Electrochimica Acta 54 (2009) 2487–2490

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Nanoscale electrodeposition of metals and compound semiconductors from ionic liquids

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ARTICLE INFO

Article history:
Received 20 November 2007
Received in revised form 20 February 2008
Accepted 25 February 2008
Available online 2 March 2008

Keywords:
Electrocrystallization
In situ scanning probe microscopy
Ionic liquid electrolyte

ABSTRACT

Employing ionic liquid electrolytes we succeeded to electrodeposit light and transition metals as well as compound semiconductors on metal and semiconductor substrates at room temperature with nanometer or atomic resolution. For this aim in situ scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) have been applied. In this article we present new and recent results of 2D phase formation and growth of Ga underpotential deposition (UPD) and of surface alloying of Cd on Au(1 1 1), as well as 3D overpotential deposition (OPD) of Ni nanocrystals and ZnSb semiconductor clusters. Particular attention is given to the respective nucleation and growth mechanisms of the selected examples. Aspects of technological applications are briefly discussed.

1. Introduction

In the fabrication of nanostructured materials by electrochemical deposition various fundamental and practical aspects have to be considered. First and most important is a detailed elucidation of the elemental steps of electrochemical phase formation, see also ref. [1]. This includes the nucleation and growth mechanism, a definition of the stability ranges of low dimensional (1D and 2D) structures forming at underpotential (UPD) conditions [2], the influence of substrates and related with this, the occurrence of surface alloying phenomena [3], and finally the nucleation kinetics. On the nanometer scale of materials surface and interfacial properties play an important role, simply because the ratio of surface to bulk states is of comparable magnitude. So, in addition to the electrochemical aspects, surface and interfacial phenomena come into play. In situ investigation of these phenomena during electrodeposition has improved considerably with the invention of scanning probe microscopy (SPM) [4], and its adaptation to measurements in an electrochemical environment [5–7].

From a more practical point of view electrodeposition methods including various modifications [8,9] have several advantages in comparison with vacuum deposition techniques. They enable fabrication at conditions near chemical equilibrium and, in particular, they are low-prized. In addition, several electrolytes are available from which the one suitable for the deposition can be chosen. Among these are ionic liquids which have a number of favourable properties for electrodeposition, many are liquid at room temperature, have a sufficiently high solubility for the respective metal or semiconductor salts, have very low vapour pressures in their pure state, and, last not least, they possess large electrochemical windows up to 6 V near room temperature, see e.g. ref. [10].

About one decade ago we have started in our group with SPM measurements employing ionic liquids and over the years succeeded in nanoscale electrodeposition of light and transition metals (Ti, Al, Zn, Ni, Fe, Co, Bi, Cd, Ga), their alloys, and compound semiconductors like AlSb and ZnSb; for a recent review see ref. [11]. In this article we present new and recent results of 2D and 3D nanostructures of metals and semiconductors electrodeposited from ionic liquid electrolytes and studied in situ by STM and STS methods. In particular, we present new measurements of 2D Ga deposition on Au(1 1 1), of Cd–Au surface alloying, of nucleation and growth of 3D Ni nanocrystals, and give an example of ZnSb compound semiconductor electrocrystallization.

2. Experimental

In the Ga, Cd and Ni electrodeposition experiments described below we have employed a Lewis acidic room temperature ionic liquid, 1-methyl-3-butylimidazolium chloride/aluminium chloride mixture (MBIC/$AlCl_3$, 42:58, mol%). In the case of ZnSb deposition, the $AlCl_3$ was replaced by $ZnCl_2$. The MBIC was freshly synthesized as described in literature [12], $AlCl_3$ was sublimed three times under vacuum, and $ZnCl_2$ was purified by heating under vacuum. High purity salts of $GaCl_3$, $CdCl_2$ and $SbCl_3$ (Alfa, >99.99%),

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doi:10.1016/j.electacta.2008.02.090

respectively, have been added to the ionic liquid corresponding to compositions of 2 mM for $SbCl_3$ and 5 mM for $GaCl_3$ and $CdCl_2$. In the case of Ni an amount of 5 mM Ni^{2+} was dissolved in the IL by anodic dissolution. All these sample preparations have been performed in an argon glove box (O_2 and H_2O concentration $\leq$1 ppm). Electrochemical measurements were performed with an Autolab potentiostat (PGSTAT30, Eco Chemie, The Netherlands) in a traditional three-electrode Teflon cell with working electrode from a Au(1 1 1) film on glass and quasi-reference being Al, Zn or Pt wire. The gold substrate was annealed in a hydrogen flame for 3 min and then slowly cooled down under nitrogen stream (Messer, Griesheim, 5 N) prior to each experiment. STM and STS measurements were carried out with a home built scanner driven by a Picoscan (Molecular Imaging) or Nanoscope E (Digital Instruments) controller. For further details on Au(1 1 1) working electrode and STM tungsten and Pt/Ir tip preparation as well as STM and STS recording, see ref. [13].

3. Results and discussion

3.1. Underpotential deposition and 2D phase formation of Ga and Cd on Au(1 1 1)

The cyclic voltammogram of Ga deposition on Au(1 1 1) from an ionic liquid is shown in Fig. 1a. A selection of four typical sweeps recorded with different cathodic limits is presented here. It is clear that the bulk oxidation of Au(1 1 1) starts only at potentials above 1.95 V. The weak redox couple at 1.72/1.75 V is always seen at the electrified Au(1 1 1)/ionic liquid interface and has been assigned to

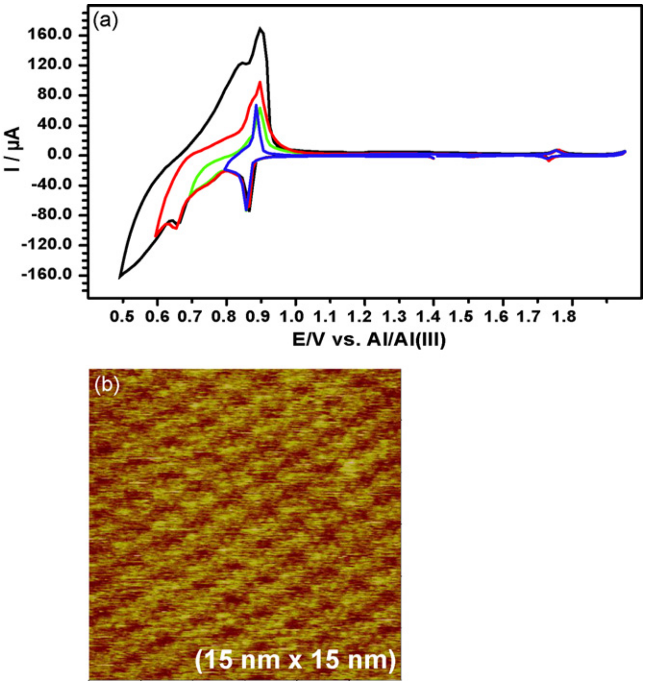

Fig. 1. (a) Cyclic voltammogram of 5 mM $GaCl_3$ in $AlCl_3$-$[C_4mim]^+Cl^-$ (58:42) on Au(1 1 1) recorded at a scan rate of 50 mVs^{-1} for different reversal cathodic potentials. (b) STM picture showing the structure of the Ga UPD layer at 0.85 V, U_{bias} = 311 mV, I_t = 1.1 nA.

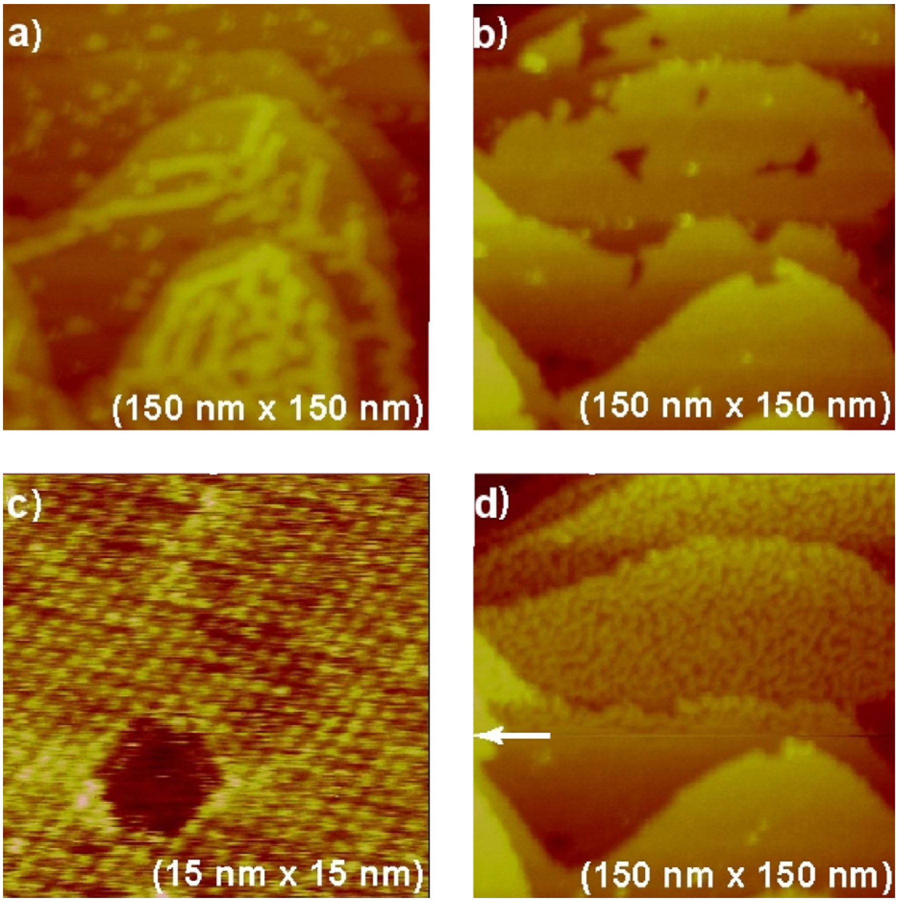

Fig. 2. STM images showing the Cd–Au surface alloy on Au(1 1 1) in MBIC-$AlCl_3$ + 5 mM $CdCl_2$ at (a) E = 0.45 V; (b) half an hour after (a). (c) High resolution STM image of (b) at E = 0.45 V; E_{tip} = 0.655 V; I_t = 1.24 nA. (d) Dissolution of a Cd–Au surface alloy layer on Au(1 1 1) at 0.85 V, U_{bias} = 100 mV; I_t = 1 nA; the arrow indicates the potential switched from 0.45 to 0.85 V.