode

ALTHOUGH the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

For electrochemical decomposition of water, a potential difference of more than 1.23 V is necessary between one electrode, at which the anodic processes occur, and the other, where cathodic reactions take place. This potential difference is equivalent to the energy of radiation with a wavelength of approximately 1,000 nm. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light. Here we describe a novel type of photo-electrochemical cell which decomposes water in this way.

Electrolysis of water can occur even without applying electric power if one of the following three conditions is fulfilled. First, oxygen evolution occurs at a potential more negative than that at which hydrogen evolution occurs in normal conditions; second, hydrogen evolution occurs at a potential more positive than that at which oxygen evolution occurs in normal conditions; third, the potential for oxygen evolution is made more negative and that for hydrogen evolution is made more positive, until the former is more negative than the latter.

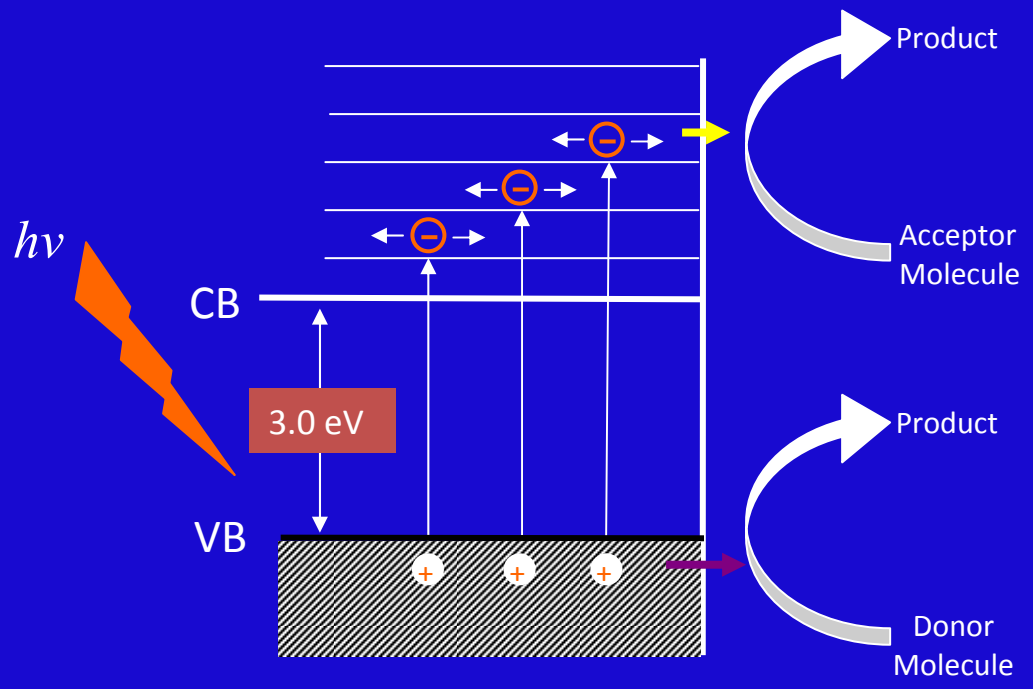
Current–voltage curves of a semiconducting n-type TiO_2



A. Fujishima and K. Honda, Nature 238 (1972) 37.

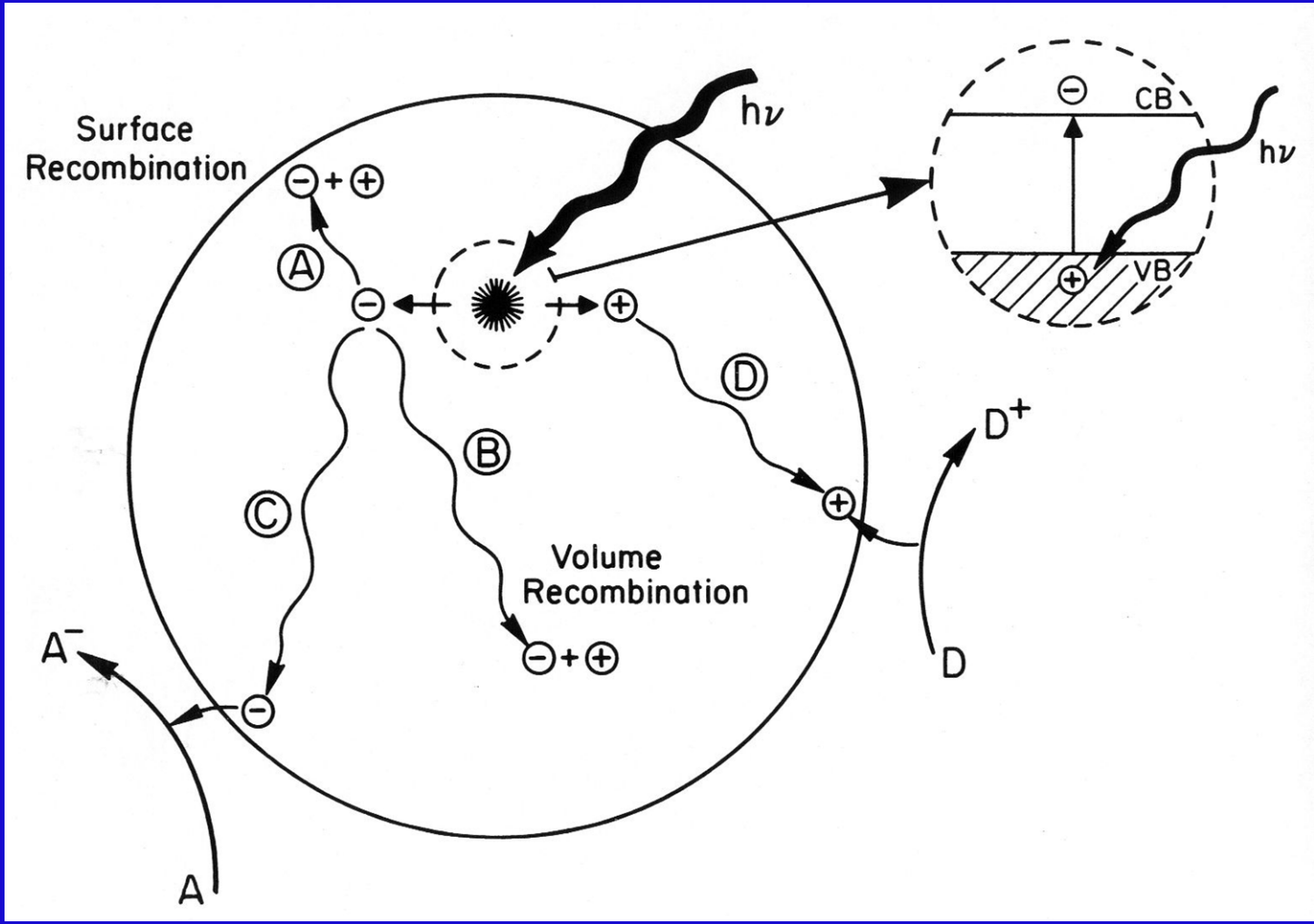
www.isiknowledge.com. Search terms = (TiO_2 OR titanium dioxide AND photo*)

Semiconductor Photoexcitation : TiO_2



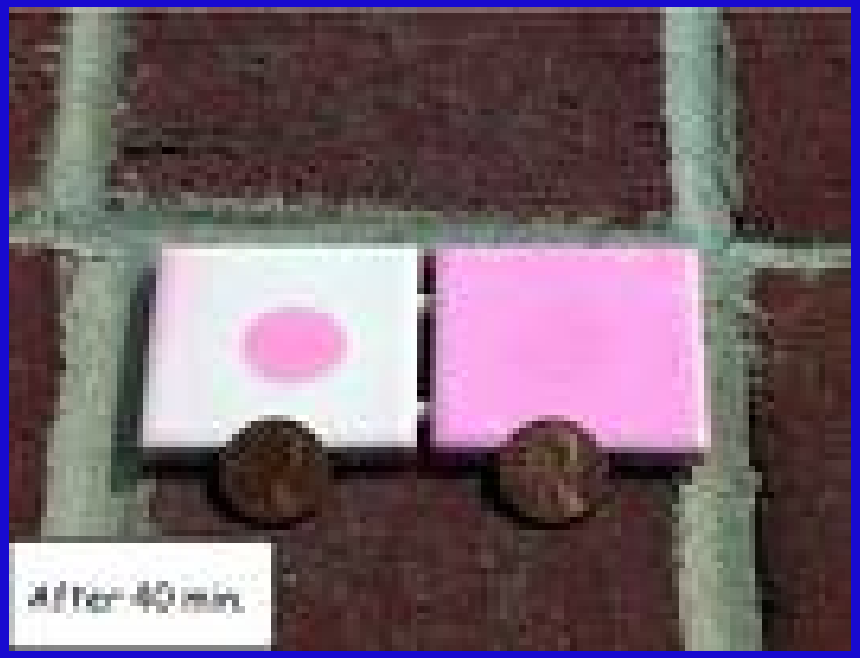
Upon UV excitation, both electrons and holes are photochemically active towards adsorbates on the TiO_2 surface.

Schematic Photo-excitation in a Solid Followed by De-excitation Events



Cleaning Organics by Photooxidation on TiO_2

Photocatalytic Removal of Dye on TiO2 Ceramic in Sunlight



Sunlight - Cleaned Roads

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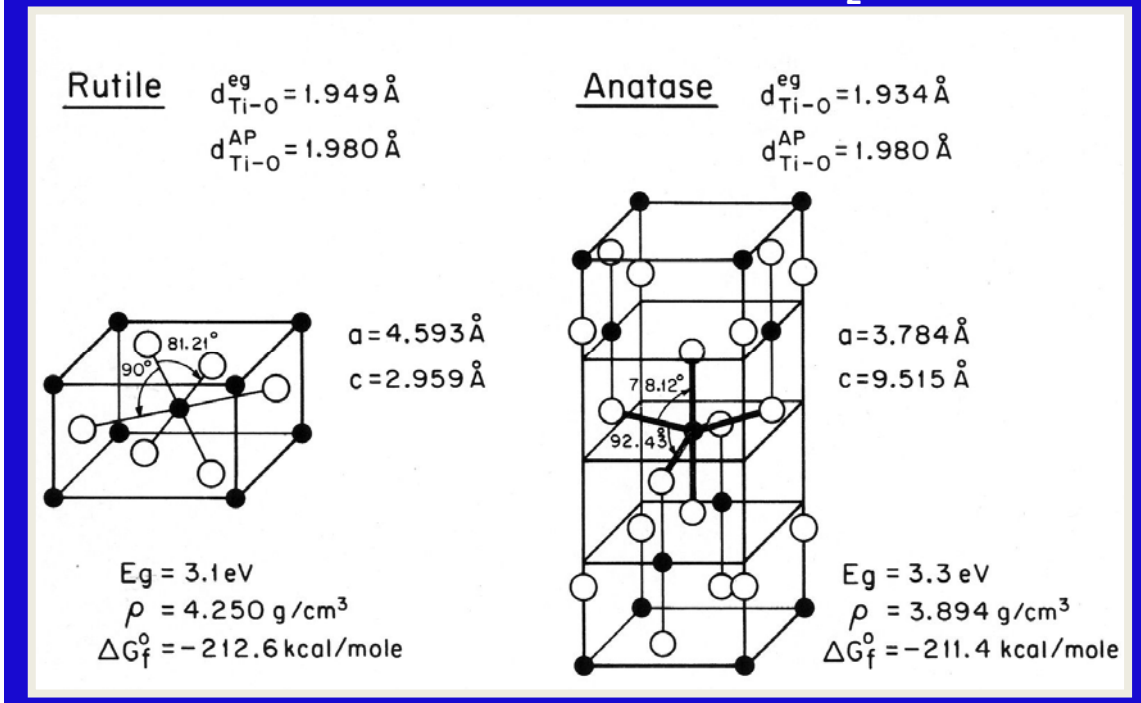
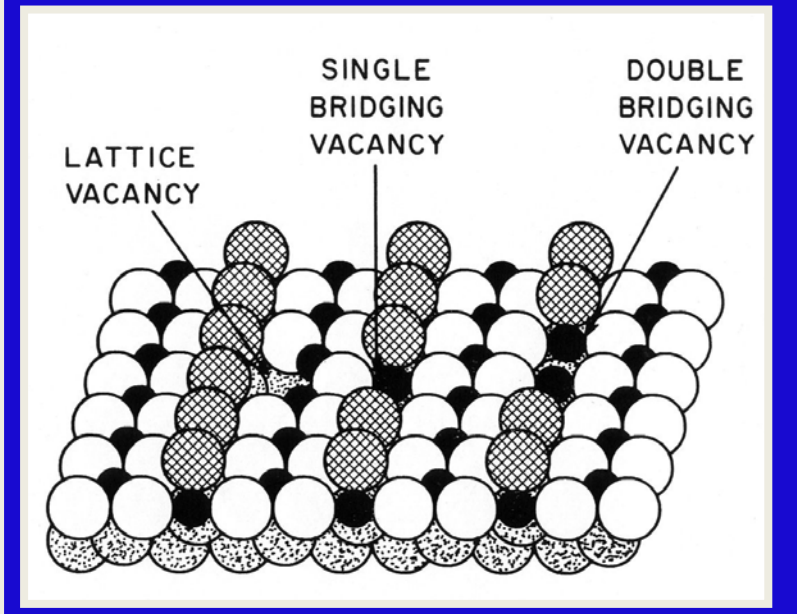
TiO_2 as a Photochemical Substrate

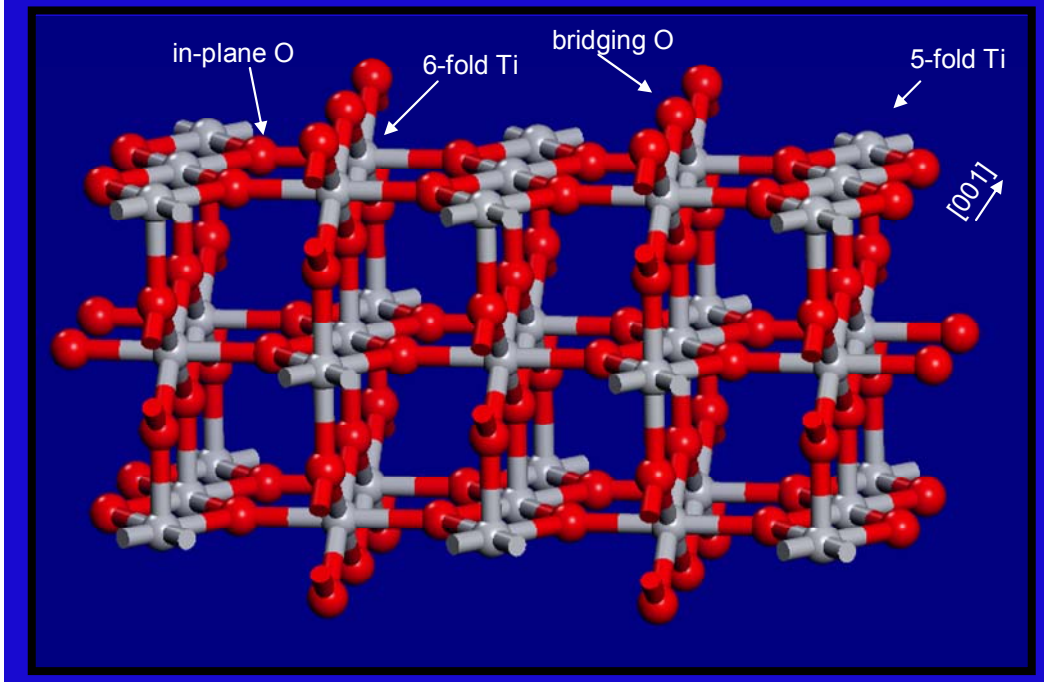
Structure of Rutile and Anatase TiO_2



TiO_2(110)-Defect sites

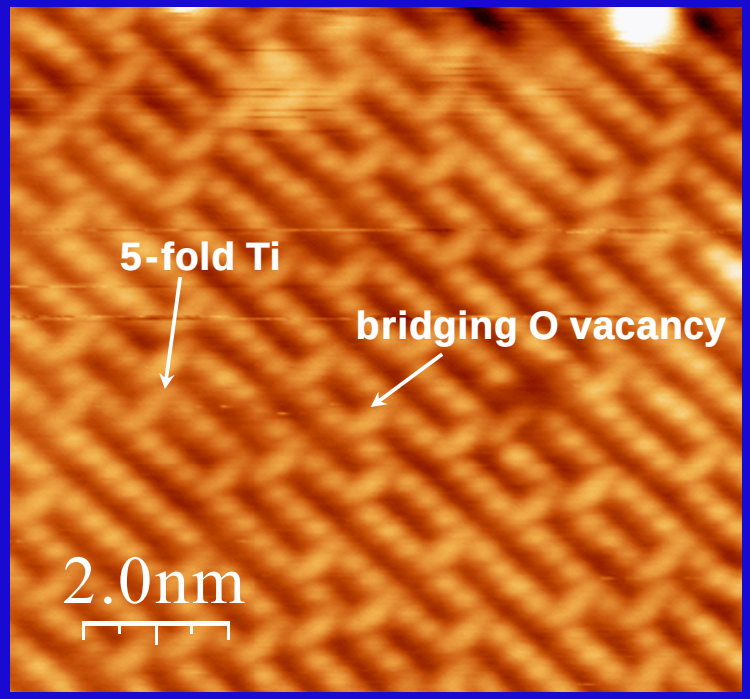


Atomic Structure of TiO_2(110) Surface



TiO_2(110)-(1x1) surface without oxygen vacancies is <u>stochiometric</u> (TiO_2)

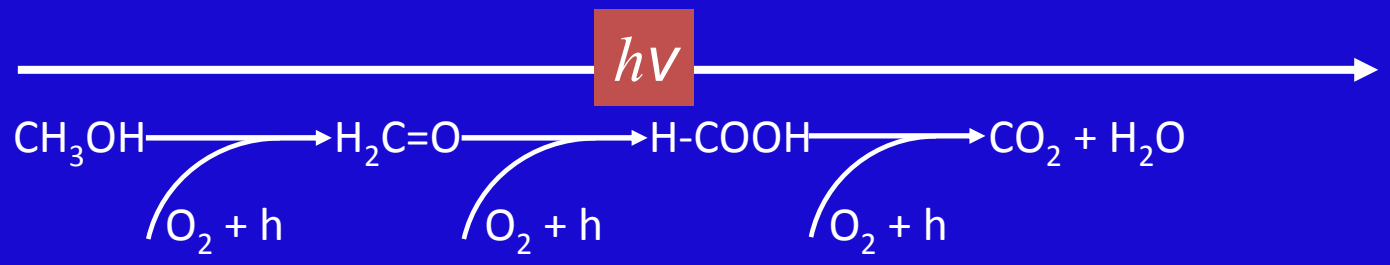
The surface density of oxygen vacancy sites is regulated by annealing conditions (time, presence of O_2)



Mezhenney et al. Chemical Physics Letters, 369 (2003) 152.

- **TiO_2 Photochemistry – Useful for Removal of Organics by Sequence of Reaction Events**

i.e.



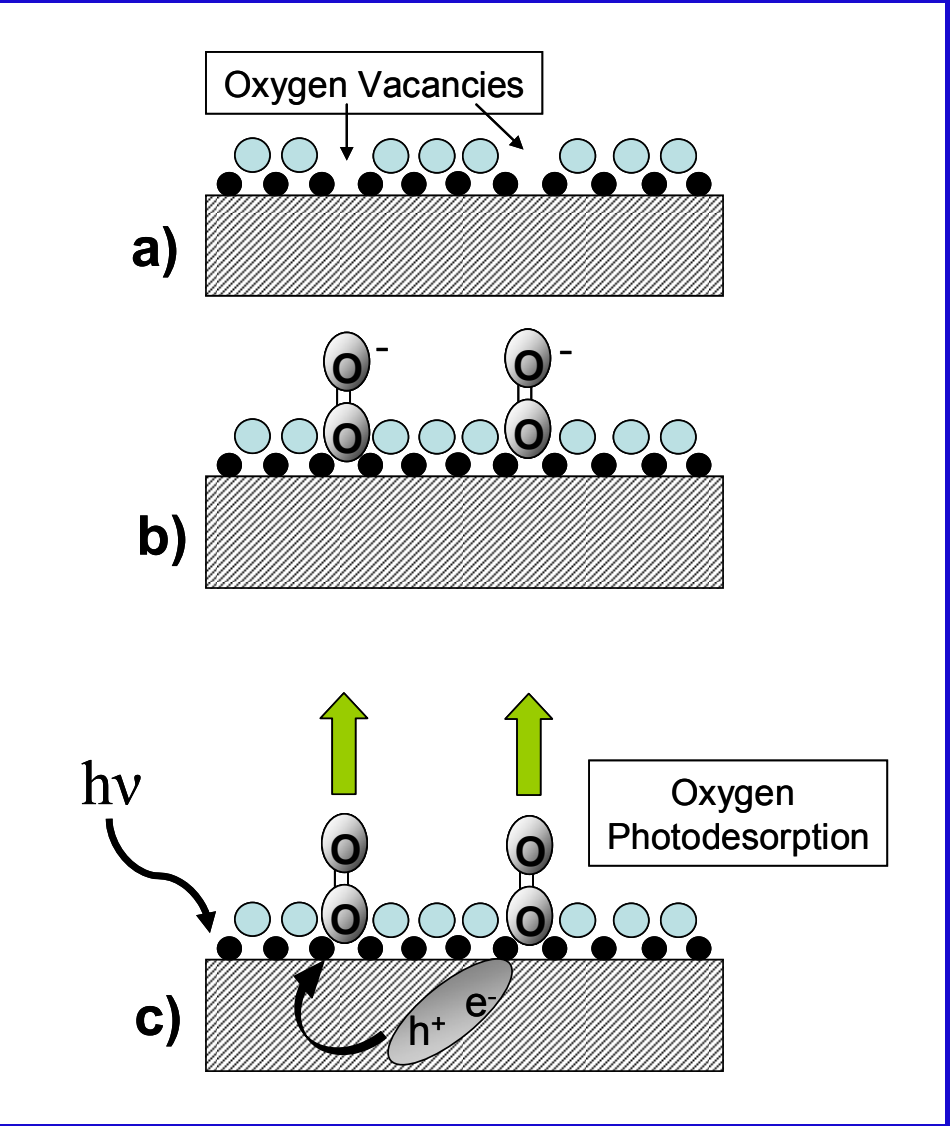
- **Sequence of complex organic oxidation reactions makes the study of photophysics difficult**

- **∴ Investigate a simple photo reaction to obtain details;**

$$h\nu + TiO_2 \longrightarrow h + e$$

$$O_2^- (a) + h \xrightarrow[TiO_2]{} O_2 (g)$$

Mechanism for Oxygen Photodesorption from $TiO_2(110)$



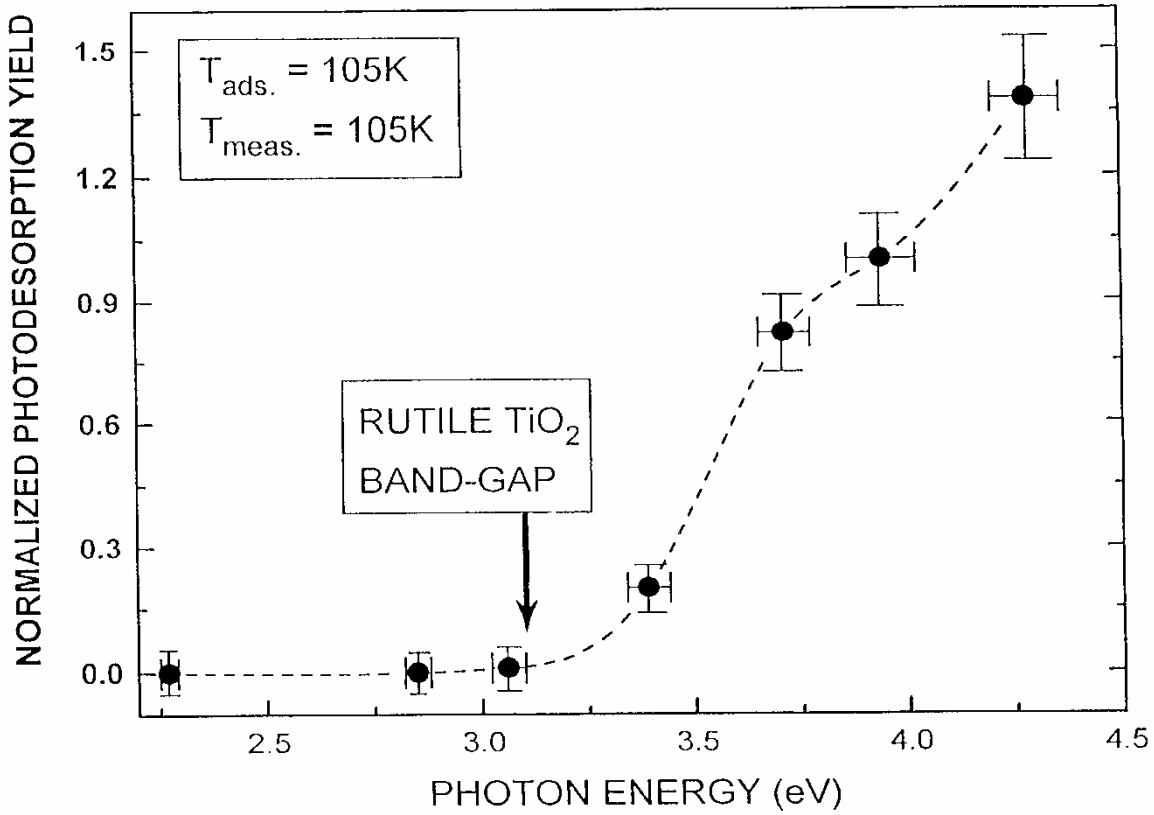
$$O_{VAC} + O_2 \longrightarrow O_2^-$$

- de Lara-Castells, M. P.; Krause, J. L. *J. Chem. Phys.* 2001, *115*, 4798-4810
- de Lara-Castells, M. P.; Krause, J. L. *Chem. Phys. Lett.* 2002, *354*, 483-490.
- Anpo, M.; Che, M.; Fubini, B.; Garrone, E.; Giamello, E.; Paganini, M. C. *Top. Catal.* **1999**, *8*, 189-198.

$$h^+ + O_2^- \longrightarrow O_2\uparrow$$

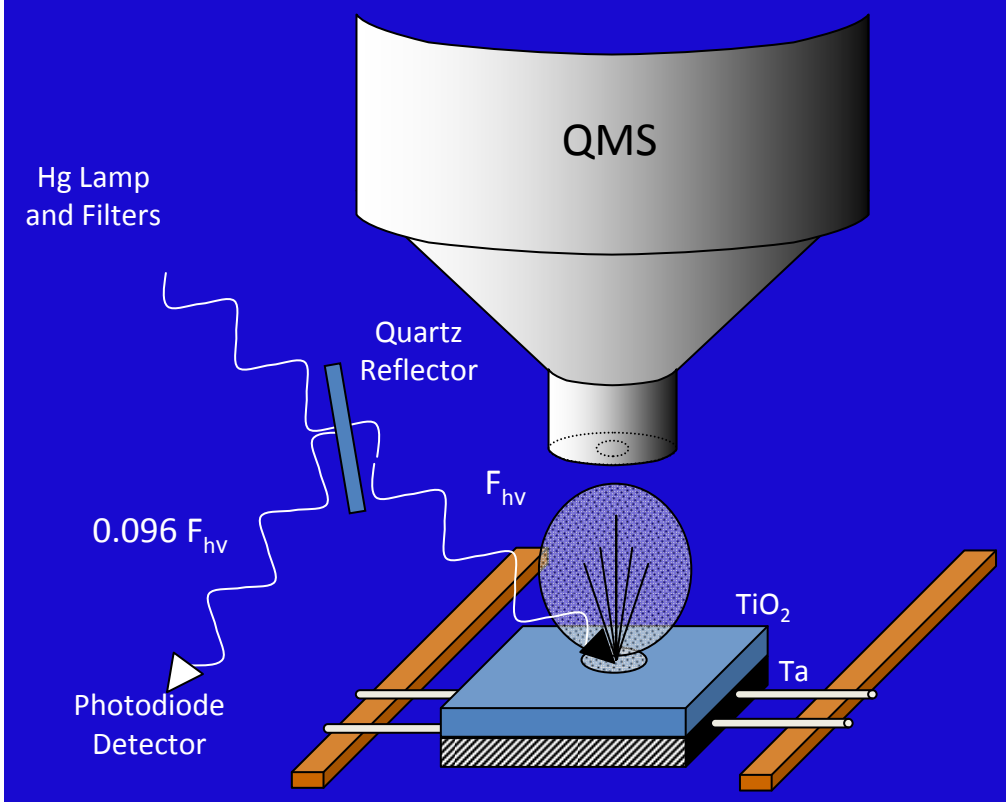
- de Lara-Castells, M. P.; Krause, J. L. *J. Chem. Phys.* **2003**, *118*, 5098-5105.

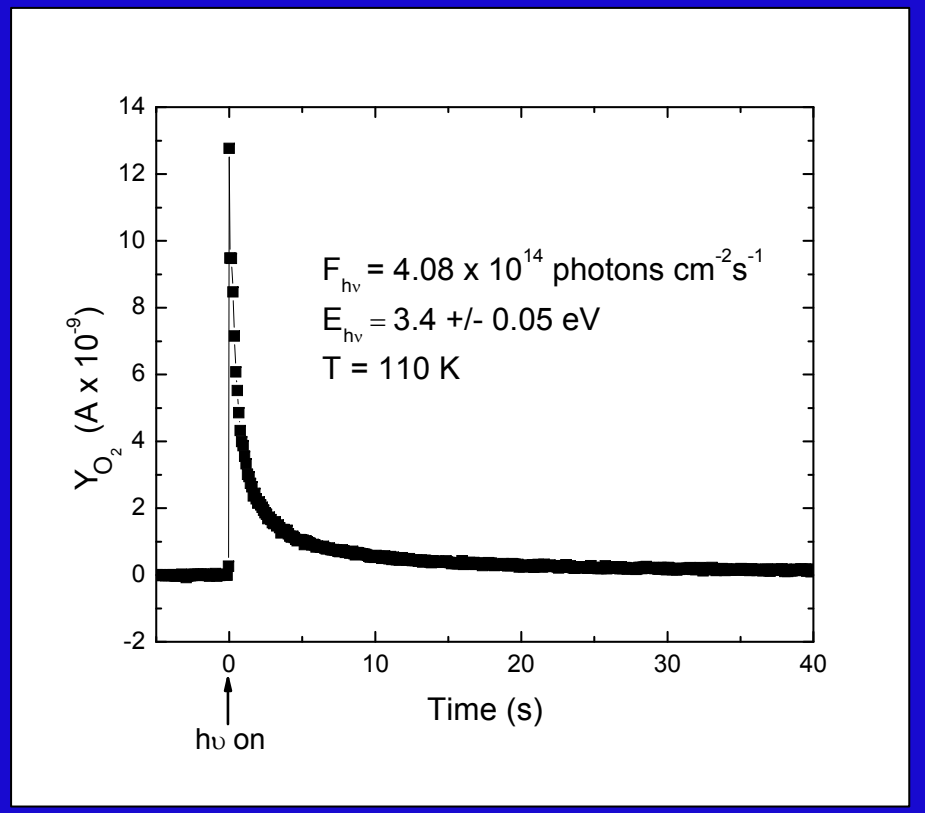
The Photon Energy Dependence of O_2 Photodesorption from $TiO_2(110)$



G. Lu, A. Linsebigler and J. T. Yates, Jr., "The Adsorption and Photodesorption of Oxygen on the $TiO_2(110)$ Surface," J. Chem. Phys. 102, 4657 (1995).

O_2 Photodesorption from TiO_2(110)





Tracy L. Thompson and John T. Yates, Jr. J. Phys. Chem. B, 109 (2005) 18230.

O_2 Photodesorption from $TiO_2(110)$:

$$h\nu + TiO_2 \xrightarrow{k_1 F_{h\nu}} e + h$$

$$h + T \xrightarrow{k_2} T^+ \quad \text{(hole capture by a hole trap)}$$

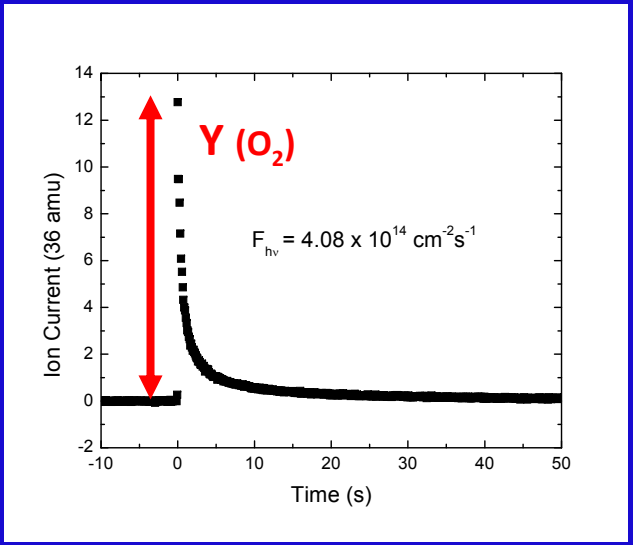
$$e + h \xrightarrow{k_3} heat \quad \text{(on recombination sites)}$$

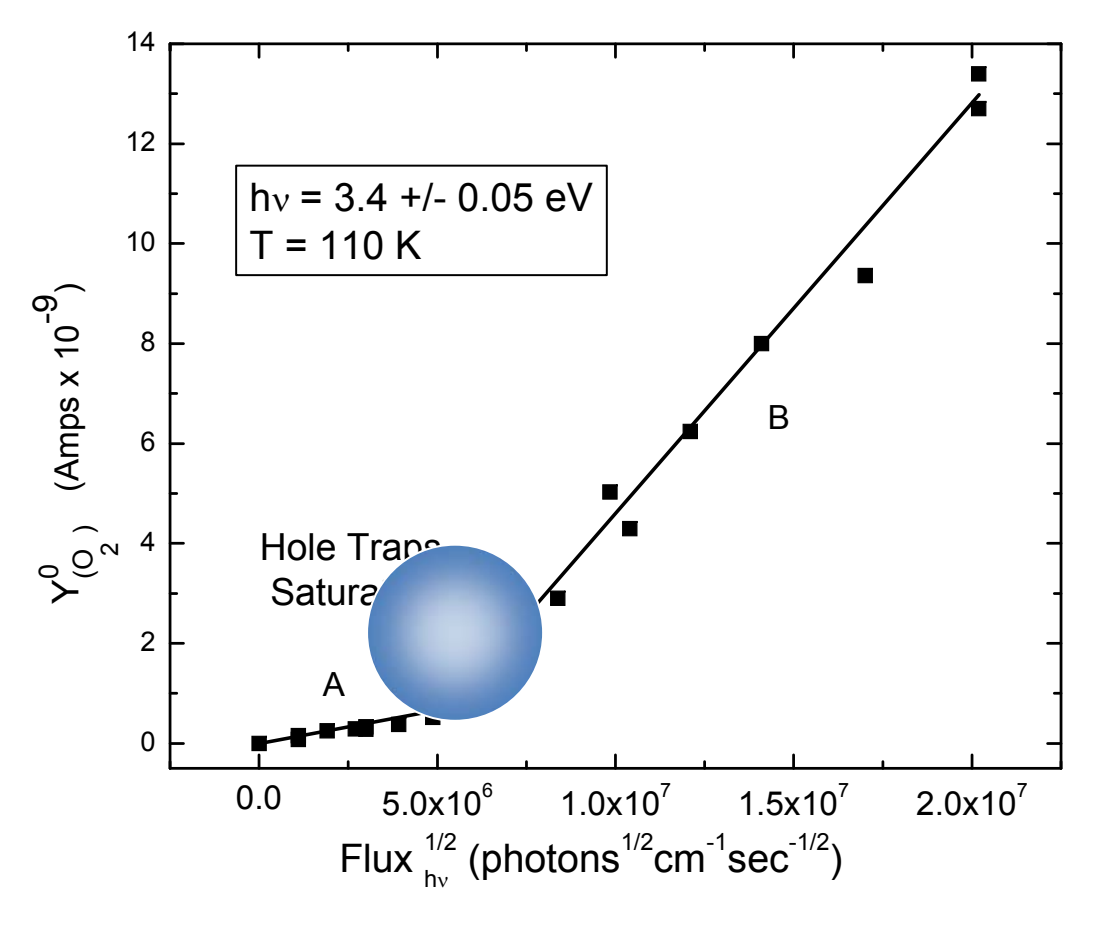
$$h + O_2^-(a) \xrightarrow{k_4} O_2(g) \uparrow$$

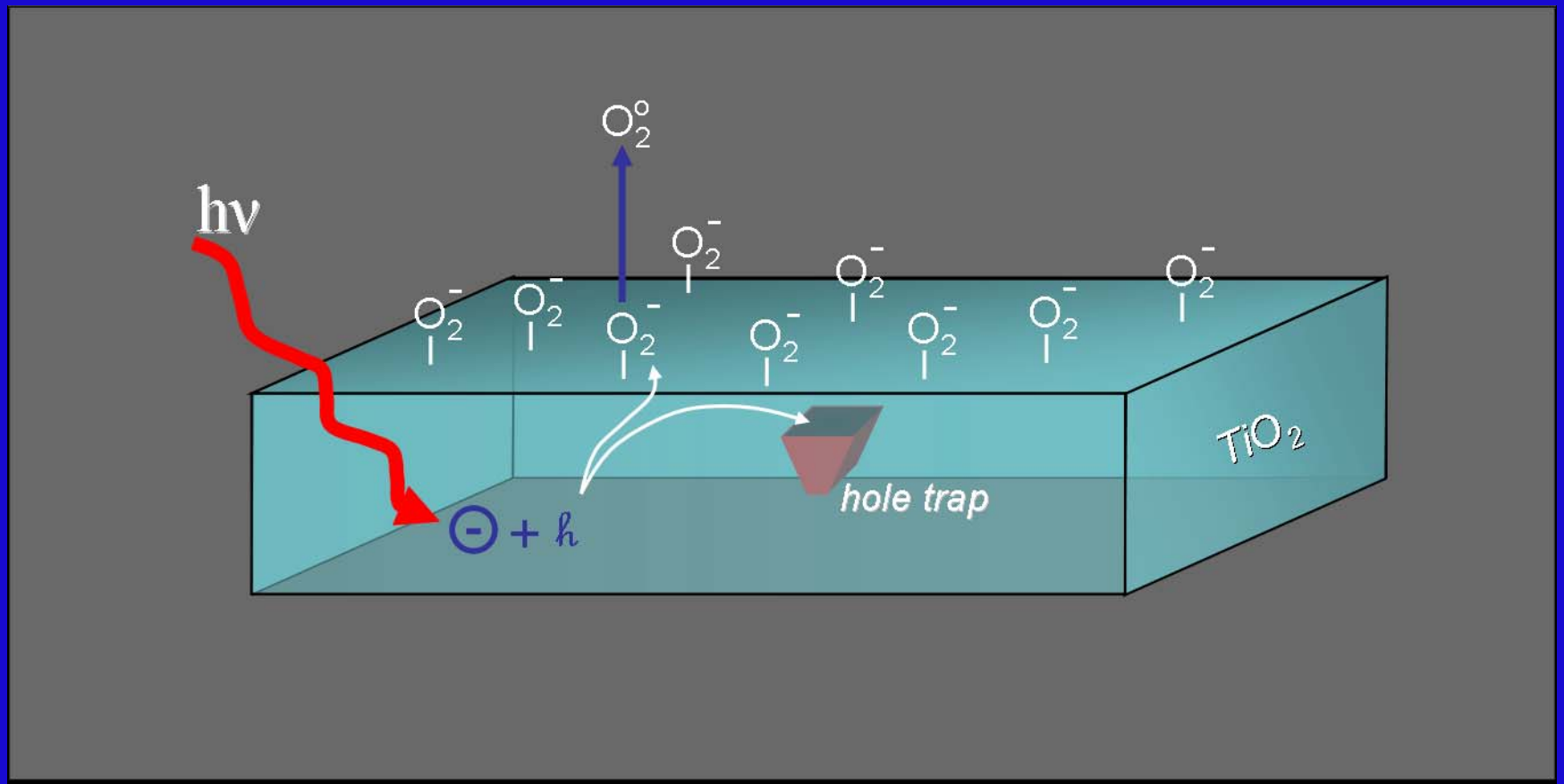
Rate of photodesorbing oxygen scales proportionally with the square root of the incident light intensity:

$$\frac{d[\theta_{O_2}]}{dt} = -k_4 \left(\frac{k_1}{k_2 + k_3} \right)^{1/2} F_{h\upsilon}^{1/2} [\theta_{O_2}]$$

$^{18}O_2$ Initial Photodesorption Yield - $TiO_2(110)$





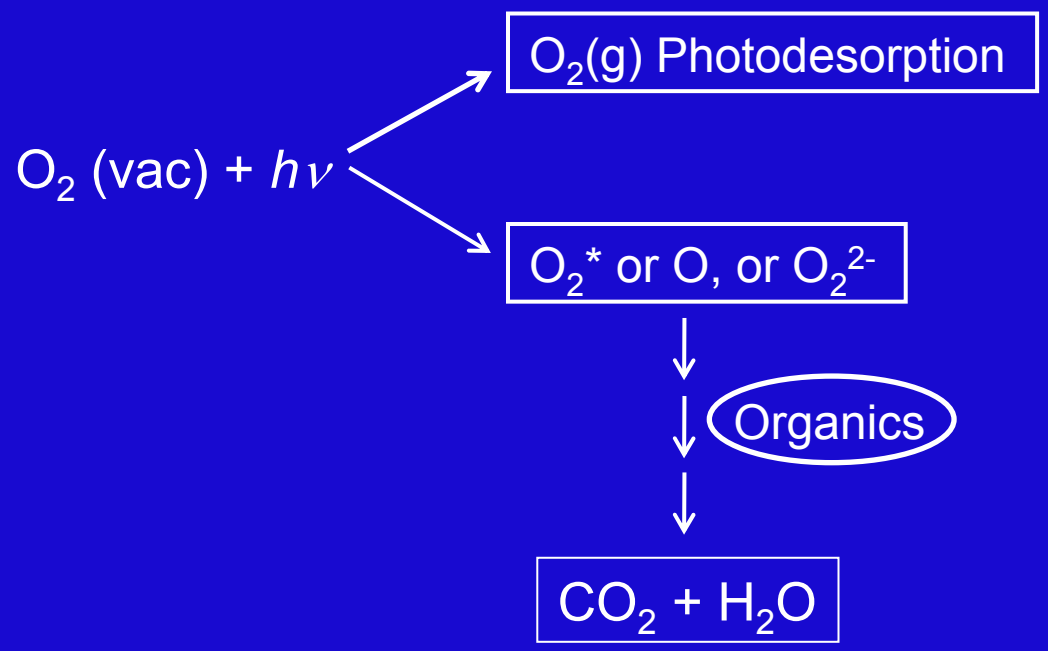

hν
O_2^o
O_2^-
O_2^-
O_2^-
O_2^-
O_2^-
O_2^-
O_2^-
O_2^-
O_2^-
O_2^-
TiO_2
hole trap
⊖ + h

What have we found?

- e-h recombination kinetics govern dependence on light intensity : $F_{h\nu}^{1/2}$ dependence.

- Trap sites for holes impede surface photo chemical processes.

O_2 Photodesorption Accompanied by Photooxidation of Organics

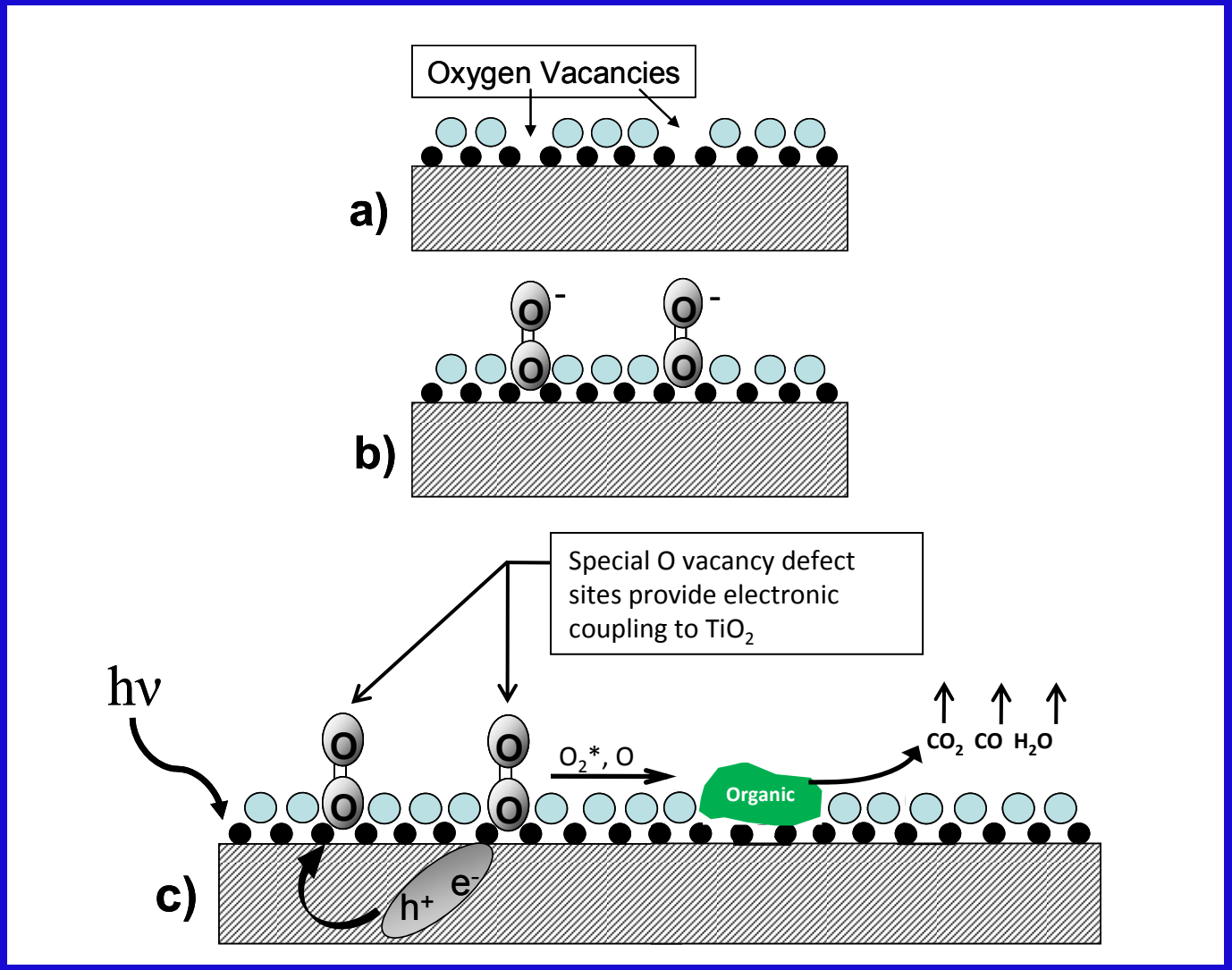


- O_2 photodesorption – hole mediated
- O_2 as photooxidant – electron or hole mediated?

What is Special about TiO_2 for Photooxidation of Organics with $h\nu$ = 100 eV?

- Different excitations than produced by $h\nu \cong 4$ eV.
- It may be that provision of an O_2 adsorption site capable of bonding O_2 which permits electronic coupling to deep TiO_2 EUV excitations will be the key to EUV mirror cleanup.

Hypothesis – TiO_2 Photooxidation in EUV

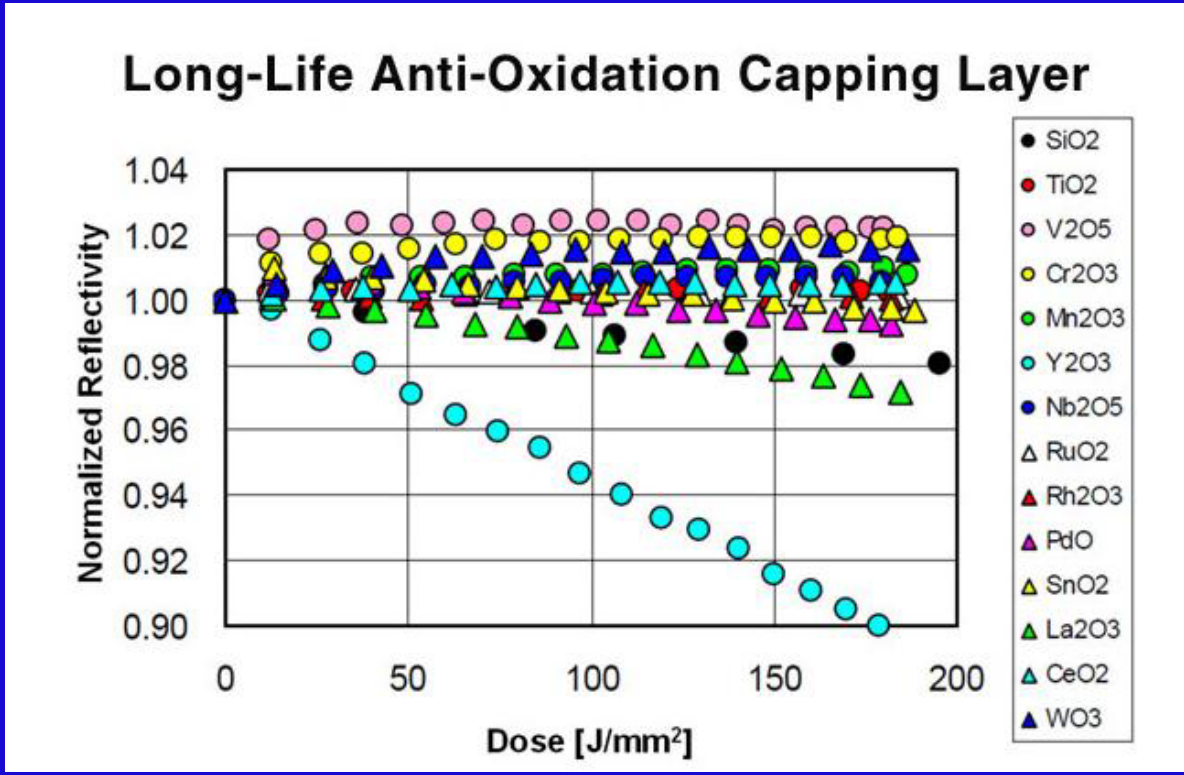


Mirror Contamination Effects

- Two deleterious processes

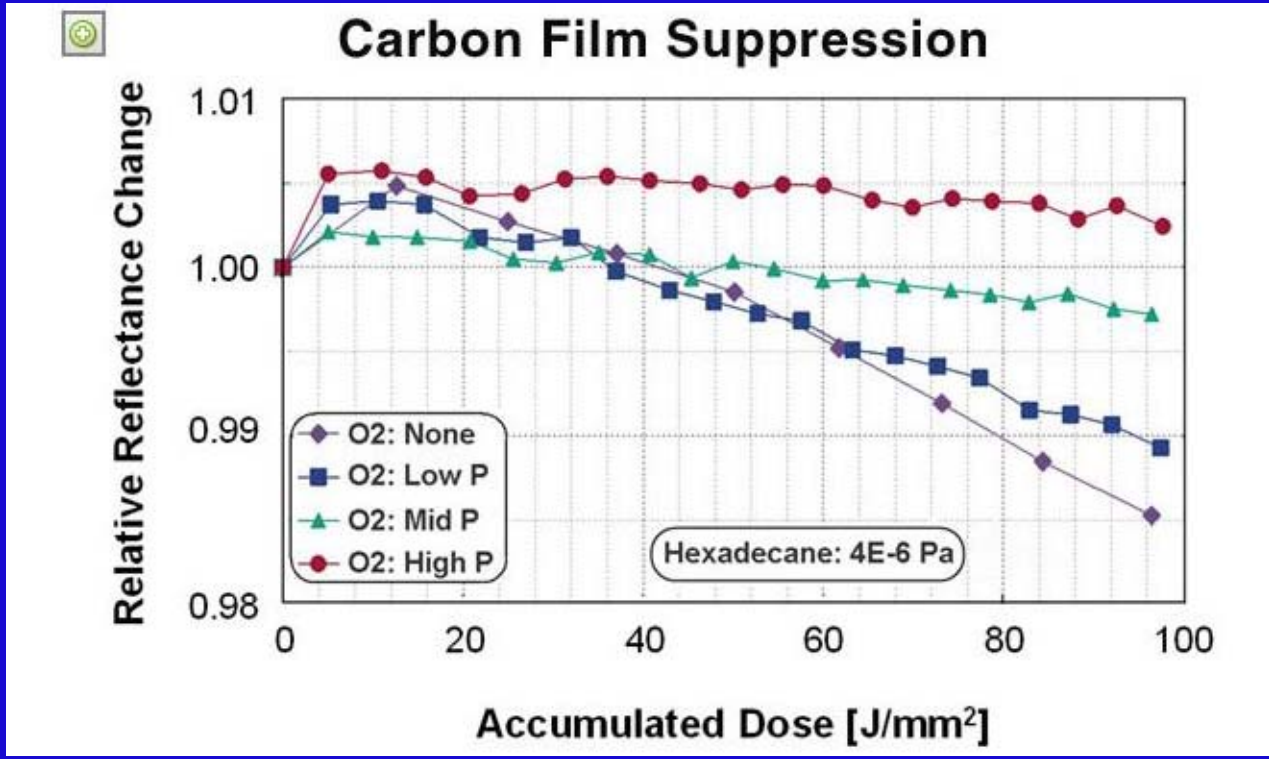
  -- Mirror oxidation

  -- Mirror carbon film contamination



- Many oxide films suppress mirror oxidation

T. Mura, K. Murakami, H. Magoon, A. Barada, M. McCullam – Nikon (2009)



- O_2(gas) + EUV radiation effective in removing C film.

T. Mura, K. Murakami, H. Magoon, A. Barada, M. McCullam – Nikon (2009)

Summary

- Electronic and thermal excitation often work together.
- Molecular fragments form and combine to make new species.
- Charge transfer to surfaces – retarded as localized electronic excitation occurs further from surface.

Summary

- High energy photons produce many secondary electrons (0-20 eV)

↓

- Secondary electrons attach to adsorbed molecules efficiently at resonant energies → temporary negative ions.

↓

- Temporary negative ions → molecular dissociation

- TiO_2 – an efficient photoactivator of adsorbed O_2

↓

- Activated oxygen on TiO_2 → photooxidation of organic layers.