

PHOTOEMISSION STUDY OF CO₂ ADSORBED ON K/Cu(110). ANALYSIS OF ADSORBATE INDUCED STRUCTURES

P. J. GODOWSKI*

Institute of Experimental Physics, University of Wrocław
Pl. Maxa Born 9, 50-204 Wrocław, Poland

J. ONSGAARD

Institute of Physics, Odense University, Campusvej 55, 5230 Odense M, Denmark

S. V. HOFFMANN

Institute for Storage Ring Facilities, University of Aarhus
Bgning 520, Ny Munkegade, 8000 Aarhus C, Denmark

AND J. NERLOV

Department of Chemistry, University of Copenhagen
Universitetsparken 5, 2100 Copenhagen, Denmark

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Using photoemission spectroscopy, adsorption and reaction of CO₂ on potassium modified Cu(110) were studied. In agreement with published results of thermally programmed desorption, apart from carbonate and carbon monoxide as the disproportionation reaction products, a linear CO₂ molecule and a bent active CO₂(-) species were identified. The reaction paths are independent on the potassium precoverage but the number of CO₃ molecules increases with the number of potassium adatoms. The presence of the CO₂(-), stable up to 200 K, suitable for the reactivity of the interface in respect of the methanol synthesis, could be confirmed in the complex valence band spectra by occurrence of the characteristic peak at binding energy of 6.8 eV.

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1. Introduction

Investigations of CO₂ adsorption on alkali modified copper surfaces using surface sensitive spectroscopies are interesting in the field of catalysis. It is known that in the methanol synthesis of CO, CO₂/H₂ mixture over the copper supported on zinc oxide catalyst, CO₂ is the main source of methanol. Consequently, the question of CO₂ applying as a reactant in hydrocarbons synthesis motivates such study on well-defined surfaces.

*e-mail: pjg@spin.ifd.uni.wroc.pl

Adsorption and reaction of CO₂ on alkali modified (or not) various metal surfaces were studied by photoelectron spectroscopy, thermally programmed desorption (TPD) and changes in work function ($\Delta\Phi$) [1–12]. It was shown that the adsorption of CO₂ and the attendant processes are substrate and face specified. Two basic species are detected on the surface: an undistorted CO₂ linear species of physisorbed state and a bent CO₂(-) anionic species of chemisorbed state. The relative concentration of the physisorbed species can be varied by changing the background CO₂ pressure, the surface temperature and photon or electron irradiation.

Although CO₂ does not adsorb on Cu(110) surface at temperatures above 110 K, the presence of preadsorbed potassium, even in small amounts, extremely increases the sticking coefficient of CO₂. TPD of CO₂ adsorbed at 110 K on the K/Cu(110) interface shows the peaks whose intensities and positions depend on the potassium coverage [6]. High intensity 44 a.m.u. peak appears at 135 K and corresponds to the physisorbed state. Relatively smaller peak at temperature range of 195–200 K corresponds to CO₂ chemisorbed state. High temperature 44 a.m.u. region consists of a broad feature around 430 K for small K coverages which develop into two high intensity peaks, depending on the potassium coverage, at temperature intervals of 475–500 K and 525–550 K for higher K coverages [9]. The different states of CO₂ are characterized basing on the energy positions and peak intensities of C 1s and O 1s core lines [6]. Both physisorbed CO₂ and chemisorbed anion CO₂(-) are detected at 110 K. The chemisorbed species decomposes onto CO₃ and CO with CO desorbing at 210 K.

Inspection of the valence band region of the CO₂/K/Cu(110) interface recorded in photoelectron spectroscopy using synchrotron radiation (PSSR) shows on the presence of different forms of adsorbed CO₂, adsorbed CO and chemisorbed CO₃. The spectra obtained with exciting photon energy of 125 eV, due to the presence of two Cu 3d satellites at binding energies (relative to the Fermi level) of 14.3 and 11.6 eV, could not be easily decomposed into its components [7]. The aim of this paper is to present new description of the levels in the valence band obtained in PSSR with the help of low energy electron diffraction (LEED) and $\Delta\Phi$ results. The incident photon energy was chosen as 40 eV to reduce the satellites intensity less than 1% of the 3d emission intensity [13] and increase ionization cross-sections of peaks induced by adsorbed molecules. Identification of the species as a physisorbed CO₂ and an ionic, bent CO₂(-) was done by means of multi-component spectra analysis. The results of the present investigations show more definitively assignment of the spectra of the CO₂/K/Cu(110) interface.

2. Experimental

The experiments were performed in a VG CLAM-2 electron spectrometer on the SX700 beam line at the Aarhus synchrotron radiation source ASTRID [14]. The pressure of residual gases in the experimental chamber was below 1.33×10^{-8} Pa during measurements. The photoelectron spectra were measured for electron emission along the surface normal, typically with exciting photon energy of 40 eV. Due to the influence of synchrotron radiation on the stability of the adsorbate layer the period of accumulation of the data was reduced to obtain the

signal to noise ratio necessary for the analysis. The overall resolution was evaluated as 200 meV in the used photon energy. The binding energy, BE_F, is related to the Fermi energy, determined as the inflection point of the Fermi edge. The IBM PC processing software was elaborated by the Synchrotron Surface Group at the Aarhus University. Work function changes were determined from the shift of the low energy tail of the secondary electron peak with a sample bias of -9 V relative to the ground potential.

The Cu(110) monocrystal of dimension 10 × 10 × 2 mm³ mounted to the manipulator holder through a tungsten wire (diameter of 0.5 mm) loop, could be cooled down to around 110 K and heated over 1000 K. The sample temperature was controlled by a chromel-alumel thermocouple fixed in a hole made at the upper edge of the sample. The surface of the crystal was cleaned by Argon ion bombardment followed by annealing to 950 K. The cleanliness of the initial and potassium predeposited surface was checked by PSSR using higher photon energies in order to reach *K* and *L* shell electrons of the characteristic impurities (C, O, P, and S). Before adsorption the sample showed a sharp (1 × 1) LEED pattern with low background intensity. The adsorption temperature did not exceed the temperature giving rise to the adsorbate induced substrate reconstruction, i.e. for K/Cu(110) $T(\text{rec.}) = 158 \text{ K}$ [15].

Potassium was evaporated from a SAES zeolite source mounted approximately 5 cm away from the copper surface [16]. The quantity of deposited potassium was evaluated from the measured work function changes [17] and the density of the saturated potassium monolayer on Cu(110) is equal to $n(\text{K}) = 3.70 \times 10^{14} \text{ at./cm}^2$. The coverage, Θ_{K} , is expressed in terms of adsorbate monolayers, AML, i.e. one monolayer $\Theta_{\text{K}} = 1 \text{ AML}$ corresponds to the mentioned density. It is easy to calculate that the saturated potassium overlayer expressed relative to the density of the substrate layer of atoms, SML, corresponds to the coverage of 0.34 SML.

CO₂ was admitted to the whole chamber via a dosing system, typically dose of 1 L (langmuir) corresponded to 20 s of $6.65 \times 10^{-6} \text{ Pa}$. It is known that within a CO₂ pressure range of 10^{-6} – 10^{-4} Pa , CO₂ interacts with ion pumps as well as hot filaments leading to formation of CO and its preferential adsorption on the sample (e.g. [1]). The gas adsorption experiments were performed with extreme care; the dosing system was flushed repeatedly with CO₂ and the ion pump was closed during admission of CO₂. The filament of the ionization vacuum meter was switched off as quickly as possible, i.e. when the steady conditions of the pressure were attained. Upon CO₂ adsorption at low temperature used, no sharp LEED pattern was observed, indicating on disordered adlayer. However, the photoemission spectroscopy can provide information on the identity and bonding of an adsorbed species and fully characterize the interface. Closely related to the solid CO₂, the often used model [1] of the relative orientation of the linear CO₂ molecules within a two-dimensional layer is postulated. For this model of a T-shaped arrangement, with the distance between C and nearest O atom of a second molecule of 0.296 nm [8], the number of molecules that complete the hypothetical monolayer on Cu(110) is equal to the density in the "solid CO₂" layer, i.e. to $n(\text{CO}_2) = 5.89 \times 10^{14} \text{ molec./cm}^2$.

3. Results

Adsorption of CO₂ on the K/Cu(110) interface can be characterized mainly on the basis of presented results with potassium coverage corresponding to work function change ($\Delta\Phi$) before minimum ($\Theta_K < 0.5$ AML). Exposition of K/Cu(110) in CO₂ increased the work function monotonically with saturation starting above 5 L of dose. For example, for the potassium adsorbed Cu(110) with the $\Delta\Phi$ decrease of -2.84 eV ($\Theta_K = 0.45$ AML), the followed adsorption of CO₂ increased $\Delta\Phi$ of +1.48 eV relative to the K-predosed surface. The secondary emission, measured as the area under the secondary peak, increased approximately 6 times after 0.45 AML K adsorption and then decreased 3.5 times after exposition in CO₂.

The 0–20 eV BE_F range of the valence band spectrum of the K/Cu(110) interface consists of the broad *s*–*p* band near the Fermi level, the Cu 3*d* band complex between 2–5 eV, whose shape and relative intensity depends on the angular arrangement of the experiment and energy of the photon beam, and finally the K 3*p* level at 18.2 eV. Because of the low cross-section for the K 4*s* level excitation (with BE_F = 0.4 eV) there was no evidence of this contribution to the total PSSR spectrum. During adsorption of CO₂ on the 0.42 AML K/Cu(110) interface the shift of the K 3*p* peak position towards lower BE_F of -0.5 eV at saturation was observed. No change in the full width at half maximum (FWHM) equal to 0.90 eV was detected. At saturation with CO₂, the intensity of the K 3*p* line, represented by the area under the peak, increased about twice.

The photoemission spectrum of the CO₂/K/Cu(110) interface obtained at $T(\text{ads}) = 125$ K is shown in Fig. 1. The Cu(110) sample with potassium coverage of $\Theta_K = 0.38$ AML was exposed to 10 L of CO₂. The energy distribution curve, apart from the Cu *s*–*p* with Cu 3*d* bands and the K 3*p* level, contains several series of overlapping peaks in the region of 5–16 eV BE_F. Heating the interface to 230 K, i.e. to the temperature greater than CO₂(phys.) desorption (135 K), K-induced substrate reconstruction (158 K), CO₂(-) desorption (195–200 K) and CO desorption (210 K), decidedly simplifies the BE_F region leaving three distinct features (Fig. 2). Three peaks of BE_F of 6.0, 9.5, and 11.8 eV were assigned to the 1e''/4e', 1a2''/3e' and 4a1 orbitals of carbonate, CO₃, respectively. Therefore, the 5–16 eV spectrum of carbonate is characterized by three features with the one at 9.5 eV of the highest amplitude (Table). It is worth noting that after CO₂(phys.) desorption and heating over $T(\text{rec.})$, apart from the sharpening of the peaks, no changes were registered. Such behaviour indicates on the ordering process on the interface which accompanies substrate reconstruction.

Inspection of the energy distribution curve of Fig. 1 shows two dominating maxima at BE_F of around 12 and 9.6 eV. The first one could be attributed only to the strongest line of CO, i.e. to the 4*σ* orbital (Table). The second maximum corresponds to the highest line of CO₃, namely to the 1a2''/3e' joint orbitals. The BE_F of the 4a1 orbital of CO₃ is very close to that one of the 4*σ* orbital of CO, leading to overlap between peaks of two species presented on the interface under investigation. After linear background subtraction from the region of 5–16 eV BE_F of the spectrum, two triplets consisting of the Gaussian peaks were fitted to the experimental points. The relative amplitudes of the lines in the groups,

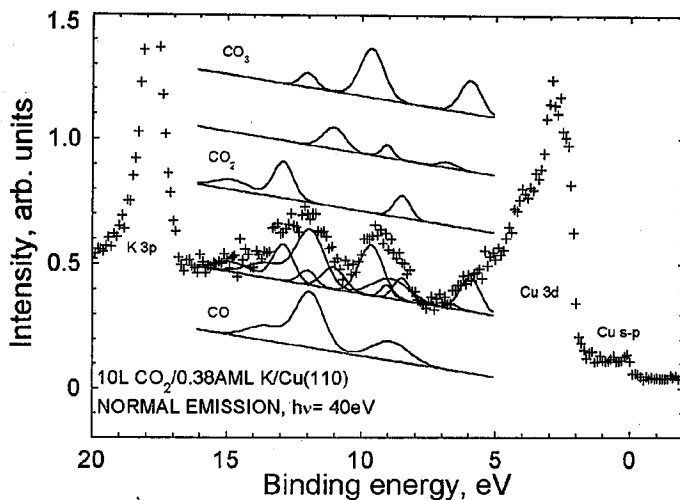


Fig. 1. Decomposition of the photoemission spectrum of the 10 L CO₂/0.38 AML K/Cu(110) interface (not smoothed data) obtained at $T = 125$ K. The analysis order of the data is as follows. First, after linear background subtraction, the CO ($1\pi/5\sigma$, 4σ , 4σ -satellite) and CO₃(-) orbitals ($1e''/4e'$, $1a2''/3e'$, $4a1$) fitted to the data are subtracted. The resulting difference spectrum shows evidence of two sets of peaks which corresponds to the CO₂ ($1\pi_G$, $1\pi_U/3\sigma_U$, $4\sigma_G$) and CO₂(-) orbitals ($1a2/4b2$, $5a1/1b1/3b2$, $4a1$). For clarity, only the background and the individual components resulting from the best fit procedure are shown as the solid lines.

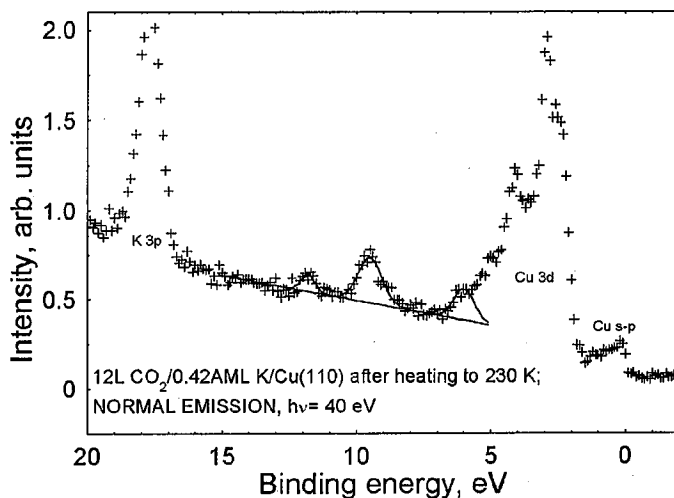


Fig. 2. The valence band spectrum of the CO₂/K/Cu(110) interface obtained by deposition of 0.42 AML K and dosing 12 L of CO₂ at $T(\text{ads.}) = 125$ K followed by heating to 230 K (not smoothed data). Three well defined features at BE_F of 6.0, 9.5, and 11.8 eV correspond to the CO₃ peaks of the $1e''/4e'$, $1a2''/3e'$, and $4a1$ orbital, respectively.

TABLE

Parameters of orbitals determined as the best fit of Gaussian lines to the data from different interfaces. The intensity I is related to the peak amplitude A and the FWHM by the equation $I = 1.062 \times A \times \text{FWHM}$. Binding energy and FWHM is expressed in eV and A in arbitrary units, the same in given group of peaks.

Interface	Orbital	BE _F	FWHM	A
CO ₂ /K/Cu(110) adsorbed at 125 K and heated to 230 K, this work	CO ₃ 1e''/4e'	6.00	0.92	0.175
	CO ₃ 1a2''/3e'	9.50	1.04	0.255
	CO ₃ 4a1	11.8	0.60	0.095
CO/K/Cu(110) adsorbed at 118 K [17]	CO 1π/5σ	8.70	1.80	0.178
	CO 4σ	11.8	1.20	0.512
	CO 4σ-satellite	13.5	1.80	0.158
CO ₂ /K/Cu(110) adsorbed at 125 K, this work	CO 1π/5σ	8.90	1.60	0.078
	CO 4σ	11.9	1.20	0.220
	CO 4σ-satellite	13.5	1.70	0.059
	CO ₃ 1e''/4e'	5.95	0.92	0.135
	CO 1a2''/3e'	9.64	1.04	0.200
	CO ₃ 4a1	12.0	0.70	0.058
	CO ₂ 1π _G	8.50	0.70	0.088
	CO ₂ 1π _U /3σ _U	12.9	0.88	0.146
	CO ₂ 4σ _G	14.8	1.54	0.040
	CO ₂ ⁻ 1a2/4b2	6.8	0.80	0.0217
	CO ₂ ⁻ 5a1/1b1/3b2	9.1	0.50	0.0512
CO ₂ ⁻ 4a1	11.0	0.96	0.0857	

their FWHM's and BE_F's positions were fixed and/or restricted to the narrow interval of values according to the determined quantities indicated in the upper part of Table. After subtraction of the peaks corresponding to the CO and CO₃ orbitals, the difference spectrum showed the presence of further six features, which could be fitted by six Gaussian functions. Three of them at BE_F of 8.5, 12.9, and 14.8 eV represent the CO₂ orbitals, i.e. the 1π_G, 1π_U/3σ_U and 4σ_G, respectively. Remaining ones at BE_F of 6.8, 9.1, and 11.0 eV were assigned as corresponding to the CO₂(-) orbitals, namely to the 1a2/4b2, 5a1/1b1/3b2 and 4a1, respectively. The results of the synthesis are shown as the solid lines in Fig. 1 and collected in Table. For clarity, the groups of peaks of different species are depicted separately on the graph once again. Despite of the above synthesis seems to be arduous and time consuming, it is believed that it provides univocally determined results. The procedure which was adopted to the complicated valence band bases on the parameters well established from the simple, reference spectra.

The photoemission spectra of the CO₂/K/Cu(110) interface for different Θ_K show qualitatively the same reaction paths. However, with increasing K coverage

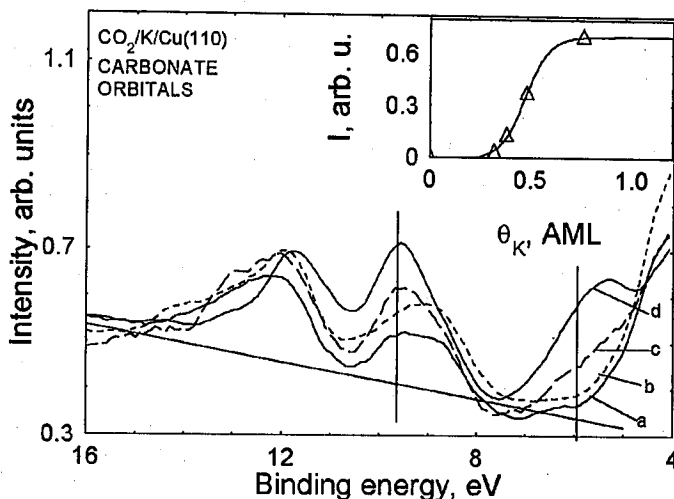


Fig. 3. Energy distribution curves of the K/Cu(110) substrate saturated with CO₂. The parameter of the curve is the potassium pre-coverage, Θ_K : a — 0.32 AML, b — 0.38 AML, c — 0.48 AML and d — 0.76 AML. The inset shows the dependence of the amplitude of the $1e''/4e'$ orbital with Θ_K .

the yield of the disproportionation increases which is observed in Fig. 3. Intensities of both: the $1e''/4e'$ and $1a2''/3e'$ orbitals of CO₃ increase with Θ_K . Evaluated amplitude of the $1e''/4e'$ orbital, as depicted in the inset in Fig. 3, follows a sigmoidal curve with Θ_K , saturating at higher potassium coverages. Thus, the number of produced CO₃ molecules could be correlated with the length of the K-islands edges (not the interior of the islands) on Cu(110).

4. Discussion

The increase in work function during dosing of CO₂ indicates on a charge transfer from the K/Cu(110) substrate to adsorbing molecules. Although CO and carbonate species appears at temperature of adsorption, here $\Delta\Phi$ increases more than for CO adsorption alone [17]. Thus, it is evidence of the formation of negatively charged CO₂(-), which agrees well with published increase of $\Delta\Phi$ on the K/Fe(film) influenced by a carbon dioxide anionic species [3]. While the chemisorbed species increases work function, the physisorbed linear CO₂ molecules can decrease it again.

Existence of mentioned anionic carbon dioxide molecule is unambiguously confirmed by the PSSR. The energy distribution curve shows the presence of the CO, CO₃, CO₂ and CO₂(-) species on the CO₂/K/Cu(110) interface at temperature of adsorption. However, there is no indication of CO₂ dissociation to adsorbed CO and O, i.e. no oxygen orbitals were found. Such behaviour is opposite to finding on a stepped Cu(332) [5]. It means that the carbonate is created by the reaction of disproportionation in which anionic carbon dioxide takes part. While the undistorted CO₂ molecule forms a linear CO₂-metal bond, the anionic species has a bent geometry with the angle between the C-O bonds of around 135°. In the

interaction with the metallic substrate they can exhibit three modes of coordination: (a) a pure carbon coordination (symmetrical upward) or (b) a pure oxygen bidentate coordination (symmetrical downward) or (c) a mixed carbon-oxygen coordination (asymmetrical). Theoretical calculations showed that (b) and (c) lead to more stable arrangement than (a) [8]. It is likely that CO₂ molecules adsorbing near the coadsorbed K atom on the Cu(110) surface react to surface carbonate through intermediate (b) and (c) configuration. This is supported by the fact that the carbonate species is readily formed on other surfaces by reaction of CO₂ with an oxygen precovered surface. The (c) coordination is accompanied by an elongation of the C-O bond distance of atoms directly involved in the interaction with the substrate. The reaction of disproportionation is favored if the binding energy for adsorbed oxygen is smaller than the energy gained by the formation of a surface carbonate. The (a) geometry relative to the substrate is less stable and has tendency to interact with neutral CO₂ e.g. to form stable anionic dimer moiety. Thus, in consequence the CO₂(-) anion can be solvated by other neutral CO₂. The chemisorbed CO₂(-) was stable on the interface up to 200 K and above this temperature it desorbed, i.e. when the temperature rises to 200 K, the CO₂(-) peaks vanish with no further increase in the amplitude of the CO₃ peaks.

It is known that molecular fragments can take up particular, well-defined orientations relative to the substrate. For example, the (1 × 2) surface structure was observed on the CO₃/Ag(110) interface [18, 19]. The adsorption geometry of the ad-molecule is that the carbonate is bounded to Ag mainly through the oxygen atoms. Assuming the same structure for the CO₃/Cu(110) interface, i.e. the (1 × 2) surface with a missing row reconstruction, the number of carbonate molecules that complete a monolayer is $n(\text{CO}_3) = 5.43 \times 10^{14}$ molec./cm². Taking into account the densities of different species on Cu(110) it can be assumed that each CO₂ molecule occupies 1.08 adsorption sites of CO₃ or 0.68 adsorption sites of CO. Thus, the reaction of disproportionation reduces the total gas coverage of the surface, e.g. from 100% to 88% for all CO₂ molecules reacting. In such a case, during reaction without desorption of any species, there is no origin of blocking mechanism to the formation of the CO₃+CO complex due to geometrical dimensions of the molecules. However, the disproportionation reaction takes place at 125 K, i.e. the dynamical process takes place during adsorption. Finally, the number of CO₃ molecules depends only on the number of edge K adatoms, i.e. only on the Θ_K .

5. Conclusions

1. The PSSR provides a clear distinction between CO₂ and CO₂(-) bent species. The characteristic features of the CO, CO₃, CO₂ and CO₂(-) at BE_F of 11.9, 9.5, 12.9, and 6.8 eV, respectively, can be indicative in establishing of the components by rough inspection of the complex valence band spectrum.
2. The surface reactions (formation of CO₂(-), disproportionation) proceed at the adsorption temperature, i.e. 125 K, on the CO₂/K/Cu(110) interface. Solved CO₂(-) species does not follow disproportionation to CO₃ with increase in temperature. The CO₂(-) readily reacts with coadsorbed hydrogen

to form formate on K/Cu(110) [20, 21]. Thus, reactivity of the interface in aspect of methanol synthesis is dependent on the ability of creation of the stable bending CO₂(-) molecules among adsorbing CO₂.

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References

- [1] B. Bartos, H.J. Freund, H. Kuhlenbeck, M. Neumann, H. Lindner, K. Muller, *Surf. Sci.* **179**, 59 (1987).
- [2] G. Iling, D. Heskett, E.W. Plummer, H.J. Freund, J. Somers, Th. Linder, A.M. Bradshaw, U. Buskotte, M. Neumann, U. Starke, K. Heinz, P.L. DeAndres, D. Saldin, J.B. Pendry, *Surf. Sci.* **206**, 1 (1988).
- [3] M. Pirner, R. Bauer, D. Borgmann, G. Wedler, *Surf. Sci.* **189/190**, 147 (1987).
- [4] J. Kiss, K. Revesz, F. Solymosi, *Surf. Sci.* **207**, 36 (1988).
- [5] I.A. Bonicke, W. Kirstein, F. Thieme, *Surf. Sci.* **307/309**, 177 (1994).
- [6] E.V. Thomsen, B. Jorgensen, J. Onsgaard, *Surf. Sci.* **304**, 85 (1994).
- [7] J. Onsgaard, J. Storm, S.V. Christensen, J. Nerlov, P.J. Godowski, P. Morgen, D. Batchelor, *Surf. Sci.* **336**, 101 (1995).
- [8] H.J. Freund, M.W. Roberts, *Surf. Sci. Rep.* **25**, 225 (1996).
- [9] M.E. Jorgensen, P.J. Godowski, J. Onsgaard, *Vacuum* **48**, 299 (1997).
- [10] G. Meyer, E. Reinhart, D. Borgmann, G. Wedler, *Surf. Sci.* **320**, 110 (1994).
- [11] J. Krause, D. Borgmann, G. Wedler, *Surf. Sci.* **347**, 1 (1996).
- [12] Th. Seyller, D. Borgmann, G. Wedler, *Surf. Sci.* **400**, 63 (1998).
- [13] M. Iwan, F.J. Himpsel, D.E. Eastman, *Phys. Rev. Lett.* **43**, 1829 (1979).
- [14] E. Uggerhoj, *Nucl. Instrum. Methods Phys. Res. B* **99**, 261 (1995).
- [15] W.C. Fan, A. Ignatiev, *J. Vac. Sci. Technol. A* **7**, 2115 (1989).
- [16] P.J. Godowski, J. Onsgaard, S.V. Christensen, J. Nerlov, *Acta Phys. Pol. A* **89**, 657 (1996).
- [17] S.V. Christensen, J. Nerlov, P.J. Godowski, J. Onsgaard, *J. Chem. Phys.* **104**, 9613 (1996).
- [18] M. Bader, B. Hillert, A. Puschmann, J. Haase, A.M. Bradshaw, *Europhys. Lett.* **5**, 443 (1988).
- [19] D.E. Ricken, J.S. Somers, A.W. Robinson, A.M. Bradshaw, *J. Chem. Phys.* **94**, 8592 (1991).
- [20] J. Onsgaard, S.V. Christensen, P.J. Godowski, J. Nerlov, S. Quist, *Surf. Sci.* **370**, L137 (1997).
- [21] J. Onsgaard, P.J. Godowski, J. Nerlov, S. Quist, S.V. Hoffmann, *Surf. Sci.* **398**, 318 (1998).