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Properties of physisorbed water layers on gold revealed in a FEM study

J. Plšek *, P. Hrubý, K. Nikiforov [1], Z. Knor

The J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3,
182 23 Prague 8, Czech Republic

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Abstract

Field emission study of thin water layers was performed to examine their properties and their changes after application of a high electric field. Comparison of field emission characteristics of water layers adsorbed on clean tungsten and gold-covered tungsten suggested that, whereas water molecules adsorbed on tungsten are oriented by oxygen atoms towards the metal surface, water layer on gold-covered tungsten has amorphous character with no preferential orientation. Both heated and non-heated layers are heavily influenced by applied high electric field strengths ($F \approx 30$ MV/cm). Decrease of the work function and of the voltage needed for a constant emission current during successive increase of the electric field was tentatively interpreted in terms of chemical and morfological changes of the water layer due to the field dissociation and solvation.

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1. Introduction

The importance of metal–water interaction in practical systems has led to a great deal of interest in the structure and dynamics of metal–ice interfaces [1]. Besides macroscopic experimental techniques also microscopic field emission (FE) techniques were used for investigation of the emission properties of metal surfaces covered by adsorbed water layers [2]. Water molecules are characterized by a high permanent dipole moment and considerable susceptibility for polarization. Therefore, the electric field applied during the measurement of a FE current I strongly influences the adsorbed water layer, namely by dissociation [3], redistribution and reorientation [4] of water molecules or a field-induced desorption [5].

The electric field effect on adsorbed water layers plays important role in electrochemical processes.

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* Corresponding author. Tel.: +420 26605 3546;
fax: +420 28658 2307.
E-mail address: jan.plsek@jh-inst.cas.cz (J. Plšek).

[1] On leave from Saint-Petersburg State University, Saint-Petersburg, Russia.

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Near the surface of an electrode, the charge is screened out within a short distance, resulting thus in high electric fields of the order of 100 MV/cm. While the role of surface electric field in electrochemistry has been theoretically studied long, since (for one representative example see Ref. [6]) experimental studies are rather few. The main difficulty is the generation of high electric field in a well reproducible way. Field emitter tip represents a promising tool, which overcomes this difficulty.

However, application of the FE microscopy for investigation of adsorbed water layers is not trouble-free because water layers are often influenced already by the electric fields needed for the work function (WF) estimation on the basis of the Fowler–Nordheim (FN) plot (i.e. when the whole FE characteristics, $I = I(F)$, is recorded). This, of course, results in a bad reproducibility of the WF estimation by the FE technique. To avoid this difficulty, a voltage U_{I_0}, needed for a constant FE current I_0, is often used in literature [4,7,8] for the estimation of the WF changes, because in this way one can cut down the time interval of measurement (only one point of the FE characteristics is measured). Thus, the perturbation of the adsorbed layer would be presumably smaller than in the preceding case.

Besides that, the possibility to create from adsorbed molecules (possessing a permanent dipole moment) a system, which would exhibit prescribed 2D (or eventually 3D) distribution of electric charges, represents an interesting problem by itself.

The experimental work, reported here, is focused on the above-mentioned principal problems of the WF estimation by FE microscopy in a system: water layers adsorbed on clean W and Au surfaces. This work concerns particularly: (i) examination of the electric field effects (problems of adsorbed layer stabilization); (ii) the interpretation of FE characteristics measured at low currents (to minimize the field effects) for these systems and (iii) discussion of a possible mechanism of the field-induced changes.

2. Experimental

Experiments have been carried out in a stainless steel UHV system USU 4 (*Acad. Sci. USSR*) described elsewhere [9,10] (base pressure $p < 1 \times 10^{-9}$ mbar). Tungsten tips, spot welded to a tungsten loop, were prepared by a standard etching procedure. The field strength F was estimated for a clean tungsten tip by means of the relation $F = U/5R$, where U is the applied voltage and R is the curvature radius of the tip apex [3,5]. R was estimated from the voltage, needed for obtaining the total emission current $I = 1 \times 10^{-5}$ A [11]. This voltage was estimated by extrapolation of the FE characteristics.

Golden layers have been deposited under UHV conditions in a ‘‘head-on-head’’ configuration onto a thermally cleaned tungsten tip. The tip temperature during deposition has been maintained at 600 K. The thickness of the golden layer, prepared by stepwise evaporation, was roughly judged from the work function changes [12]. It was estimated to be approximately two–three monolayers in the reported experiments. This thickness of Au layers is sufficient for preventing the dissociation of water molecules on the tungsten surface [4].

Prior to dosing, water was degassed by several freeze-thaw cycles [3]. Water vapor was handled in an all-glass system connected with a stainless steel UHV system by a sapphire leak-valve. To avoid a dissociation of water on hot cathodes, the water vapor pressure has been measured during dosing by a magnetron gauge VMB-1/8-001 (*Acad. Sci. USSR*). Magnetron gauge was calibrated for N_2 by a quadrupole mass-spectrometer (QMG 064 Balzers). All adsorbed layers were prepared by condensation on the tip held at 78 K (virgin layers).

The FE images have been recorded by a CCD camera. FE currents I were measured at the screen, held at a ground potential. FE characteristics of the clean surface and of the surface covered with adsorbed water layers were usually measured by an amplifier in the low current range (0.1–7 nA), without recording the field emission image, which was not visible under these conditions. During measurements of the FE characteristics the field strength never exceeded 30 MV/cm. Slopes and intercepts of FN plots were estimated from the experimental FE characteristics. The voltages U_{I_0} needed for a constant current were obtained by interpolation of FE characteristics.

3. Experimental results and discussion

High electric fields applied in FE measurements seriously influence the adsorbed water layers, and thus