THE PASSIVITY OF CO IN 0.1 M NAOH STUDIED BY IN SITU STM AND XPS

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Co is an important metal and alloy component for various tools in industry and implants in the human body due to its hardness and its excellent corrosion resistance. The knowledge of the protecting anodic layers of Co is rather poor, which might be a consequence of its property to form various oxides and hydroxides. XPS and in situ STM have been applied to study the passive behaviour of Co in 0.1 M NaOH, pH 13. XPS yields quantitative information on the composition and thickness of passive layers, whereas in situ STM investigations reveal high resolution structural information down to the atomic scale. For the XPS studies, the preparation of the anodic oxide layers has been performed potentiostatically with sputter cleaned samples within a closed system under the protection of purified argon with a subsequent transfer to the UHV of the XP- spectrometer [1]. These conditions permit to start with oxide free specimens and a transfer without any contamination or oxidation of the lower valent cations in air, and therefore mirror the in situ conditions applied in the presented STM studies. The evaluation of the XPS results occurs on the basis of well characterized standards, which yields the composition of the passive layer i.e. the contribution of the cobalt and oxygen species Co(0), Co(II), Co(III), OH^-, O^{2-} and H_2O [2].

In 0.1 n NaOH the current density voltage curve (CV) of Co is characterized by a remarkably sharp oxidation peak at E = 0.35 V, which divides the CV in the range of pimary and secondary passivity as shown in Fig. 1. According to XPS studies $Co(OH)_2$ covers the metal surface in the primary passive range, which is formed by a dissolution precipitation mechanism. When reaching the range of secondary passivity a CoOOH and Co_3O_4 layer develops, with an observed increase of the Co(III) amount with increasing potential and passivation time. Details of these investigations have been published already previously [3,4].

The structure of these passive layers has been examined with atomic resolution with in situ STM on Co(0001) single crystals. In the under potential range (UPR, Fig.1) of oxide formation at E < -0.6 V / SHE a moiré pattern is formed on the surface. Atomic resolution shows a hexagonal surface lattice with a parameter P = 0.31 nm, which corresponds to the structure of hexagonal (0001) oriented $Co(OH)_2$ (Fig. 2). A sequence of STM images recorded within 12 min shows that several surface reactions are involved in the reduction process of this hydroxide at E = -1.0 V which lead to a conclusive model. Small hexagonal islands, which are supposed to be crystallisation nuclei, appear at t < 60 sec, they enlarge and grow together to terraces. Simultaneously 2D adatomic arrays are distributed on the surface forming uncompleted hexagons, triangles and rhombuses (Fig. 3). The arrays are supposed to consist of adsorbed OH^--Co^{2+}-OH^- trimers. With time they diffuse to the step edges of the metal terraces, accumulate there and finally decorate the steps. In addition 2-D clusters of 2 nm diameter are left on top of the terraces after reduction, which are supposed to consist of Co metal atoms.

The thicker $Co(OH)_2$ films observed at higher potentials are difficult to image with STM due to their low conductivity. However, potentiodynamically formed $Co(OH)_2$ shows at E = -0.15 V a faceted surface morphology, which indicates, that the former formed moiré pattern has a precursor function for further hydroxide formation. In contrast to the observed facets in the range of primary passivity, potentiostatically prepared oxide layers in the range of secondary passivity at E = 0.40 V show up to 40nm wide terraces with kinked step edges.

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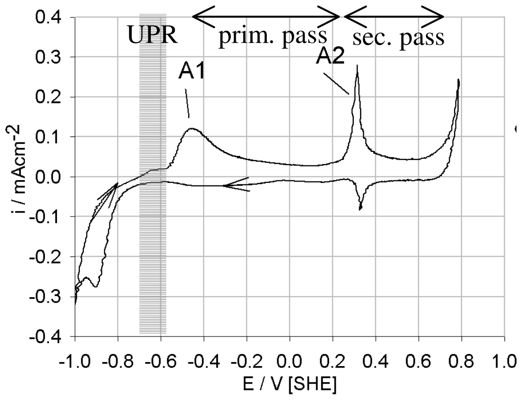

Fig. 1: Potentiodynamic polarization curve of polycrystalline Co in 0.1 M NaOH, scan rate 5 mV/s.

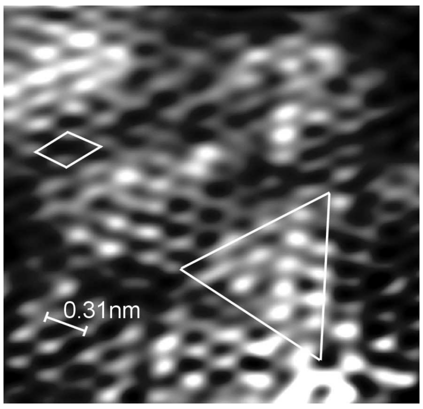

Fig. 2: Topographic in situ STM image of Co(0001) in 0.1 M NaOH showing the atomically resolved superstructure of $Co(OH)_2(0001)$ at E = -0.62 V, E_{tip} = -0.78 V, I_t = 2.5 nA, z-range: 0.1 nm

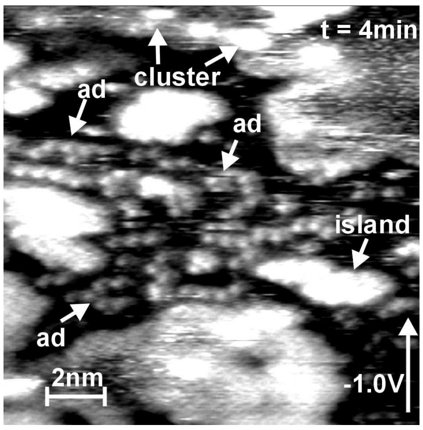

Fig. 3:Topographic in situ STM image of Co(0001) in 0.1 M NaOH showing the reduction process of $Co(OH)_2$ at E = -1.0 V; t = 4 min; E_{tip} = -0.64 V, z range: 1 nm, I_{tip} = 3.0 nA. Clusters, islands and adatomic units are marked.