Oxidation of Mg films monitored with Mg/*p*-Si(111) Schottky diodes

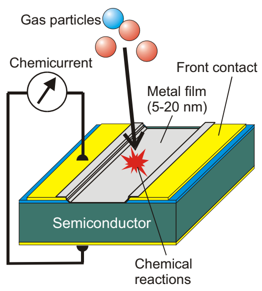
Project A1 – H. Nienhaus
Co-workers: S. Glass, R. Nünthel, D. Krix

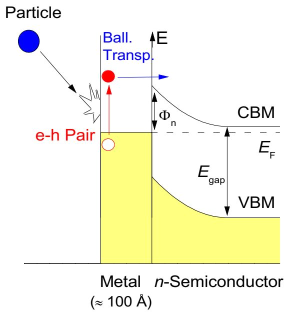
SFB616 Energy dissipation at surfaces

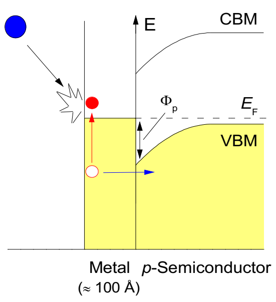
UNIVERSITÄT DUISBURG ESSEN

Principle of chemicurrents

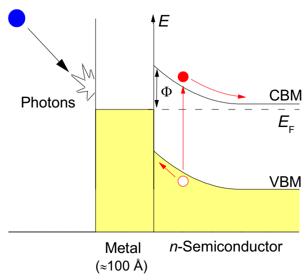
- Non-adiabatic dissipation of chemical reaction energy
- Hot charge carrier detection with thin metal-film Schottky diodes:
  hot electrons → *n*-type diodes
  hot holes → *p*-type diodes
- Schottky barrier height Φ[Si] ≈ 0.5 – 1 eV





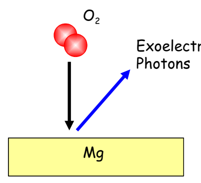


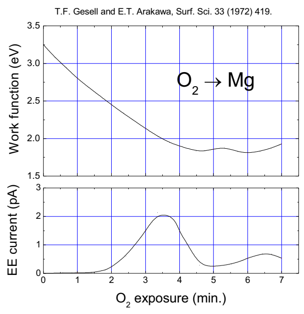
- Detection of surface chemiluminescence by photoeffect or internal photoemission

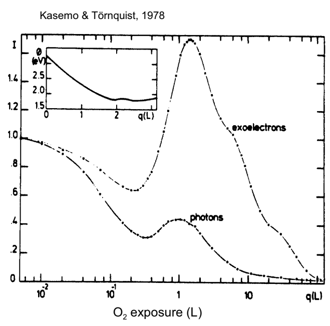


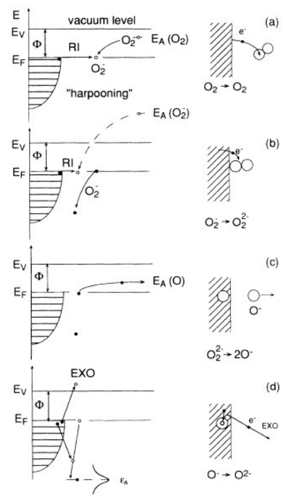
Exoemission and chemiluminescence with O_2 → Mg

- Deposited energy: ≈ 2.4 eV/molecule
- Chemiluminescence (CL) and exo-electron emission (EE) with O_2 adsorption on Mg surfaces
- Work function (Φ) reduction with O coverage
- Open question:
  CL and EE transients due to Φ variation??





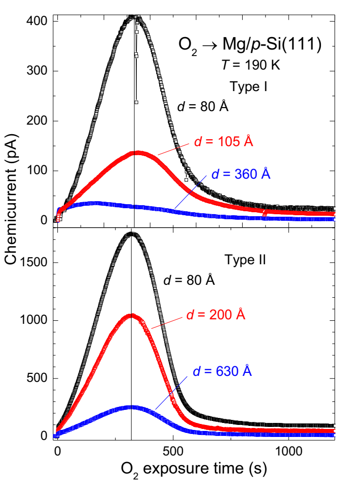


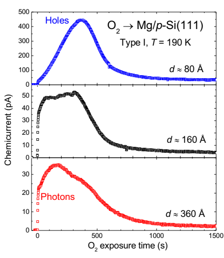


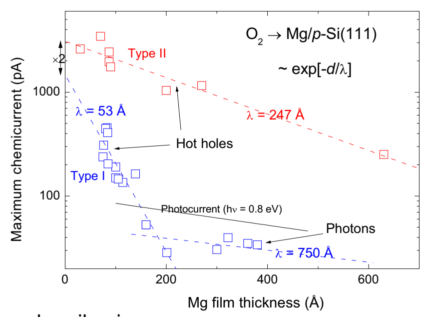
- Harpooning: $O_2 \rightarrow O_2^-$
- Acceleration due to image force; second electron transfer: $O_2^- \rightarrow O_2^{2-}$
- Dissociation: $O_2^{2-} \rightarrow 2\,O^-$
- Non-adiabatic electron transfer: $O^- \rightarrow O^{2-}$ and exoelectron emission

(T. Greber et al., 1994)

Chemicurrents in Mg/*p*-Si Schottky diodes during O_2 exposure







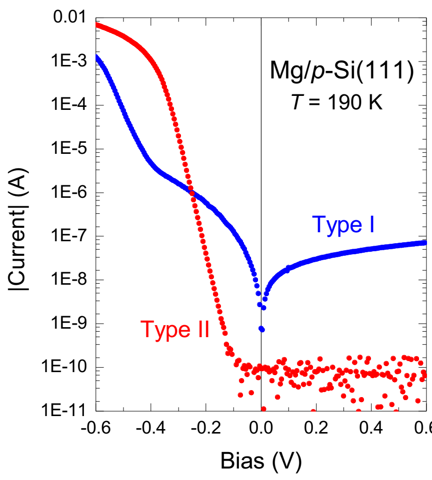
- Evidence of surface chemiluminescence with type I-diodes
- Exponential attenuation
- Larger attenuation constants with type II-diodes

<u>Diode preparation:</u>

- Low-temperature (LT, 190 K) evaporation of Mg films on H-terminated Si(111) substrates
- Type I: **no** annealing before and after Mg evap.
  Type II: annealing at 700 K before evap. and warming to RT after evaporation

<u>Diode properties from I-V curves:</u>

	Type I	Type II
Interface	inhomogeneous	homogeneous
Ideality factor	*n* = 1.4 – 2.7	*n* = 1.0 – 1.2
Effect. barrier	Φ_{eff} = 0.6 - 0.76 eV	Φ_{eff} = 0.66 – 0.72 eV
Homog. barrier	Φ_{hom} = 0.8 eV	Φ_{hom} = 0.7 eV

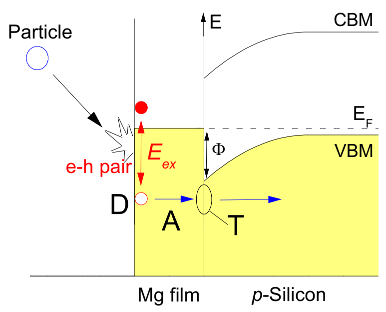


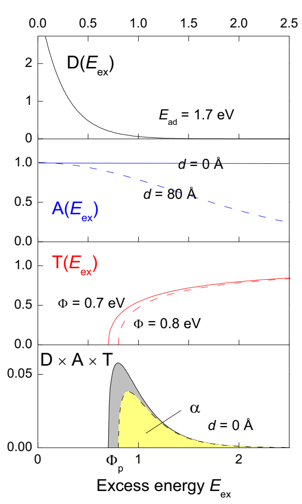
Spectroscopy of hot charge carriers

Three-step-model:

$$\alpha = \int_0^\infty dE_{ex}\, D(E_{ex}) A(E_{ex}) T(E_{ex})$$

D: Hot hole distribution
A: Attenuation
T: Transmission



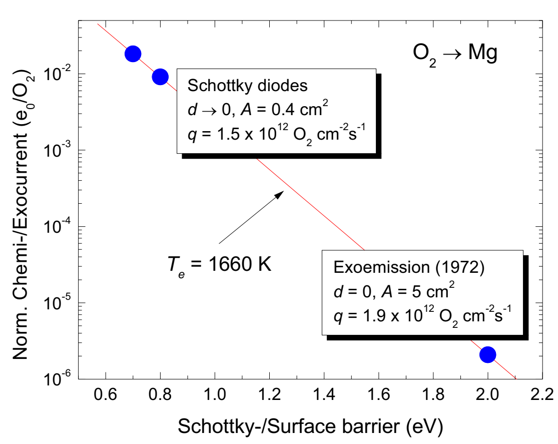


$$D = \frac{6.9}{E_{ex}} \exp\left[-\frac{6.9 E_{ex}}{E_{ad}}\right]$$

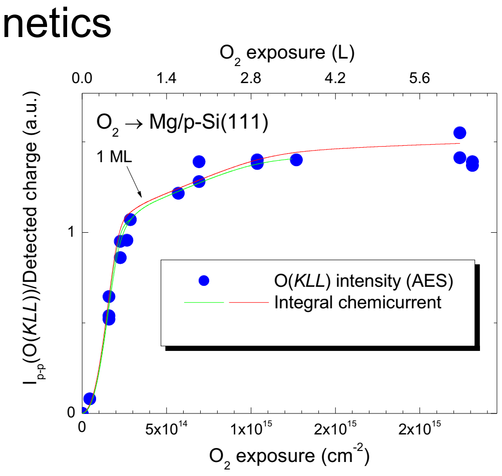
$$A = \exp\left[-\frac{d}{\lambda(E_{ex})}\right]$$

$$T = 4 \times \frac{\sqrt{(E_{ex}-\Phi)(E_{ex}+E_F)}}{\left(\sqrt{E_{ex}+E_F}+\sqrt{E_{ex}-\Phi}\right)^2}$$

Results:
α(Φ = 0.7 eV) = 2.6 %
α(Φ = 0.8 eV) = 1.7 %



Kinetics



- Oxygen coverage proportional to detected charge in the diode:

$$\Theta \propto \int_0^t I_{CH}(t)\, dt$$

- Chemicurrent represents chemical kinetics of surface reaction, i.e.,

$$I_{ch}(t) = \alpha\, e_0\, F \frac{dN}{dt}(t)$$

α: chemicurrent efficiency

- Electron-hole pair excitation cross section independent of exposure and coverage

Conclusions

- Chemicurrent method much more sensitive than exoelectron emission
- Efficiency correlated to diode preparation and homogeneous Schottky barrier height
  ⇒ maximum efficiency ≈ 0.022 holes/incident O atom
- No work function effect! Chemicurrent transient with maximum exclusively related to chemical reaction kinetics
  ⇒ reaction rate increases with O coverage in the low-coverage regime