Electrodeposited iron-based nanofoams as precursors for transducers

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Abstract. The aim of this work is the electrochemical preparation of iron-based oxide (Fe₂O₃, Fe₃O₄) nanofoams on metal substrate by accompanying hydrogen-evolution as promising precursors for transducers. Various metal substrates have been tested and the most satisfying electrolyte composition have been determined. However, various deposition parameters determine various nanofoam properties, like pore-size, density, pore-type, thickness of interconnections etc. The crystallographic composition and morphology of the electrodeposited samples have been studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

1. Introduction

Semiconductor nano- and microstructures may have great utility in transducers industry. For instance, various sensing applicability can be considered of magnetite regarding to their magnetic or superparamagnetic response of external electrical [1,2] and magnetic field [3]. The fast and well described abreaction in change of resistance by changing the temperature make iron-oxides great candidates as thermistors [4,5]. The usability of iron-oxide semiconductors as precursors of transducers are not well established [6 and references wherein]. Even we talk about sensors, thermistors, actuators [7-14] etc., there are several physical parameters [15] concerning the structural and morphological properties that should be satisfied. The main physical parameters regarding the structure of the semiconducting materials include but not are limited to high porosity, high specific surface area, open porous for fast transport of gas/liquid and piezoelectric potential. Different physical and chemical preparation techniques are available for the fabrication of nano- or microscale structures considering layers, wires, tubes and foams. Widespread and most popular preparation methods are sputtering [16,17], evaporation [18,19], chemical vapor deposition [20-25] and electrochemical deposition [26-31]. To bring together the requirements with the given facilities a three dimensional (3D) foam-like nanostructure would mean a distinguished solution. The nanofoams exhibit many excellent properties to the respect of the above listed requisites. The development of the state of the art preparation procedures includes a novel preparation technique of the iron-based nanostructures according to the requirements of increase in efficiency [6]. The electrochemical preparation of nano- and microscale metalfoams, metal alloy foams or metal oxide foams has been started in the last decade, namely it can be considered as novel method. Also, it can emulate with the other techniques
well due to its low-costs, good versatility of parameters in terms of desired properties and simple handling [26].

2. Theoretical Background of electrodeposition using bubbles

The Dynamic Hydrogen Bubble Template (DHBT) is an excellent method for the fabrication of macrostructures with nanoporous side walls [32,33]. The method has been named from the phenomena when a series of hydrogen-bubbles generated on the surface of the substrates act like a dynamic negative template. Figure 1 demonstrates the theoretical approach of the technique. Fig 1(a) Where the hydrogen-evolution takes place on the surface there is no metal/metal-oxide deposition. The size of the bubbles increasing along the distance from the substrate surface. [34] Fig 1(b) shows the SEM-image of copper nanofoams prepared by DHBT [35].

![Figure 1](image.png)

Figure 1. (a) Simplified description of DHBT generated metal/metal-based foams [34] (b) Honeycomb-like Cu-deposit structure made by DHBT [35].

2.1. Materials and Methods

The nanostructures were electrodeposited onto copper substrate. The substrates were mechanically polished with 800 and 2000 emery papers, respectively. Henceforward, the polished substrates were ultrasonically cleaned in deionized water, ethanol and acetone, respectively [28]. The 2 cm² active surface area of the substrates were ensured by commercial nail-polish and insulating tape. The galvanostatic deposition was carried out in a two electrode cell using a DC Power Supply. Platinum-mesh was used as counter electrode. The electrolytic bath was a strongly alkaline solution with pH 12.5 [27] made of 0.037 M Fe₂(SO₄)₃ 0.1 M triethanolamine (TEA) and 2 M NaOH. After mixing the components following the described protocol [29] at T = 80 °C the solution had greyish-green color and no turbidity was observed. The parameters of the deposition process were varied in the terms of current density, bath temperature and deposition time. The range of cathodic current density was chosen j = 5-15 mA cm⁻², the deposition time was given from 5 min to 6 hours and the bath temperature was adjusted T = 60-90 °C. The nominal thicknesses of the prepared structures were calculated by using the Faraday-law [36].

The surface morphology of the deposited layers were studied by scanning electron microscope (Nova NanoSEM 230) and the crystallographic characterization was determined by X-ray diffraction (Bruker D8 Advance, Cu radiation-40kV, 35mA).

2.2. Results and Discussion

Several samples were deposited with different conditions. The preferred deposits checked by optical microscope (ZEISS) were sent for structural and morphological characterization.

2.2.1. Scanning electron microscopy

Figure 2 demonstrates 4 different SEM-images of the prepared samples. Fig 2(a) was taken on a sample prepared in 300 s deposition period in 60°C bath with -7.5 mA cm⁻² current density, and the nominal thickness was 2.24 μm. In Fig 2(b) can be seen the morphology of the sample prepared in 300 s at 70°C with-5 mA cm⁻² current density with nominal thickness of 23.55 μm. Fig 2(c) shows the SEM-result of the sample deposited with the same bath temperature and current density as 2(b) but extended deposition time: Δt = 900 s (dₐ = 30.28 μm). Fig 2(d) represents the SEM-image of the sample
prepared in the highest bath temperature 90°C with 5 min deposition time, -7.5 mA cm\(^{-2}\) current density (\(d_1 = 4.42\ \mu m\)).

The SEM-images clearly show the structural changes by increasing the bath-temperature. Filamentous deposit structure has been observed at 90 °C. This flake-like structure was observed in the corresponding literatures [30,31], where the authors conclude that the generation of the filaments is in function of more negative deposition potentials but not of the bath temperature. Due to the galvanostatic deposition mode the potential values have been not recorded. For better understanding of the structural formations potentiostatic deposition mode should be done.

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\text{Figure 2. SEM-images of the electrodeposited iron-oxide samples with different deposition parameters (a) } \Delta t = 300 \text{s}, T = 60^\circ C, j = -7.5 \text{ mA cm}^{-2} \text{ at 50000X magnification (b) } \Delta t = 300 \text{s}, T = 70^\circ C, j = -5 \text{ mA cm}^{-2} \text{ at 15 000X magnification(c) } \Delta t = 900 \text{s}, T = 70^\circ C, j = -5 \text{ mA cm}^{-2} \text{ at 10000X magnification (d) } \Delta t = 300 \text{s}, T = 90^\circ C, j = -7.5 \text{ mA cm}^{-2} \text{ at 10000X magnification.}
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2.2.2. X-ray diffraction

Crystallographic study of the iron-oxide samples were done. Figure 3 represents the identification of the observed peaks. Fig 3(a) shows the results of sample prepared in 3300 s in 70 °C bath with -5 mA.cm\(^{-2}\) current density. Grazing incidence XRD patterns of this sample indicate the presence of magnetite (blue lines) and copper substrate (green lines). Grazing angle was 2 (red curve) and 6 degrees (blue curve), respectively. In Fig 3(b) the results of sample with same conditions as in Fig 3(a) can be seen, but in this case the current density was -9 mA.cm\(^{-2}\). Here, grazing incidence XRD patterns indicate iron (grey lines) and copper (green lines). Grazing angle was 2 (red curve) and 6 degrees (blue curve), respectively. Fig 3(c/1) and (c/2) show the results of XRD taken from the same sample with deposition conditions of 2 hours deposition time in 85 °C bath and -12.5 mA.cm\(^{-2}\) current density.

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\text{Figure 3. X-ray diffractograms of the iron-oxide electrodeposited samples prepared under different conditions. a, } \Delta t = 3300 \text{s}, T = 70^\circ C, j = -5 \text{ mA cm}^{-2}; \text{ b, } \Delta t = 3300 \text{s}, T = 70^\circ C, j = -9 \text{ mA cm}^{-2}; \text{ c/1}, \Delta t = 7200 \text{s}, T = 85^\circ C, j = -12.5 \text{ mA cm}^{-2}; \text{ c/2, powder scratched from the surface of sample c/1.}
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In Fig 3(c/1) the grazing incidence XRD patterns were done on the sample with the substrate. Clear evidence of magnetite (blue lines), iron (grey lines) and copper as substrate (green lines). Grazing angle was 2 (red curve) and 6 degrees (blue curve), respectively. Fig 3(c/2) demonstrates grazing incidence XRD pattern of loose powder from the same sample as (c/1). Only magnetite phase (blue lines) is detected. Grazing angle was 2 degrees.

The XRD results show clear evidence of magnetite if the current density does not exceed 8 mA.cm\(^{-2}\) cathodic current density (see Fig 3(a) and (b)).

3. Conclusion

Attempts have been carried out for the electrochemical preparation of iron-based nanofoams by galvanostatic electrodeposition mode. Different conditions were set in. According to the SEM-results, no foam-like nanostructures were observed on the surface, but filamentous structures can be achieved by increasing the bath temperature. However, this conclusion have been not declared by other authors. Potentiostatic study, cyclic voltammetric studies and potentiostatic deposition mode could help for better understanding the substrate/electrolyte interface reactions and the structural formation of the deposits. Base on the XRD results it can clearly concluded that the electrochemical deposition of iron or iron-oxide structures can be achieved when the current density does not exceed the value of 8 mA.cm\(^{-2}\). More negative cathodic current leads to higher Fe-content in the deposit.

3.1. Future plan

Based on the preliminary experiments it can be concluded that the next steps for iron-based nanofoam preparation might be the application of more negative cathodic current or, in case of potentiostatic mode, more negative potential values (vs. SCE). The problem of the pure iron deposition by increasing the applied current/potential can be prevented by testing different additives and chelating agents in the electrolytic bath. Other possible way for the acceleration of H\(_2\)-liberation on the substrate surface could be achieved with higher H\(_2\)-content in the bath. Also, the cell construction can be improved by using close cell-structure and external over-pressure to slower and control the generation of H\(_2\)-bubbles on the surface substrate for the time of deposition.

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4. References

[1] J. M. D. Coey, Magnetism and Magnetic Materials, Cambridge University Press., New York (2009).
[2] E. Hristoforou and A. Ktena, Magnetoststriction and magnetostrictive materials for sensing applications, J. Magnetism and Magnetic Materials 316 (2007) 372.
[3] K. Larsson et al., Magnetic transducers in biosensors and bioassays, Analusis 27 (1999) 617.
[4] N. M. B. El Badramany et al., Electrical resistivity of magnetite and nickel ferrous ferrites above 300 °K, J. American Ceramic Soc. 62 (3-4) (1979) 113.
[5] J. Certo et al., α-FeO. ceramics as negative coefficient thermistors J. European Ceramic Society 11 (1993) 401.
[6] A. Tawfik and A. El-Sharif, Electromechanical properties of magnetite transducer, J. Magnetism and Magnetic Materials 278 (2004) 195.
[7] E. Hristoforou and R.E. Reilly, Nonuniformity in Amorphous Ribbon Delay Lines After Stress and Current Annealing, J. Appl. Phys., 69 (1991) 5008.
[8] E. Hristoforou and D. Niarchos, Fast Characterisation of Magnetostriective Delay Lines, IEEE Trans. Magn., 29 (1993) 3147.
[9] E. Hristoforou et al., Sound Velocity in Magnetostriective Amorphous Ribbons and Wires, J. Phys. D: Applied Physics, 27 (1994) 1595.
[10] H.Chiriac et al., Design and Fabrication of Microminiature Delay Line Using Thin Film Technology, Sensors and Actuators A, 59 (1997) 280.
[11] H. Chiriac et al., Magnetoelastic Characterization of Thin Films Dedicated to Magnetomechanical Microsensor Applications, Sensors and Actuators A, 68 (1998) 414.
[12] H. Chiriac et al., Magneto-Surface-Acoustic-Waves Microdevice Using Thin Film Technology: Design
and Fabrication Process, *Sensors & Actuators A*, 91 (2001) 107.

[13] M. Pletea et al., Miniaturized Magnetostrictive Delay Line Arrangement Using Multilayer-Like Structure, *Sensors & Actuators A*, 92 (2001) 115.

[14] Youroudi, C. Orfanidou and E. Hristoforou, Circumferentially oriented Ni cylindrical thin films for torque sensor applications, Sensors and Actuators A, 106 (2003) 179

[15] E. Hristoforou, Magnetic Effects in Physical Sensor Design, *J. Opt. Adv. Mat.*, 4 (2002) 245.

[16] D. Depla et al., Handbook of deposition technologies for films and coatings, 3rd Edition, Chapter 5. Sputter deposition processes, Elsevier Inc. (2016).

[17] M. Santamaria et al., Physicochemical characterization and photoelectrochemical analysis of iron oxide films, *J. Solid State Electrochem.* 17 (2013) 3005.

[18] I. Shah et al., Handbook of deposition technologies for films and coatings, 3rd Edition, Chapter 4. Evaporation:Processes, Bulk microstructures and mechanical properties, Elsevier Inc. (2016).

[19] T. Furubayashi, Magnetite films prepared by reactive evaporation, *J. of Magnetism and Magnetic Materials* 272–276 (2004) e781.

[20] J. O. Carlsson et al., Handbook of deposition technologies for films and coatings, 3rd Edition, Chapter 7. Chemical Vapor Deposition, Elsevier Inc. (2016).

[21] R. Mantovan et al., CVD synthesis of polycrystalline magnetite thin films: structural, magnetic and magnetotransport properties *J. Phys. D: Appl. Phys.* 43 (2010) 065002.

[22] N. Papadopoulos et al., Synthesis and characterization of cobalt precursors for the growth of magnetic thin films by the MOCVD method, *J. Optoelectronics and Advanced Materials* 10 (2008) 1098.

[23] ND Papadopoulos et al., Cyclodextrin inclusion complexes as novel MOCVD precursors for potential cobalt oxide deposition, *Applied Organometallic Chemistry* 24 (2010) 112.

[24] ND Papadopoulos et al., MOCVD Cobalt Oxide Deposition from Inclusion Complexes: Decomposition Mechanism, Structure, and Properties, *Journal of the Electrochemical Society* 158 (2011) 5.

[25] N. Papadopoulos et al., Effects of MOCVD thin cobalt films’ structure and surface characteristics on their magnetic behavior, *Chemical Vapor Deposition*, 17 (2011) 211.

[26] M. Paunovic and M. Schlesinger, Fundamentals of Electrochemical Deposition, 2nd Edition, A John Wiley & Sons, Inc. Publication, Hoboken, New Yersey (2006).

[27] H. M. Kothari et al., Electrochemical deposition and characterization of Fe₃O₄ films produced by the reduction of Fe(III)-triethanolamine, *J. Mater. Res.* 21 (2006) 293.

[28] S. Mitra et al., Growth and electrochemical characterization versus lithium of Fe₃O₄ electrodes made via electrodeposition, *Adv. Funct. Mater.* 16 (2006) 2281.

[29] C. Goujon et al., Electrochemical deposition of thick iron oxide films on nickel based superalloy substrates, *Electrochim. Acta* 176 (2015) 230.

[30] D. Li et al, Electrodeposition of micro-nanosize Fe₃O₄ crystals anchored on flexible buckypaper. *J Solid State Electrochem.* 19 (2015) 3053.

[31] S. H: Jeon et al., Effects of deposition potentials on the morphology and structure of iron-based films on carbon steel substrate in an alkaline solution, *Advances in Materials Science and Engineering* 2016 (2016).

[32] B. J. Plowman et al., Building with bubbles: The formation of high surface area honeycomb-like films via hydrogen bubble templated electrodeposition, *Chem. Commun.* 51 (2015) 4331.

[33] T. Nguyen et al., Hydrogen bubbling-induced micro/nano porous MnO films prepared by electrodeposition for pseudocapacitor electrodes, *Electrochim. Acta* 202 (2016) 166.

[34] H. C. Shin et al., Nanoporous structures prepared by an electrochemical deposition process *Adv. Mater.* 15 (2003) 1610.

[35] H. Zhang et al. Effect of bubble behavior on the morphology of foamed porous copper prepared via electrodeposition *J. Electrochem. Soc.* 160 (2013) D441.

[36] M. Faraday, Experimental researches in electricity *Phil. Trans. R. Soc. London* 124 (1834) 77.