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Nonthermal UV-laser induced diffusion and desorption processes of CO on nano-sized Pd aggregates adsorbed on an epitaxial Al_2O_3-support

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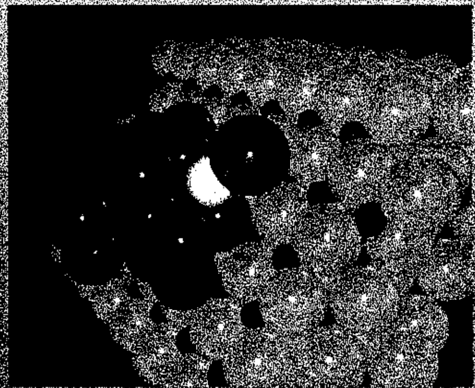
A. Wille [a)], K. Al-Shamery [a)], H.-J. Freund [b)]



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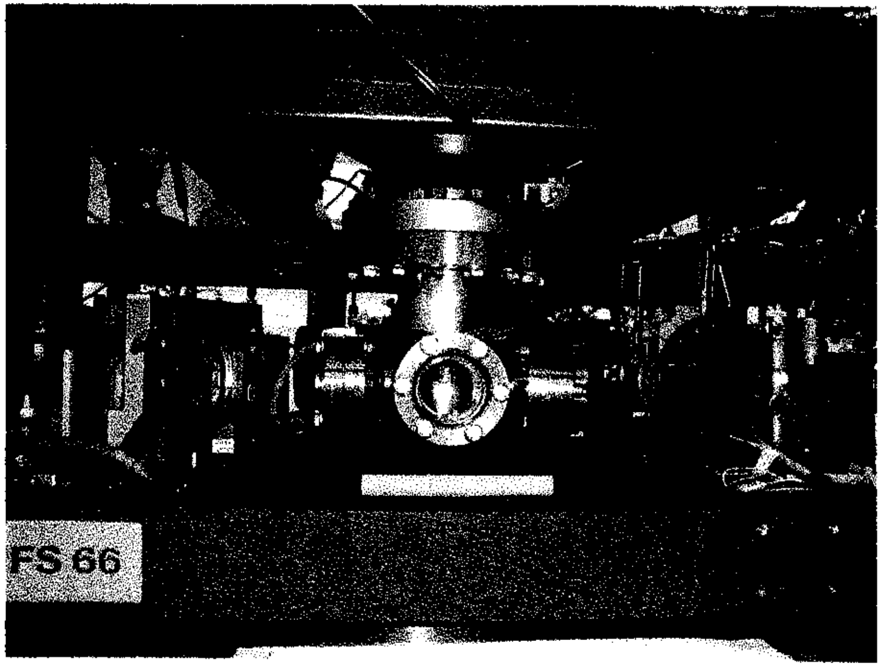
Contents

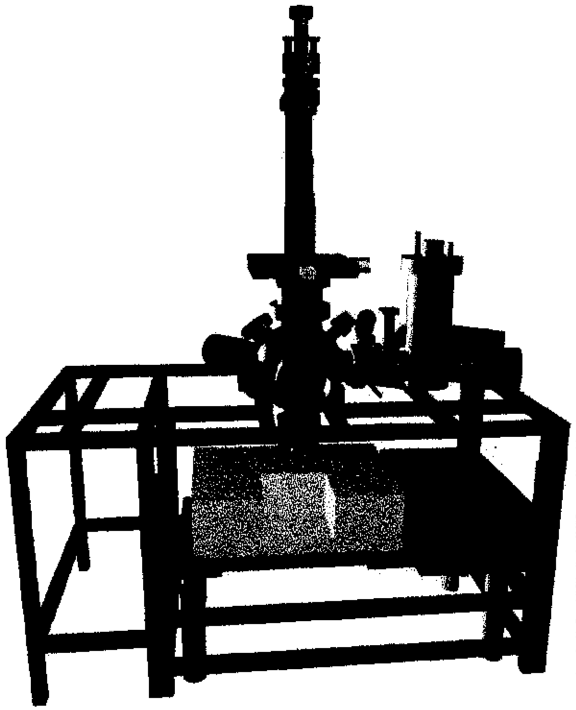
Motivation

- ⇒ **Nanostructured metal particels important for many catalytic reactions**
- ⇒ **Closing of the „material gap“**
- ⇒ **Size and morphology dependence of photodissoziation and photodesorption of methane on $Pd/Al_2O_3/NiAl(110)$**
- ⇒ **Variation of aggregate size as tool to control surface photo reactions**
- ⇒ **Better understanding of the relevant mechanisms by probing CO on $Pd/Al_2O_3/NiAl(110)$**

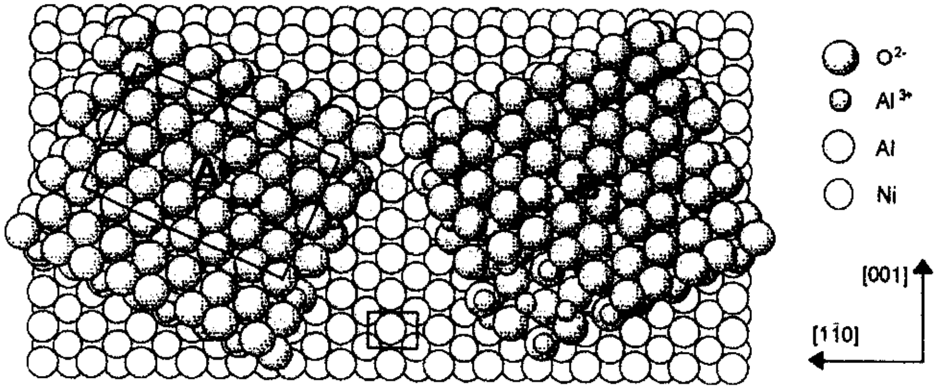
Experimental setup

- Standard ultra high vacuum chamber
- Spectroscopic utilities: purged FTIR system, LEED, Auger
- Laser system: Nd/YAG laser, 10 pulses per second, 0.3 mJ/cm^2 at 355 nm



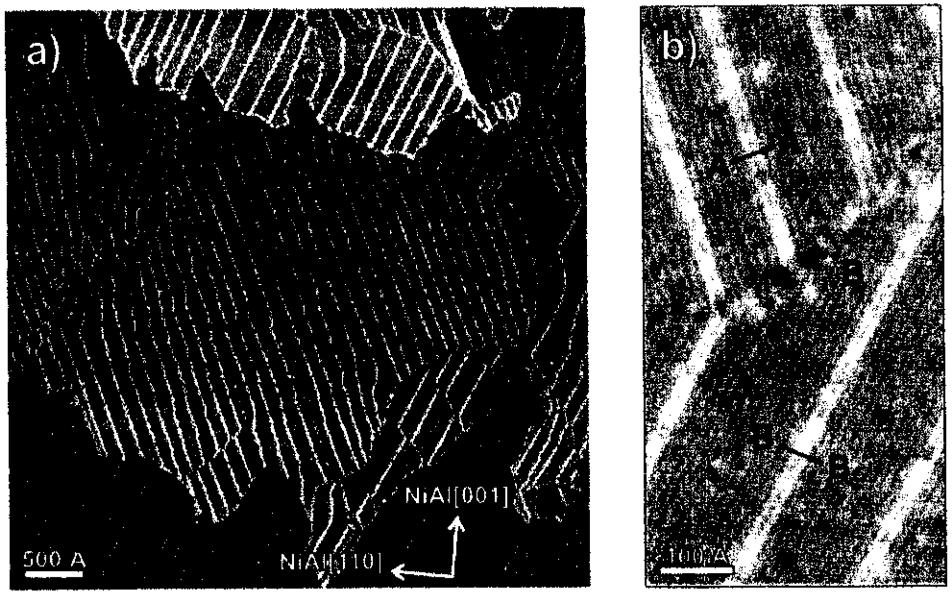


The alumina film



Structure model of Al_2O_3/ NiAl(110), derived from a distorted g-Al_2O_3 structure

[J. Libuda, M. Bäumer, H.-J. Freund, *J. Vac. Sci. Technol.* A **12** (1994) 2259]



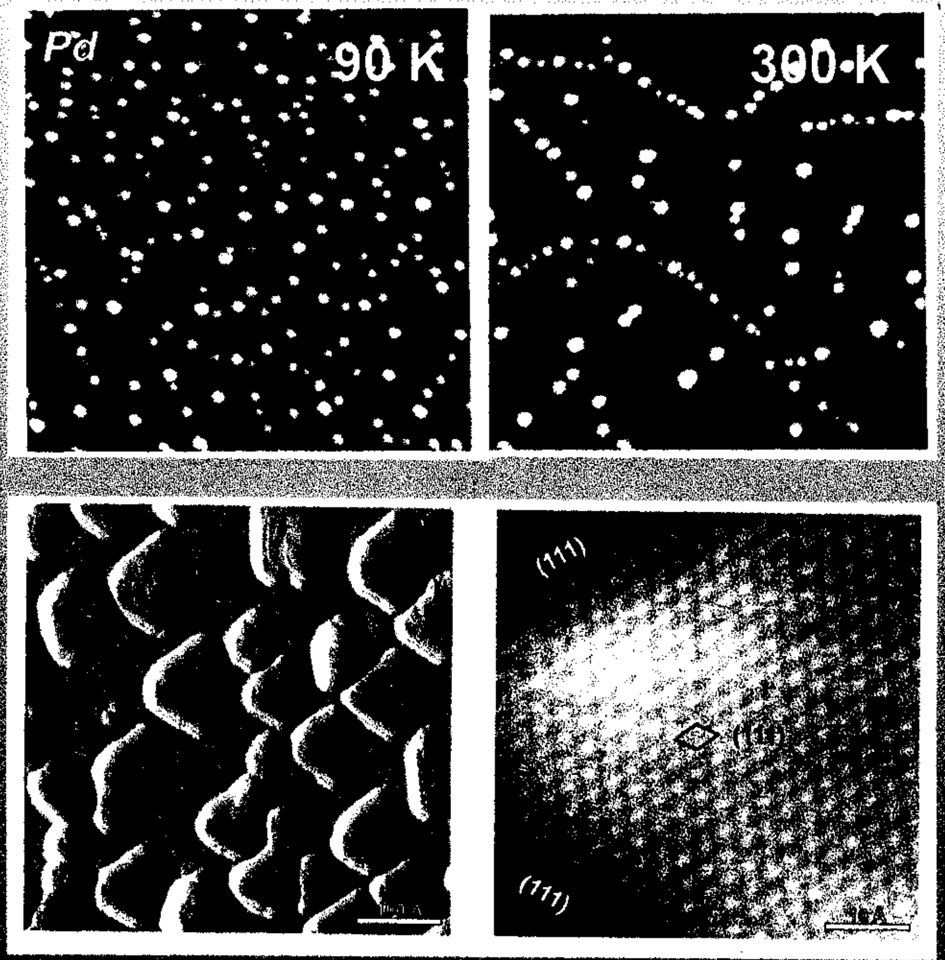
STM images of the alumina film:

a) STM image of the thin alumina film grown on NiAl(110) (CCT, 5000 A^2)

b) Close-up showing the various domain boundaries in more detail (CCT, 775 A x 400 A); (A-A), (B-B): antiphase domain boundaries, (A-B): reflection domain boundaries

[illegible] to be published]

Pd deposition at 300 K and 90 K



STM images taken after deposition of small amounts of Pd (CCT, 1000 Å^2)

Left: amorphous aggregates

Right: crystalline aggregates

[M. Frank, M. Bäumer, to be published]

Left: Differentiated STM image of crystalline Pd aggregates grown at 300 K (CCT, 500 Å^2)

Right: Close-up showing an

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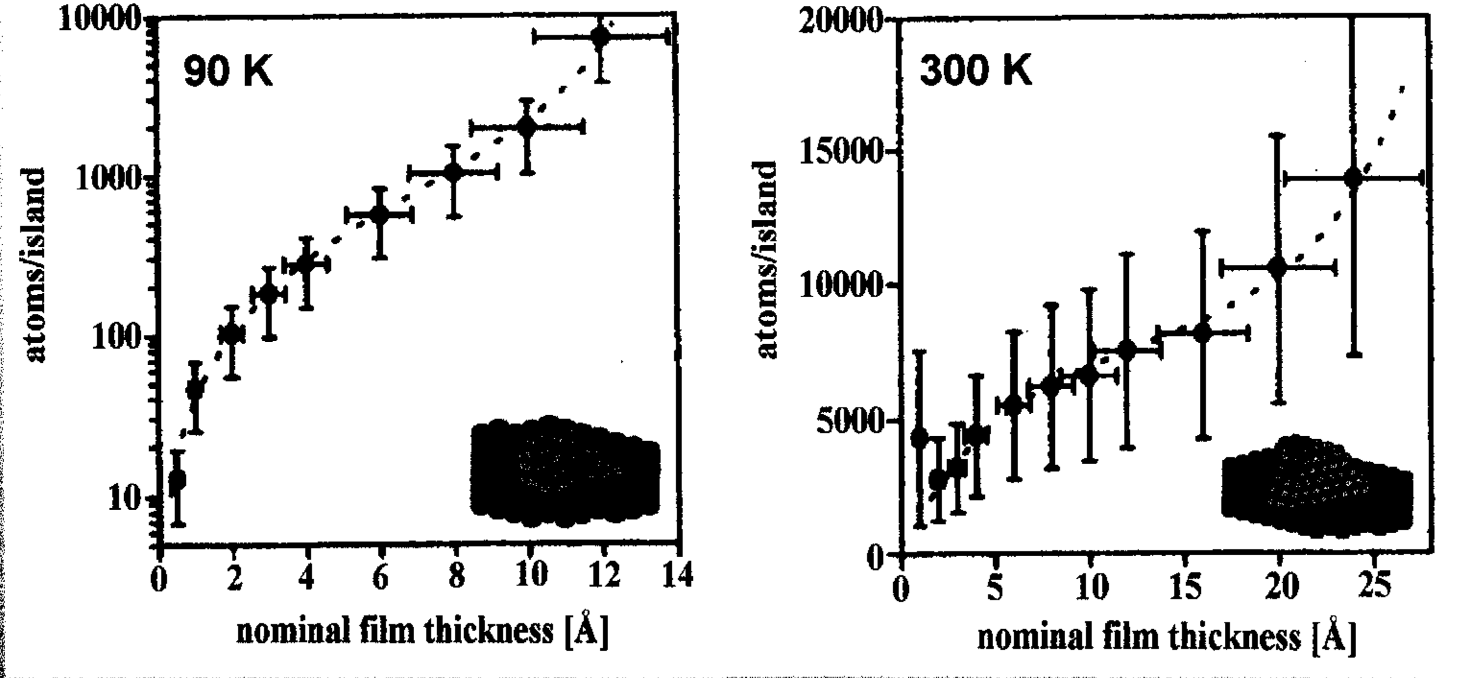
Average sizes of Pd aggregates



Average number of atoms per island determined by LEED spot-profile analysis

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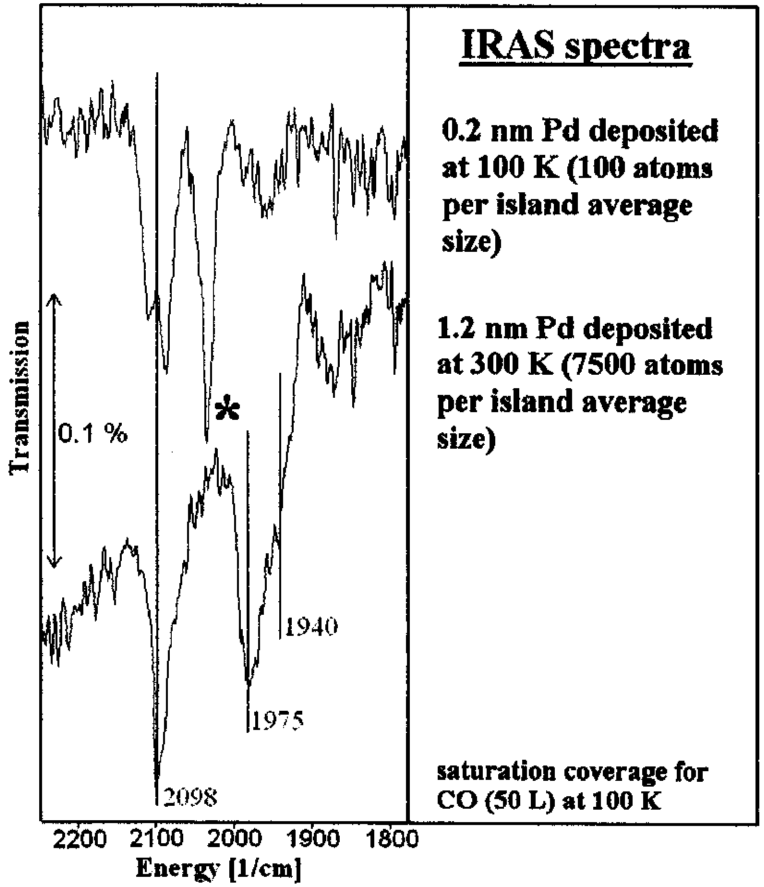
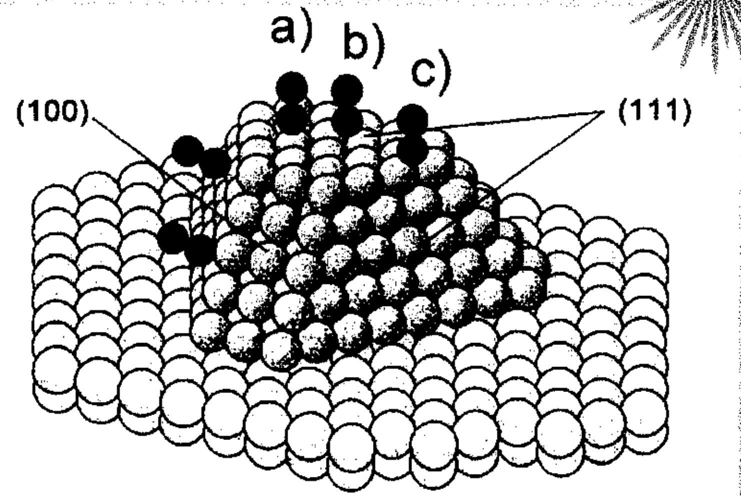
CO on Pd/Al_2O_3/NiAl(110)





Schematic model of a crystalline Pd particle and the specific adsorption sites of CO:

a) Terminal bonded CO on terraces: 2080-2100 cm^{-1}

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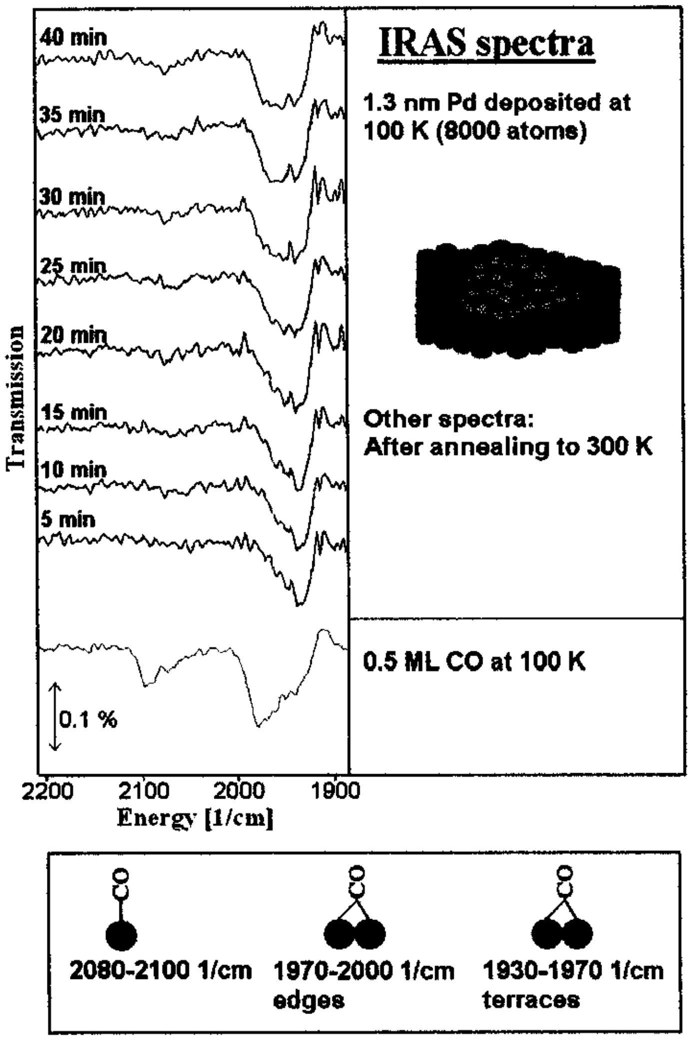
Annealing and cooling experiment



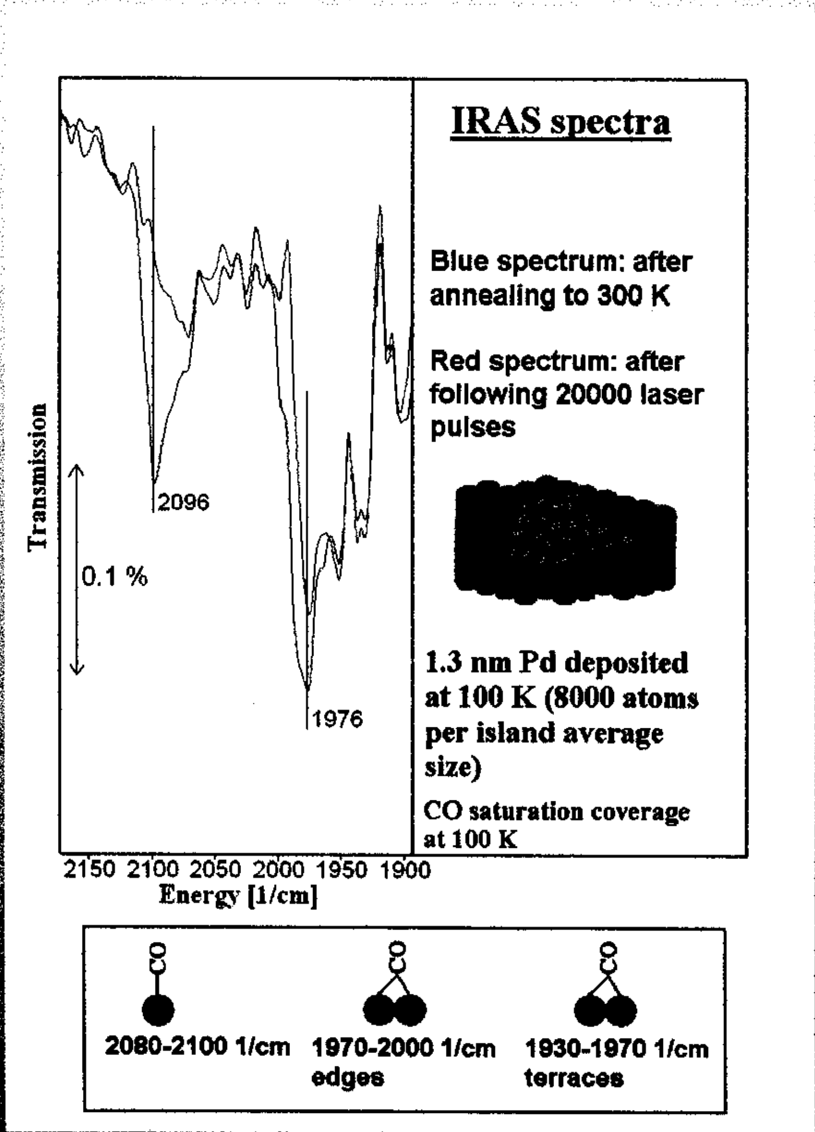
⇒ Terminal bonded CO species and bridge bonded species on the edges disappear by annealing to 300 K.

⇒ Slight reoccupation of terminal bonded species during cooling period

⇒ Partially reoccupation of the bridge bonded adsorption site on the edges

⇒ No changes at 100 K

Annealing experiments



8000 atoms per island (amorphous)

⇒ Obvious increase in band intensity of terminal bonded CO caused by laser exposure

⇒ Small increase in band intensity of bridge bonded CO species on the edges

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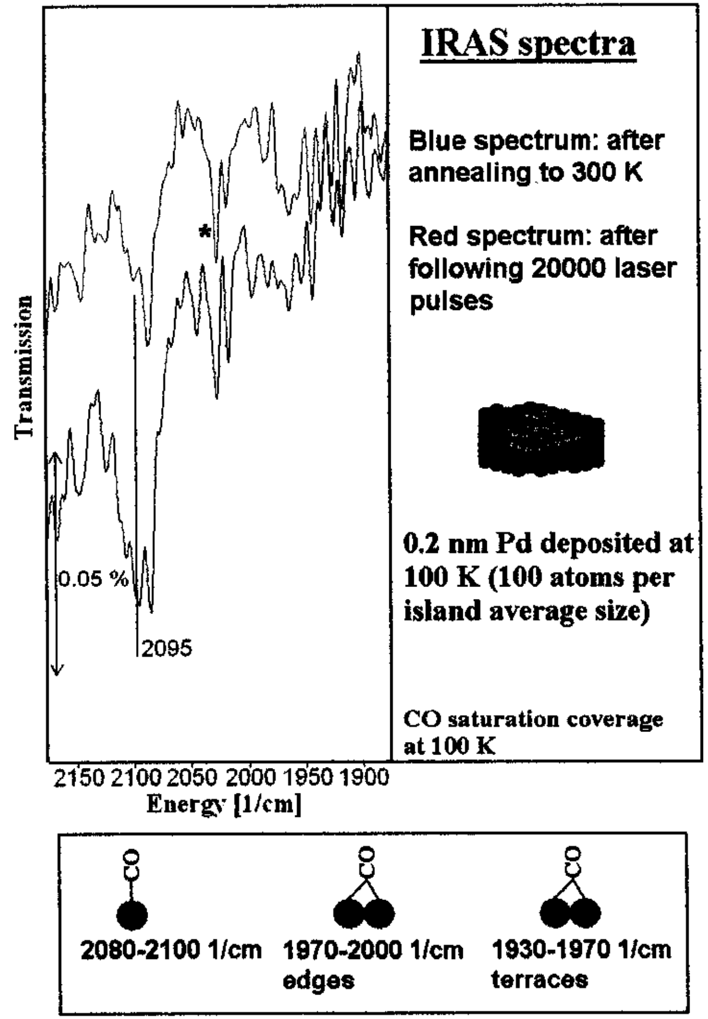
Annealing experiments

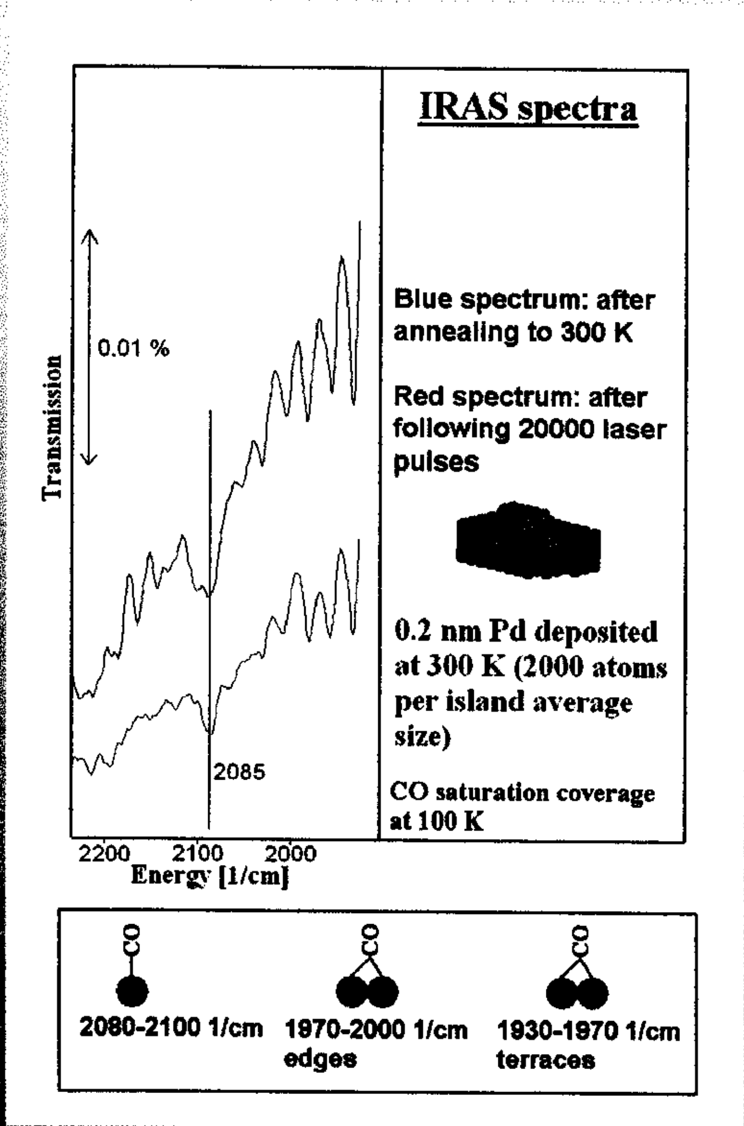


100 atoms per island

(amorphous)

⇒ **Obvious increase in band intensity of terminal bonded CO caused by laser exposure**

Annealing experiments



2000 atoms per island

(crystalline)

⇒ Obvious increase in band intensity of terminal bonded CO caused by laser exposure

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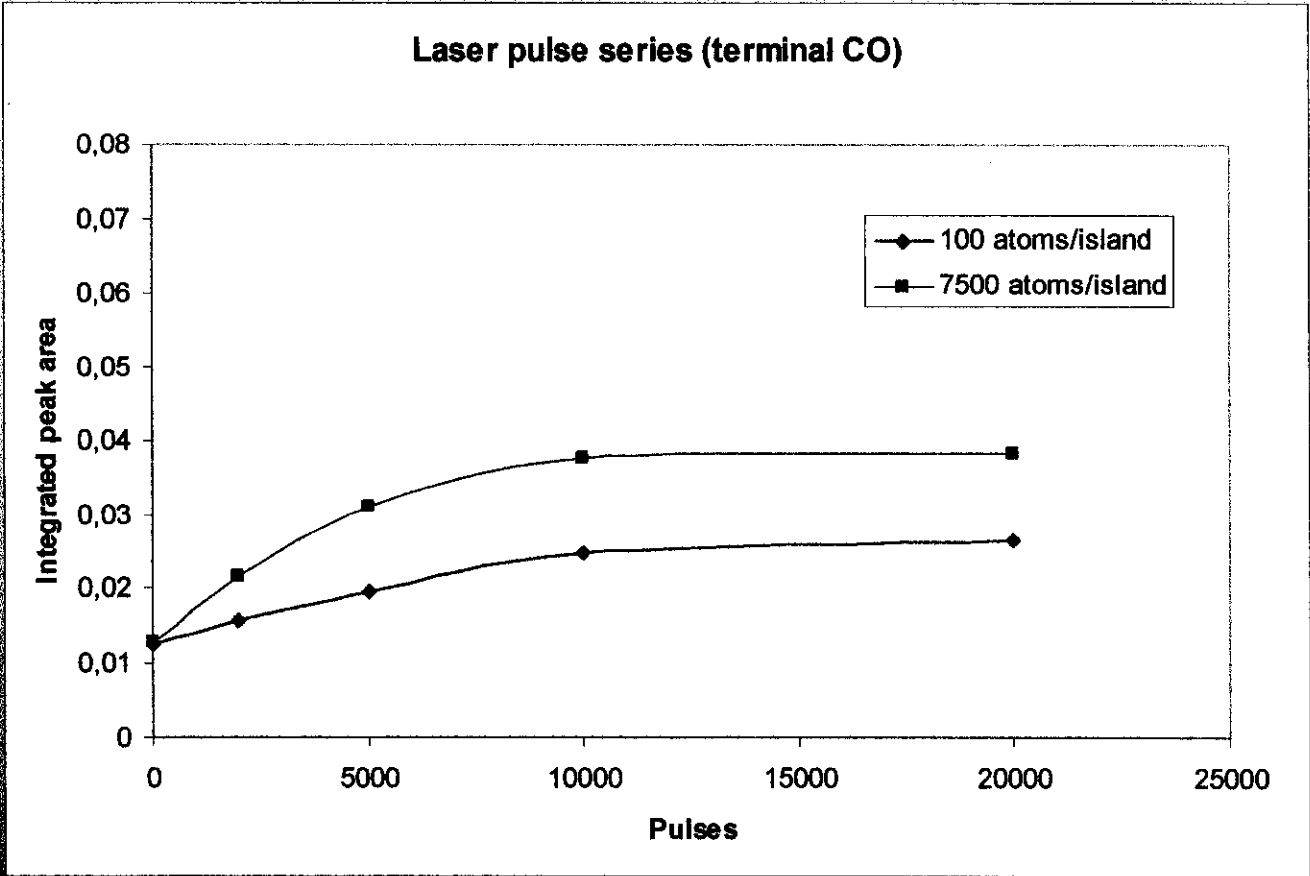
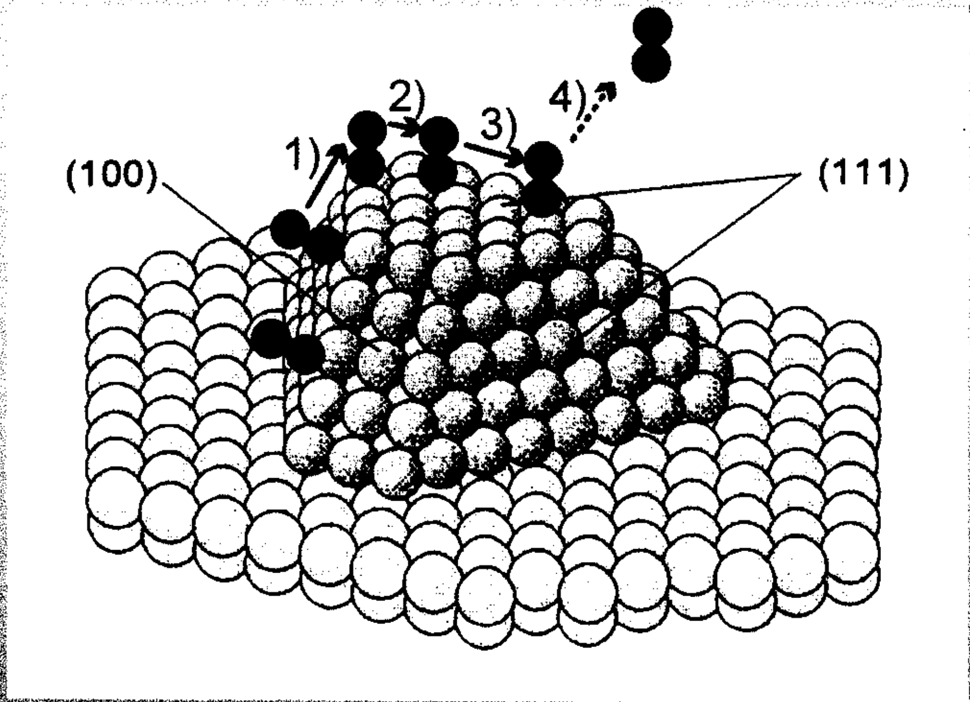
Laser pulse series



bonded

Possible diffusion mechanism



1) CO diffusion from non-infrared active adsorption sites on the particle facets onto infrared active on-top sites

Summary

Effects of laser exposure:

⇒ **Obvious increase in band intensity of terminal bonded CO**

⇒ **Increase in band intensity of bridge bonded CO on the edges**

⇒ **Size dependent effects by laser exposure**

⇒ **Suggestion of a laser induced diffusion mechanism**

Acknowledgement

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