

Preface

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Great advances have recently been achieved in the preparation, characterization and application of materials at a nanometre scale. Electrochemistry is currently an emerging technique in nanotechnology. Due to its low cost, wide applicability, easy upgrading, it has the potential to be a technology of the future. Downsizing the dimension of structures can be achieved by various electrochemical techniques leading to numerous new applications in the fields of semiconductors, surface science, corrosion science, biotechnology and energy.

In September 2004, we have organized the “First Summer School on Electrochemistry and Nanotechnology”, held on the island of Porquerolles, on the Provence coast in south France. This school was attended by about 50 scientists, half of them being post-docs and graduate students. The beautiful and undisturbed environment of Porquerolles (the main instrument for mobility is the bicycle) permitted a studious and fruitful teaching and learning experience with 7 introductory lectures by recognized “senior” scientists, 30 oral presentations and a lot of open discussions.

This special volume of the “Journal of Electroceramics” summarizes some of the most substantial contributions to this summer school. According to the topics developed during the workshop, four clusters of work can be outlined.

1. Nanostructuring of semiconductors and oxides

This is the largest cluster of work presented at the summer school. In their introductory article, Djenizian and Schmuki present nanostructuring of surfaces using electron-beam lithographic approaches combined with electrochemical techniques, such as electroplating of metals and electrochemical etching of substrates. The paper describes how to exploit these electron beam-writing techniques for highly

selective electrochemical reactions at various surfaces. Electron beam-induced nanomasking even under extreme conditions can be used for the fabrication of structures in the sub-100 nm range.

The growth of silicon nanowires by “chemical” methods is described in the article by Boukherroub et al. Here, silicon nanowires grow on oxidized silicon substrates using different approaches for gold catalyst deposition. The gold nanoparticles are either dispersed or spotted at different concentrations using a robot, or formed on a patterned Si/SiO₂ substrate by metal evaporation. A high density of silicon nanowires is subsequently obtained by decomposition of silane gas (SiH₄).

Electrochemical formation of nanopores in various semiconductors and oxides was the subject of 3 contributions. The morphology of porous n-GaP is strongly dependent on the anion present in the electrolyte. Etching in HF led to a statistically porous structure with no evidence for higher ordering. Etching in HCl caused a localized attack of the surface with porous insular areas. In HBr, highly defined rectangular pores grow perpendicular to the (100)-surface forming several μm thick well defined porous layers. In HI, pores are aligned parallel to equipotential lines along defects. Pore formation in H₃PO₄ and HNO₃ can lead to highly complex ordered structures.

Self-organized porous titania nanotubes are formed by electrochemical anodization of titanium under specific experimental conditions. The influence of different electrolyte compositions on the structure of self-organized porous layers and the conditions for ideal pore growth are studied. Using SO₄²⁻/F⁻ electrolytes with different cations can drastically influence the final morphology of the nanotubes. The nanotubes consist of TiO₂ and remain unchanged when annealed.

The initiation and growth of porous oxide on tantalum was investigated in mixed H₂SO₄/HF electrolytes. Under selected potentiodynamic conditions, nearly uniform porous Ta₂O₅

layers are formed, consisting of self-organized pore arrays with single pore diameters ranging from 2 to 10 nm. The morphology and the thickness of the layer depend strongly on the applied potential, the scan rate and on HF presence.

2. Corrosion protection

Corrosion protection is a very important topic for industrial applications, e.g. automobile industry. In this domain also, nanostructured materials appear currently as full of promise for the future.

Roche et al. presented a new nanostructured lamellar fluorinated diblock copolymer coating for corrosion protection, elaborated by Controlled Radical Polymerization and then deposited on steel. This type of polymeric coating has wide variability and great interest for automobile industry. Several parameters were taken into account to evaluate their influence on corrosion protection properties: polymer molar mass, solvent type, coating thickness and nature of nanostructuration (lamellae or spheres).

Thin “passive” oxide films, formed on metal and alloy surfaces in an electrolyte, play an important role in preventing material degradation due to corrosion. Tsuchiya et al. studied semiconductor properties of passive Fe-Cr films on stainless steel and correlated semiconductor properties and corrosion behaviour. Band gap energy of the passive films was estimated from a photoelectrochemical spectrum that could be separated into two components, from Cr hydroxide and Cr oxide layer. Donor densities of the passive films, estimated by Mott-Schottky plots, depended on passivation time, film formation potential and additives.

3. Copper electrodeposition: influence of surface modifications and additives

Copper is a model metal for study of electrodeposition. In the summer school, several important aspects were covered by contributions: i) influence of additives, ii) organic monolayers for patterning, iii) nanostructuring using scratches.

The effect of polyethylene glycol (PEG) and chloride ions on Cu electrodeposition mechanism is investigated by Eyraud and coworkers. Alternative current techniques and electrochemical quartz crystal microbalance experiments show that PEG adsorption on the Cu electrode is weak at open circuit, but increases under polarisation. Whatever the substrate, the addition of PEG and Cl^- has a beneficial effect by reducing the hysteresis due to H_2 production. For Cu electrolytes, the PEG addition to solution has little effect, while the simultaneous PEG and Cl^- addition inhibits both Cu^{2+} reduction current and mass increase.

Various methods can be used to pattern the surfaces with small features. In the work by Zhang et al., a micro-indenter was used to scratch the Si surface to create sub-micrometer structures. The influence of the electrochemical potential on copper nucleation, growth and morphology was studied on this scratched silicon surface. Copper deposition either in the opening of an insulating oxide layer made by scratching with an indenter tip or on oxide free Si surface was observed by Scanning Electron Microscopy (SEM). The nucleation and growth morphology of copper at high voltage pulse on both oxide-covered and oxide-free silicon surfaces were also studied. Thin oxide layers can act as a very efficient resist even at comparably high voltages.

Organic covalently attached monolayers (CAMs) are useful resist layers for patterning Si surfaces. Balaur et al. studied selective plating of Cu on n-type Si (111) surfaces chemically modified with different organic monolayers and subsequently directly patterned by an electron-beam and by AFM induced scratching. The organic molecules (1-undecylenic acid, 1-decene and 1-octadecene) were covalently attached to a hydrogen-terminated Si surface. A masking effect can be clearly observed, the efficiency of which depends on the type of molecule. Selectivity of deposition strongly depends on applied e-beam dose. Electron-beam-modified CAMs can be used as positive tone resist if treated with medium e-beam doses and as negative tone resist if treated with high doses for both copper immersion plating and electrodeposition. CAMs can also be used as negative tone resists for AFM induced scratching. By optimizing the electroless deposition parameters, homogeneous deposition with a complete selectivity can be achieved, leading to a high lateral resolution of the Cu patterns.

4. Biosensors

Biological applications of electrochemistry are another exciting topic for research. At the summer school, the topic of electrochemical biosensors was particularly covered with contributions on amperometric and conductometric sensors.

Lojou and Bianco review amperometric biosensors with special emphasis on enzymatic electrodes developed for medical or environmental applications. Electrode processes and basic principles of amperometric methods currently used in biosensor electrochemistry are described. Strategies that combine control of electrode surface structure with stable enzyme immobilization are examined.

Schäf et al. discuss the possibility of developing size and shape-selective resistive gas sensors based on microporous oxides. This concept is demonstrated for the zeolite Stilbite and various alcohol molecules with different shape and size. The electrical impedance of natural Stilbite single crystals decreases in presence of methanol, 2-propanol and

3-pentanol, but increases with increasing water vapour pressure. The interaction can be described by a Langmuir-type adsorption equation.

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Editors

Philippe Knauth
Thierry Djenizian
Patrik Schmuki