225

STM studies of real and quasi-perfect silver single crystal surfaces used in electrochemical experiments

M. Höpfner, W. Obretenov, K. Jüttner, W.J. Lorenz

Institute of Physical Chemistry and Electrochemistry, University of Karlsruhe, Karlsruhe, Germany

G. Staikov, V. Bostanov and E. Budevski

Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia, Bulgaria

Received 18 July 1990; accepted for publication 7 November 1990

Real and quasi-perfect silver single crystal surfaces, which have been used intensively in different electrochemical investigations, are studied by STM to determine the surface profile on an atomic level. The measurements were carried out on chemically polished macroelectrodes and electrolytically grown microelectrodes in contact with air as well as under potentially controlled electrochemical conditions. The real macroelectrodes show a much higher surface corrugation than the quasi-perfect microelectrodes which have large atomically flat terraces separated by monoatomic steps. The possibility to observe the dynamics of monoatomic steps under anodic and cathodic polarization conditions on quasi-perfect single crystal surfaces is demonstrated. Nucleation and crystal growth processes are observed by means of in situ STM investigations of lead electrocrystallization on Ag(111) macroelectrodes. The results demonstrate the possibility to study fundamentally the initial steps of electrocrystallization by in situ STM under electrochemical well-defined conditions.

1. Introduction

Fundamental electrochemical studies at welldefined single crystal surfaces of metals have been carried out in the last two decades in order to correlate interfacial phenomena with the structure of the electrode. Such studies contributed significantly to obtain a completely new insight on an atomic level in the following fields: double layer structure and sorption effects (see ref. [1] and literature cited therein), underpotential deposition (UPD) of metals [2–39], underpotential–overpotential transitions (UPD–OPD) [4,9,12,16,20, 23,40], and electrocatalysis [41–55].

In most of these investigations so-called real single crystal surfaces of macro- or micro-electrodes have been used which are prepared either by thermal, chemical or electrochemical pretreatments or by vapor deposition techniques. These real single crystal surfaces contain a great density of crystal imperfections, especially emergence points of edge and screw dislocations, which lead to the appearence of mono- and multi-atomic steps and a relatively high surface corrugation.

Much better defined single crystal surfaces of silver and cadmium can be prepared by electrolytic growth according to the so-called capillary method developed by the Bulgarian school for electrocrystallization studies [56-58]. Under certain growth conditions, the low-index planes of such single crystals are obtained free of screw dislocations and atomically smooth. Therefore, these surfaces can be considered as quasi-perfect ones and provide ideal model systems for fundamental studies of metal/electrolyte interfaces. The modern knowledge of the mechanism of the electrocrystallization of metals is based on microelectrode experiments with quasi-perfect surfaces of silver single crystals. Later on, some investigations on the double layer structure and sorption effects

[1], UPD [4,9,11,12,16,20,22,23,25], and UPD-OPD transitions [4,9,12,16,20,23] have been carried out on quasi-perfect silver single crystal surfaces and the results were compared with those obtained on real ones.

From the experimental results obtained on real and quasi-perfect silver single crystal faces, structural and kinetic UPD interpretations were made which presume a quasi-perfect, regular atomic structure of the substrate surface. Indeed, different ex situ and in situ surface analysis methods such as LEED, RHEED, EXAFS, etc. confirmed, for example, the existence of UPD superlattice structures.

Very recently, first electrochemical STM studies on substrates of real silver single crystal faces showed, however, drastic surface corrugations in the nm range [59–62]. Therefore, it is surprising that the structural UPD interpretations based on the quasi-perfect surface assumption provide reasonable good agreement between theory and experimental results obtained on real single crystal surfaces. This has already been interpreted in terms that surface corrugations formed mainly by monoatomic steps may behave similarly to quasi-perfect single crystal faces [11,16].

In situ STM studies of lead and copper UPD on real (100) and (111) single crystal faces of gold have been carried out very recently. Atomic resolution of ordered surface structures could be achieved on the Au(111) face only [63–66].

The aim of this paper is to study real silver single crystal surfaces (Ag) and quasi-perfect silver single crystal surfaces (Ag*) of the orientations (100) and (111) by means of electrochemical ex situ and in situ STM and to compare the corresponding structures on an atomic level.

2. Experimental

2.1. STM set-up and electrochemical cell

The STM observations were carried out with a standard Nanoscope II STM (Digital Instruments, Santa Barbara, CA, USA). Bare or epoxy-isolated Pt-Ir tips (Pt-E3-010-12-R, Longreach Scientific Resources, Orr's Island, MN, USA) were em-



Fig. 1. Electrochemical cell. RE: reference electrode (Ag or Pb); CE: counter electrode (Pt).

ployed providing a background current of about 10 pA for the electrochemical measurements. Vibration isolation was achieved by mounting the whole STM assembly on an air table. The STM and the sample were screened by a steel shield grounded at a common point.

A teflon electrochemical cell with a volume of about 0.5 cm^3 (fig. 1) was screwed on the STM support plate allowing the use of either real single crystal macroelectrodes or quasi-perfect electrolytically grown silver single crystal microelectrodes. A platinum wire watertightly fixed at the wall of the cell served as the counter electrode for the electrochemical measurements. A Ag wire and

a Pb-coated Pt wire were used as reference electrodes in the systems Ag/Ag^+ and Ag/Pb^{2+} , respectively.

The potentials of both the working electrode and the STM-tip were independently controlled by means of a four-electrode potentiostat analogous to that developed by Siegenthaler et al. [59,60]. This means that the tunneling voltage is determined by the difference between the applied tip and working electrode potentials. This potentiostat could be used for potential control of both macro- and micro-electrodes. The current of the working electrode was measured by a sensitive electrometer (Keithley 617). The current of the tip was fed directly to the Nanoscope II hardware.

2.2. Electrode preparation

Macroelectrodes of silver single crystals of the orientations (100) and (111) with a diameter of 4.0 mm were embedded in teflon tubes using epoxy resin. The single crystals were oriented with an accuracy of about 1°. The surface was mechanically polished with diamond paste of different grain sizes down to 1 μ m and subsequently chemically etched for 10 s in a solution containing 4.8% CrO₃, 4% HCl, and 20% HClO₄, for 20 s in 4M H₂SO₄, and for 300 s in a solution containing 25% NH₃. Then, the macroelectrodes were thoroughly rinsed with four-time quartz-destilled water taking care to preserve a water drop on the surface.

The ex situ STM investigations in contact with air were performed by removing the water drop from the surface before mounting the electrode in the STM cell. For the electrochemical in situ STM investigations, the water drop at the surface was removed exactly prior filling the electrochemical STM cell with electrolyte.

Microelectrodes of silver single crystals of the orientation (100) were electrolytically grown in teflon capillaries (diameter about 300 μ m) in a separate and specially designed electrochemical cell containing a solution of 6M AgNO₃ and 0.1M HNO₃ according to the well-known capillary method [56–58]. After the crsytal growth, the microelectrodes were cleaned with four-time quartz-destilled water and then transfered to the STM cell.

2.3. Electrolyte solutions

For in situ STM measurements in the systems Ag/Ag^+ , Ag^*/Ag^+ and Ag/Pb^{2+} , the electrolytes consisted of $1.7 \times 10^{-2}M$ AgClO₄ and $5 \times 10^{-3}M$ Pb(ClO₄)₂ + $5 \times 10^{-2}M$ NaClO₄ at pH = 2.5 (adjusted with HClO₄), respectively. The electrolytes were freshly prepared from suprapure grade chemicals (Merck, Darmstadt) and four-time quartz-destilled water.

2.4. Measuring routine

For the STM investigations in contact with air, a tunneling voltage of typically -100 mV (tip positive vs. substrate) was applied and the tunneling current was adjusted to 2 nA. The course approach of the sample to the tip was achieved by means of microscrews, the fine approach was operated by the Nanoscope II software. Scanning rates of 8.7 lines/s $\leq v \leq 78$ lines/s were employed corresponding to sampling times of $22 \text{ s} \geq t \geq 3$ s. The STM images were automatically recorded in the computer memory for subsequent treatments (filtering, focusing, different display modes etc.). Both, constant current and constant height imaging modes were employed.

For in situ STM imaging in electrolyte solutions, tip potentials of typically 300 mV (tip potential versus Ag/Ag^+ or Pb/Pb^{2+} reference electrode) and only isolated tips were used in order to avoid electrochemical reactions at the tip itself. A typical value of the faradaic current flowing through a well isolated tip was about 10 pA at this tip potential.

The drift in x-y direction depended strongly on the electrochemical cell used and on the external vibration conditions. Under favorable conditions, x-y drift of less than 0.01 nm s⁻¹ could be obtained.

The experimental set-up for the in situ STM technique has been checked by cyclic voltammetric measurements of UPD of lead on real and quasi-perfect Ag(100) single crystal faces. The voltammograms were identical with previous results obtained in usual electrochemical cells [10-16].

M. Höpfner et al. / STM of real and quasi-perfect Ag single crystal surfaces



Fig. 2. Ex situ STM image (surface profile, constant current mode) of a real Ag(100) surface in contact with air.

3. Results and discussion

Fig. 2 shows a STM image of a real Ag(100) surface of a macroelectrode in contact with air after the standard pretreatment including chemical polishing and precleaning as usually and succesfully applied in UPD and electrocrystallization studies [2-28]. The structure is characterized by a relatively high surface corrugation in the order of 10 nm similar to the results of Siegenthaler et al. [59,60] and van der Eerden et al. [61,62]. A similar STM image was obtained on a real Ag(111) face. No features characteristic for the crystallographic orientations of the substrates were observed under the applied lateral resolution.

For comparison, fig. 3 represents a corresponding STM image of a quasi-perfect Ag*(100)



Fig. 4. Ex situ STM image (surface profile, constant current mode) of a quasi-perfect $Ag^*(100)$ surface in contact with air showing monoatomic steps as demonstrated in the cross section on line A-B.

surface in contact with air. In contrast to the real surfaces (e.g., fig. 2), a rather smooth surface profile consisting of flat terraces separated by only a few growth steps is observed. It should be noted that the surface profile strongly depends on the



Fig. 3. Ex situ STM image (surface profile, constant current mode) of a quasi-perfect Ag*(100) surface in contact with air.



Fig. 5. Ex situ STM image (surface profile, constant current mode) of an atomically smooth area (300 nm×300 nm) of a quasi-perfect Ag*(100) surface in contact with air.



Fig. 6. In situ STM images (top view, constant height mode) of a quasi-perfect $Ag^{*}(100)$ surface in the system $Ag^{*}/AgClO_{4}$ recorded at the equilibrium potential (a) and under cathodic polarization conditions ($\eta = -10 \text{ mV}$, $i_{-} = -0.1 \text{ mA cm}^{-2}$) at time intervals of about 100 s (b, c).

electrolytic growth conditions and the roughening during the cleaning and transfer procedure.

The surface profile of another sample exhibiting a relatively smooth surface area and only two growth steps is shown in fig. 4 under higher vertical resolution. From the cross section in fig. 4 it is clearly seen, that the growth steps are of monoatomic height. These results give direct evidence for the existence of monoatomic steps separated by atomically smooth terraces on quasi-perfect silver single crystal faces as it was predicted only indirectly by coulometric measurements in electrocrystallization studies [56]. It should be noted that atomically smooth large areas exist on quasi-per-



Fig. 7. In situ STM images (top view, constant height mode) of a quasi-perfect $Ag^{*}(100)$ surface in the system $Ag^{*}/AgClO_{4}$ recorded at the equilibrium potential (a) and under anodic polarization conditions ($\eta = +30 \text{ mV}$, $i_{+}=3 \text{ mA cm}^{-2}$) at time intervals of about 100 s (b, c).

fect single crystal faces in contrast to real single crystal surfaces as shown in fig. 5.

First results of electrochemical in situ STM measurements on quasi-perfect silver single crystal surfaces are presented in figs. 6 and 7 for the system Ag*(100)/AgClO₄ (1.7×10^{-2} M) at the equilibrium potential ($\eta = 0$) as well as under

cathodic $(\eta < 0)$ and anodic $(\eta > 0)$ polarization conditions, respectively. These STM images indicate that the time-dependent changes of the surface structure can be followed by means of in situ STM technique. For example, movement of growth steps along the surface is detectable in fig. 7 under anodic polarization conditions. In contrast to this,



Fig. 8. In situ STM images (surface profile, constant current mode) of a real Ag(111) surface in the system Ag/Pb²⁺ on the bare substrate (a) and after 3D lead nucleation and crystal growth (b, c, d). (a) $\eta = 0$ mV, $t \le 0$ s; (b) $\eta = -2$ mV, t = 280 s; (c) $\eta = -2$ mV, t = 300 s; (d) $\eta = -2$ mV, t = 320 s.

no pronounced growth steps on real silver single crystal faces could be observed under anodic polarization.

Another possibility of electrochemical in situ STM measurements is related to the electrocrystallization of metals on a foreign substrate. Figs. 8



Fig. 9. In situ STM image (surface profile, constant current mode) indicating monoatomic growth steps on a Pb(111) face of a 3D Pb crystallite on top of a real Ag(111) substrate.

and 9 show the electrodeposition of lead on a real silver single crystal surface in the $Ag(111)/Pb^{2+}$ system under cathodic polarization. Fig. 8 demonstrates the possibility to study the kinetics of lead nucleation and growth. The formation of 3D lead crystallites of triangular shape and their growth is clearly seen. The crystallites are oriented with the (111) face parallel to the Ag(111) substrate as reported in previous papers [4,9,12,16,20,23]. Monoatomic steps on a growing Pb(111) face can easily be recognized on a larger scale in fig. 9. Studies to measure accurately the propagation of monoatomic steps are in progress.

4. Conclusions

The results show the existence of large atomically smooth areas separated by monoatomic steps on quasi-perfect silver single crystal surfaces as accepted previously on the basis of electrochemical measurements only. On the other hand, real silver single crystal surfaces are shown to have relatively high surface corrugations and small terraces. Obviously, the step density is much higher on real single crystal faces than on quasi-perfect ones.

The results demonstrate that quasi-perfect silver single crystal faces provide ideal model electrodes for fundamental electrochemical and in situ STM studies in the following fields: double layer structure, sorption effects, UPD, electrocrystallization, UPD-OPD transitions, and electrocatalysis.

Moreover, the results encourage more detailed in situ STM studies of the electrodeposition and dissolution processes of quasi-perfect silver single crystal faces and demonstrate also the possibility to study the nucleation and dynamics of crystal growth of different metals on a foreign substrate.

The relatively high roughness of real silver single crystal faces on an atomic scale opens the discussion on the existence of superlattice structures of adsorbates in UPD experiments. Certainly, such superlattice structures will exist on relatively small terraces. The previously succesfully applied superlattice structure hypothesis will remain valid only, if surface corrugations are formed by monoatomic steps and if the superlattice structure is not influenced by the relatively high monoatomic step density. Besides of this thermodynamic and structural problem, the kinetics of UPD of metals were assumed to depend strongly on the monoatomic step density [7,19]. Furthermore, surface reconstruction phenomena were indirectly correlated to the monoatomic step density [25]. An exact confirmation of these results will be possible by in situ STM measurements using quasi-perfect silver single crystal surfaces which are in progress.

Acknowledgements

The authors would like to thank the Deutsche Forschungsgemeinschaft for financial support in the R & D program "Kristallkeimbildung und -wachstum" (Lo 184/21-1,2,4,5), the purchase of the Nanoscope II (Lo 184/21-3), and the cooperation with the Bulgarian Academy of Sciences. We

are also indebted to H. Siegenthaler for succesfull scientific cooperation and helpful discussions.

References

- A. Hamelin, in: Modern Aspects of Electrochemistry, No. 16, Eds. B.E. Conway, R.E. White and J.O'M. Bockris, (Plenum, New York, 1985) p. 1.
- [2] W.J. Lorenz, H.D. Herrmann, N. Wüthrich and F. Hilbert, J. Electrochem. Soc. 121 (1974) 1167.
- [3] D.M. Kolb, in: Advances in Electrochemistry and Electrochemical Engineering, Vol. 11, Eds. H. Gerischer and C.W. Tobias (Wiley, New York, 1978) p. 125.
- [4] K. Jüttner and W.J. Lorenz, Z. Phys. Chem. NF 122 (1980) 163.
- [5] W.J. Lorenz, Chem. Ing. Tech. 4 (1973) 175.
- [6] F. Hilbert, C. Mayer and W.J. Lorenz, J. Electroanal. Chem. 47 (1973) 167.
- [7] H.D. Herrmann, N. Wüthrich, W.J. Lorenz and E. Schmidt, J. Electroanal. Chem. 68 (1979) 273, 289.
- [8] K. Jüttner, G. Staikov, W.J. Lorenz and E. Schmidt, J. Electroanal. Chem. 80 (1977) 67.
- [9] W.J. Lorenz, E. Schmidt, G. Staikov and H. Bort, Faraday Symp. Chem. Soc. 12 (1977) 14.
- [10] G. Staikov, K. Jüttner, W.J. Lorenz and E. Schmidt, Electrochim. Acta 23 (1978) 305.
- [11] G. Staikov, K. Jüttner, W.J. Lorenz and E. Budevski, Electrochim. Acta 23 (1978) 319.
- [12] K. Jüttner, W.J. Lorenz, G. Staikov and E. Budevski, Electrochim. Acta 23 (1978) 741.
- [13] H. Bort, K. Jüttner, W.J. Lorenz, and E. Schmidt, J. Electroanal. Chem. 90 (1978) 413.
- [14] H. Siegenthaler, K. Jüttner, E. Schmidt and W.J. Lorenz, Electrochim. Acta 23 (1978) 1009.
- [15] K. Jüttner and H. Siegenthaler, Electrochim. Acta 23 (1978) 971.
- [16] G. Staikov, W.J. Lorenz and E. Budevski, Commun. Dept. Chem. Bulg. Acad. Sci. XI (1978) 474.
- [17] H. Siegenthaler and K. Jüttner, Electrochim. Acta 24 (1979) 109.
- [18] J.P. van der Eerden, D. Kashchiev, G. Staikov, W.J. Lorenz and E. Budevski, Surf. Sci. 82 (1979) 364.
- [19] K. Engelsmann, W.J. Lorenz and E. Schmidt, J. Electroanal. Chem. 114 (1980) 1, 11.
- [20] W.J. Lorenz, in: Proc. Symp. on Electrocrystallization, Hollywood, Florida, 1980, Eds. R. Weil and R.G. Barradas, Vol. 81-6 (The Electrochemical Society, Pennington, NJ, 1981) p. 81.
- [21] M. Klimmeck and K. Jüttner, Electrochim. Acta 27 (1982) 83.
- [22] H. Bort, K. Jüttner, W.J. Lorenz and G. Staikov, Electrochim. Acta 28 (1983) 993.
- [23] N. Bort, K. Jüttner, W.J. Lorenz, G. Staikov and E. Budevski, Electrochim. Acta 28 (1983) 985.

- [24] H. Siegenthaler and K. Jüttner, J. Electroanal. Chem. 163 (1984) 327.
- [25] T. Vitanov, A. Popov, G. Staikov, E. Budevski, W.J. Lorenz and E. Schmidt, Electrochim. Acta 31 (1986) 981.
- [26] J.R. Vilche and K. Jüttner, Electrochim. Acta 32 (1987) 1567.
- [27] A. Bewick and B. Thomas, J. Electroanal. Chem. 65 (1975) 911; 70 (1976) 239; 84 (1977) 127; 85 (1977) 329.
- [28] A. Bewick, J. Jovicevic and B. Thomas, Faraday Symp. Chem. Soc. 12 (1977) 24.
- [29] H.O. Beckmann, H. Gerischer, D.M. Kolb and G. Lehmpfuhl, Faraday Symp. Chem. Soc. 12 (1977) 51.
- [30] D.M. Kolb, K. Kötz and K. Yamamoto, Surf. Sci. 87 (1979) 20.
- [31] K. Takayanagi, D.M. Kolb, K. Kambe and G. Lehmpfuhl, Surf. Sci. 100 (1980) 407.
- [32] R. Adzic, E. Yeager and B.D. Cahan, J. Electrochem. Soc. 121 (1974) 474.
- [33] J. Horkans, B.D. Cahan and E. Yeager, J. Electrochem. Soc. 122 (1974) 1585.
- [34] D. Dickertmann, F.D. Koppitz and J.W. Schultze, Electrochim. Acta 21 (1976) 967.
- [35] J.W. Schultze and D. Dickertmann, Surf. Sci. 54 (1976) 489.
- [36] D. Dickertmann and J.W. Schultze, Electrochim. Acta 22 (1977) 117.
- [37] J.W. Schultze and D. Dickertmann, Faraday Symp. Chem. Soc. 12 (1977) 36.
- [38] J.W. Schultze and D. Dickertmann, Ber. Bunsenges. Phys. Chem. 82 (1978) 528.
- [39] J.W. Schultze and K.R. Brenske, J. Electroanal. Chem. 137 (1982) 331.
- [40] O.R. Melroy, M.F. Toney, G.L. Borgers, M.G. Samant, J.B. Kortright, P.N. Ross and L. Blum, J. Electroanal. Chem. 258 (1989) 403.
- [41] R.R. Adzic, in: Advances in Electrochemistry and Electrochemical Engineering, Vol. 13, Eds. H. Gerischer and C.W. Tobias (Wiley, New York, 1984) p. 159.
- [42] K. Jüttner, Electrochim. Acta 31 (1986) 917.
- [43] C. Mayer, K. Jüttner and W.J. Lorenz, J. Appl. Electrochem. 9 (1979) 161.
- [44] A.M. Abd. El-Halim, K. Jüttner and W.J. Lorenz, J. Electroanal. Chem. 106 (1980) 193.
- [45] A. Zwetanova and K. Jüttner, J. Electroanal. Chem. 119 (1981) 149.
- [46] K. Jüttner and W.J. Lorenz, in: Proc. Symp. on Electrocatalysis, Vol. 82-2 (The Electrochemical Society, Pennington, NJ, 1982) p. 323.

- [47] G. Kokkinidis and K. Jüttner, Electrochim. Acta 26 (1981) 971.
- [48] M. Alvarez-Rizzatti and K. Jüttner, J. Electroanal. Chem. 144 (1983) 351.
- [49] S.M. Sayed and K. Jüttner, Electrochim. Acta 28 (1983) 1635.
- [50] K. Jüttner, Electrochim. Acta 29 (1984) 1597.
- [51] M. Alvarez and K. Jüttner, Electrochim. Acta 33 (1988) 33.
- [52] M. Alvarez and K. Jüttner, in: 27. Tutzing Symposium der DECHEMA "Instationäre Messmethoden in Katalyse, Elektrochemie und Korrosion", 6–9 März 1989, DE-CHEMA-Monographs Series, Vol. 120 (VCH, Weinheim, 1989) p. 345.
- [53] R. Adzic and N. Markovic, J. Electroanal. Chem. 138 (1982) 443.
- [54] R. Adzic, A. Tripkovic and W. O'Grady, Nature 296 (1982) 137.
- [55] J. Clavillier, R. Parsons, R. Durand, C. Lamy and J.M. Leger, J. Electroanal. Chem. 124 (1983) 321.
- [56] E.B. Budevski, in: Comprehensive Treatise of Electrochemistry, Vol. 7, Eds. B.E. Conway, J.O'M. Bockris, E. Yeager, S.U.M. Khan and R.E. White (Plenum, New York, 1983) p. 339.
- [57] E. Budevski, V. Bostanov, T. Vitanov, Z. Stoynov, A. Kotzeva and R. Kaischev, Electrochim. Acta 11 (1966) 1697.
- [58] V. Bostanov, A. Kotzeva and E. Budevski, Bull. Inst. Chem. Phys. Bulg. Acad. Sci. 6 (1967) 33.
- [59] P. Lustenberger, H. Rohrer, R. Christoph and H. Siegenthaler, J. Electroanal. Chem. 243 (1989) 225.
- [60] R. Christoph, H. Siegenthaler, H. Rohrer and H. Wiese, Electrochim. Acta 34 (1989) 1011.
- [61] M. Hottenhues, M. Mickers, J. Gerritzen and J.P. van der Eerden, Surf. Sci. 206 (1989) 259.
- [62] J.P. van der Eerden, M. Mickers, J. Gerritzen and M. Hottenhues, Electrochim. Acta 34 (1989) 1141.
- [63] J. Wiechers, T. Twomey, D.M. Kolb and R.J. Behm, J. Electroanal. Chem. 248 (1988) 451.
- [64] O.M. Magnussen, J. Hotlos, R.J. Nichols, D.M. Kolb and R.J. Behm, Phys. Rev. Lett. 64 (1990) 2929.
- [65] M.P. Green, K.J. Hanson, D.A. Scherson, X. Xing, M. Richter, P.N. Ross, R. Carr and I. Lindau, J. Phys. Chem. 93 (1989) 2181.
- [66] D.J. Trevor, C.E.D. Chidsey and D.N. Loiacono, Phys. Rev. Lett. 62 (1989) 929.