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Electrodeposition of Ti from TiCl₄ in the ionic liquid l-methyl-3-butyl-imidazolium bis (trifluoro methyl sulfone) imide at room temperature: study on phase formation by in situ electrochemical scanning tunneling microscopy

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Abstract

Titanium was electrodeposited from a nominal 0.24 M TiCl₄ in l-methyl-3-butyl-imidazolium bis (trifluoro methyl sulfone) imide ([BMIm]BTA) at room temperature on a Au(1 1 1) substrate. The process of electrodeposition was studied by cyclic voltammetry, chrono amperometry and in situ scanning tunneling microscopy (STM). In a first step TiCl₄ is reacted to TiCl₂, which is subsequently reduced to metallic Ti. Two dimensional (2D) clusters form preferentially on the terraces in the under potential deposition range. 2D clusters presumably of TiCl₃ precipitates grow and coalesce to cover the whole substrate with a 2D film at a substrate potential below -1.1 V versus ferricenium/ferrocene ([Fc]⁺/[Fc]) redox couple. At a potential of -1.8 V a dense layer of three dimensional (3D) clusters of titanium of 1–2 nm thickness is formed. The features of the I-U tunneling spectra and the relative reduction of the effective tunneling barrier by 0.8 eV with respect to gold clearly indicate the metallic character of Ti deposits. Observation of circular holes on the Au(1 1 1) substrate after dissolution of the deposited Ti indicates the formation of Au–Ti surface alloying.

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1. Introduction

Electrodeposition of titanium and its alloys like titanium–aluminium compounds is of particular technological interest. These materials combine a high tensile strength and ductility with a special corrosion resistance. The electrochemistry of titanium, however, is complicated due to the existence of various oxidation states of Ti(II), Ti(III) and Ti(IV) species in solution. Numerous electrochemical and spectroscopic studies of the titanium complex chemistry have been reported in recent years which have been performed in both the inorganic high temperature and organic room temperature molten salts, see e.g. [1-7]. In an electrodeposition study of titanium from alkalihal-ide melts containing TiCl2/TiCl3 mixtures at high temperatures (450-850 °C) it has been shown that a clear redox peak for the Ti(II) to Ti reduction exists together with a broad shoulder for the Ti(II)-Ti(III) reduction [3]. In a fluoride/chloride mixture it has been reported that Ti(III) species are reduced directly to Ti(0) [4]. The electrochemistry of TiCl₄ in a strongly Lewis acidic room temperature molten salt (AlCl₃-EtMelmCl) has been examined [5]. It was found that Ti(IV) is reduced to Ti(III) and Ti(II) in two one-electron steps, whereby Ti(III) is deposited at the electrode as a brown film, probably the β -TiCl₃ phase. At lower TiCl₃-concentrations the amount of this precipitate is clearly decreased [5]. Similar, observations were reported by Hussey et al. in their investigation of Al-Ti alloy deposition from a Lewis acidic AlCl₃-EtMeImCl electrolyte at 50.2 °C [6].

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The experimental studies above have focused on the electrochemistry of titanium in various ionic liquids and have employed different spectroscopic and electrochemical methods. In this investigation we have tried to resolve the initial stages of titanium electrodeposition in the underpotential (UPD) and overpotential (OPD) range with nanometer resolution. For this aim in situ electrochemical scanning tunneling microscopy (STM) and spectroscopy (STS) experiments have been applied for the first time for the titanium electrodeposition in an ionic liquid. The potential of this technique to elucidate the electrocrystallization and two dimensional (2D) and three dimensional (3D) electrochemical phase formation has been proven in a variety of applications for aqueous electrolytes, see e.g. [8–12]. In these cases atomic resolution can be achieved. An extension of this method for studies in ionic liquids was demonstrated recently for the electrodeposition of several transition metals and semiconductors like Ge [13–16]. In a previous communication we reported first results of titanium nanowire formation on HOPG-step edges obtained by electrodeposition from the ionic liquid l-methyl-3-butyl-imidazolium bis trifluoro (methyl sulfone) imide ([BMIm]BTA) [17]. In the present work we have employed [BMIm]BTA as an ionic liquid to investigate the possibility of pure titanium electrodeposition at room temperature. We focus here on in situ STM and STS characterization of titanium 3D cluster formation and compare these results with conventional electrochemical measurements.

2. Experimental

All parts of the electrochemical cell were thoroughly cleaned in a 50/50 vol.% concentration H₂SO₄ and 30% H₂O₂ mixture at ambient temperature, followed by thorough cleaning in a stream of mili-Q (Milipore) water. The ionic liquid, [BMIm][BTA] ($[BMIm]^+[Q[(CF_3SO_2)_2N]^-$, 98% pure) was obtained from Solvent Innovation, Germany. The liquid was dried under vacuum at 120 °C and was kept in an argon glove box (O_2 and $H_2O < 2 ppm$) before use. TiCl₄ (99.999%) was obtained from Alfa Aceser, Germany and showed good solubility in the ionic liquid. Although the ionic liquid was extremely hydrophobic, saturated by <2 mass% H₂O, the whole processes of cell assembly for all the electrochemical measurements and EC-STM studies were performed in an argon filled glove box in order to avoid any contamination by H₂O or O₂ of either the ionic liquid or the extremely hygroscopic active electrolyte, TiCl₄.

A teflon electrochemical cell with three electrode configuration was used for all the studies. The working electrode was Au(111) obtained by evaporating gold on chromium coated special heat resistive quartz glass (Berliner Glass KG). The thickness of the Au coating was about 300 nm with grain size varying between 1 and 3 nm. Atomically flat terraces were obtained by annealing the clean Au(111) surface under hydrogen flame at orange/red colour for 3 min and then rapidly quenching the substrate in mili-Q water at room temperature. With such treatment flat terraces measuring about 50–100 nm were achieved. The Au(1 1 1) substrate (with an effective surface area of $3.6 \times 10^{-5} \text{ m}^2$) was sealed to the teflon cell by a teflon coated silicone O-ring. A Pt ring and a Pt wire (99.99% pure, both with a diameter of 0.5 mm) served as the counter and reference electrodes, respectively. A major part of the electrochemical studies were carried out by a PAR 273 (USA) poten-tiostat coupled to a computer with commercial M-270 software for experimental control and data acquisition. Concentration dependence of the active electrolyte on the deposition process was studied by using two different concentrations of TiCl₄. The probability of impure species deposition from the ionic solvent was checked by performing separate control experiments.

The EC-STM experiments were carried out by a home built STM driven by a Picoscan controller of Molecular Imaging Company, USA. The potential of the working electrode was controlled during in situ measurements by a Picostat potentiostat coupled to the STM controller. The tips were prepared by etching Pt-Ir wires of 0.25 mm diameter in 4 M KCN solution. In order to avoid the effect of Faraday currents on the tip, it was properly insulated except the apex by electropaint (BASF, ZQ 84-32250201, Germany) via electrophoresis and cured first at 150 °C for 2 h followed by heating at 250 °C for 10 min. Such an electropaint coated tip showed very negligible Faraday current (<50 pA). The tunneling current was set to 1 nA for imaging experiments taken in the constant current mode. The STS data were acquired at a set point current of 20 nA and an initial tip bias voltage of 0.3 V. For reasons of clarity, we present here the average spectrum acquired at three different places of a particular scan area (200 nm \times 200 nm) in the bias voltage range of -0.5 to 0.5 V. Since the tip bias was scanned in a wide range of voltage during acquisition of STS data, the quality of tip coating was carefully monitored before and after the STS data acquisition, which showed a constant Faraday current less than 50 pA. The adverse effect of thermal drift on the quality of STS data was carefully minimized by acquiring the spectra in only 20 ms in comparison with the imaging scan rate of three lines per second. Since the reference electrode was Pt, all the potentials cited here were calibrated indirectly against the ferricenium/ferrocene ([Fc]⁺/[Fc]) redox couple. Always a freshly prepared Au(111) surface was used in a new measurement. The whole set-up for the EC-STM studies was mounted in a clean, dried and Ar filled stainless steel container which was air tight to ensure relatively long measurement times. Unless mentioned otherwise all potentials are cited with respect to the $[Fc]^+/[Fc]$ reference.

3. Results and discussion

Solubility data of TiCl₄ in the present ionic liquid are not known and we cannot exclude that the real solubility of TiCl₄ is lower than the nominal concentrations added. Furthermore, to our knowledge no electrochemical or spectroscopic information exists concerning the electroactive species in this neutral melt. The STM measurements performed with nanometer resolution give no unambiguous answer of precipitation of β -TiCl₃. So, we cannot exclude the formation of ultra-thin passivating films. For all these reasons the following presentation of the electrochemical measurements has to be limited to a qualitative description and we focus on the STM and STS evidence of Ti electrochemical phase formation and surface alloying with Au(1 1 1).

3.1. Cyclic voltammetry (CV)

The CV for the Ti electrodepostion from a nominal concentration of 0.24 M TiCl₄ in [BMIm]BTA on a Au(111) substrate is shown in Fig. 1. The first cathodic peak at -0.39 V is attributed to the Ti(IV) to Ti(II) reduction process. It has been observed that Ti(TV) generally is reduced to Ti(II) in two one-electron steps at higher temperature in alkali chloride or chloride-fluoride mixtures [3,4]. In the electrolyte studied here we find some experimental indications that a two electron transfer process in one step seems to be possible. First, the current time transient around the Ti(IV) to Ti(II) reduction potential does not show any signature of an appreciable Ti(III) precipitation reaction which appears due to passivation of the substrate by TiCl₃ species. Furthermore, the relevant redox couple remains constant in several subsequent cycles at constant sweep rate and, in particular, in the first cycle the violet coloration expected for the Ti (111)complexes in the presence of ferrocene is not observed [17]. We observe the violet color only after the first cycle. The time delay possibly can be due to conversion of Ti(IV) to Ti(III) via a disproportionation reaction, i.e. $Ti^{2+} + Ti^{4+} \rightarrow 2Ti^{3+}$. There is a shoulder around -0.8 V, which we tentatively assign to Ti(III) reduction on the basis of STM observations, see Section 3.2. The hump in the CV at -1.45 V is assigned to the UPD of Ti metal from the Ti(II) state since the STM pictures at this potential show the formation of clusters and



Fig. 1. Cyclic voltammogram of 0.24 M TiCl₄ in [BMIm]BTA on Au(111) substrate vs. [Fc]⁺/[Fc] obtained at a sweep rate of $10 \text{ mV} \text{ s}^{-1}$ at room temprature.

films of two-three monolayer height. With the small hump at -1.61 V, another UPD process can possibly be correlated to the formation of a binary alloy of Au-Ti. In situ STM images and STS spectra show that 3D-Ti starts to deposit near an applied potential of -1.9 V. Hence the peak at -1.9 V is attributed to the three dimensional growth of Ti clusters in the over potential deposition (OPD) regime of Ti. The low current density in the CV in this potential range presumably is due to a thin passivating layer at the electrode. The current inflection at the extreme cathodic direction is due to the reduction of the organic cation of the solution. At the anodic side we observe a relatively broad peak at -1.27 V, which can be due to stripping of Ti and oxidation to Ti(II) species. At an anodic potential of ~ 0.22 V we note the quasi reversible peak for the oxidation of Ti(II) to Ti(IV). Application of an anodic potential of ~ 0.8 V leads to the step edge oxidation of the Au(111) substrate beyond which (\sim 1.2 V) the anionic part of the ionic liquid undergoes oxidation.

3.2. UPD of Ti on Au(111): 2D phase formation

STM images of the electrolyte/electrode interface in the potential range from -0.5 to -1.1 V are shown in Fig. 2. At the open circuit potential conditions clear Au(111) steps of monoatomic height of ~ 2.4 Å, with a rough appearance of the step-edges are observed. As the potential of the Au(111)substrate is made negative stepwise, we first observe the formation of 2D islands on the terraces at -0.5 V which is shown in Fig. 2a. Interestingly, we notice preferential nucleation on the terraces rather than at the step edges of the Au(111) substrate. Initially, these islands are about 2.5 Å in height and exhibit a narrow lateral size distribution-see me z-profile in Fig. 2a. As the process of deposition is continued, we do not find any sensible change in the number of nuclei but their growth is clearly noticed with time and applied potential. Fig. 2b shows an image of the deposits when the applied potential is at -0.8 V, about 80% of the substrate surface is covered with the islands. When the applied potential reaches -1.1 V, we observe a complete coverage of the Au(111) substrate (Fig. 2c). The nature of these islands/clusters in the potential range from -0.5 to -1.1 V is not clear. From the STS spectra below a deviation from the Ti characteristics is indicated. So we cannot exclude deposition of TiCl₃ precipitates with sub-nanometer thickness in this potential range formed according to toe disproportionation reaction above. In the UPD region below -1.4 V a complete coverage of the substrate by nearly two atomic layers of Ti has been observed (images not shown).

3.3. Over potential deposition of Ti on Au(111): 2D–3D transition

We have already noticed that the UPD process leads to complete coverage of the Au substrate by Ti of nearly two monolayer height. Therefore, depending on the degree of lattice misfit and the substrate-deposited film interaction, the



Fig. 2. STM images for Ti UPD on Au(111) from 0.24 M TiCl₄ in [BMIm]BTA: (a) initial stage of 2D island formation (150 nm × 150 nm) with a typical z-profile, sample potential of -0.5 V, tip potential -0.3 V; (b) nearly complete coverage of the Au(111) substrate by the deposits (135 nm × 135 nm), at a sample potential of -0.8 V, tip potential -0.6 V; (c) fully covered substrate with a 2D layer (160 nm × 160 nm), sample potential of -1.1 V, tip potential -0.9 V. Tunneling current in all the cases is set to 1 nA.

OPD process is expected to take place either in a layer by layer or in the 'Stranski–Krastanov' growth mode [18]. However, in view of the irreversibility of the CV also kinetic growth limitations may have to be considered. Shown in Fig. 3 is the appearance of the deposits when the potential of the working electrode is kept at -1.8 V at room temperature. 3D clusters grow all over the surface, which are about 10–20 Å high. It can be argued from the 3D representation, which is shown in Fig. 3b, that the OPD of Ti on Au(111) from the present ionic liquid leads to the formation and growth of bulk titanium.

3.4. Current transients

Fig. 4a shows a selection of current transients, which have been obtained with starting potentials of 0.5 V and at step potentials in the region of the first cathodic peak in the CV, see Fig. 1. At longer times the *I* versus *t* curves are indicative of a limiting Cottrell behaviour, i.e. diffusion control characteristics. According to previous studies of the electrochemistry



100x 100 nm



Fig. 3. OPD of Ti on Au(111) from 0.24 M TiCl₄ solution: (a) 1 nm thick 3D layer of Ti on Au(111), sample potential -1.8 V, tip potential -1.5 V (100 nm \times 100 nm); (b) the 3D view of the deposited clusters.



Fig. 4. Current transients obtained during electrodeposition of Ti from 0.24 M TiCl₄ in [BMIm]BTA at different step potentials: (a) belongs to the potential region where Ti(IV) is reduced to Ti(II) species; (b) corresponds to the UPD–OPD transition region of Ti on bare Au(111) substrate; (c) a fit of the experimental current transient obtained at -1.7 V by a double layer charging, a 2D nucleation and growth and 3D nucleation and diffusion limited model (see text).

of TiCl₄ in various ionic liquids and molten salts [5–7], the formation of Ti(II) and Ti(HI) species has to be discussed in the potential range of interest here. If TiCl₃ precipitates at the electrode to an appreciable amount a passivation layer should form and one could expect a correspondingly sharp passivation transient. This is not visible in the curves of Fig. 4a. So these results agree with the STM-observations that there is no high concentration of TiCl₃ precipitates during TiCl₄ reduction in the ionic liquid under study.

Approaching the UPD–OPD transition region around -2.0 V characteristic changes in the current transients are observed, see Fig. 4b. A clear bump occurs at shorter times, which is less pronounced in the curve at -2.0 V. In order to get a first insight into the time behaviour of these transients we have considered the following contributions: a double-

layer charging dominating at shorter times (I_{dl}) , a 2D nucleation term including lattice incorporation (I_{2D}) , and a 3D nucleation process followed by diffusion controlled growth (I_{3D}) :

$$I(t) = A \exp\left(\frac{-t}{\tau}\right) + p_1 t \exp\left(-p_2 t^2\right) + p_3 t^{-1/2} \\ \times \left(1 - \exp\left(-p_4\left(t - \left(1 - \exp\left(\frac{-p_5 t}{p_5}\right)\right)\right)\right)\right)$$
(1)

For a detailed description of the different contributions in Eq. (1) and the definitions of the parameters A, τ and p_1 we refer to the literature [19,20]. Since in the following we focus on the contribution of I_{3D}, we give here the expressions for p_3 , p_4 and p_5 only:

$$p_3 = \pi^{-1/2} z F D^{1/2} c, \quad p_4 = \pi N_0 D k, \quad p_5 = k_n$$
 (2)

with

$$k = \frac{4}{3} \left(\frac{8\pi c}{\rho}\right)^{1/2}.$$
(3)

Here D = diffusion coefficient, c = bulk concentration of the electroactive species, N_0 = number density of active nucleation sites, k_n = nucleation rate constant; the other symbols have their usual meaning. A fit of the current transients by Eq. (1) is shown in Fig. 4c for the example of an *I* versus *t* curve at a potential of -1.7 V versus [Fe]⁺/[Fe] taking for c the nominal concentration of Ti⁴⁺. As can be seen a reasonable fit can be obtained in this potential range where the commencement of 3D phase formation is observed in the STM measurements. The long time behaviour is well described by the I_{3D} term. From the fitting parameters of this contribution we derive a diffusion coefficient of $D \sim 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ which is the same order of magnitude in comparison with literature data of Ti(II) in a similar ionic liquid [6]. The fit result of $k_n \sim$ $10^{-2} \,\mathrm{s}^{-1}$ is comparable in magnitude with typical values in aqueous solutions [19]. As for the other parameters, the fit result of p_4 has a high uncertainty –it is strongly correlated with D, see Eq. (2), so that only a rough estimate of $N_0 \sim 10^9 \,\mathrm{cm}^{-2}$ is obtained, which is uncertain by at least one order of magnitude. This analysis shows that the long time behaviour of the current transients in Fig. 4 can be qualitatively described by a 3D nucleation and diffusion control mechanism. However, it should be critically commented, mat with the large number of fitting parameters a quantitative interpretation e.g. of the 2D nucleation and double layer charging contribution is difficult.

3.5. Dissolution and surface alloying

Similar to the electrodeposition process we have monitored in situ the dissolution of Ti layers deposited on the Au(1 1 1) substrate. At first a thick layer of approximately 1 nm of Ti was deposited on the Au(1 1 1) surface, which is then dissolved at an anodic potential of 0.5 V. A representative image is shown in Fig. 5a. In the initial stage of the dissolution process, typical worm like vacancy clusters are observed which are controlled by mass transport through peripheral diffusion [21]. As the dissolution process is continued the original surface of Au(1 1 1) becomes visible. However, the whole Au(1 1 1) surface presented in Fig. 5b shows a large number of holes which are of about monatomic depth (confirmed from the cross section analysis). This is indicative of surface alloying of Ti with Au. The presence of very small clusters all over the surface is also evident from Fig. 5b. These clusters disappear with time and surface atoms diffuse very fast over the surface and heal the holes within about 15–20 min.



500x500 nm²



200x200 nm²

Fig. 5. STM images acquired during the dissolution of $\sim 1 \text{ nm}$ thick Ti layer from the Au(1 1 1) substrate: (a) Typical signature of mass transport through peripheral diffusion, sample potential 0.5 V, tip potential 0.6 V (500 nm × 500 nm), (b) holes of monatomic height on Au(1 1 1) satistrate indicating possible surface alloying, sample potential 0.5 V and tip potential 0.2 V (200 nm × 200 nm).



Fig. 6. Tunneling spectra, I-U curves, obtained for Ti and Au(111): (a) I-U spectra obtained in the applied bias range of -0.5 to 0.5 V and (b) variation of the effective barrier height as a function of sample potential (see text).

3.6. I-U spectra and electronic properties of the deposits

Typical I-U spectra received from the bare Au(1 1 1) substrate and Ti covered Au(1 1 1) surfaces are presented in Fig. 6a. Although the raw data are noisy, they exhibit a clear metallic behaviour. These spectra are used to determine the effective tunneling barrier (ϕ) by assuming a constant density of states for sample and tip. In such a case the tunneling current is given by the following approximation [22]:

$$I = \text{const.} \int_{0}^{U} \exp\left[-2(2m)^{0.5}\hbar^{-1}\left(\phi - \frac{eU}{2}\right)^{0.5}d\right] dU, \quad (4)$$

where *d* is the distance between the tip and the surface and the other symbols have their usual meaning. The magnitude of *d* is found to be ~3 Å at a set point tunneling current of 20 nA, by the distance tunneling spectroscopy in the present ionic liquid. In Fig. 6b we show the variation of ϕ as a function of the applied potential during electrodeposition. It can be seen that the magnitude of ϕ for Au(1 1 1) is 2.0 eV, which is about 3.0 eV less in this ionic liquid than the vacuum value of the work function (-5.1 ± 0.2 eV). Adsorption of ions on the Au(1 1 1) surface clearly can reduce the work function by such an amount [23]. At the initial stage of deposition, the thin Ti layer shows a lower value of ϕ in the under potential region. However, after a certain applied potential of ~-1.4 V, once a minimum thickness of about 1 nm is reached, a constant value of ϕ is observed. A thick layer of bulk Ti shows an effective barrier ϕ of 1.25 eV. The relative difference of the effective barrier between Ti and Au(1 1 1) in this ionic liquid medium is -0.8 eV, which compares surprisingly well with the difference of the respective work functions. Similar observations have been made recently in the Ni and Co deposition on Au(1 1 1) from ionic liquids [13,14].

4. Conclusions

Titanium metal has been electrodeposited from TiCl₄ in a new class of ionic liquid, [BMIm]BTA, for the first time at room temperature with in situ monitoring of the 2D and 3D phase formation by electrochemical STM. Interestingly, the severe problem of Ti(III) precipitation before metal deposition seems to be reduced in this medium. At room temperature the predominant reaction is that from Ti(IV) to Ti(II). In the initial steps of deposition clusters of 2.5 Å height are formed all over the surface without any site preference. At an applied potential of -1.1 V the whole substrate is covered with a thin layer, presumably β -TiCl₃. The OPD of Ti starts near -1.8 V. The growth continues with the formation of 3D clusters. Finally the clusters coalesce to form a 3D bulk phase. Dissolution of a thick layer of Ti indicates Au-Ti surface alloying. STS results confirm the metallic nature of the deposit. Moreover, the difference in the barrier height of the deposited Ti and Au(111) substrate in the present ionic liquid nicely matches with the difference in magnitude between their work functions in vacuum.

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