

The adsorption of bipyridine molecules on Au(110) as measured by reflection anisotropy spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 S4385

(<http://iopscience.iop.org/0953-8984/16/39/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 17:56

Please note that [terms and conditions apply](#).

The adsorption of bipyridine molecules on Au(110) as measured by reflection anisotropy spectroscopy

C I Smith¹, G J Dolan¹, T Farrell¹, A J Maunder¹, D G Fernig²,
C Edwards² and P Weightman^{1,3}

¹ Department of Physics, University of Liverpool, L69 7ZE, UK

² School of Biological Sciences, University of Liverpool, L69 7ZB, UK

Received 1 April 2004

Published 17 September 2004

Online at stacks.iop.org/JPhysCM/16/S4385

doi:10.1088/0953-8984/16/39/013

Abstract

The reflection anisotropy spectra of 2,2'-bipyridine and 4,4'-bipyridine adsorbed onto an Au(110) surface in an electrochemical cell demonstrate that both systems form ordered structures. It is shown that reflection anisotropy spectroscopy can be used to distinguish between structural isomers adsorbed on the Au(110) surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The adsorption of organic molecules onto electrode surfaces has been widely studied in recent years [1, 2] and such modified electrodes are of importance technologically in the field of metal plating additives, corrosion inhibitors, electrocatalysis, molecular electronics, chemical and biosensor technology.

The development of *in situ* techniques such as scanning tunnelling microscopy (STM), atomic force microscopy (AFM) and optical spectroscopies as well as x-ray techniques have contributed to the rapid growth in the study of the electrochemical surfaces [3, 4], and when applied to well defined single-crystal substrates these techniques can give detailed structural information about film formation. It is now possible to obtain thermodynamic analysis of adsorption at solid electrodes allowing Gibbs surface excess, adsorption energies and film pressure to be determined and the presence of phase transitions within organic films to be established.

Pyridine has a simple molecular structure (figure 1) and its adsorption on electrodes has been extensively studied by a variety of methods including electrochemistry [5–11], surface-enhanced Raman spectroscopy (SERS) [12–14], radioactive labelling [15], *in situ* Fourier

³ Author to whom any correspondence should be addressed.

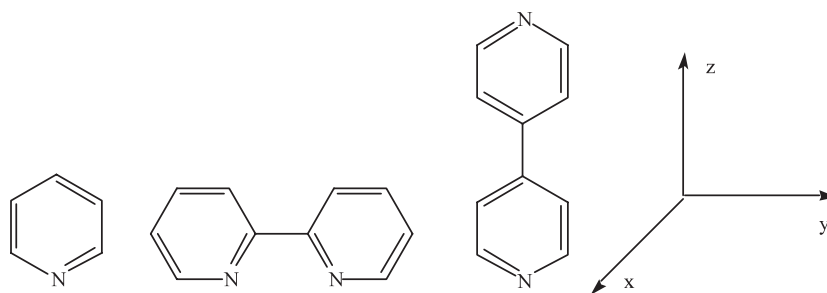


Figure 1. Structures of pyridine, 2,2'-bipyridine and 4,4'-bipyridine. The molecules are shown in the orientation they are expected to adopt on the Au(110). In the axis system shown z is normal to the Au(110) surface and x and y are in the surface plane.

transform infra-red (FTIR) spectroscopy [16–19], electroreflectance [20–22] and STM [23–25]. Studies of the adsorption of pyridine onto various gold crystallographic faces established that it adopts only one orientation on the (110), (210) and (311) faces but that changes in electrode potential induce reorientations of the molecule on the (111), (100) and polycrystalline faces. These studies have probed the nature of the interaction between the adsorbed pyridine and the metal and show that the molecule can interact through either the delocalized π orbitals on the ring, which results in the molecule lying flat on the surface, or through the lone pair of electrons localized on the N atom, which results in a vertical orientation. Recent infra-red adsorption studies [26, 27] suggest that even when it adopts the flat orientation pyridine bonds to the Au(111) surface through the N atom.

The advances made in the understanding of the adsorption of pyridine have led to similar studies of the more complex bipyridine species such as 2,2'-bipyridine and 4,4'-bipyridine (figure 1). 2,2'-bipyridine exists in a planar *trans* configuration in its crystalline form and in solution but on complexation to metal ions it adopts the *cis* configuration shown in figure 1. The adsorption of 2,2'-bipyridine onto various electrodes has been studied by electrochemistry [28], SERS [29], second harmonic generation (SHG) spectroscopy [30], ac impedance [30, 31], STM [31–33] and surface x-ray scattering [34, 35]. On an Au(111) electrode at negative potentials the *trans* configuration is preferred with the 2, 2'-bipyridine adopting a flat orientation, while at positive potentials the *cis* configuration is adopted with a vertical orientation [36].

4,4'-bipyridine is a structural isomer of 2,2'-bipyridine and is considered as a bifunctional, non-chelating molecule that is employed as a bridging ligand in coordination chemistry [37]. The adsorption of 4,4'-bipyridine onto solid electrodes was used to study the electron transfer of cytochrome *c* [38, 39], which showed that the 4,4'-bipyridine bound 'end on' through one nitrogen while the other nitrogen was pointing into the solution. Further studies showed a potential induced reorientation at -0.1 V versus SCE [40] but very little change in the mass in the electrochemical quartz crystal microbalance (EQCM) experiments [41, 42]. An STM/AFM study [43] showed the self-assembly of 'polymer chains' of perpendicular 4,4'-bipyridine molecules and another study [44] showed the presence of three phase transitions on Au(111).

Reflectance anisotropy spectroscopy (RAS) is a non-destructive surface sensitive optical probe capable of operation within a wide range of environments. The technique was originally developed as a method of studying semiconductor surfaces [45], and as an *in situ* monitor of semiconductor growth [46]. It has been applied to the study of metal surfaces [47], to metal/liquid interfaces [48–50] and recently to the study of pyridine on Au(110) in an

electrochemical environment [51] where it was shown to be a sensitive monitor of the time dependence of the adsorption process.

In this work RAS has been applied to studies of the adsorption of 2,2'-bipyridine and 4,4'-bipyridine molecules onto Au(110) electrodes. Improved experimental results are presented for the pyridine/Au(110) system.

2. Experimental details

The Au(110) single crystal (purity 99.999%) was a disc with diameter 10 mm and a thickness of 2 mm with an exposed area of 0.5 cm². The crystal was orientated to an accuracy of 0.1° using x-ray diffraction, mechanically polished to 0.25 μm with diamond paste and cleaned in an ultrasonic bath. A butane micro-torch was used to clean the crystal by flame annealing prior to the experiments. The crystal was then cooled for a minute in air before quenching in ultra-pure water (Millipore Q system, 18 MΩ cm) before being covered by a droplet of ultra-pure water to prevent contamination from the laboratory air and transferred into the electrochemical cell. This procedure preserves the (1 × 2) missing row reconstruction of Au(110) [52–54].

The electrochemical cell was a typical three-electrode cell with a platinum counter-electrode and a saturated calomel electrode (SCE) as the reference electrode. A silica strain free disc was used as the window in the cell for the light to pass through. All potentials quoted are referenced to the SCE. The potentiostat used was an Autolab PGSTAT 30 with GPES software (Eco Chemie).

All solutions were prepared from NaClO₄ (Merck, Analar grade), pyridine (Merck, Aristar grade), 2,2'-bipyridine (Merck, Analar grade) or 4,4'-bipyridine (Aldrich) with Millipore water (18 MΩ cm). The solutions were made oxygen free by purging with argon prior to use.

Ultra-violet–visible (UV–vis) absorbance spectroscopy measurements were carried out on a Hitachi model U-2000 double-beam spectrophotometer. The solutions from the electrochemical experiments were run against a background of 0.1 M NaClO₄ in far-UV quartz cells.

The RAS instrument used in this work was of the Aspnes design [55] and operated in the range 1.5–5.5 eV. The measured RA signal is given by

$$\text{Re} \left\{ \frac{\Delta r}{r} \right\} = \text{Re} \left\{ \frac{r_{[1\bar{1}0]} - r_{[001]}}{r} \right\}.$$

Since the publication of our previous study of the pyridine/Au(110) system [51] minor improvements have been made to the RA spectrometer for working in the ultra-violet (UV) region of the spectrum by the introduction of mirrors with an enhanced response in the UV. The pyridine experiments were repeated with a slight extension of the spectral range and the results are shown in figure 2.

3. Results

In preliminary experiments we found that the strong adsorption of the molecules in solution for photon energies above 3.9 eV prevented any information being obtained on the adsorbed species in this spectral range at concentrations above 0.5 mM. However, by injecting a known quantity of the molecules into the electrochemical cell after taking the RA spectrum of the Au(110) electrode the RA spectrum of the adsorbed species can be obtained. The full curves in figures 2–4 show the RA spectra of the Au(110) surface after flame annealing. The dotted curve in figure 2 shows the RA spectrum obtained after 5 ml of 1 mM pyridine is added to the cell. Experimental results obtained in the same way for 2,2'-bipyridine and 4,4'-bipyridine are

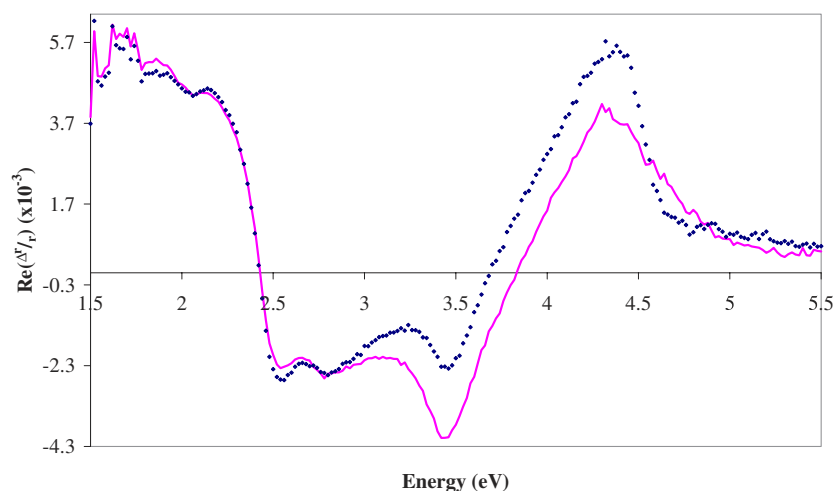


Figure 2. RA spectrum of Au(110) in 0.1 M NaClO₄ at 0.4 V versus SCE (solid curve) and Au(110) in 0.1 M NaClO₄ + 5 ml of 1 mM pyridine at 0.4 V versus SCE (◆).

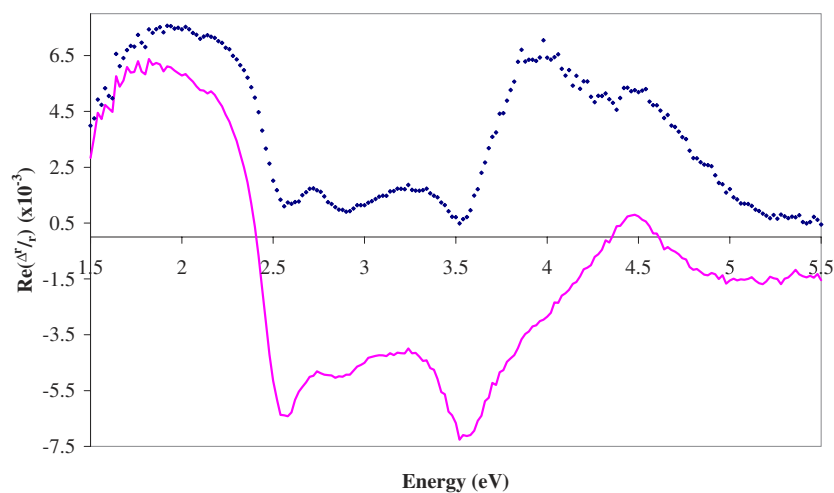


Figure 3. RA spectrum of Au(110) in 0.1 M NaClO₄ at 0.4 V versus SCE (solid curve) and Au(110) in 0.1 M NaClO₄ + 5 ml of 1 mM 2,2'-bipyridine at 0.4 V versus SCE (◆).

shown in figures 3 and 4 respectively. In each case the Au(110) electrode was held at +0.4 V versus SCE. In all three cases the adsorption of the molecule significantly changed the RA spectra of the Au(110), indicating that the molecules form ordered structures on the Au(110) electrode.

The experimental results obtained for the RA spectra of the Au(110) electrodes in the experiments on the three pyridine species (figures 2–4) vary slightly. This variation is probably due to slight differences in the azimuthal alignment of the crystal in the three experiments and to differences in surface morphology following the flame annealing procedure. The sensitivity of the RA spectra to the surface morphology of the Au(110) surface has been discussed in the literature [48, 49, 56, 57] and we do not expect this sensitivity to have a major impact on the results reported here.

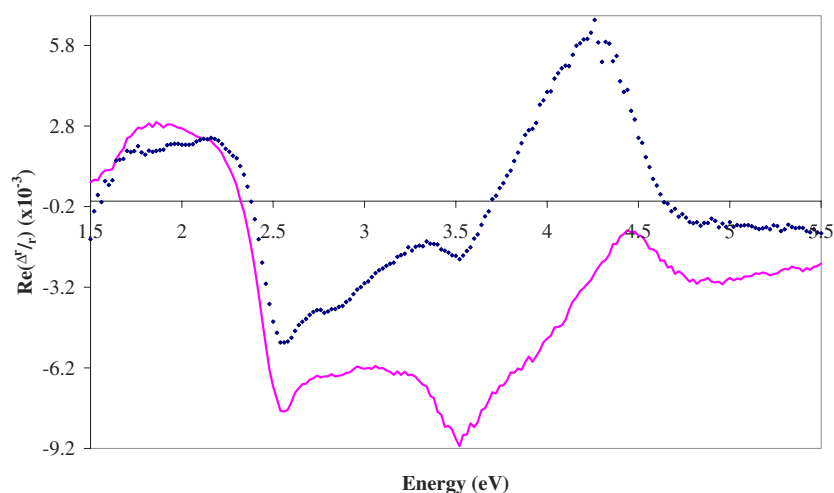


Figure 4. RA spectrum of Au(110) in 0.1 M NaClO₄ at 0.4 V versus SCE (solid curve) and Au(110) in 0.1 M NaClO₄ + 5 ml of 1 mM 4,4'-bipyridine at 0.4 V versus SCE (◆).

The 2,2'-bipyridine and 4,4'-bipyridine molecules are known to adsorb on Au(111) [28, 30, 31, 33–36, 43, 44, 59] and Au(100) [32] surfaces and would therefore be expected to adsorb onto the Au(110) electrode. Although these molecules are structural isomers (figure 1), the variation in the location of the N atoms is expected to give rise to different binding modes to the electrode surface. The 2,2'-bipyridine is expected to bind to the Au(110) surface by the two nitrogens while the 4,4'-bipyridine is expected to bind through only one of the end nitrogen atoms. These differences in the expected orientation of the molecules on the Au(110) surface are illustrated in figure 1.

4. Discussion

It is more difficult to interpret the RAS results for the two bipyridine species adsorbed at the Au(110)/electrolyte interface than it was for pyridine [51], since while there are a number of studies, using a variety of techniques, of these molecules adsorbed on the Au(111) surface [31, 33, 34, 43, 58, 59] and some information on adsorption on the Au(100) surface [32] we have not found any previous studies of these molecules adsorbed on the Au(110) surface. However, the observation of a non-zero RA spectrum demonstrates that both molecules adopt an ordered structure at the Au(110)/electrolyte interface. The studies of adsorption on the Au(111) surface show that there are major differences in the orientation of the two molecules on this surface which are caused by the fact that 2,2'-bipyridine is able to bond to the surface through both N atoms while 4,4'-bipyridine can only bond through a single N atom. It is likely that the major differences in the RA spectra of the two molecules adsorbed on the Au(110) electrode at the same potential arise from differences in the way these molecules are orientated on the surface (figure 1).

The difference between the RAS of the Au(110) surface and the RAS of the bipyridine/Au(110) systems shown in figures 3 and 4 should correspond to the RAS of the adsorbed bipyridine plus any changes induced in the Au(110) surface by the adsorption. These latter changes are expected to be small and they are clearly reversible since changing the electrode potential in order to desorb the molecules gave rise to identical RA spectra of Au(110) to those observed prior to adsorption.

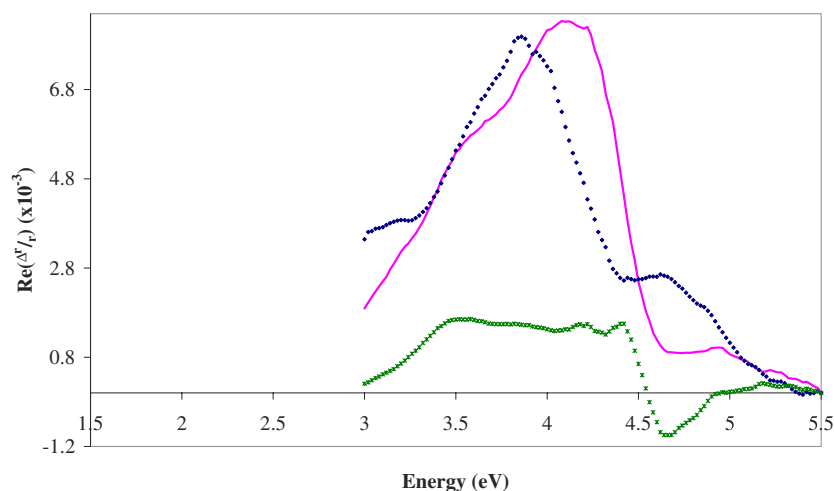


Figure 5. Comparison of RA spectra of 2,2'-bipyridine (◆), 4,4'-bipyridine (solid curve) and pyridine (●) all recorded at +0.4 V versus SCE. These results were obtained by the subtraction of the RAS of the Au(110) from the RAS of the adsorbed species shown in figures 2–4.

In figure 5 we show the difference between the RA spectra of each adsorbed species and RA spectra of the corresponding Au(110) electrode. In the absence of theoretical calculations of the optical spectra of these molecules it is not possible to provide detailed interpretations of the RAS obtained. However it is possible to make a few general observations based on the expected symmetry of the adsorbed species (figure 1). The difference spectra for pyridine and 4,4'-bipyridine have a roughly similar shape but very different intensity (figure 5). The similarity in the shape of the spectra may be due to the fact that if 4,4'-bipyridine adsorbs vertically through an N atom it adopts a very similar orientation on the surface to that of pyridine (figure 1). The RAS of all three species is given by $(r_x - r_y)$ and in the case of pyridine and 4,4'-bipyridine this arises from the difference in intensity of the reflection arising from transitions polarized at right angles to the molecular plane and from transitions polarized in the in-plane y direction. Since the 4,4'-bipyridine will have contributions from two pyridine rings this could explain the greater intensity of the RAS observed for this species over that of pyridine (figure 5). The similar intensities of the RAS observed from 2,2'-bipyridine and from 4,4'-bipyridine are probably due to the fact that both molecules have two active pyridine rings. The difference in the shape of the RAS observed from these two species is probably associated with the fact that while the RAS of 2,2'-bipyridine will have contributions from transitions polarized along the in-plane long axis of the molecule such transitions will not contribute to the RAS of 4,4'-bipyridine.

Figure 6 shows a comparison of our measurements of the UV adsorption spectra of the bipyridine molecules in the 0.1 M NaClO₄ solution used in the RAS experiments with the corresponding RA spectrum from figure 5. One should not expect to see a close resemblance between the adsorption spectra of these molecules in solution and the RA spectra of the molecules adsorbed on the Au(110) surface since in the latter case the molecules adopt a specific spatial orientation and the relative intensity of components of the spectrum will be influenced by geometric factors. However, it is clear that for both species the first maxima in the adsorption spectra of the free molecules in solution occur at ~ 0.5 eV higher energy than the peaks in the RA spectra. Experience of applying a Fresnel three-phase model to the interpretation of the RAS of Au(110) [48] leads us to expect that such shifts together with

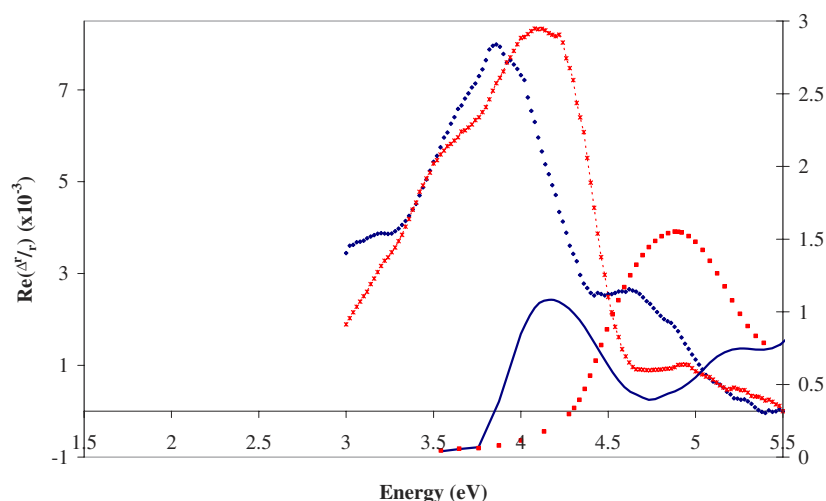


Figure 6. A comparison of the UV adsorption spectrum of 2,2'-bipyridine (solid curve) and 4,4'-bipyridine (— —) with the RA spectrum of 2,2'-bipyridine (◆) and 4,4'-bipyridine (— * —).

significant broadening and spectral distortion are likely to arise from the interaction between the molecular transitions and the optical response of the substrate.

5. Conclusion

The RAS results establish that all three molecules adopt an ordered arrangement when adsorbed on the Au(110) surface. The intensity of the RAS observed from the bipyridine species is greater than that observed from pyridine and this may arise from the presence of two pyridine rings in these molecules. The difference in the shape of the RAS observed from the bipyridine species probably arises from the difference in the orientation of the two species on the Au(110) surface and shows that the technique can distinguish between adsorbed structural isomers.

Acknowledgment

This work was supported by the UK Engineering and Physical Science Research Council (EPSRC).

References

- [1] Buess-Hermann C 1992 *Adsorption of Molecules at Metal Electrodes* ed J Lipkowski and P Ross (Weinheim: Verlag Chemie) p 77
- [2] Lipkowski J and Stolberg L 1992 *Adsorption of Molecules at Metal Electrodes* ed J Lipkowski and P Ross (Weinheim: Verlag Chemie) p 171
- [3] Bard A J, Abruna H D, Chidsey C E, Faulkner L R, Felberg S W, Itaya K, Majda M, Melroy O, Murray R W, Porter M D, Soriaga M P and White H S 1993 *J. Phys. Chem.* **97** 7147
- [4] Haiss W, Roelfs B, Port S N, Bunge E, Baumgärtel H and Nichols R J 1998 *J. Electroanal. Chem.* **454** 107
- [5] Hamelin A 1983 *J. Electroanal. Chem.* **144** 365
- [6] Stolberg L, Richer J, Lipkowski J and Irish D E 1986 *J. Electroanal. Chem.* **207** 213
- [7] Stolberg L, Lipkowski J and Irish D E 1990 *J. Electroanal. Chem.* **296** 171
- [8] Stolberg L, Morin S, Lipkowski J and Irish D E 1991 *J. Electroanal. Chem.* **307** 241

- [9] Yang D F, Stolberg L, Lipkowski J and Irish D E 1992 *J. Electroanal. Chem.* **329** 259
- [10] Stolberg L, Lipkowski J and Irish D E 1992 *J. Electroanal. Chem.* **322** 357
- [11] Efimov I O and Heusler K E 1996 *J. Electroanal. Chem.* **414** 75
- [12] Pettinger B, Wenning U and Wetzell H 1980 *Surf. Sci.* **101** 409
- [13] Stolberg L, Lipkowski J and Irish D E 1991 *J. Electroanal. Chem.* **300** 563
- [14] Lipkowski J, Stolberg L, Morin S, Irish D E, Zelenay P, Gamboa M and Wieckowski A 1993 *J. Electroanal. Chem.* **355** 147
- [15] Zelenay P, Rice-Jackson L M and Wieckowski A 1990 *Langmuir* **6** 974
- [16] Ikezawa Y, Sawatari T, Goto T K H and Toriba K 1998 *Electrochim. Acta* **43** 3297
- [17] Nanbu N, Kitamura F, Ohsaka T and Tokuda K 1999 *J. Electroanal. Chem.* **470** 136
- [18] Ikezawa Y, Sawatari T and Terashima H 2001 *Electrochim. Acta* **46** 1333
- [19] Li C, Zamlyny V, Lipkowski J, Henglein F and Pettinger B 2002 *J. Electroanal. Chem.* **524/525** 43
- [20] Henglein F, Lipkowski J and Kolb D M 1991 *J. Electroanal. Chem.* **303** 245
- [21] Henglein F, Kolb D M, Stolberg L and Lipkowski J 1993 *Surf. Sci.* **291** 325
- [22] Lipkowski J, Stolberg L, Yang D-F, Pettinger B, Mirwald S, Henglein F and Kolb D M 1994 *Electrochim. Acta* **39** 1045
- [23] Andreassen G, Vela M E, Salvarezza R C and Arvia A J 1997 *Langmuir* **13** 6814
- [24] Cai W-B, Wan L-J, Noda H, Hibino Y, Ataka K and Osawa M 1998 *Langmuir* **14** 6992
- [25] Andreassen G, Vela M E, Salvarezza R C and Arvia A J 1999 *J. Electroanal. Chem.* **467** 230
- [26] Tadjeddine A, Le Rille A, Pluchery O, Hébert P, Zheng W Q and Marin T 1999 *Nucl. Instrum. Methods Phys. Res. A* **429** 481
- [27] Hoon-Khosla M, Fawcett W R, Chen A, Lipkowski J and Pettinger B 1999 *Electrochim. Acta* **45** 611
- [28] Dretschkow Th and Wandlowski Th 1999 *Electrochim. Acta* **45** 731
- [29] De Bonis A, Compagnini G, Cataliotti R S and Marletta G 1999 *J. Raman Spectrosc.* **30** 1067
- [30] Yang D, Bizzotto D, Lipkowski J, Pettinger B and Mirwald S 1994 *J. Phys. Chem.* **98** 7083
- [31] Dretschkow Th, Lampner D and Wandlowski Th 1998 *J. Electroanal. Chem.* **458** 121
- [32] Dretschkow Th and Wandlowski Th 1998 *J. Electroanal. Chem.* **467** 207
- [33] Noda H, Minoha T, Wan L-J and Osawa M 2000 *J. Electroanal. Chem.* **481** 62
- [34] Wandlowski Th, Ocko B M, Magnussen O M, Wu S and Lipkowski J 1996 *J. Electroanal. Chem.* **409** 155
- [35] Wu S, Lipkowski J, Magnussen O M, Ocko B M and Wandlowski Th 1998 *J. Electroanal. Chem.* **446** 67
- [36] Hoon-Khosla M, Fawcett W R, Goddard J D, Tian W-Q and Lipkowski J 2000 *Langmuir* **16** 2356
- [37] Steel P 1990 *Coord. Chem. Rev.* **106** 227
- [38] Eddowes M J and Hill H A O 1977 *Chem. Commun.* 3154
- [39] Alberty W J, Eddowes M J, Hill H A O and Hillman A R 1981 *J. Am. Chem. Soc.* **103** 3904
- [40] Uosaki K and Hill H A O 1981 *J. Electroanal. Chem.* **122** 321
- [41] Wilde C P and Durig T 1992 *J. Electroanal. Chem.* **327** 279
- [42] Zheng X and Hatton R 2000 *Electrochim. Acta* **45** 3629
- [43] Cunha F, Tao N J, Wang X W, Jin Q, Duong B and D'Agnese J 1996 *Langmuir* **12** 6410
- [44] Mayer D, Dretschkow Th, Ataka K and Wandlowski Th 2002 *J. Electroanal. Chem.* **524/525** 20
- [45] Aspnes D E and Stunda A A 1985 *Phys. Rev. Lett.* **54** 1956
- [46] Aspnes D E, Harbison J B, Stunda A A and Florez L T 1988 *Appl. Phys. Lett.* **52** 21
- [47] Martin D S and Weightman P 2001 *Surf. Interface Anal.* **31** 915
- [48] Sheridan B, Martin D S, Power J R, Barrett S D, Smith C I, Weightman P, Lucas C A and Nichols R J 2000 *Phys. Rev. Lett.* **85** 4618
- [49] Mazine V, Borensztein Y, Cagon L and Allongue P 1999 *Phys. Status Solidi a* **175** 311
- [50] Harrison P, Farrell T, Maunder A, Smith C I and Weightman P 2001 *Meas. Sci. Technol.* **12** 2185
- [51] Smith C I, Maunder A J, Lucas C A, Nichols R J and Weightman P 2003 *J. Electrochem. Soc.* **150** E233
- [52] Clavilier J, Faure R, Guinet G and Durand R 1980 *J. Electroanal. Chem.* **107** 205
- [53] Kolb D M 1993 *Structure of Electrified Interfaces* ed J Lipkowski and P N Ross (New York: VCH) p 65
- [54] Robinson K M, Robinson I K and O'Grady W E 1992 *Surf. Sci.* **262** 387
- [55] Aspnes D E, Harbison J P, Stunda A A and Florez L T 1988 *J. Vac. Sci. Technol. A* **6** 1327
- [56] Mazine V and Borensztein Y 2002 *Phys. Rev. Lett.* **88** 147403
- [57] Weightman P, Smith C I, Martin D S, Lucas C A, Nichols R J and Barrret S D 2004 *Phys. Rev. Lett.* **92** 199707
- [58] Yang D, Bizzotto D, Lipkowski J, Pettinger B and Mirwald S 1994 *J. Phys. Chem.* **98** 7083
- [59] Cunha F and Tao N J 1995 *Phys. Rev. Lett.* **75** 2376