

Electrodeposition of cadmium on copper surfaces:
Atomic structure and anion influence
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Controlled electrochemical phase formation on the nanometerscale, like ultrathin film growth or cluster deposition, requires detailed information about the growth mechanism and the resultant structure on the atomic scale as a function of the process parameters like substrate structure, nature of the counter-ions, concentrations etc. Scanning tunneling microscopy (STM) nowadays provides these informations in-situ, i.e. in solution, with the same precision as we are used to from ultrahigh vacuum (UHV) based surface science. In this contribution the underpotential deposition of cadmium on Cu(111) and Cu(100) in the presence of Cl^- , SO_4^{2-} and S^{2-} -anions is studied by in-situ STM as well as ex-situ surface analytical methods, like AES, XPS, ISS and LEED. The in-situ electrochemical STM is fully home-built and enables a direct correlation of cyclic voltametric measurements with simultaneous potentiostatic, potentiodynamic and quasi-spectroscopic STM measurements. The ex-situ studies are carried out in a transfer-chamber which permits a contamination-free transport of the sample from the solution into UHV and vice versa.

Fig. 1 displays the Moiré-type superstructure of a Cd up-layer on Cu(111) in HCl-solution, which does not correspond to a simple (4×4) structure. Instead, a careful analysis of the STM image results in a very large unit cell of the overlayer indicating a rather weak interaction with the substrate. In fact, all in-situ and ex-situ data support the notion of a CdCl_2 -like overlayer. This overlayer is stable again emersion and transfer into UHV as judged by LEED; the LEED-derived $\sqrt{19} \times \sqrt{19} R 23.4^\circ$ superstructure is fully consistent with the in-situ STM results. By contrast, the higher corrugation of the Cu(100) surface leads to unidirectional registry between a CdCl_2 -overlayer and the (100) substrate structure, resulting in a striped superstructure as shown in Fig. 2. On both surfaces the Cd layer is in direct contact with the Cu surface underneath, and capped by a chloride layer.

In sulfuric acid Cd deposition on Cu(111) does not lead to any ordered Cd-layer structure, while on Cu(100) a rather open $2\sqrt{2} \times 2\sqrt{2} R 45^\circ$ structure is observed, probably co-adsorbed with SO_4^{2-} anions.

Quite different is the upd-behavior of Cd on Cu(111) in the presence of S^{2-} anions. With increasing negative electrode potential sulfide forms a Moiré-like superstructure, a $\sqrt{7} \times \sqrt{7} R 19,1^\circ$ - and a $2\sqrt{7} \times 2\sqrt{7} R 19,1^\circ$ -structure on Cu(111). Cd deposition on the perfect $\sqrt{7}$ -layer leads again to a $\sqrt{7}$ -structure with a dense network of domain walls (Fig. 3). This suggests that unlike chloride the S^{2-} -structure on Cu(111) is the structure-determining factor for the resultant CdS overlayer. The electrochemical deposition of Cd-chalcogenide layers, for instance, may become an interesting route for the production of optoelectronic devices.

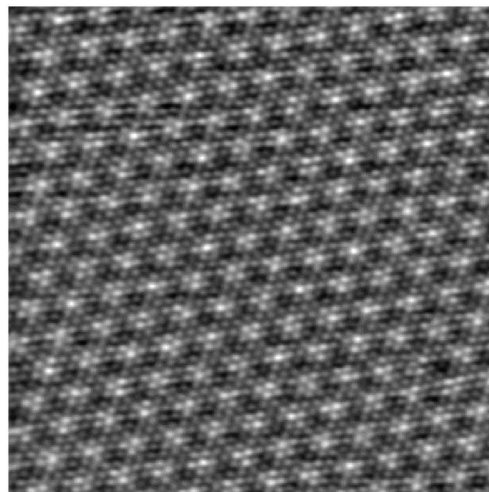


Fig. 1 STM image of a Cd up-layer on Cu(111) in hydrochloric acid; $(16,63 \text{ nm})^2$

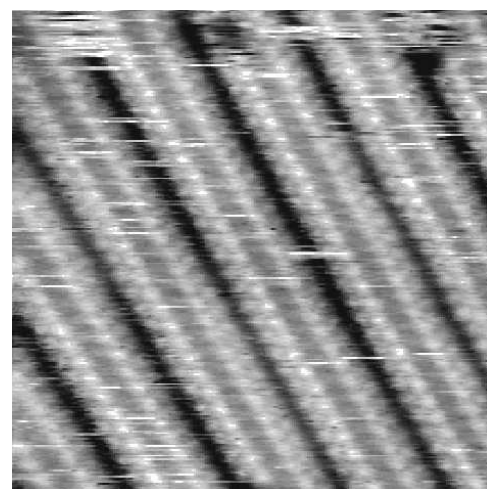


Fig. 2 STM image of a Cd up-layer on Cu(100) in hydrochloric acid; $(8 \text{ nm})^2$

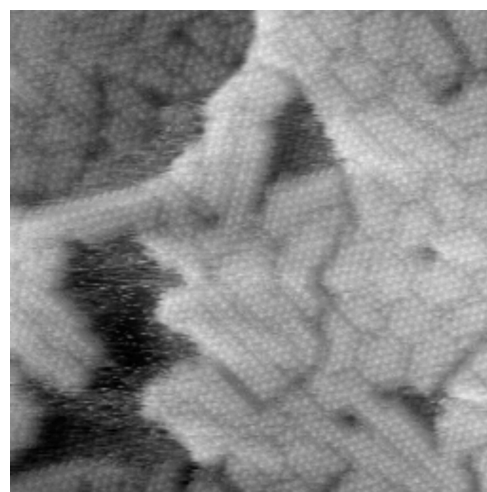


Fig. 3 STM image of a CdS - layer on Cu(111); $(34 \text{ nm})^2$