

Unusual stability of electrodeposited magnetic nanostructures

P. Hugelmann and W. Schindler

Institut für Hochfrequenztechnik und
Quantenelektronik, Universität Karlsruhe (TH),
Kaiserstr. 12, DE-76131 Karlsruhe (Germany),
email: P.Hugelmann@etec.uni-karlsruhe.de

Electrochemistry combined with in situ STM allows to present the deposition of nanostructures with lateral widths below 20 nm [1-6]. The unique advantage of our technique is the possibility to nucleate and to grow locally such small structures at predefined positions on a single crystal substrate surface without any irreversible modifications of neither the nanostructure nor the substrate [1,2]. This is important in order to measure the intrinsic properties of nanostructures, since such small structures consist mainly of interfacial atoms.

We have studied the growth and dissolution of solely electrochemically deposited Co clusters using the system Au(111)/Co²⁺. Utilizing the tip of a scanning tunneling microscope (STM) as a reversible nanoelectrode we are able to deposit metal ions from the electrolyte solution onto the substrate surface via a special polarization routine of the STM tip. This generates a Co²⁺ supersaturation underneath the tip, resulting in a local increase of the Co/Co²⁺ Nernst potential which initiates the local Co nucleation onto the Au substrate. It is an important feature of this preparation method that the cluster diameter and height can be adjusted independently of each other, allowing an arbitrary adjustment of the aspect ratio [2]. In order to avoid undesired defects, the tip is retracted from the substrate surface by approximately 20 nm during the polarization routine. Nanostructuring of gold and silicon surfaces have been demonstrated by similar techniques, however, with the tip in tunneling contact [3,4].

The stability of nanostructures is one essential requirement in view of future applications. The observed unusual stability behaviour of deposited metal clusters differs significantly from the known stability behaviour of bulk deposits. Possible explanations for this unusual stability behaviour might be oxidation, anion stabilization [7,8], alloy formation, kinetic and / or thermodynamic effects [9,10], and different electronic structure compared to the bulk material [11].

Detailed studies of the stability of Co clusters on Au(111) have been performed in carefully deaerated ultrapure electrolyte solutions in order to exclude any oxygen corrosion reactions before, during or after the deposition of the nanostructures. The influence of different anions on the stability behaviour of the deposited Co clusters has been investigated in detail. The experiments have been performed with ClO₄⁻, Cl⁻ and SO₄²⁻ anions which are known to be adsorbed differently at surfaces and step edges [7].

Subsequently, controlled growth of the deposited Co nanostructures has been achieved by a slight negative shift of the substrate potential with respect to the Co/Co²⁺ equilibrium potential. A controlled dissolution of the deposited clusters has been achieved by adjusting the substrate potential more positive than the Co/Co²⁺ equilibrium potential. We observe overpotentials up to several hundreds of mV being necessary to dissolve some clusters completely. At step edges, the clusters have been observed to be more stable than on atomically flat surfaces due to different binding and crystallographic properties.

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