



Experiment title: X-RAY ELECTROCHEMICAL LITHOGRAPHY	Experiment number: CH-3523
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The proposal was aimed to understand the chemistry and electrochemistry of photoelectrons created at solid/liquid interface under X-ray illumination. The idea of combining electrochemistry with X-ray photolithography and involving photoelectrons to electrochemical circuit was originated from experimental observation of the variation in electrochemical deposition/etching rates at the working electrode under illumination. Generally, absorption of a high-energy photon by the electrode surface leads to numerous secondary events with an avalanche-type creation of low-energy excited electrons. In cases the energy of the electron exceeds the Volta potential difference, it can escape from the surface to the electrolyte volume. In case of cathodic polarization low-energy electrons emitted from the electrode surface can further reduce cations in the Helmholtz layer, while high-energy electrons get through the electric double layer to electrolyte volume (Fig. 1). Thus, emitted photoelectrons generally produce an additional electric current at the electrode-electrolyte interface that involves electrochemical transformation. Unlike the radiolysis products, these electrons have no oxidizing pairs, which obviously shifts electrochemical equilibrium and enhances deposition rates on the illuminated areas of the electrode. The holes on core levels generated by X-rays move away from the electrode surface under applied potential and annihilate effectively in the electrode volume. The circuit completes through electrochemical reactions on the anode.

In frames of CH-3523 experiment several tasks were addressed:

- 1) Cyclic voltammetry of Ni and Pd deposition/etching in corresponding electrolyte solutions at different X-ray intensities and energies.
- 2) Potentiostatic X-ray assisted deposition/etching of Ni and Pd at different X-ray energies.
- 3) X-ray electrochemical lithography experiments through Ni deposition in potentiostatic regimes using Talbot imaging of 4.2 μm grating and ultimate resolution determination using silicon multilens interferometer.

All the experiments were performed on Pt and Cu microelectrodes with diameter of $\sim 500 \mu\text{m}$. Sets of CRL lenses were used to adjust illuminated area to fit the size of microelectrodes and homogeneously illuminate it. The experiments on cyclic voltammetry revealed a substantial current increase for both anodic and cathodic polarisation under X-ray illumination. One should note, while an increase in cathodic current is well understood in frames of proposed photoelectron current model, an increase of current for anodic polarisation needs further interpretation.

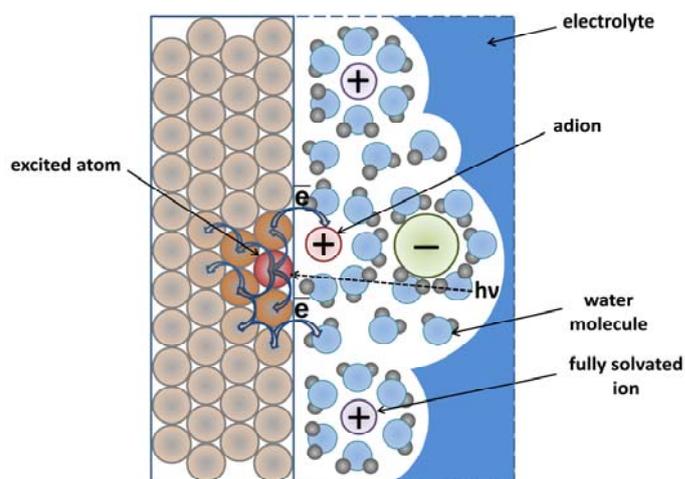


Fig. 1. Schematic representation of charge transfer during the X-ray assisted electrochemical deposition.

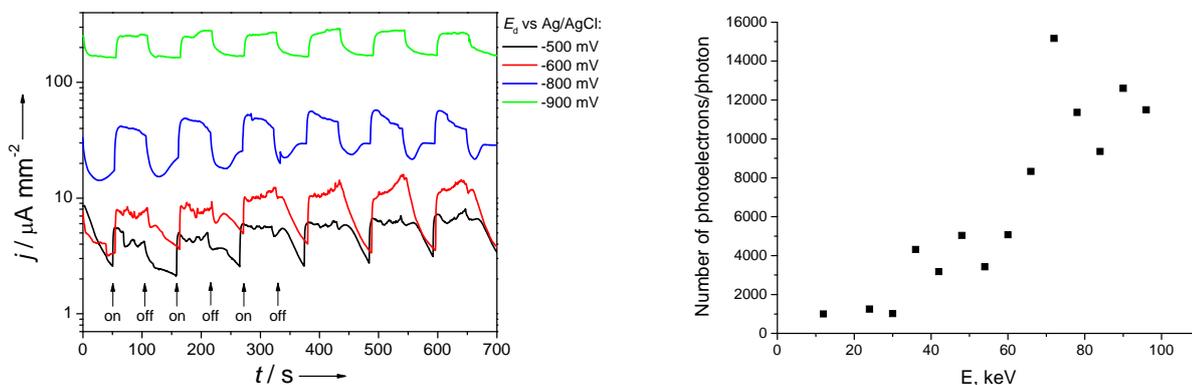


Fig. 2. Current transients recorded for potentiostatic deposition of Ni under periodic illumination of electrode by X-rays (note $j(t)$ curves are plotted on a logarithmic scale) and total number of photoelectrons generated per photon at different energies.

Current transients recorded during potentiostatic deposition of Ni under periodic illumination of an electrode by X-rays revealed an extensive increase in current on switching X-ray illumination (Fig. 2). The effect of X-rays is observed even under an open circuit conditions, resulting in a slow metal deposition that is pronounced only in long-term experiments (>10 h). The photocurrent increased significantly (10-100 times) then applying cathodic polarization. An increase in photocurrent with an applied potential suggests the low-energy secondary electrons to govern the process of X-ray assisted electrochemical deposition.

Photocurrent yield measured for different X-ray energies varies from ~ 1000 electrons ejected into the electrolyte volume per one absorbed photon at 24 keV to ~ 15000 at 96 keV (Fig. 2). This dependence is obviously indicative for multiple secondary processes and thermalization of photoelectrons. Unfortunately we fail to observe a reasonable photoelectron current increase while shifting excitation energy over Pd X-ray absorption edge (in the Pd electrodeposition experiments).

To testify the possibility of electrochemical X-ray photolithography and determine an ultimate resolution for the method, Talbot imaging of the diffraction phase grating and multilens CRL interferometer were performed. In the first case the grating to sample distance was adjusted to provide maximal contrast at minimal feature size. The use of multilens interferometer enabled us to control interline spacing, however achieved B/W contrast ($\sim 1:3$) was not enough to improve the resolution. The resulting structures illustrated an ultimate B/W resolution of the method below 360 nm governed probably by lifetime of radiolysis products, spur radii and electron inelastic mean free paths in condensed matter. Further increase of resolution can be possible through minimising X-rays energy (to minimize electron IMFP) and improvement of B/W contrast by X-ray optics.

The results of CH-3523 experiment were partly used for the preparation of manuscript [1].

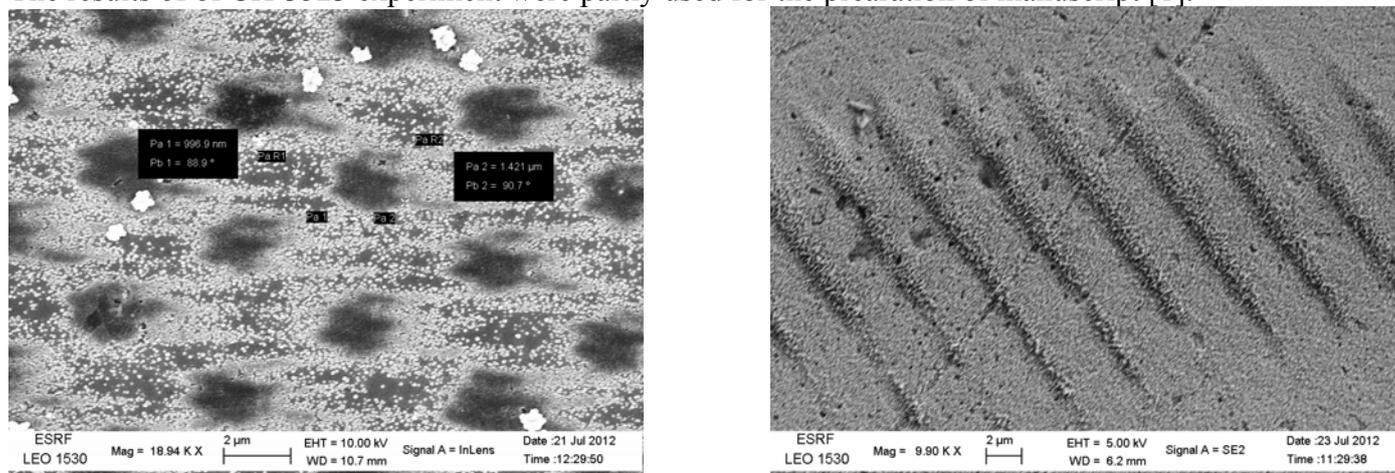


Fig. 3. Microphotographs of nickel film obtained by electrochemical X-ray photolithography through Talbot imaging of 4.2 μm pitch grating and silicon multilens interferometer. B/W resolution <360 nm.

References

- [1] A.A. Eliseev, N.A. Sapoletova, I. Snigireva, A. Snigirev, K.S. Napolskii, Electrochemical X-ray Photolithography // *Angewandte Chemie International Edition* (2012), v. 51 (46), pp. 11602–11605.