

Available online at www.sciencedirect.com



SURFACE SCIENCE

Surface Science 600 (2006) 3971-3977

www.elsevier.com/locate/susc

# 2D compound formation during copper dissolution: An electrochemical STM study

P. Broekmann \*, N.T.M. Hai, K. Wandelt

Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany

Available online 6 May 2006

#### Abstract

The reversible formation of a 2D-CuI film on Cu(100) is studied by means of cyclic voltammetry in combination with electrochemical scanning tunneling microscopy.

Exposing the Cu(100) electrode surface to an acidic and iodide containing electrolyte (5 mM H<sub>2</sub>SO<sub>4</sub>/1 mM KI) leads to the formation of a well ordered  $c(p \times 2)$ -I adsorbate layer at potentials close to the onset of the anodic copper dissolution reaction. Copper dissolution starts at slightly more positive potentials preferentially at step edges in the presence of the iodide adlayer via the removal of copper material from kink sites at step edges. This increase of mobile Cu<sup>+</sup> ions causes the local exceeding of the CuI solubility product (pKL = 11.3), thereby giving rise to the nucleation and growth of a laterally well ordered 2D-CuI film. Key structural motifs of the growing CuI film are closely related to the (111) plane of bulk CuI. Quite intriguing, the 2D-CuI film does not act as a passive layer. Copper dissolution proceeds even in the presence of this binary compound via an inverse step flow mechanism. © 2006 Elsevier B.V. All rights reserved.

Keywords: STM; Electrified interfaces; Corrosion; Anion effects

# 1. Introduction

Copper as one of the key materials of the twenty-first century has attracted tremendous attention over the last two decades due to its nowadays realized application as wiring material in the state-of-the-art chip design [1], here replacing the former aluminium technology. However, the on-going trend of miniaturization towards the nanometer scale requires a more sophisticated understanding of the relevant interface properties and processes of those devices containing reactive materials like as copper. An atomic scale understanding of corrosion phenomena, corrosion inhibition by organics, oxidation, anodic dissolution and the formation of passivating films on copper is thus of vital interest and has consequently been in the focus of numerous fundamental studies. Since modern processing lines of chip fabrication also involves more and more "wet" chemical deposition processes the mastering of copper-electrolyte interfaces with or without additional potential control can be regarded as a particular challenge.

The anodic Copper Dissolution Reaction (CDR) in acidic electrolytes has been intensively studied in particular by Bard et al. [2,3] and Magnussen/Behm et al. [4–8] using in situ STM. Active sites for the dissolution or deposition are exclusively kinks at step edges as stated by Stranski in 1920 [9]. Magnussen and co-workers elaborated that the local structure of kink sites can be significantly altered by the presence of specifically adsorbed anions thus leading to changes in the overall surface reactivity [4]. State-of-the-art video STM techniques even allow the direct correlation of "global" parameters such as the exchange current density on the one hand and the "local" and microscopic dissolution rates at kink sites on the other hand [6,7].

Substantial contributions to the microscopic understanding of the anodic CDR in alkaline electrolytes came from Marcus/Strehblow et al. [10–13]. Quite contrary to the behavior in acidic media the CDR under alkaline

<sup>\*</sup> Corresponding author. Tel.: +49 228 73 3292; fax: +49 228 73 2551. *E-mail address:* broekman@thch.uni-bonn.de (P. Broekmann).

<sup>0039-6028/\$ -</sup> see front matter  $\odot$  2006 Elsevier B.V. All rights reserved. doi:10.1016/j.susc.2006.01.109

conditions is interfered by a binary compound formation, namely the formation of a passivating  $Cu_2O$  film at lower potentials and a  $Cu_2O/CuO$ ,  $Cu(OH)_2$  duplex film at higher potentials. Experimental conditions such as the pH, the applied potential and the polarization time sensitively control the atomic scale ordering, the overall film morphology and the thickness of the formed passive layers [13].

In the present study we report a new dissolution/corrosion mechanism observed on a Cu(100) electrode surface which comprises characteristic elements of the dissolution mechanism observed in both acidic and alkaline electrolytes. A binary compound formation is observed even in acidic electrolytes when the solution phase contains strongly adsorbing species like iodide which is known to form insoluble salts with  $Cu^+$  ions. The main focus of the present paper lies in the structural characterization of a well ordered 2D-CuI layer which forms and, by contrast to the  $Cu_2O/CuO$  film, does not passivate the electrode against on-going CDR.

## 2. Experimental

In order to study the initial stage of anodic CDR in the presence of inorganic salts we use a home-built in situ STM [14].

The tunneling tips were electrochemically etched in 2M KOH solution from 0.25 mm tungsten wire and subsequently coated with commercially available hot glue.

For all solutions high purity water (Milli-Q purification system; conductivity  $< 18 \text{ M}\Omega \text{ cm}$ ; TOC < 5 ppb) and reagent grade chemicals were used. Given the high affinity of copper towards oxygen the electrolyte had to be degassed with argon for several hours before use. All potentials given in the text refer to a RHE reference electrode.

Prior to each experiment to the copper surface had to be treated by an electrochemical etching procedure as described in Ref. [14].

All experiments started routinely with the characterization of the Cu(100) electrode in the presence of pure 5 mM H<sub>2</sub>SO<sub>4</sub> which served as supporting electrolyte for all subsequent dissolution experiments in the presence of iodide anions. For the latter experiments the pure supporting electrolyte was exchanged under potential control, e.g. at E = +80 mV, by a mixture of 5 mM H<sub>2</sub>SO<sub>4</sub> and 1 mM KI solution. The "intermediate step" via the pure sulfuric acid is important in order to avoid the instantaneous formation thick CuI films.

## 3. Results and discussion

### 3.1. Electrochemistry

A representative cyclic voltammogram of Cu(100) in 5 mM H<sub>2</sub>SO<sub>4</sub>/1 mM KI solution is presented in Fig. 1 (grey curve). It reveals a number of striking deviations to other CVs of Cu(100) in various acidic electrolytes [4,15]. These



Fig. 1. Cyclic voltammograms of Cu(100) in pure 5 mM  $H_2SO_4$  (black curve) and in 5 mM  $H_2SO_4/1$  mM KI (grey curve), dE/dt = 10 mV/s.

deviations are related to the appearance of a pronounced anodic peak system with P1 at +175 mV and P2/3 centered at about +215 mV. In the reverse potential scan characteristic cathodic current waves emerge at +120 mV (P'1), -110 mV (P'2) and +40 mV (P'3). The lack of an exponentially increasing anodic current, at least within the given potential range, is clearly indicative for a passivation of the copper surface with respect to the CDR after passing the anodic peak system P1–P3. An exponential increase of the CDR is only observed when potentials above +360 mV are applied [16]. Note that the pure supporting electrolyte (black curve in Fig. 1) the CDR starts already at about +275 mV.

A similar electrochemical behavior as presented in Fig. 1 has been reported by Inukai et al. [17] for a Cu(111) surface exposed to an iodide containing perchloric acid. The additional anodic current features were explained in terms of copper oxidation in the presence of iodide anions leaving CuI behind. In principle the same explanation as given by Inukai et al. [17] holds for the Cu(100) electrode in the iodide containing sulfuric acid. Recent SXPS (Synchrotron X-ray Photoelectron Spectroscopy) studies, indeed, evidenced the formation of CuI after passing the anodic peak system. The discussion of the particular reaction mechanism will be addressed in a separate paper [25].

It is, actually, this thick insulating film of CuI which leads to the observed passivation of the copper electrode with respect to the CDR. The large separation/hysteresis of about 320 mV between the oxidation (P2) and the corresponding reduction peak (P'2) points to a strong kinetic hindrance in particular of the reduction processes [16]. With this pronounced passivation behavior the Cu/I system seems to be closer to the electrochemical behavior of Cu in alkaline electrolytes [13] than to other acidic electrolytes [4,15,16]. A detailed analysis of all subtle current features showing up in Fig. 1 will be given in forthcoming papers [16,25]. Here we restrict ourselves to the surface dynamics occurring within the potential range between +80 mV and +130 mV at the onset of the anodic peak system where copper oxidation remains restricted to the monolayer regime only.

## 3.2. STM results

An electrolyte exchange procedure at +80 mV as described in the experimental section leads instantaneously to the formation of a laterally well ordered iodide adlayer (Fig. 2(a)). Iodide anions form a distorted "pseudo"square structure on Cu(100) [18,19] which is commensurate in only one of the substrate (011) directions giving rise to an additional one-dimensional height modulation perpendicular to this "commensurate direction". To first approximation we can understand this structure in terms of a distorted  $c(2 \times 2)$  lattice which is expanded parallel to only one of the original  $c(2 \times 2)$  unit-cell vectors leading to a  $c(p \times 2)$  unit cell. Characteristically, this *p*-vector decreases (increases) with increasing (decreasing) electrode potentials in terms of a so-called electrocompression (electrodecompression) process [18,19]. A schematic hardsphere model of the  $c(p \times 2)$  is presented in Fig. 2(c). At the given potential of +80 mV (Fig. 2(a)) the iodide saturation coverage of  $\Theta = 0.4$  ML is already reached corresponding to p = 2.5 and an NND (nearest neighbor distance) of 0.409 nm. Similar electrocompressible iodide phases are reported for the Cu(111) electrode [24].

Sweeping the electrode potential into positive direction from E = +80 mV to E = +100 mV causes the initiation of local dissolution processes (Fig. 3(a) and (b)) in the presence of the  $c(p \times 2)$ -I overlayer. Local dissolution starts at step edges and proceeds via an "inverse step-flow" mechanism. Steps stabilize themselves during dissolution along preferential directions (Fig. 3(b)) which coincide with main symmetry axes of the iodide lattice [18]. Besides the local removal of copper material one observes the 2D growth of an ordered film in close proximity of the ongoing copper dissolution (Fig. 3(b)). For two reasons it can be excluded that the observed film growth is a simple re-deposition of afore dissolved copper material: firstly, the emergence of a striped long-range superstructure does not correspond to the  $c(p \times 2)$ -I overlayer. Secondly, the growth of a completely new phase is inferred from one-dimensional cross sections over the growing film in the sub-monolayer regime (Fig. 3(c) and (d)). Step heights do not correspond to the value of 0.18 nm expected for step heights of the bare or anion covered Cu(100) surface. Using the height difference between two iodide covered Cu(100) terraces as internal reference (Fig. 3(c)) one determines a height difference of  $0.39 \pm 0.01$  nm between an iodide covered (100) terrace and the growing film (Fig. 3(d)) which is actually even more than twice the mono-atomic step height on Cu(100). The height difference between two adjacent terraces both covered by this new phase amounts to 0.18 nm



Fig. 2. (a) Structure of the  $c(p \times 2)$ -I layer at the onset of the CDR, 15.1 nm × 15.1 nm,  $I_t = 5$  nA,  $U_{\text{bias}} = 1$  mV,  $E_{\text{work}} = +80$  mV; (b)  $4.7 \times 4.7$  nm,  $I_t = 5$  nA,  $U_{\text{bias}} = 1$  mV,  $E_{\text{work}} = +80$  mV; (c) Hard sphere model of the  $c(p \times 2)$ -I layer, the *p*-value amounts to p = 2.5 at  $E_{\text{work}} = +80$  mV.



Fig. 3. Simultaneously occurring copper dissolution and 2D-CuI film growth, (a) 108 nm × 108 nm,  $I_t = 0.25$  nA,  $U_{\text{bias}} = 224$  mV,  $E_{\text{work}} = +110$  mV; (b) 108 nm × 108 nm,  $I_t = 0.25$  nA,  $U_{\text{bias}} = 224$  mV,  $E_{\text{work}} = +120$  mV; (c) cross section along the marked white line in (b); (d) cross section along the marked white line in (b).

which reflects again a single Cu–Cu step. Characteristically, the 2D film growth starts within a narrow potential range of only 10 mV between  $\pm$ 100 mV and  $\pm$ 110 mV at the onset of the anodic peak system P1/P2 and proceeds until the entire surface is covered with this new phase. One reasonable explanation for all these observations is the formation of an ultra-thin 2D film of CuI. Dissolved copper material does not leave the iodide covered copper surface into the solution but increases the local concentration of copper ions directly at the surface, with the consequence that the low solubility product of CuI (pKL = 11.3) becomes locally exceeded. This actually gives rise to the heterogeneous nucleation and growth of a surface confined 2D compound, namely CuI, as argued in the following.

Since the usual STM imaging mode does not provide any chemical sensitivity our assignment to 2D-CuI is based on a comparison to the work by Andryushechkin et al. [21] dealing with characterization of CuI, obtained after exposing Cu(100) to an excess of molecular iodine under UHV conditions. In fact, these authors observed with STM the same sequence of iodine phases and CuI films as a function of iodine exposure in UHV [20–23] as we have seen by in situ STM with a Cu(100) electrode under electrochemical conditions. Beyond this "gross" similarity there is even a striking correspondence between the atomic structure of our supposed CuI film (Fig. 4) and that grown under UHW conditions. This latter UHV-grown film could, indeed, be identified as CuI using Auger electron spectroscopy [21].

The 2D-CuI phase presented in Fig. 4 is characterized by stripes arranged in a strictly parallel manner with two periodicities distinct of  $d1 = 1.7 \pm 0.2$  nm and  $d2 = 3 \pm 0.2$  nm. However, there is no apparent regularity in the sequence of these characteristic stripe distances. The almost ideal hexagonal symmetry of the 2D-CuI phase becomes obvious from Fig. 4(b). The averaged NND amounts to  $0.44 \pm 0.02$  nm. Local deviations from that value are due to the existence of periodically arranged line dislocations. Close packed rows in adjacent stripes exhibit a pronounced anti-phase behavior as indicated by the dashed lines in Fig. 4(b). The enclosing angle between the propagation direction of the stripe pattern and the close packed rows on the atomic scale amounts to  $8 \pm 2^{\circ}$  [16]. All these observations are in excellent agreement with the assump-



Fig. 4. Atomic structure of the stable 2D-CuI film, (a) 27.3 nm × 27.3 nm,  $I_t = 1.3$  nA,  $U_{\text{bias}} = 10$  mV,  $E_{\text{work}} = +120$  mV; (b) 3 nm × 3 nm,  $I_t = 1.3$  nA,  $U_{\text{bias}} = 10$  mV,  $E_{\text{work}} = +120$  mV.

tion of a CuI(111) phase formed on the iodide pre-covered Cu(100) surface. Bulk CuI crystallizes in a ZnS-type structure (zinc blende) with a tetrahedral coordination (KZ = 4) of Cu<sup>+</sup> and I<sup>-</sup> respectively. Note, the formal oxidation states (+I) for copper and (-I) for iodide, however, do not imply an ionic bonding character. Quite in contrast, all solid monovalent copper halide phases reveal a highly covalent bonding between copper and halide particles which is actually the chemical reason for the low solubility of these compounds.

A preliminary model for the 2D-CuI surface film is based on the following stacking sequence: Cu(100)/  $c(p \times 2)$ -I/Cu/I (Fig. 5) which is in agreement with the results of Andryushechkin et al. [21]. Due to the reduced symmetry of the  $c(p \times 2)$ -I adsorbate phase with respect to the underlying substrate (Fig. 2) there are also somewhat distorted "quasi"-threefold hollow sites available within the iodide adsorbate layer as potential adsorptions sites for Cu<sup>+</sup> ions (Fig. 2(c)). With an additional iodide particle on-top of this single Cu<sup>+</sup> ion it is possible to form a slightly



Fig. 5. Schematic drawing illustrating the vertical stacking sequence of Cu(100)/I/Cu/I system; this model explains the observed step height in Fig. 3(b).

distorted tetrahedron with a central monovalent Cu species surrounded by four iodide particles as a characteristic structure motif of the growing 2D-CuI film. However, due to the different lattice symmetries and the slight mismatch between nearest neighbor spacings in the  $c(p \times 2)$ -I phase  $(NND_{iodide} = 0.41 \text{ nm})$  and an ideal CuI(111) plane  $(NND_{iodide} = NND_{Cu} = 0.422 \text{ nm})$ , respectively, those lattices are apparently not in full registry. The appearance of striped dislocation lines (Fig. 4) in combination with the pronounced anti-phase behavior could be explained in terms of a partial release of strain which originates from the inherent lattice mismatch. It should be stressed, however, that an ultimate structure model including these "buried" interfaces cannot be achieved only on the basis of STM work. Forthcoming in situ X-ray diffraction experiments on this system will certainly help to improve our preliminary structure model.

One of the most prominent properties of this 2D-CuI film is related to the on-going CDR at slightly more positive potentials (+120 mV). It appears quite intriguing that the 2D-CuI film does not effectively passivate the electrode surface against the CDR as it is reported for the  $Cu_2O/$ CuO duplex film in alkaline solution [12,13]. Fig. 6 demonstrates an on-going dissolution reaction in the presence of the 2D-CuI film. Time resolved STM images clearly indicate an inverse step flow mechanism with receding step edges leaving the same CuI film at the lower terraces behind. Considering the stacking sequence at the interface (Fig. 5) it becomes obvious that the dissolution mechanism in the presence of the 2D-CuI film must be much more complex than for electrode surfaces which are covered by monolayers of regular adsorbate phases [4,8]. In this latter case only two layers are involved into the dissolution reaction, namely the anion overlayer and the metallic substrate layer underneath while in the present case four layers must participate in the "collective receding" of steps (Fig. 6). This concerted process is indicated in Fig. 5 by four dark arrows.



Fig. 6. CDR in the presence of the 2D-CuI film, (a)–(c) 70 nm × 70 nm,  $I_t = 1$  nA,  $U_{\text{bias}} = 5$  mV,  $E_{\text{work}} = +120$  mV, one prominent defect within the 2D-CuI film is marked in all 4 STM images, the in-set in panel (c) shows the structure of the 2D-CuI film which can be imaged on terraces affected by the CDR.

Increasing the dissolution rate by applying potentials above +130 mV leads to the formation of 3D-CuI/iodine clusters [16,25] until the entire surface is covered with an about 5–8 nm thick passive film.

## 4. Conclusions

In this paper we could show that a well defined binary compound is formed at the electrode surface close to the onset of the copper dissolution reaction (CDR). An ultimate prerequisite for such a binary compound formation is the extraordinarily low solubility of this binary compound.

A laterally well ordered 2D-CuI film is formed on Cu(100) at potentials (+100 mV to +110 mV) below the potential range of the corresponding bulk CuI formation (above +130 mV). Due to this separation of the potential regime of the 2D-CuI formation on the one hand and the 3D-CuI bulk formation on the other we denote the observed films growth as Under Potential Formation (UPF) of a binary compound similar to the well known phenomenon of Under Potential Deposition (UPD) of metals. In this latter case, however, the metal "deposit" comes from

the solution phase while in our case the metal cations originate directly from the electrode surface as a consequence of an oxidative dissolution reaction of the electrode material. The observed structural features are in good agreement with the assumption of a Cu(100)/I/Cu/I stacking sequence. Due to the pronounce hexagonal symmetry of the growing film we propose a lateral structure of the CuI film which is closely related to the (111)-plane of bulk CuI with a "pseudo"-tetrahedral coordination of Cu<sup>+</sup> ions placed in a kind of "sandwich" of two adjacent iodide layers. Quite surprisingly, the formation of the 2D-CuI film does not efficiently suppress the anodic dissolution of copper. Only the ongoing CDR in the presence of the 2D-CuI film at higher reaction rates leads to the growth of 3D-CuI clusters thus explaining the final passivation against the CDR as observed in the CV.

#### References

- T.G. Koetter, H. Wendrock, H. Schuehrer, C. Wenzel, K. Wentzig, Microelectron. Reliab. 40 (2000) 1295.
- [2] D.W. Suggs, A.J. Bard, J. Am. Chem. Soc. 116 (1994) 10725.
- [3] D.W. Suggs, A.J. Bard, J. Phys. Chem. 99 (1995) 8349.

- [4] M.R. Vogt, A. Lachenwitzer, O.M. Magnussen, R.J. Behm, Surf. Sci. 399 (1998) 49.
- [5] O.M. Magnussen, M.R. Vogt, Phys. Rev. Lett. 85 (2000) 357.
- [6] O.M. Magnussen, L. Zitzler, B. Gleich, M.R. Vogt, R.J. Behm, Electrochem. Acta 46 (2001) 3725.
- [7] O.M. Magnussen, W. Polewska, L. Zitzler, B. Gleich, R.J. Behm, Faraday Discuss. 121 (2002) 43.
- [8] O.M. Magnussen, Chem. Rev. 102 (2002) 679.
- [9] I.N. Stranski, Z. Phys. Chem. 136 (1928) 259.
- [10] V. Maurice, H.-H. Strehblow, P. Marcus, Surf. Sci. 458 (2000) 185.
- [11] V. Maurice, L.H. Klein, H.-H. Strehblow, P. Marcus, J. Electrochem. Soc. 150 (2003) B316.
- [12] J. Kunze, V. Maurice, L.H. Klein, H.-H. Strehblow, P. Marcus, J. Electroanal. Chem. 554–555 (2003) 113.
- [13] J. Kunze, V. Maurice, L.H. Klein, H.-H. Strehblow, P. Marcus, Corr. Sci. 46 (2004) 245.
- [14] M. Wilms, M. Kruft, G. Bermes, K. Wandelt, Rev. Sci. Instr. 70 (7) (1999) 3641.
- [15] P. Broekmann, M. Anastasescu, A. Spaenig, W. Lisowski, K. Wandelt, J. Electroanal. Chem. 500 (2001) 241.

- [16] P. Broekmann, N.T.M. Hai, K. Wandelt, J. Appl. Electrochem., in press.
- [17] J. Inukai, Y. Osawa, K. Itaya, J. Phys. Chem. B 102 (1998) 10034.
- [18] P. Broekmann, A. Spaenig, A. Hommes, K. Wandelt, Surf. Sci. 517 (1–3) (2002) 123.
- [19] A. Hommes, A. Spaenig, P. Broekmann, K. Wandelt, Surf. Sci. 547 (2003) 239.
- [20] B.V. Andryushechkin, K.N. Eltsov, V.M. Shevlyuga, U. Bardi, B. Cortigiani, Surf. Sci. 497 (2002) 59.
- [21] B.V. Andryushechkin, K.N. Eltsov, V.M. Shevlyuga, Surf. Sci. 566–568 (2004) 203.
- [22] B.V. Andryushechkin, K.N. Eltsov, V.M. Shevlyuga, Surf. Sci. 472 (2001) 80.
- [23] B.V. Andryushechkin, K.N. Eltsov, V.M. Shevlyuga, Surf. Sci. 584 (2005) 287.
- [24] B. Obliers, P. Broekmann, K. Wandelt, J. Electroanal. Chem. 554–555 (2003) 183.
- [25] P. Broekmann, N.T.M. Hai, S. Hümann, R. Hunger, K. Wandelt, in preparation.