



ELSEVIER

Surface Science 498 (2002) L71–L77



www.elsevier.com/locate/susc

Surface Science Letters

# Study of CO adsorption on crystalline-silica-supported palladium particles

Javier B. Giorgi<sup>\*</sup>, Thomas Schroeder, Marcus Bäumer, Hans-Joachim Freund

*Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*

Received 31 July 2001; accepted for publication 19 October 2001

## Abstract

Supported palladium particles have been studied using a recently developed crystalline silica film. The SiO<sub>2</sub> film, as seen for the first time by scanning tunnelling microscopy (STM), is sufficiently flat to be used for model catalyst studies. Palladium particles grown on silica at room temperature are round and somewhat disordered as seen by STM, suggesting a strong interaction between the Pd particles and the silica support. The structural properties of the palladium particles were probed by CO adsorption at 90 K, and monitored by IRAS. The same general adsorption sites are observed for the Pd particles grown on silica as have previously been observed for crystalline Pd particles on alumina, however a larger fraction of on-top sites was observed on silica, indicative of the smaller and more disordered particles. These first results obtained for the Pd/SiO<sub>2</sub>/Mo(1 1 2) system are encouraging for the use of the crystalline SiO<sub>2</sub> substrate as a model-catalyst support. © 2001 Published by Elsevier Science B.V.

*Keywords:* Palladium; Carbon monoxide; Silicon oxides; Adatoms; Clusters; Vibrations of adsorbed molecules; Infrared absorption spectroscopy; Scanning tunneling microscopy

## 1. Introduction

Supported metal particles are commonly used heterogeneous catalysts. The active catalytic material is dispersed as small particles in order to maximise surface area. However under these conditions particle-size effects and metal–support interactions play an important role in the material's catalytic behaviour. An important part of catalytic research is dedicated to the exploitation of these effects to improve catalytic activity or selectivity [1]. Despite this, understanding of the activity–

structure relationship at a fundamental level is still quite limited. In this direction, our group has performed a number of studies of metal particles supported on thin, well-ordered oxide films, which are grown on a metal single-crystal surface [2–4]. Using a thin film oxide grown on a metal substrate has the advantage of good electrical and thermal conductivity relative to bulk oxides, thereby allowing experimental investigation by electron spectroscopies and scanning tunnelling microscopy (STM) without charging effects [5–7].

The simplest method of producing a thin oxide film is by oxidation of a metallic substrate. This approach has been used to obtain a crystalline, well-ordered alumina film (Al<sub>2</sub>O<sub>3</sub>) grown on NiAl(1 1 0) [8]. This film grows reproducibly with a

<sup>\*</sup> Corresponding author. Fax: +49-30-8413-4101.

E-mail address: giorgi@fhi-berlin.mpg.de (J.B. Giorgi).

well-defined defect structure [4,9,10]. The  $\text{Al}_2\text{O}_3/\text{NiAl}(110)$  support has been used to study small metal particles of a wide range of sizes and characteristics [2,4,11], grown with a relatively narrow size distribution without the necessity of a complicated experimental set-up for mass-selected cluster deposition. Further investigation of the metal–support interaction was also pursued by hydroxylation of the alumina support [12,13].

An alternative, more complicated method of producing a well-ordered oxide film involves the hetero-epitaxial growth of the oxide on a crystalline metal substrate [14]. This approach has made possible for the first time the preparation of a crystalline silica ( $\text{SiO}_2$ ) film grown on  $\text{Mo}(112)$  [15–17]. It is the purpose of this work to show that this silica film is well suited for model-catalyst studies.

The development of the crystalline silica film and its use as a catalytic support is based on the aim to understand the role of the support in catalytic systems by comparing the structure and reactivity of metal particles grown on different supports (in this case, silica vs. alumina). In real catalysts, these two common supports have shown differences in their interactions with metal-particle systems [1,18–20]. Silica–metal interactions tend to be weaker, although the reason for this is usually ascribed to the smaller hydroxyl content of the silica supports with respect to the alumina supports [19,20].

In this article we report first results for the growth of palladium particles on the well-ordered, crystalline silica film. The Pd particles are observed by STM and their structural properties are probed by CO adsorption.

## 2. Experimental

Experiments were performed in an ultra-high-vacuum (UHV) system equipped with LEED, an XPS/UPS set-up, an STM, and IRAS capability. Only STM and IRAS results will be shown here, LEED and XPS/UPS are routinely used as checks during the oxide preparation procedure. The background pressure in the different areas of the system is lower than  $2 \times 10^{-10}$  mbar.

The silica film preparation was performed as described previously [15–17]. The procedure results in a crystalline  $\text{SiO}_2$  film, approximately 6 Å in thickness. Palladium was evaporated from a rod (purity >99.9%) by electron bombardment with the sample at room temperature. The sample was maintained at the same potential as the Pd rod to avoid sputtering of the surface by Pd ions. Flux calibration has been performed with a quartz microbalance. The deposition rate was measured as 0.815 Å/min. Carbon monoxide (AGA, purity >99.997%) was further purified by a liquid nitrogen trap during dosing, which was achieved utilising a pinhole doser.

Surface images were recorded by an Omicron Variable-Temperature STM, operated at room temperature. Infrared spectra were measured using a Bruker IFS 66v/S spectrometer with a liquid-nitrogen cooled MCT detector. The IRAS geometry involves an 84° grazing incidence, and p-polarised light is detected and accumulated for 4096 scans to obtain each spectrum.

## 3. Results and discussion

The use of a crystalline silicon dioxide film as a support for model catalytic studies has several advantages over the commonly used amorphous material. The film used in this study is stoichiometric  $\text{SiO}_2$ , contains no holes, is atomically flat, has long-range order, and can be prepared reproducibly to a thickness of  $6 \pm 2$  Å [15–17]. These characteristics make it a suitable support for model catalysts, on which metal particles can be grown reproducibly.

The use of a crystalline film also allows us to take full advantage of diffraction techniques for characterisation [15–17], and STM for imaging. It is worth noting that STM images of amorphous-silica supported Cu particles have been obtained [14,21]. Although some structure in the Cu particles was seen, the amorphous silica film was too rough for imaging.

A typical STM image of our crystalline silica film is shown in Fig. 1, a full discussion of the STM results is the subject of a subsequent paper [22]. Briefly, the image shows a large area

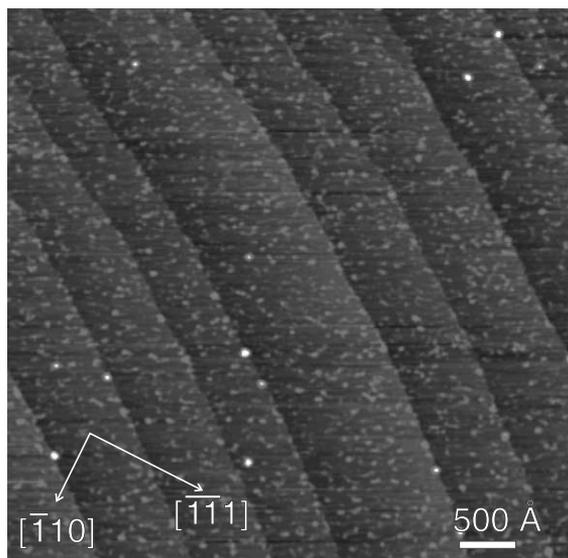


Fig. 1. Large area STM image of SiO<sub>2</sub>/Mo(1 1 2). Image taken with  $V_{\text{tip}} = -5.88$  V and  $I = 0.73$  nA. The crystal orientation of the underlying Mo(1 1 2) surface is indicated; steps correspond to steps in the Mo surface.

(500 × 500 nm<sup>2</sup>) where steps due to the underlying Mo(1 1 2) are clearly visible. Ad-islands can also be seen which are consistent with the growth mode of the silica film previously suggested by SPA-LEED [15]. The corrugation on the terraces is ~1 Å, with ad-islands (1–10 Å) present above the terrace plane. The film has a RMS roughness smaller than 2 Å.

Palladium particles were grown on the silica film while maintaining the sample at room temperature. Under these conditions, the palladium particles appear to be 30–60 Å in diameter for the coverages studied (Fig. 2). However, STM has often been found to overestimate particle size [23,24], and these numbers should be regarded as an approximation, or upper limits. It seems more valuable to describe the particles in terms of their metal content and distribution on the surface. The measured particle density is approximately constant at  $\sim 5 \times 10^{12}$  particles/cm<sup>2</sup> for the measured intermediate coverages (1–5 Å Pd). From the average metal thickness and the number of particles, the number of atoms per particle can be easily calculated. The number of atoms per particle will be used in the rest of this paper.

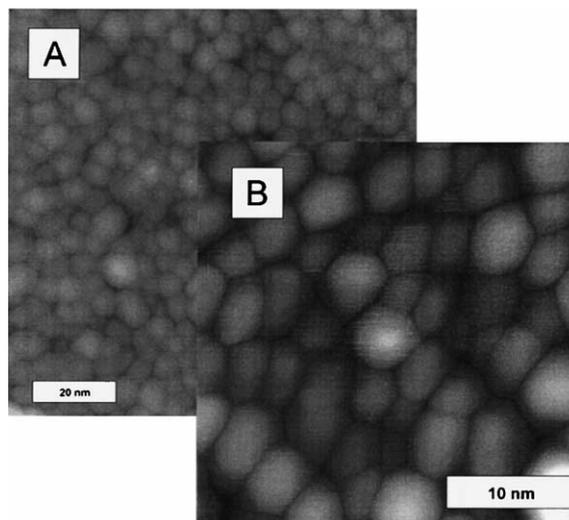


Fig. 2. STM images of supported Pd particles. (A) 4.9 Å Pd on SiO<sub>2</sub>/Mo(1 1 2), 850 atoms/particle.  $V_{\text{tip}} = -2.36$  V,  $I = 0.10$  nA. (B) Close up. 1.1 Å Pd on SiO<sub>2</sub>/Mo(1 1 2), 110 atoms/particle.  $V_{\text{tip}} = -2.19$  V,  $I = 0.11$  nA.

The particles on the surface seem to be homogeneously distributed for the coverages used. It seems reasonable to suggest that ad-islands of the silica film would act as nucleation sites. However, ad-island density is variable from film to film, and in all cases it is higher than the observed Pd particle density. A closer look at the morphology of the Pd particles grown on SiO<sub>2</sub> (Fig. 2B) shows that most particles seem to have a round top and be irregular in shape, but some particles with sharp edges can be observed. Flat facets on the particles were not observed, in contrast with Pd particles grown on alumina where predominantly (1 1 1) facets are seen [2,25], and with Pd particles grown on MgO where (1 1 1) or (1 0 0) facets can be observed for particles of varying size [26,27]. The irregular, non-faceted particles observed here seem to be more consistent with Pd particles as grown on alumina at 90 K, where kinetic restraints prevent the particles forming crystallites even after allowing the particles to reach room temperature [4].

The structural properties of the Pd particles grown on SiO<sub>2</sub> were probed by CO adsorption. The extensive literature regarding the adsorption of carbon monoxide to Palladium single crystals



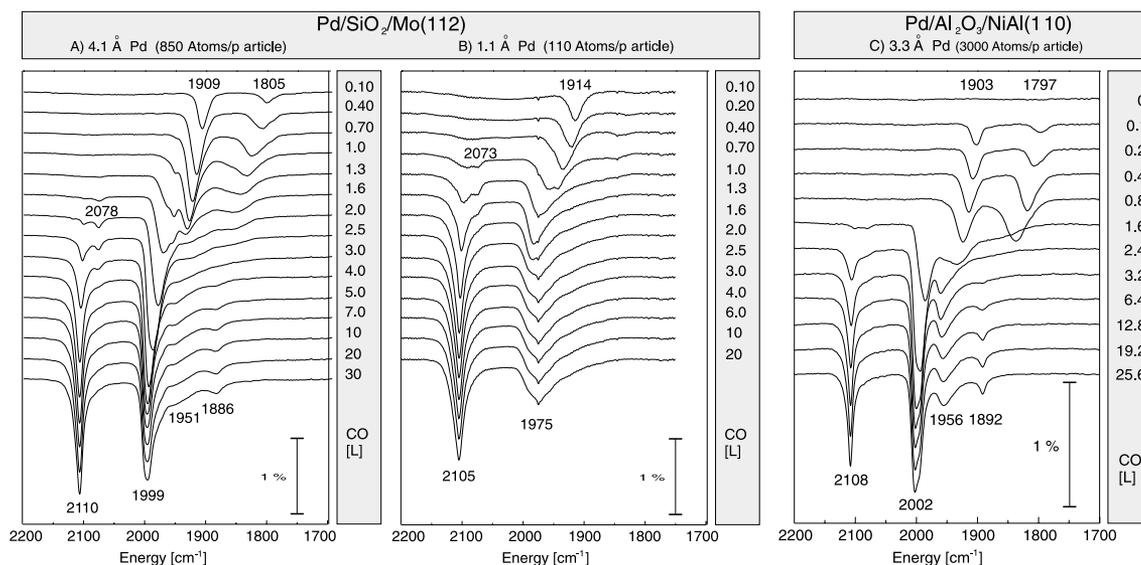


Fig. 3. Infrared spectra of increasing doses of CO adsorbed on Pd particles grown at room temperature. CO dosage and measurement performed at 90 K: (A) 4.1 Å Pd on  $\text{SiO}_2/\text{Mo}(112)$ , (B) 1.1 Å Pd on  $\text{SiO}_2/\text{Mo}(112)$  and (C) 3.3 Å Pd on  $\text{Al}_2\text{O}_3/\text{NiAl}(110)$  [4]. The “blip” seen in all the spectra of (B) at  $1975\text{ cm}^{-1}$  is an artefact during the measurement of the background spectrum.

A look at smaller palladium particles (110 atoms/particle, Fig. 3B) confirms the trends and assignments described above. The fraction of on-top bound CO (low coordination) is larger than for bigger particles, which is not surprising since this is a common trend for decreasing particle size [4]. An indication of increasing disorder with decreasing size is given by the bridge and threefold-hollow site peaks, which become much broader and smeared. Interestingly, while the aggregates become more disordered, the peak at  $2073\text{ cm}^{-1}$  is still clearly visible corroborating its assignment as on-top sites at edges.

Overall, STM shows palladium particles that are quite disordered, but the IRAS results indicate at least at higher coverages Pd particles with well-defined adsorption sites for CO, which can be assigned to different crystal facets of Pd. To understand this better it is useful to extend the discussion to previously obtained results for Pd particles grown on  $\text{Al}_2\text{O}_3$ .

Palladium particles grown on alumina ( $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ ) at room temperature have been shown to grow as Pd crystallites with predominant (111) facets. The particles are cubo-octahedral truncated-pyramids that exhibit a flat top (111) surface, with

(111) and (100) lateral facets [25]. The particles aggregate along the line defects of the oxide substrate and align azimuthally to the oxide lattice [4,11,47]. At a coverage of about  $3\text{ \AA}$ , the average particle density is at  $\sim 5 \times 10^{12}\text{ atoms/cm}^2$ . The Pd particles grown on  $\text{SiO}_2$  are somewhat more disordered and, due to higher particle density, smaller than Pd particles grown on  $\text{Al}_2\text{O}_3$ . This suggests that Pd has less mobility on the  $\text{SiO}_2$  film.

However, it is noteworthy that the general trends in the IR spectra of CO adsorbed on Pd/ $\text{SiO}_2/\text{Mo}(112)$ , the peak positions, and the peak widths coincide with those observed for CO adsorbed on Pd/ $\text{Al}_2\text{O}_3/\text{NiAl}(110)$  (shown on Fig. 3C for comparison), with the implication that a certain degree of crystallinity is also present for the Pd particles on the silica support. Note however the higher fraction of on-top bound CO (low coordination) over bridge bound CO (higher coordination) for the CO/Pd/ $\text{SiO}_2$  system, in agreement with the previously stated trends that the Pd particles on silica are smaller and less ordered than on alumina. This is further inferred from the absence of the threefold-hollow site peak at  $1805\text{ cm}^{-1}$  for Pd small particles on silica, which was observed for similar palladium coverages on alumina [39].

#### 4. Conclusion

The question of the role of the support in model catalysts has led to the development of new, well-defined oxide films to be used as supports. Here we show for the first time STM images of a flat, crystalline silica film that has been recently developed. The film is used for the first time as an oxide support for a catalytic system (Pd particles) and the initial results regarding particle morphology and CO adsorption are compared with a similar system of Pd particles supported on an alumina film.

The results show that palladium particles are more disordered and smaller, implying a stronger overall interaction with the silica film than with the alumina film. This conclusion is in agreement with the stronger adhesion energy observed for the more covalent oxide [48], but is surprising in the catalytic field where silica is considered as one of the more innocuous supports [1,18]. An explanation may be found in the difference of the surface morphology (and particle nucleation sites) for the pristine surfaces compared here. Also, the intrinsic presence of hydroxyl groups in the oxide supports used in real catalytic systems play an important role in the metal–support interaction. A comparison between model and real catalytic systems will necessarily have to include hydroxylated films. Work in this direction is being pursued for a hydroxylated silica film to be compared with available results on a hydroxylated alumina film [12,13].

The CO adsorption sites on Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> seem to be identical, indicating the similarity of the two systems, but the different ratios of sites confirm the STM observation of smaller and more disordered particles on silica than on alumina. The first results presented here are encouraging for the use of crystalline SiO<sub>2</sub> films grown on Mo(1 1 2) as a support for model-catalyst studies. A systematic comparison of silica and alumina supported catalysts is expected to provide further insight into the role of the support in these systems.

#### Acknowledgements

We are thankful to a number of agencies for their financial support: Deutsche Forschungs-

gemeinschaft (DFG), Bundesministerium für Bildung und Forschung (BMBF), and Fonds der Chemischen Industrie. We also thank the Alexander von Humboldt Foundation and the National Science and Engineering Research Council of Canada for granting of fellowships.

#### References

- [1] M. Che, C.O. Bennet, *Adv. Catal.* 20 (1989) 153.
- [2] M. Bäumer, H.-J. Freund, *Prog. Surf. Sci.* 61 (1999) 127.
- [3] H.-J. Freund, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 452.
- [4] M. Frank, M. Bäumer, *Phys. Chem., Chem. Phys.* 2 (2000) 3723.
- [5] S.C. Street, C. Xu, D.W. Goodman, *Annu. Rev. Phys. Chem.* 48 (1997) 43.
- [6] C.R. Henry, *Surf. Sci. Rep.* 31 (1998) 235.
- [7] C.T. Campbell, *Surf. Sci. Rep.* 27 (1997) 1.
- [8] R.M. Jaeger, H. Kühlenbeck, H.-J. Freund, M. Wuttig, W. Hoffmann, R. Franchy, H. Ibach, *Surf. Sci.* 259 (1991) 235.
- [9] J. Libuda, F. Winkelmann, M. Bäumer, H.-J. Freund, T. Bertrams, H. Neddermeyer, K. Müller, *Surf. Sci.* 318 (1994) 61.
- [10] M. Adelt, S. Nepijko, W. Drachsel, H.-J. Freund, *Chem. Phys. Lett.* 291 (1998) 425.
- [11] M. Bäumer, M. Frank, M. Heemeier, R. Kühnemuth, S. Stempel, H.-J. Freund, *Surf. Sci.* 454–456 (2000) 957.
- [12] M. Heemeier, M. Frank, J. Libuda, K. Wolter, H. Kühlenbeck, M. Bäumer, H.-J. Freund, *Catal. Lett.* 68 (2000) 19.
- [13] J. Libuda, M. Frank, A. Sandell, S. Andersson, P.A. Brühwiler, M. Bäumer, N. Märtensson, H.-J. Freund, *Surf. Sci.* 384 (1997) 106.
- [14] D.W. Goodman, *Surf. Rev. Lett.* 2 (1995) 9.
- [15] T. Schroeder, A. Hammoudeh, M. Pykavy, N. Magg, M. Adelt, M. Bäumer, H.-J. Freund, *Solid State Electron.* 45 (2001) 1471.
- [16] T. Schroeder, M. Adelt, B. Richter, M. Naschitzki, M. Bäumer, H.-J. Freund, *Microelectron. Reliab.* 40 (2000) 841.
- [17] T. Schroeder, M. Adelt, B. Richter, M. Naschitzki, M. Bäumer, H.-J. Freund, *Surf. Rev. Lett.* 7 (2000) 7.
- [18] G.C. Bond, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, VCH Verlagsgesellschaft mbH, Weinheim, 1997, pp. 752–770.
- [19] Y. Iwasawa, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, VCH Verlagsgesellschaft mbH, Weinheim, 1997, pp. 853–873.
- [20] J.R. Anderson, *Structure of Metallic Catalysts*, Academic Press, London, 1975.
- [21] X. Xu, S.M. Vesecky, D.W. Goodman, *Science* 258 (1992) 788.
- [22] T. Schroeder, J.B. Giorgi, M. Bäumer, H.-J. Freund, in preparation.

- [23] S. Stempel, M. Bäumer, H.-J. Freund, Surf. Sci. 402–404 (1998) 424.
- [24] D. Keller, Surf. Sci. 253 (1991) 353.
- [25] K.H. Hansen, T. Worren, S. Stempel, E. Lægsgaard, M. Bäumer, H.-J. Freund, F. Besenbacher, I. Stensgaard, Phys. Rev. Lett. (1999) 4120.
- [26] H. Graoui, S. Giorgio, C.R. Henry, Surf. Sci. 417 (1998) 350.
- [27] C.R. Henry, C. Chapon, C. Duriez, S. Giorgio, Surf. Sci. 253 (1991) 177.
- [28] F.M. Hoffmann, Surf. Sci. Rep. 3 (1983) 107.
- [29] M. Tüshaus, Hochauflösende Schwingungsspektroskopie an adsorbierten Molekülen, Ph.D., Frei Universität, Berlin, 1990.
- [30] M. Tüshaus, W. Berndt, H. Conrad, A.M. Bradshaw, B. Persson, Appl. Phys. A 51 (1990) 91.
- [31] W.K. Kuhn, J. Szanyi, D.W. Goodman, Surf. Sci. Lett. 274 (1992) L611.
- [32] X. Xu, J. Szanyi, Q. Xu, D.W. Goodman, Catal. Today 21 (1994) 57.
- [33] J.C. Cook, S.K. Clowes, E.M. McCash, J. Chem. Soc., Faraday Trans. 93 (1997) 2315.
- [34] B. Bourguignon, S. Carrez, B. Dragnea, H. Dubost, Surf. Sci. 418 (1998) 171.
- [35] K. Fukui, H. Miyauchi, Y. Iwasawa, J. Phys. Chem. 100 (1996) 18795.
- [36] R. Raval, S. Haq, M.A. Harrison, G. Blyholder, D.A. King, Chem. Phys. Lett. 167 (1990) 391.
- [37] R. Raval, G. Blyholder, D.A. King, J. Electron. Spectrosc. Relat. Phenom. 54/55 (1990) 629.
- [38] K. Wolter, O. Seiferth, J. Libuda, H. Kuhlenbeck, M. Bäumer, H.-J. Freund, Surf. Sci. 402–404 (1998) 428.
- [39] K. Wolter, O. Seiferth, H. Kuhlenbeck, M. Bäumer, H.-J. Freund, Surf. Sci. 399 (1998) 190.
- [40] D.R. Rainer, C. Xu, P.M. Holmblad, D.W. Goodman, J. Vac. Sci. Technol. A 15 (1997) 1653.
- [41] C. Goyhenex, M. Croci, C. Claeys, C.R. Henry, Surf. Sci. 352–354 (1996) 475.
- [42] X. Xu, D.W. Goodman, J. Phys. Chem. 97 (1993) 7711.
- [43] P. Hollins, Surf. Sci. Rep. 16 (1992) 51.
- [44] P. Gelin, A.R. Siedle, J.T. Yates Jr., J. Phys. Chem. 88 (1984) 2978.
- [45] A.M. Bradshaw, F.M. Hoffmann, Surf. Sci. 72 (1978) 513.
- [46] J. Szanyi, W.K. Kuhn, D.W. Goodman, J. Vac. Sci. Technol. A 11 (1993) 1969.
- [47] M. Bäumer, J. Libuda, A. Sandell, H.-J. Freund, G. Graw, T. Bertrams, H. Neddermeyer, Ber. Bunsenges. Phys. Chem. 99 (1995) 1381.
- [48] C. Noguera, Physics and Chemistry at Oxide Surfaces, Cambridge University Press, Cambridge, 1996.
- [49] A. Ortega, F.M. Hoffmann, A.M. Bradshaw, Surf. Sci. 119 (1982) 79.
- [50] T. Gießel, O. Schaff, C.J. Hirschmugl, V. Fernandez, K.-M. Schindler, A. Theobald, S. Bao, R. Lindsay, W. Berndt, A.M. Bradshaw, C. Baddeley, A.F. Lee, R.M. Lambert, D.P. Woodruff, Surf. Sci. 406 (1998) 90.