Electrochemical cell for *in situ* x-ray diffraction under ultrapure conditions

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An electrochemical cell has been developed for *in situ* x-ray diffraction from a working electrode under clean conditions equivalent to ultrahigh vacuum conditions of 5×10^{-10} mbar. The substrate crystals can be prepared *ex situ* and transferred into the cell under protection of ultrapure water within a few seconds. The oxygen level in the electrolyte is reduced by continuous N_2 flow to less than 0.2% compared to that of a fresh electrolyte. This can be done while rotating the cell by 360° about the surface normal. The electrode potential is accurately measured at the position of the crystal using a Luggin capillary and a standard reference electrode. We demonstrate the performance of our cell by *in situ* synchrotron x-ray diffraction measurements on ultrathin Co layers electrodeposited on Cu(001) in an aqueous H_2SO_4/$CoSO_4$ solution. © *1998 American Institute of Physics.* [S0034-6748(98)00204-4]

I. INTRODUCTION

Numerous electrochemical cell designs have been published in the literature for x-ray diffraction measurements with synchrotron radiation in transmission and reflection geometry.[1–5] These cells have been usually machined out of Teflon or Kel-F with o-ring sealings. Mylar windows and a thin electrolyte layer in front of the substrate surface are usually used to achieve low x-ray absorption. However, a fast sample transfer into these cells with the sample surface protected from air would be difficult and an *in situ* removal of oxygen from the electrolyte is not possible. Significant changes in the cyclic voltammograms during diffraction measurements have been repeatedly reported.[5,6] It is known that Cu easily oxidizes in aqueous electrolytes in the presence of oxygen.[7–10] We have shown that the reproducible electrodeposition and *in situ* investigation of ultrathin magnetic films requires oxygen removal from the electrolyte and clean conditions which are equivalent to ultrahigh vacuum conditions of 5×10^{-10} mbar.[11] Therefore, x-ray diffraction at such base metal substrates, at surfaces with a high affinity to oxidation, or at overpotential deposited thin films [particularly Co on Cu(001)], requires an electrochemical cell which fulfills additional requirements compared to the usual cell designs:

(i) It must be deaerateable by inert gases, like noble gases or N_2, to reduce the oxygen content in the electrolyte to a minimum, thereby avoiding unwanted reactions at the substrate surface and avoiding unwanted cathodic currents in the double layer range. Low base currents in the current–voltage characteristics are required to achieve a charge resolution equivalent of 0.02 ML during thin film deposition;[11]

(ii) the transfer of the substrate, which may have to be prepared *ex situ* (as, e.g., Cu), into the cell has to be done fast, under ultrapure conditions and protected from contact to air to avoid contamination and oxidation of the substrate surface; (iii) the potential of the working electrode [WE, i.e., the crystal] should be measured accurately in a three electrode configuration using a Luggin capillary and a standard reference electrode in order to achieve reproducible current–voltage characteristics; (iv) the cell should be rotatable by 360° about the surface normal of the crystal to allow a proper alignment of the crystal; (v) the Mylar window should be easily and quickly exchangeable without contamination of the cell.

We present a cell which has been proven to fulfill these requirements (Fig. 1). We demonstrate its performance by an x-ray diffraction study of ultrathin Co films deposited from an aqueous H_2SO_4/$CoSO_4$ solution onto Cu(001) which would sensitively react to dissolved oxygen in the electrolyte.

II. CELL DESIGN

The cell (Fig. 1) has been made of Duran glass to achieve the cleanest conditions similar to a previous cell for electrochemical scanning tunneling microscope (STM) measurements.[12] The connections to the cell are made by glass joints to prevent contamination by other materials.

The 6 μm thick Mylar window is sealed with Apiezon wax on top of a specially machined male joint. It is the outermost point at this end of the cell (Fig. 1, right side). Thus, angles of incidence down to 0° can be realized.

The substrate is mounted at the end of a glass tube; the
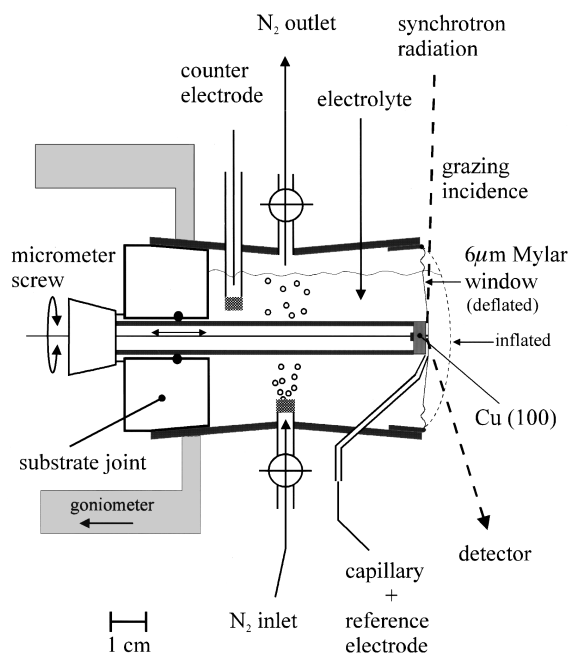
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FIG. 1. Electrochemical thin electrolyte layer cell: The cell is mounted horizontally on the diffractometer which is schematically indicated at the left side of the figure. The cell can be rotated about its horizontal axis.

electrical contact is made by a Pt wire glued to the back of the substrate using a silver epoxy glue. All electrically conducting areas of the crystal except for the oriented surface are isolated with a lacquer against the electrolyte. The tube (and substrate) can be adjusted towards the Mylar window by means of a micrometer screw which is mounted on the male substrate joint (Fig. 1, left side). This joint, micrometer screw, substrate holder (i.e., glass tube), and crystal can be exchanged as a whole, if the corresponding joint of the cell points upwards, so that the electrolyte cannot flow out. This enables particularly a fast insertion of WE into the electrolyte under potential control. Additionally, the crystal can be electrochemically polished or cleaned *ex situ*, and then transferred into the cell with the crystal surface protected against contamination by a drop of ultrapure water (Milli-Q plus). This can be easily repeated if necessary. The crystal surface is also protected during removal from the cell, since a drop of electrolyte remains on the crystal surface while the crystal is pulled out of the liquid. This is essential if surfaces have to be investigated which cannot be cleaned *in situ* (e.g., Cu) in the electrochemical cell.

We use a saturated calomel electrode (SCE) as reference electrode (RE), since this standard reference provides reproducible cell potentials during long measurement times. It is connected to the Luggin capillary in the cell by an approximately 1 m long polyethylene tube to allow the rotation of the cell. Using a Luggin capillary, we are able to measure accurately the WE potential at the substrate position as indicated in Fig. 1. The counter electrode (CE) is a Pt wire, separated by a frit from the volume of the cell to avoid pollution of the electrolyte by reaction products. A large surface area of CE is not necessary, because of the low cell currents which do not exceed significantly 100 μA during the film deposition.

N_2 bubbles are generated by a frit as indicated in Fig. 1. These bubbles are a second reason for using glass as a material for the cell, because the bubbles would stick to the walls of the cell if they were machined out of Teflon. Inlet and outlet to the cell can be closed by valves to apply over- and underpressure to the interior of the cell.

The voltammetry in the cell can be done with the Mylar window inflated by a slight N_2 overpressure, providing an approximately 2 mm thick electrolyte layer between the crystal surface and the Mylar window, to avoid diffusion limitation of the cell current, as is the case in the thin layer geometry used for the x-ray measurements.

A thin layer geometry during the x-ray diffraction measurements is realized by stopping the N_2 flow, closing the valve at the bottom of the cell, and by applying a small underpressure to the interior of the cell. This provides an electrolyte layer thickness of 10–20 μm[13] and a smooth Mylar window across the substrate surface.

The small N_2 gas reservoir at the top of the cell does not influence the measurements, since the geometry guarantees contact of all electrodes to the electrolyte during a 360° rotation of the cell. In particular, there is no interference of the gas bubbles with the electrodes.

All parts of the cell are routinely cleaned in a mixture of concentrated H_2SO_4/H_2O_2 and sterilized in ultrapure water. Thus, we achieve the required clean conditions mentioned above.

III. VOLTAMMETRY

To test the performance of our cell, we investigated ultrathin Co layers electrodeposited onto a Cu(001) surface in an aqueous electrolyte of 0.1 M H_2SO_4+1 mM $CoSO_4$. The details of the preparation of the Cu(001) surface by electrochemical polishing in H_3PO_4 have been published in Ref. 12.

The current in the double layer range between -100 and -600 mV is reduced to less than 1 μA/cm^2 if the electrolyte is carefully deaerated (solid curve in Fig. 2). This residual current results mainly from the charging of the electrolytical double layer during the voltage sweep of 10 mV/s. The typical increase of the cathodic current in the double layer range around -300 mV, related to O_2 reduction,[14] as seen in the dotted curve in Fig. 2 (partially deaerated electrolyte) is completely missing. The current variation around -300 mV, which could be attributed to O_2 reduction, is less than 0.05 μA/cm^2. A possible electrochemisorption of oxygen species [e.g., Cu–(OH)$_{ads}$], as reported for Cu(111) electrodes in aqueous electrolytes,[15] cannot be observed. The dashed curve in Fig. 2 shows the cyclic voltammogram of a freshly prepared electrolyte. Comparison of the current–voltage characteristics of the completely deaerated and of the fresh electrolyte shows that the oxygen level in the electrolyte is suppressed by more than a factor 500 after *in situ* bubbling with N_2. Oxidation of Cu to Cu_2O or CuO would be observed around -550 mV (and is expected only in alkaline solutions).[16] The measured anodic charge between -100 and -50 mV is related to the oxidation of Cu to Cu^{2+}. This anodic charge equals the corresponding cathodic charge during the re-deposition of Cu within the accuracy of
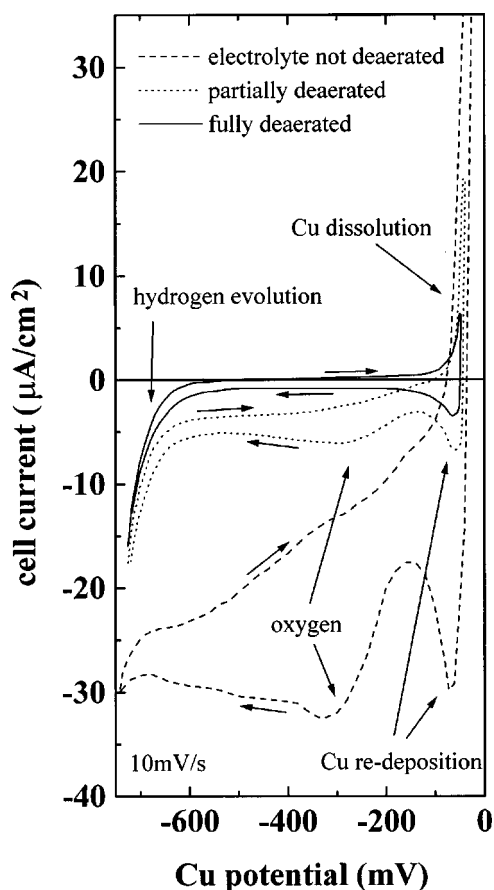
FIG. 2. Current–voltage characteristics in an aqueous electrolyte of 0.1 M H_2SO_4 without $CoSO_4$ to show the effects of oxygen removal on the voltammetry. The potentials are measured with respect to the saturated calomel electrode (SCE). The arrows indicate the cycling direction of the voltage sweep with 10 mV/s. The increase of the cathodic current below -600 mV is caused by H_2 evolution at the substrate. The Cu dissolution (increase of anodic current) starts around -80 mV. (Dashed curve) cyclic voltammogram of a fresh electrolyte; (dotted curve) incompletely deaerated electrolyte still showing the increase of cathodic current in the double layer range around -300 mV caused by O_2 reduction to H_2O_2 or H_2O; (solid curve) carefully deaerated electrolyte. The remaining current between -100 and -600 mV is mainly caused by the charging of the electrochemical double layer during the voltage sweep.

IV. X-RAY DIFFRACTION

As an example for the application of our electrochemical cell, we show x-ray diffraction measurements of the electropolished Cu(001) crystal without Co and with 12 ML Co/Cu(001). The experiments were carried out at the BW2 beamline at HASYLAB, using focused radiation of the 56 pole hybrid Wiggler. The photon energy was 8.5 keV, 0.5
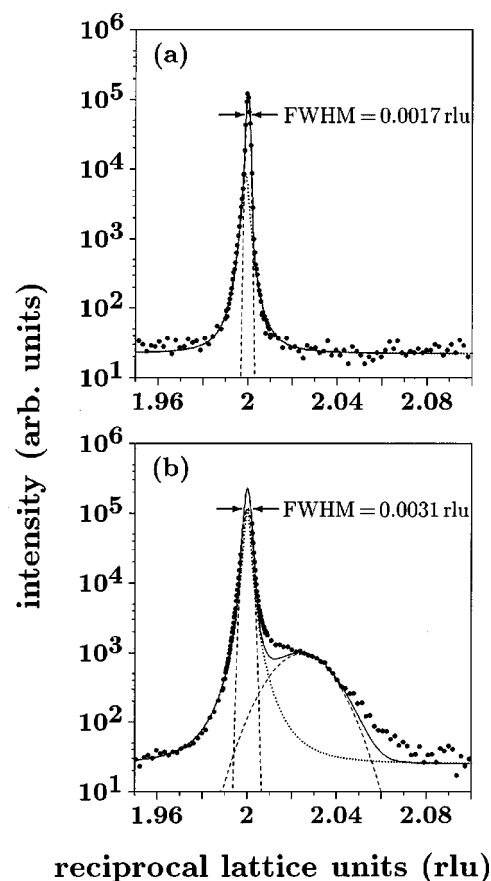

FIG. 3. (a) In-plane $[2,-2]$ diffraction peak of the clean Cu(001) surface. (b) In-plane $[2,-2]$ diffraction peak of 12 ML Co/Cu(001). Both scans are in the in-plane $[2,-2]$ direction. The presence of Co is detectable by an asymmetric broadening of the peak profile compared to (a). Gauss fits are drawn as dashed lines, Lorentz fits as dotted lines, and the sum of both as solid lines. The angle of incidence was $0.3°$ with respect to the surface plane, the photon energy was 8.5 keV.

keV below the K edge of Cu. Surface sensitivity was achieved by an angle of incidence of $0.3°$ with respect to the crystal surface.

The in-plane $[2,-2]$ diffraction peaks of clean Cu(001) and 12 ML Co/Cu(001) are shown in Figs. 3(a) and 3(b), respectively. The Cu peak [Fig. 3(a)] was fitted using a Gaussian line shape with a small contribution (8% of the total peak height) of a Lorentzian line shape. The full width half maximum (FWHM) of the Gauss peak is 0.0017 reciprocal lattice units (rlus), that of the Lorentzian component is 0.0026 rlu. The origin of this two component line shape is basically the diffraction from surfaces showing atomic-scale roughness which results in a Bragg and a diffuse scattering intensity component.[17,18] The electrodeposited Co [Fig. 3(b)] is detectable by a broadening of the Cu diffraction peak at 2.000 rlu and by an additional peak in the line shape compared to (a). This additional peak is centered at 2.022 rlu, which corresponds to an in-plane lattice constant of 3.575 Å, 1.1% smaller than the in-plane lattice constant of Cu (3.6147 Å).

The detailed crystallographic investigation of ultrathin electrochemically grown Co/Cu(001) will be published in Ref. 19.

the measurement in the case of the completely deaerated electrolyte (solid curve in Fig. 2), whereas it is approximately three times larger than the corresponding cathodic charge during the re-deposition of Cu in the case of the fresh electrolyte (dashed curve in Fig. 2). This strongly suggests that there is oxidation or electrochemisorption at the Cu surface even in acidic solutions mediated by the dissolved oxygen in the electrolyte.

V. DISCUSSION

The electrochemical cell described here allows x-ray diffraction measurements of surface and surface–electrolyte interface properties at clean conditions equivalent to the state of the art in electrochemical laboratories. The possibility of an *ex situ* preparation of substrates and their fast transfer into the cell without contamination from air, as well as immediate potential control, allows reliable surface sensitive investigations at base metal surfaces. In particular the reproducible and accurate *in situ* voltammetry, as well as the *in situ* removal of dissolved oxygen from the electrolyte open up new prospects into the investigation of overpotential deposited ultrathin films like Co/Cu (001). The cell permits the investigation of such films in the monolayer range for several hours under ultrapure and reproducible conditions.

ACKNOWLEDGMENTS

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