UNIVERSITÄT DUISBURG ESSEN

SFB 616 A2

Revealing reaction kinetics on gold surfaces by chemically induced tunnel currents

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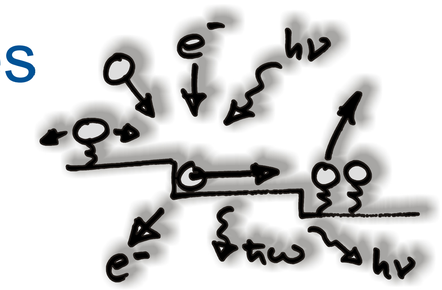


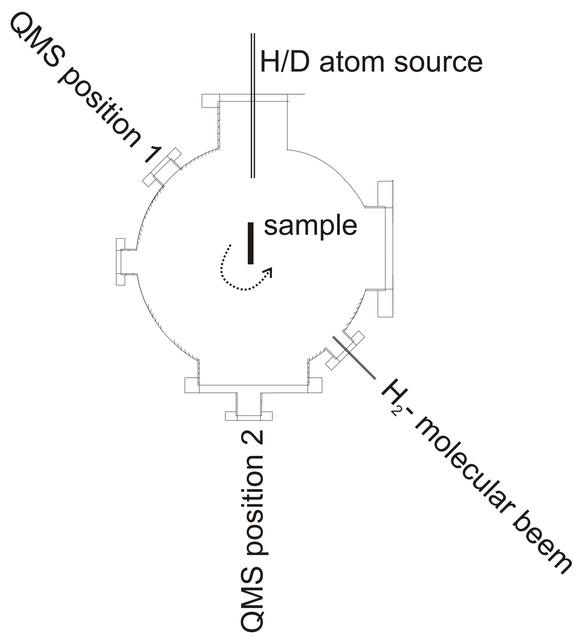
Our work

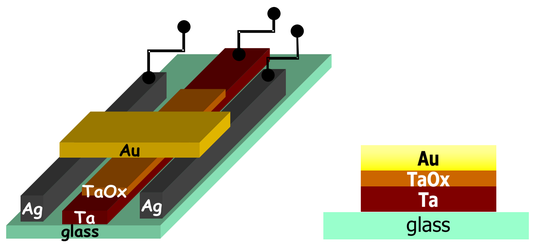
- Studying electronic excitation processes in the course of adsorption, chemisorption and surface reactions
- Understanding the role of single reaction steps in the entire process of chemically induced electronic excitation
- Determination of the excitation energy

Methods

- Detection of electronic excitation as tunnel current with 0 V tunnel bias in thin metal-insulator-metal junctions
- Characterisation of reaction kinetics by guiding a bunch of atoms or molecules on the surface
- Energy selective detection of the electronic excitation by the application of a bias tunnel voltage
- Comparison of chemically induced excitations with photo excitations

Experimental Setup





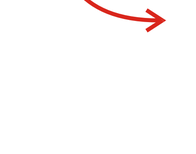
Layer system:

- 30 nm thick tantalum evaporated by e-beam
- 3.4 nm amorphous tantalum oxide produced by local electrochemical oxidation. Thickness adustable to +/- 0.2
- 15 nm thick gold film in situ prepared in UHV, polycristalline surface, preferentially 111 oriented

Some reaction kinetics

Atomic adsorption

Au + H > H(ad) + E



$$\frac{d}{dt} = s \; j_H \quad 1 \quad \frac{}{N}$$

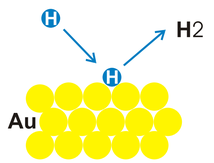
Langmuir-Hinshelwood reaction (LH)

H(ad) + H(ad) > H_2 (ad) > H_2 (gas) + E

$$\frac{d}{d} = \frac{}{N} \quad ^2 \exp \frac{e \; E_d}{k_B T}$$

Eley-Rideal reaction (ER)

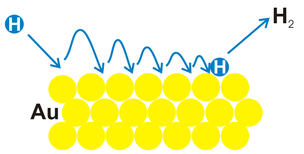
H(ad) + H(gas) > H_2 (gas) + E



$$\frac{d}{dt} = j_H \quad \frac{}{N}$$

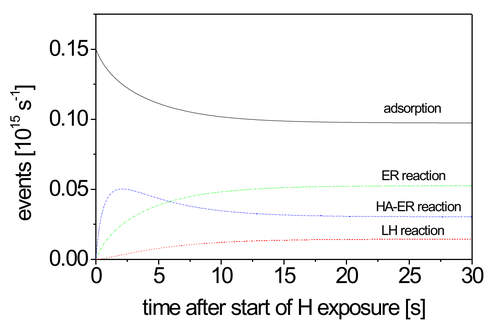
Hot atom Eley-Rideal reaction (HA-ER)

H(ad) + H(hot) > H_2 (gas) + E



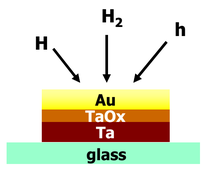
Incident H-atom samples n empty surface sites before reacting with an accomodated H-atom

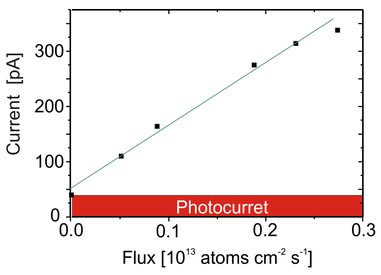
$$\frac{d\Theta}{dt} = j_H \cdot n \cdot \frac{\Theta}{N}\left(1 - \frac{\Theta}{N}\right)^n$$

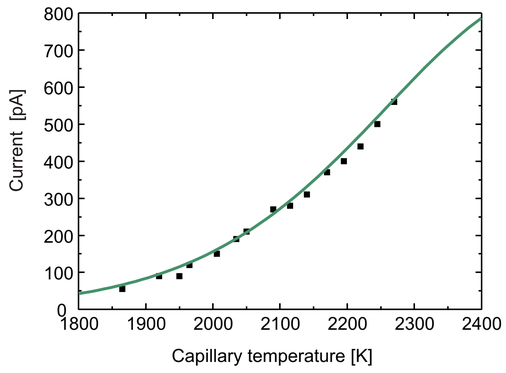


Experimental results

Possible sources of the signal





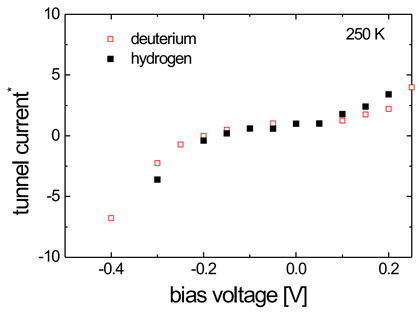


→ Capillary induced photocurrent plays minor role

→ Tunnel current induced by H atom impact

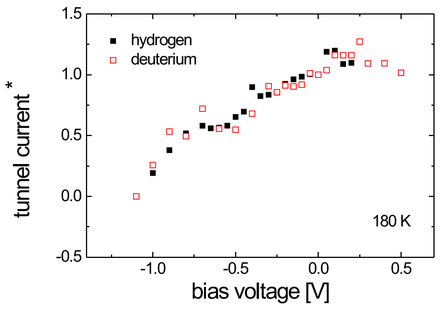
Energy selective detection of e-h pairs

In the course of adsorption and LH reactions



* normalised at 0 V

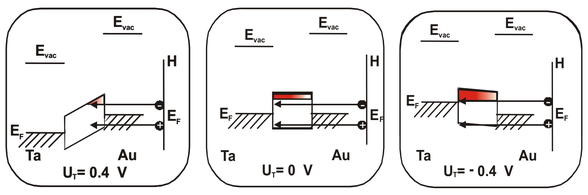
In the course of adsorption and HA-ER reactions



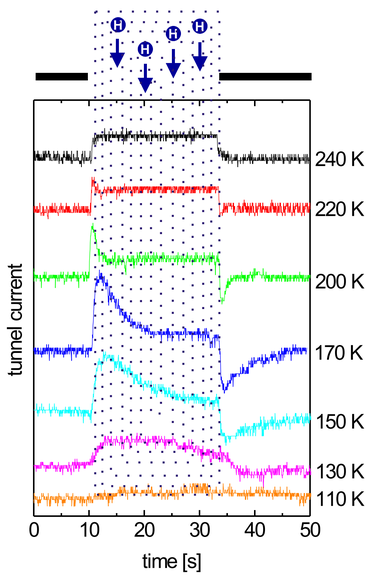
Change of polarity in the H induced tunnel current indicates:

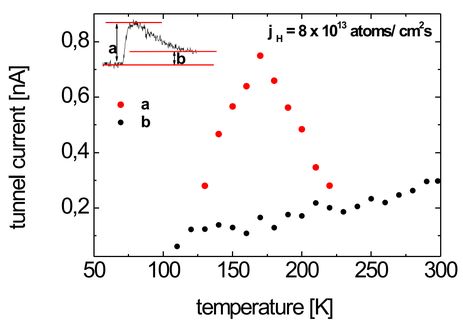
→ a simultaneous detection of electrons and holes

→ a detection method which acts as an two band tunnel device



Chemically induced tunnel current as a function of sample temperature





→ Simple square form for temperatures T > 250 K

→ Prominent overshoot of the tunnel current at the beginning and the end of H exposure in the temperature range 150 - 200 K

→ Linear dependence of the steady state signal over the whole temperature range

Theoretical consideration

$$f_{excitation} = A \quad \exp \quad \frac{(E \quad E_F)}{k_B \quad T}$$

$f_{excitation}$ taken to be Maxwell distribution

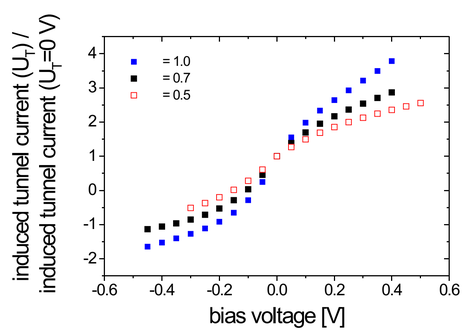
→ exactly founded by TDDFT calculations by group E. Pehlke

$$A = 1 \quad 10^{\;9}$$

$$T = 1000K$$

band gap = 4.0 eV

barrier height = 2.0 eV



Small influence of the bias voltage on deuterium induced signal

→ wider distribution of excited electrons for D than for H