GROWTH OF RuO_2 BY ELECTROCHEMICAL- AND GAS-PHASE-OXIDATION OF A Ru(0001) SURFACE

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Ruthenium is important as a catalyst in gas-phase catalysis and as a co-catalyst material in Pt-Ru fuel-cell electrocatalysis. In electrocatalysis, it provides active oxygen that facilitates the oxidation of CO, which blocks the Pt surface for H_2 or methanol oxidation. This behavior is a strong incentive for studying the surface oxidation of Ru. RuO_2 grows epitaxially at elevated temperatures (600-800 K) in the presence of a large amount of molecular oxygen on the Ru(0001) surface; its (110) face is oriented parallel to the substrate's surface [1]. In contrast, an *ex situ* UHV-electrochemical study shows that the oxidation at very high positive potentials (1.37 V *vs.* RHE) results after annealing at 800 K in RuO_2 epitaxial growth with its (100) plane parallel to the Ru(0001) surface, [2]. Both the electrochemical and *in situ* surface x-ray scattering studies revealed that the surface oxidation of Ru(0001) in acid solutions is limited to an one-electron process involving the uptake of one monolayer oxygen at potentials below the onset of bulk oxidation at 1.25 V *vs.* RHE [3]

In this work, we discuss our findings on the electrochemical oxidation of an Ru(0001) surface to RuO_2 in 0.05 M H_2SO_4 solution at high positive potentials, and also describe a new simple method for growing RuO_2(110) by the oxidation of Ru(0001) in argon containing 115 ppm of O_2.. We compare these two oxidation processes. In the electrochemical reaction, a large number of RuO_2 islands formed, randomly distributed on terraces and steps, while in gas-phase oxidation, large stripes of ordered RuO_2(110) grew from the edges of the steps.

A disk-shaped Ru(0001) single crystal was mechanically polished and then annealed by inductive heating in a stream of Ar-15% H_2 gas mixture on an Al_2O_3 support inside a quartz tube. The crystal was heated to approximately 1400 K, and held there for 30-60 s. After cooling to room temperature in the Ar-15% H_2 atmosphere, a droplet of 0.05 M H_2SO_4 was placed on the crystal's surface. Thus protected, the crystal was transferred to an electrochemical cell filled with 0.05 M H_2SO_4 for investigation. Such annealing yields a well-ordered Ru(0001) surface of comparable quality to one prepared by the UHV method. Chemical oxidation was initiated by inductive heating in a mixture of Ar and 115 ppm O_2. The oxide was formed during cooling period at temperatures ranging from 600-800 K.

In situ ECSTM showed that the oxidation of the Ru(0001) surface starts at steps' edges (inset of Fig. 1), and proceeds through the formation of randomly distributed RuO_2 islands (Fig.1). Oxidizing Ru(0001) by O_2 (115 ppm) in Ar generates an entirely different morphology, with the RuO_2 oxide deposited as rectangular stripes of monolayer height (Fig. 2). The growth of these stripes is globally initiated at the step edges; their orientation is unidirectional, forming a 60° angle with the steps' direction. The difference in RuO_2 growth in the two cases probably is because electro-oxidation took place at room temperature, whereas chemical oxidation was carried out at elevated temperatures (600 – 800 K) that mobilized the reaction species, thus facilitating ordering of the oxide layer.

Further analysis of RuO_2 growth and the results of the potentiostatic pulse measurements also will be discussed.

Acknowledgements

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References

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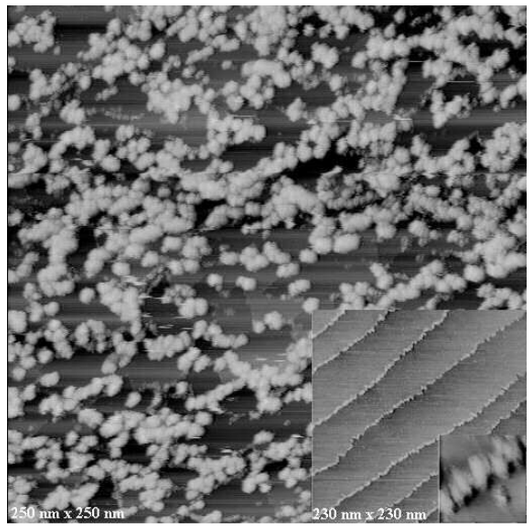

Fig.1. RuO_2 on Ru(0001) oxidized in 0.05 M H_2SO_4 at 1.35 V *vs.* RHE. Inset shows oxidation of step edges obtained at 1.17 V *vs.* RHE.

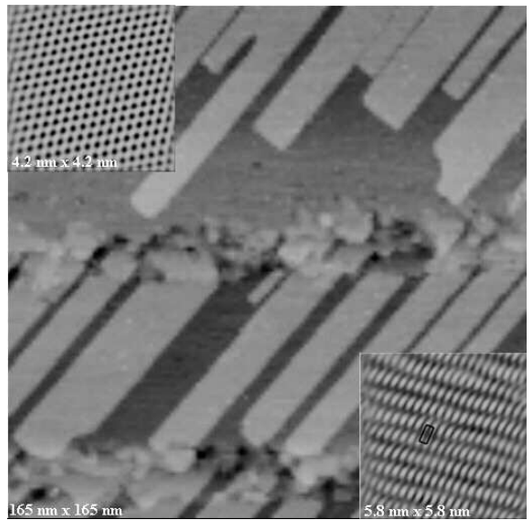

Fig. 2. ECSTM image of Ru(0001) oxidized in Ar + 115 ppm of O_2 obtained in 0.05 M H_2SO_4. The upper left inset is Fourier transform of an atomically resolved flat region between rectangular stripes corresponding to "bare" Ru(0001) surface, while the bottom right inset shows the RuO_2(110) lattice seen in Fourier transform of an atomically resolved image of rectangular stripes.