Ionic Liquids: The Link to High-Temperature Molten Salts?

SHERIF ZEIN EL ABEDIN[†] AND
FRANK ENDRES*

Faculty of Natural and Materials Sciences, Clausthal University of Technology, Robert-Koch-Strasse 42, 38678 Clausthal-Zellerfeld, Germany

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ABSTRACT
Due to their wide thermal windows, ionic liquids can be regarded as the missing link between aqueous/organic solutions and high-temperature molten salts. They can be employed efficiently for the coating of other metals with thin layers of tantalum, aluminum, and presumably many others at reasonable temperatures by electrochemical means. The development of ionic liquids, especially air and water stable ones, has opened the door for the electrodeposition of reactive elements such as, for example, Al, Ta, and Si, which in the past were only accessible using high-temperature molten salts or, in part, organic solvents.

1. Introduction

Ionic liquids are in a wider sense molten salts with melting points below 100 °C, and they consist solely of cations and anions. In contrast to simple metal halides, both cations and anions are relatively complicated ions where in most cases the charge is delocalized or shielded by side groups. This is one reason why the melting points of ionic liquids are remarkably low. A fascinating aspect of ionic liquids is their variety: 10^{12}–10^{18} different liquids, binary and ternary mixtures with versatile properties, have been predicted. Most of the liquids known hitherto have at or near room temperature vapor pressures of 10^{-11}–10^{-10} mbar which enables experiments at temperatures at up to 300 °C on a longer time scale and up to 400 °C on a short time scale. In this context, ionic liquids are the missing link between aqueous/organic solvents, which can

be handled up to 100 °C, and classical molten salts with melting points of ≥ 400 °C. The extremely low vapor pressures allow experiments under vacuum conditions; thus, the surface of the liquid can be investigated, for example, by XPS, UPS, AES, and other surface sensitive techniques. Nevertheless, some liquids can be distilled even at elevated temperatures under vacuum.[1] Another important advantage of ionic liquids is their large electrochemical windows (>5 V), and hence, they give access to elements which cannot be electrodeposited from aqueous or organic solutions such as, for example, Al, Mg, Ti, and Ta, at moderate temperatures, although Mg and Ti in particular have not yet been electrodeposited as elements in the bulk phase. Moreover, the high thermal stability of ionic liquids (see refs 2 and 3) allows the direct electrodeposition of crystalline metals and semiconductors at elevated temperatures, and in this context, ionic liquids can be regarded as the link to molten salts. To obtain more information about the ionic liquids in general and their use as solvents for electrodeposition of metals and semiconductors, we refer to recently published review articles.[4–8]

In this Account, we summarize and discuss some results of the electrodeposition of aluminum, tantalum, and silicon in ionic liquids and discuss the prospects of ionic liquids for variable-temperature electrochemistry. It is demonstrated that adherent layers of Ta can be obtained in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide ([BMP]Tf$_2$N) containing TaF$_5$ at 200 °C, under the right conditions. Nano- and microcrystalline aluminum are made in the ionic liquids [BMP]Tf$_2$N and [EMIm]Tf$_2$N [1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide], respectively. Moreover, well-adhering aluminum layers can be made on mild steel in chloroaluminate and [EMIm]Tf$_2$N ionic liquids after in situ electrochemical etching. Elemental semiconducting silicon is obtained in the ionic liquid [BMP]Tf$_2$N.

2. Experimental Section

The ionic liquids 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) amide ([BMP]Tf$_2$N), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ([EMIm]Tf$_2$N), and 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) were purchased via Merck KGaA (EMD) in ultrapure quality. The liquids were dried under vacuum for 12 h at 100 °C to water contents below 3 ppm (by Karl-Fischer titration) and stored in an argon-filled glovebox with water and oxygen levels below 1 ppm (OMNI-LAB from Vacuum-Atmospheres). Anhydrous AlCl$_3$ grains (Fluka, 99%), TaF$_5$ (Alfa, 99.99%), and SiCl$_4$ (Alfa, 99.999%) were used without further purification.

Frank Endres, born in 1966, is a Full Professor of Electrochemistry at Clausthal University of Technology. He studied chemistry at the University of Saarbrücken (Saarbrücken, Germany) from 1988 to 1993. In 1996 he received his doctorate degree in Physical Chemistry from the University of Saarbrücken. In the same year, he moved to the University of Karlsruhe where he filled the position of a university lecturer at the Institute of Physical Chemistry. In 2002, he got his *habilitation* and moved to Clausthal where he is currently working as Professor of Electrochemistry and Electrochemical Nanotechnology. His main research interests are focused on the application of ionic liquids in electrochemistry as well as study of nanoscale processes at the electrode–ionic liquid interface using in situ (electrochemical) scanning tunneling microscopy.

Sherif Zein El Abedin (born 1970, Kalyoub, Egypt) is Associate Professor at the National Research Centre (Cairo, Egypt). He received his M.Sc. (1996) and Ph.D. (1999) degrees in Physical Chemistry from Zagazig University (Zagazig, Egypt). He carried out his postdoctoral studies on high-temperature molten salts and electrodeposition of metals and semiconductors in ionic liquids at the Institute of Physical Chemistry, Karlsruhe University (Karlsruhe, Germany). He joined the Chair of Prof. Endres at Clausthal University of Technology in 2003, where he is currently working on the nanoscale electrodeposition of metals and semiconductors as well as electropolymerization in ionic liquids. His research interests involve the application of ionic liquids in electrochemistry and corrosion of metals and alloys.

* Corresponding author. E-mail: frank.endres@tu-clausthal.de. Fax: +49-5323-722460.
† Permanent address: Electrochemistry and Corrosion Laboratory, National Research Centre, Dokki, Cairo, Egypt.

All electrochemical measurements were performed in the glovebox using a Parstat 2263 potentiostat/galvanostat (Princeton Applied Research) controlled by PowerCV and PowerStep software. Au(111) on mica (Molecular Imaging), platinum sheets (Alfa, 99.99%), and highly oriented pyrolytic graphite (HOPG) were used as working electrodes. In case of Al electrodeposition, Al wires (Alfa, 99.999%) were used as quasi-reference and counter electrodes. However, in Ta and Si electrodeposition, Pt wires (Alfa, 99.99%) were used as quasi-reference and counter electrodes. A quartz round flask was used as an electrochemical cell. Prior to use, all parts in contact with the solution were thoroughly cleaned in a 50/50 volume mixture of H_2SO_4 and H_2O_2 followed by refluxing in bi-distilled water. A high-resolution field emission scanning electron microscope (Carl Zeiss DSM 982 Gemini) was utilized to investigate the surface morphology of the deposited films, and energy dispersive X-ray analysis (EDX) was used to determine the film composition. The X-ray diffractograms of the deposited samples were recorded using a Siemens D-500 diffractometer with Co Kα radiation.

In situ STM experiments were performed with in-house-built STM heads and scanners under inert gas conditions (H_2O and O_2 at <1 ppm) with a Molecular Imaging Pico Scan 2500 STM controller in feedback mode. STM tips were prepared by electrochemical etching of tungsten wires (0.25 mm diameter) and electrophoretically coated with an electropaint (BASF ZQ 84-3225 0201). During the STM experiments, the electrode potential was controlled by the PicoStat from Molecular Imaging. For the current–voltage tunneling spectroscopy, the tip was positioned on the site of interest and the tip voltage was scanned between an upper and lower limit. During this procedure, the feedback is switched off.

3. Results and Discussion

3.1. Electrodeposition of Aluminum. The electrolysis of molten cryolite (Na_3AlF_6) in which aluminum oxide is dissolved at 1000 °C[9] is still the main industrial method for primary aluminum production. However, it is not suitable for coating other metals with a layer of aluminum, since the electrolysis is performed at a temperature where Al is liquid. At present, there are various methods for aluminum coating such as hot dipping, thermal spraying, sputter deposition, vapor deposition, and electroplating in, for example, organic solvents. The electroplating process offers some advantages. The deposits are usually adherent and do not affect the structural and mechanical properties of the substrate. Furthermore, the thickness and the quality of the deposits can be adjusted by controlling the experimental parameters. Moreover, the electroplating process is rather cost-efficient, since it can be performed at moderate temperatures.

Because of its high reactivity (-1.67 V vs NHE), the electrodeposition of aluminum from aqueous solutions is not possible. Therefore, electrolytes for Al deposition must be aprotic such as ionic liquids or organic solvents. The electrodeposition of aluminum in organic solutions is
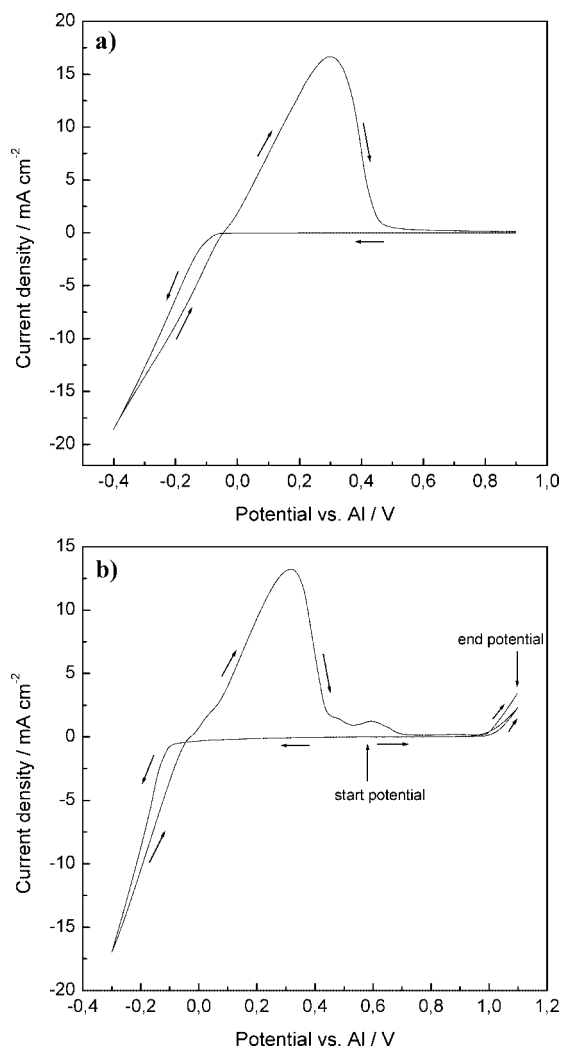

FIGURE 1. (a) Cyclic voltammogram of Al deposition on mild steel substrate in a Lewis acidic ionic [EMIm]Cl/$AlCl_3$ liquid (40 mol %/60 mol %) at room temperature with a scan rate of 10 mV/s. (b) Cyclic voltammogram recorded on mild steel substrate in a Lewis acidic ionic [EMIm]Cl/$AlCl_3$ liquid commenced from an anodic scan and terminated at 1100 mV instead of open circuit potential. The scan rate was 10 mV/s.

commercially available [SIGAL process (Siemens-Galvano-Aluminium)[10,11]], but due to volatility and flammability, there are some safety issues. Therefore, the development of room-temperature ionic liquids in recent years resulted in another potential approach for aluminum electrodeposition. Many papers have been published on the electrodeposition of aluminum from chloroaluminate (first-generation) ionic liquids.[12–20] It was shown that mild steel can be coated by electrodeposition with adhering aluminum at room temperature in a first-generation [EMIm]Cl/$AlCl_3$ (40 mol %/60 mol %) ionic liquid.[20] The cyclic voltammogram of aluminum deposition/stripping on conventionally pretreated mild steel shows only a rising cathodic current due to Al plating and an oxidation peak due to stripping of aluminum (Figure 1a). An Al deposit made on such mild steel is high in quality, but it does not adhere well to the mild steel surface. It is quite easy to remove the deposit, resulting in nice free-standing aluminum sheets. Iron oxide layers that are not chemically
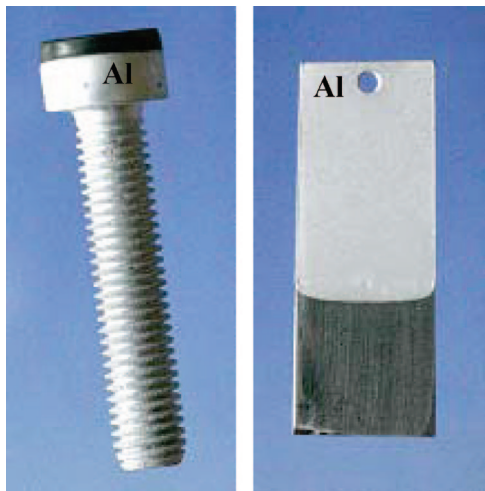
FIGURE 2. Optical photos of Al deposits manufactured from the employed ionic liquid with uneven surface and screw geometry.

dissolved in the ionic liquid seem to prevent an adhesion of aluminum to steel. However, an anodic electrochemical pretreatment of mild steel leads reproducibly to well-adhering Al coatings on steel which resist even mechanical scratching. This pretreatment removes the iron oxide layers. Cyclic voltammetry measurements reveal that iron is oxidized during anodic polarization, removing the iron oxide layers (Figure 1b). Subsequent electrodeposition of Al might lead to a codeposition of iron or alloy formation. With the electrochemical pretreatment in the ionic liquid, not only steel sheets but also complex shapes like, for example, screws can be coated with well-adhering aluminum. Figure 2 shows optical photos of a mild steel sheet with hole and a screw, coated by Al layers prepared by galvanostatic electrodeposition at -10 mA/cm^2 for 2 h. The Al layers on those mild steel components all display attractive brightness and adhere well to the surface due to the application of the in situ electrochemical etching prior to electrodeposition. The aluminum adheres so well that it can be polished mechanically to mirror brightness. An immersion test of semicoated mild steel in an aqueous NaCl solution shows that the mild steel surface is subjected to strong corrosion whereas the Al layer is unaffected. Therefore, we believe that an Al electrodeposition process in ionic liquids has the potential to replace the industrial procedure based on the SIGAL process. Ionic liquids based on AlCl$_3$ have no significant vapor pressure up to 150 °C; they are nonflammable, and they deliver high-quality Al deposits. Furthermore, Al can be employed as a sacrificial anode so that such a bath would require an only small amount of maintenance, provided it is held under at least dry air. For corrosion protection, Al-coated steel would be highly interesting as Al forms, in contrast to zinc layers, self-passivating oxide layers.

Recently, we employed for the first time air and water stable ionic liquids for the electrodeposition of aluminum. We could show that nano- and microcrystalline aluminum can be electrodeposited in three different air and water stable ionic liquids, namely, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) amide ([BMP]Tf$_2$N),
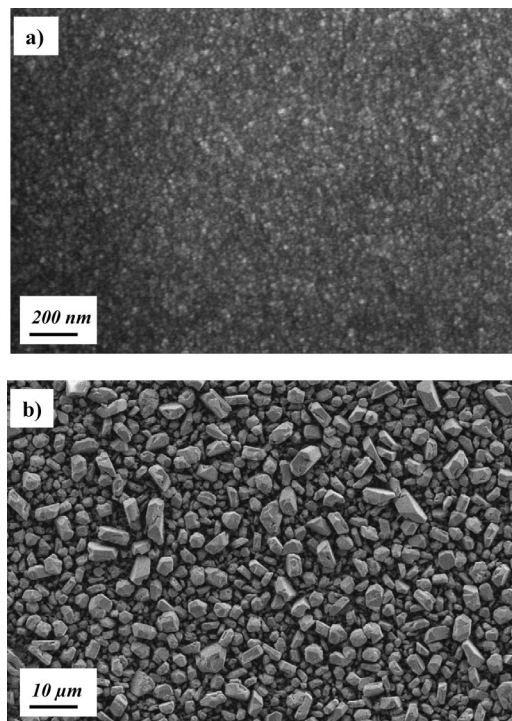

FIGURE 3. (a) SEM micrograph of an electrodeposited Al film on gold formed in the upper phase of the AlCl$_3$/[BMP]Tf$_2$N mixture after potentiostatic polarization at -0.45 V (vs Al) for 2 h at 100 °C. (b) SEM micrograph of an electrodeposited Al film on gold made in the upper phase of the AlCl$_3$/[EMIm]Tf$_2$N mixture after potentiostatic polarization at -0.05 V (vs Al) for 2 h at 100 °C.

1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ([EMIm]Tf$_2$N), and trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl) amide (P$_{14,6,6,6}$Tf$_2$N).[21] It was found that the ionic liquids [BMP]Tf$_2$N and [EMIm]Tf$_2$N form biphasic mixtures in the concentration range of AlCl$_3$ from 1.6 to 2.5 mol/L and from 2.5 to 6 mol/L, respectively.[21] Moreover, the electrodeposition of aluminum at room temperature occurs only from the upper phase at AlCl$_3$ concentrations of ≥1.6 and ≥5 mol/L in ionic liquids [BMP]Tf$_2$N and [EMIm]Tf$_2$N, respectively. The biphasic behavior of such liquids was first reported by Wasserscheid,[22] but a complete understanding of the aluminum species in the phases is still lacking. Interestingly, we have found that Al can be electrodeposited only from the upper phase of the biphasic mixture. This means that the reducible aluminum-containing species exists only in the upper phase of the biphasic mixtures, and hence, the electrodeposition of Al occurs only from the upper phase.

In the case of the ionic liquid [BMP]Tf$_2$N, shiny, dense, and adherent deposits with very fine crystallites in the nanometer regime can be obtained without any addition of organic brighteners or using pulse plating techniques (Figure 3a). In contrast, coarse cubic-shaped aluminum particles in the micrometer regime are obtained in the ionic liquid [EMIm]Tf$_2$N (Figure 3b). As the temperature and electrochemical parameters were varied, it is unlikely that this observation is due to viscosity effects alone. As one explanation, the [BMP]$^+$ cation acts as a grain refiner and it might play its role by adsorption on the substrates
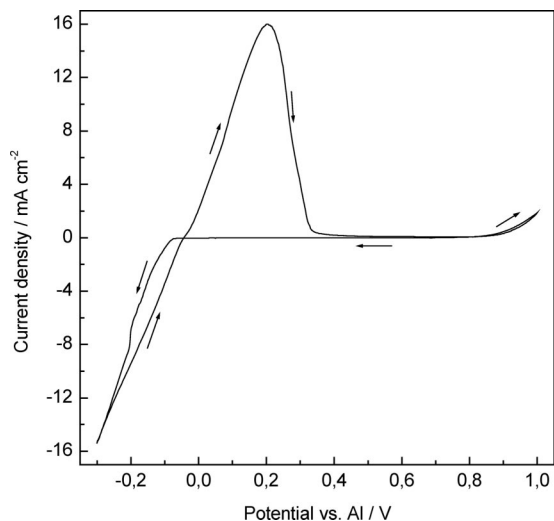
FIGURE 4. Cyclic voltammogram recorded at mild steel substrate in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide containing 6 M AlCl$_3$ (from the upper phase of the mixture) at room temperature. The scan rate was 10 mV/s.

and on growing nuclei, thus hindering the further growth of crystallites. A detailed study on the electrodeposition of nano- and microcrystalline aluminum in different air and water stable ionic liquids was recently published.[21]

We reported in a recent paper that dense, adherent aluminum layers can be electrodeposited on mild steel in the water and air stable ionic liquid [EMIm]Tf$_2$N containing AlCl$_3$ as a source of aluminum.[23] Figure 4 shows the cyclic voltammogram of the upper phase of the biphasic [EMIm]Tf$_2$N/6 M AlCl$_3$ mixture on a mild steel electrode, first and second cycles. The potential was scanned from the open circuit potential (0.56 V vs Al) in the negative direction down to a potential of –0.3 V. It is clearly seen that the bulk deposition of aluminum occurs at a potential of approximately –0.07 V. In the reverse scan, the cathodic branch of the cyclic voltammogram crosses the anodic one at a potential of –0.05 V, producing a current loop which is attributable to nucleation. The recorded anodic peak at a potential of 0.2 V is correlated with the stripping of electrodeposited aluminum. The increase in the anodic current at a potential of 0.9 V is due to the anodic oxidation of the substrate. Well-adhering aluminum layers can be obtained after anodic oxidation of the substrate in the employed electrolyte prior to bulk deposition of aluminum. This is attributed to the dissolution of the air-formed iron oxide layer on anodic polarization producing an oxide-free surface. Figure 5 shows a SEM micrograph of the cross section of a deposited aluminum layer on mild steel substrate obtained galvanostatically at a current density of –5 mA/cm^2 for 2 h. Prior to Al electrodeposition, the electrode was anodically polarized at a potential of 1 V (vs Al) for 2 min. As shown in the SEM micrograph, the deposited Al layer adheres well to the mild steel substrate and the layer is homogeneous with a thickness of 10 μm. The corrosion behavior of mild steel without and with coating by an aluminum layer with a thickness of 10 μm in 3.5% NaCl solutions was reported in ref 23. Compared to the uncoated sample,

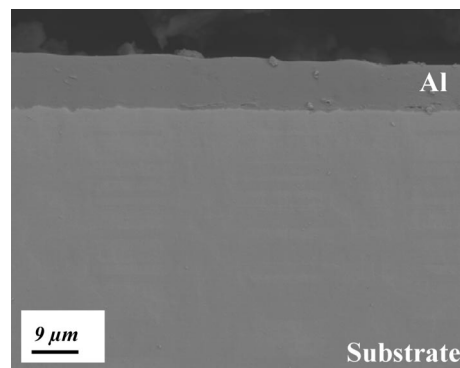FIGURE 5. SEM micrograph of the polished cross section of an 10 μm Al layer electrodeposited galvanostaticllay on mild steel substrate at –5 mA/cm^2 in [EMIm]Tf$_2$N/6 M AlCl$_3$.

the Al-coated mild steel exhibited a lower corrosion current and a higher polarization resistance, indicating the improvement of the corrosion resistance by Al coating.[23]

In our opinion, the electrodeposition of Al is a good example of the prospects of ionic liquids in the electrodeposition of reactive elements. In contrast to the SIGAL (Siemens-Galvano-Aluminium) and REAL (room-temperature electroplated aluminum) processes for Al deposition, there are no flammable organic solvents and the electrodeposition can be performed at elevated temperatures up to 180 °C. An advantage over the NaCl/AlCl$_3$ system with a melting point of 150 °C is the wider thermal window between 0 and 180 °C. Furthermore, via cation and anion effects, the structure of the deposit can be influenced, a field which is practically unknown with classical molten salts. Thus, these liquids behave like molten salts, but there is more chemistry behind it with many prospects for future developments.

3.2. Electrodeposition of Tantalum. Many efforts have been made to develop a process for the electrodeposition of Ta. High-temperature molten salts were found to be efficient baths for the electrodeposition of tantalum.[24–29] Senderoff and Mellors reported the first results on the electrodeposition of Ta using the ternary LiF/NaF/KF eutectic mixture as a solvent and K$_2$TaF$_7$ as a source of Ta between 650 and 850 °C.[24,25] Despite enormous importance, these baths have many technical and economic problems such as the loss in current efficiency of the electrolysis process, due to the dissolution of metal after its deposition,[30] and severe corrosion problems at high temperatures. Furthermore, from a practical point of view, molten salts are hardly suited for the coating of sensitive materials like NiTi shape memory alloy with tantalum since the electrolysis process is performed at overly high temperatures. With ionic liquids, a technical electroplating process might be performed at moderate temperatures, but we have to point out clearly that the electrodeposition of metals with several oxidation states of the precursors can lead to nonstoichiometric subvalent deposits, i.e., with an oxidation state of >0, which are easily misinterpreted as metallic deposits.

Recently, we reported for the first time that tantalum can be electrodeposited as thin layers in the water and
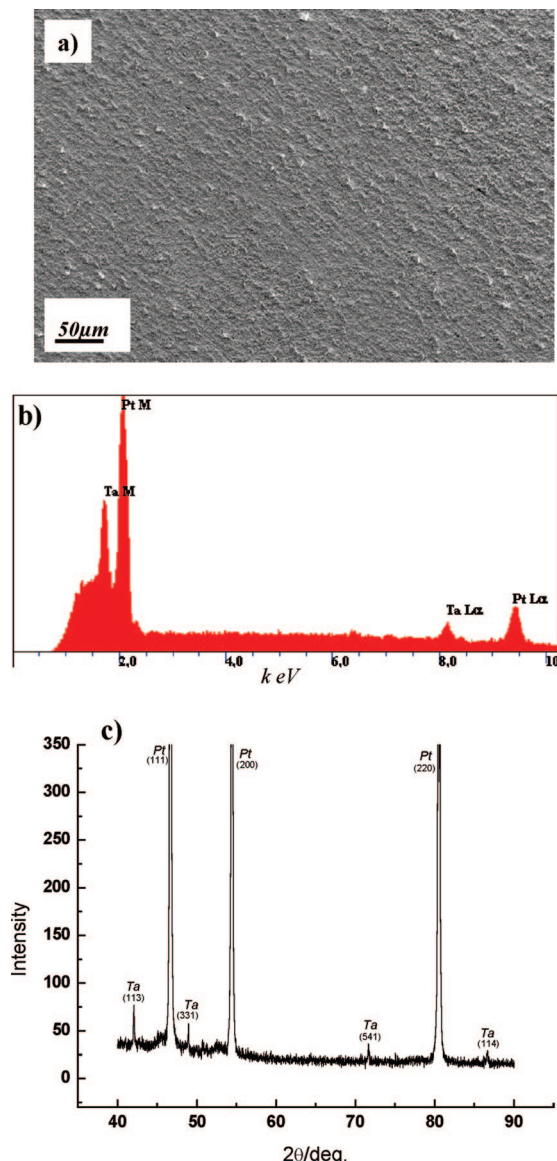
FIGURE 6. (a) SEM micrograph of the Ta electrodeposit formed potentiostatically on Pt in [BMP]Tf$_2$N containing 0.25 M TaF$_5$ and 0.25 M LiF at a potential of −1.8 V for 1 h at 200 °C. (b) EDAX profile of the area shown in the SEM micrograph. (c) XRD patterns of the deposited layer.

air stable ionic liquid [BMP]Tf$_2$N at 200 °C using TaF$_5$ as a source of tantalum.[31] The quality of the deposit was found to be improved upon addition of LiF to the deposition bath. The SEM micrograph of the Ta electrodeposit (Figure 6a) made potentiostatically at −1.8 V in [BMP]Tf$_2$N containing 0.25 M TaF$_5$ and 0.25 M LiF on a Pt electrode at 200 °C for 1 h shows a smooth, coherent, and dense layer. The deposit was analyzed as tantalum as revealed in the corresponding EDX profile of Figure 6b. XRD patterns of the electrodeposit clearly show the characteristic patterns of crystalline tantalum (Figure 6c). However, tantalum deposition is not straightforward in ionic liquids. Under the wrong conditions (high current density), mainly subvalent XRD-amorphous tantalum species with an oxidation state of >0 are obtained. There seems to be a limiting current density: above, one obtains only subvalent deposits, and below, thin crystalline tan-

talum layers are obtained. At present, we are able to deposit 1 μm thick tantalum layers at 200 °C. At room temperature, only ultrathin tantalum layers can be deposited as an element at the moment.

How can we understand that nonstoichiometric subvalent tantalum species form? It is well known that in molten salts like LiCl and NaCl tantalum can be obtained in crystalline layers at temperatures around 600–700 °C. Thermodynamically, Ta should be deposited at electrode potentials below −400 mV versus NHE. On the other hand, a look in textbooks of inorganic chemistry shows a rich cluster chemistry for Ta, Nb, W, Mo, and many other transition and refractory metals. One example is [Ta$_6$Cl$_{12}$]$^{2+}$ where in a Ta$_6$ cluster the metal atoms are bound to Cl$^-$ and bridged via Cl$^-$. In the case of this cluster, Ta has an average oxidation state of 14/6 (≈2.33). Such cluster compounds can be made by means of solid state chemistry. Indeed, with TaCl$_5$ as a precursor, we never succeeded in depositing elemental tantalum. These complexes seem to be that stable that at low temperatures they are not reduced to the element. In high-temperature molten salts, however, elemental tantalum can be obtained, and the results are better with TaF$_5$ in fluoride melts. Metal fluorides exhibit a less rich cluster chemistry than the chlorides or bromides. It is known in molten salts (in part also in aqueous electrochemistry, e.g., in Cr deposition) that the addition of Li$^+$ ions enhances the metal deposition. One explanation is that the Li$^+$ destabilizes the metal–halide bonds, thus facilitating deposition. This is maybe also the role of LiF in our ionic liquid, as without LiF the deposition of crystalline Ta seems to be fairly difficult. Nevertheless, the deposition of Ta is possible in ionic liquids at 200 °C, far from the limits of water or organic solvents.

We showed furthermore that adhering, dense, and uniform layers of Ta can be electrodeposited on NiTi alloy in the ionic liquid [BMP]Tf$_2$N containing 0.25 M TaF$_5$ and 0.25 M LiF at a moderate temperature of 200 °C.[32] NiTi alloys are widely used as orthodontic wires, self-expanding cardiovascular and urological stents, and bone fracture fixation plates and nails.[33–35] The biocompatibility of NiTi implants depends on their corrosion resistance. The major risk associated with NiTi implants is the breakdown of the passive film which occurs because of the aggressiveness of human body fluids, leading to a release of Ni ions that may cause allergic, toxic, and carcinogenic effects.[36–38] We found that the electrodeposition of an only 500 nm thick film of Ta on NiTi alloy improves its corrosion resistance considerably, leading to a decreased amount of Ni ions released into the solutions which, in turn, enhances its biocompatibility.[32] Avoiding the release of Ni ions into the human body fluid is greatly important when NiTi alloy is used in medical implantation because of the allergic and carcinogenic effects of Ni ions.

In this context, ionic liquids are again the link between water/organic solvents and molten salts. One can investigate the tantalum chemistry at low temperatures and draw conclusions about the chemistry of tantalum species; on the other hand, it is possible to deposit tantalum in
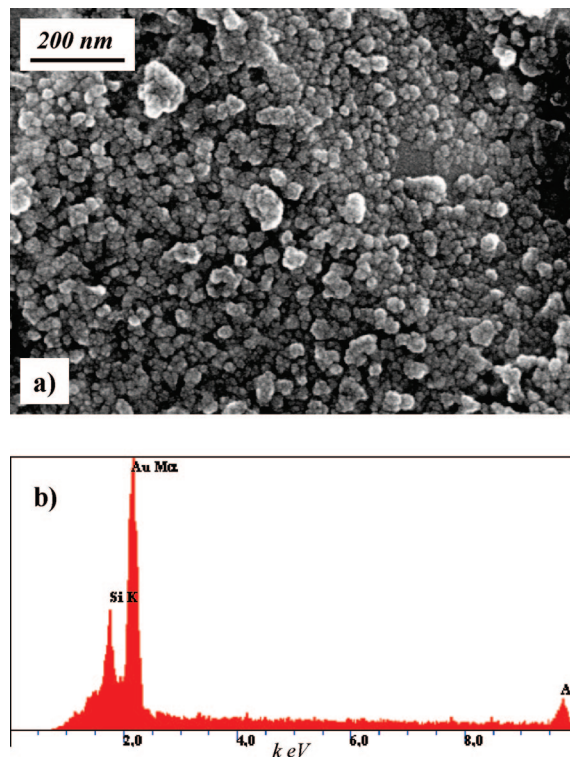
FIGURE 7. (a) SEM micrograph of electrodeposited silicon obtained potentiostatically on gold in [BMP]Tf$_2$N saturated with SiCl$_4$ at a potential of –2.7 V vs Fc/Fc$^+$ for 2 h at room temperature. (b) EDAX profile of the area shown in the SEM micrograph.

thin layers at 200 °C. We are convinced that there will be liquids available in the future which allow the deposition at temperatures of up to 300 °C. The Tf$_2$N, unfortunately, starts to be decomposed in the presence of LiF and TaF$_5$ at 250 °C.

3.3. Electrodeposition of Silicon. Silicon cannot be electrodeposited from aqueous solutions because of its very negative reduction potential which favors hydrogen evolution instead of element deposition. As a consequence, most of the work on the electrodeposition of silicon was done in aprotic solvents or in molten salts. Silicon can be obtained in high-temperature molten salts using K$_2$SiF$_6$, Na$_2$SiF$_6$, or SiO$_2$ as sources of silicon.[39–41] Furthermore, there were several attempts in the past to electrodeposit silicon from organic solvents,[42–44] and smooth and uniform silicon deposits up to 0.25 μm thick could be obtained. The electrodeposition of silicon from its halides in nonaqueous solutions was also reported quite recently.[45] However, the authors also report a strong oxidation of the electrochemically made silicon. It was stated that silicon can also be electrodeposited in a low-temperature molten salt.[46] In this study, the authors employed 1-ethyl-3-methylimidazolium hexafluorosilicate, and at 90 °C, they could deposit a thin layer of silicon. However, upon being exposed to air, the deposit reacted completely to SiO$_2$. Thus, it is an open question whether the obtained silicon was semiconducting. Recently, we showed that silicon can be well electrodeposited on the nanoscale in the room-temperature ionic liquid [BMP]Tf$_2$N saturated with SiCl$_4$.[47,48] Figure 7a shows a high-resolution SEM picture of an electrodeposited silicon
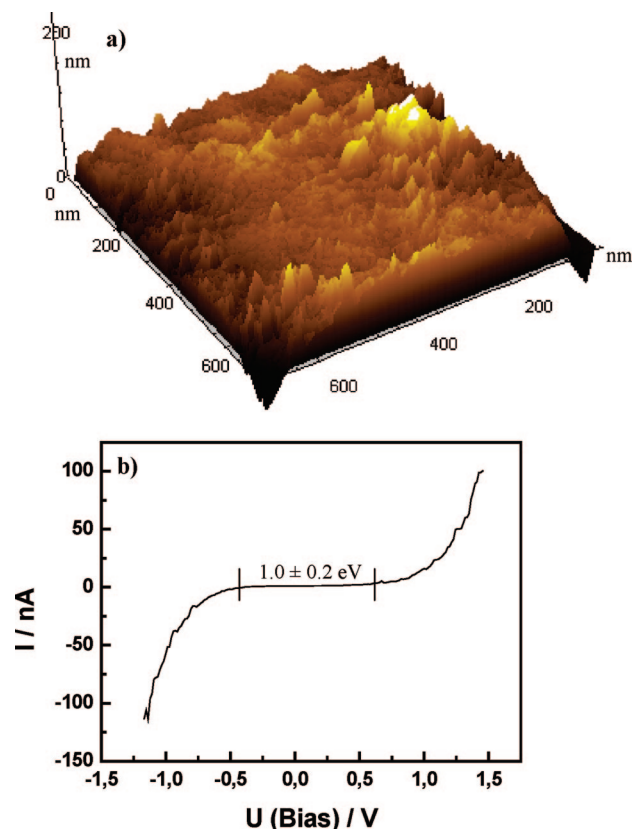

FIGURE 8. (a) In situ three-dimensional STM picture of an 100 nm thick silicon film formed on HOPG in [BMP]Tf$_2$N saturated with SiCl$_4$ at a potential of –1.7 V vs Fc/Fc$^+$. (b) In situ current–voltage tunneling spectrum of the silicon electrodeposit on HOPG.

layer on gold substrate. As seen, the deposit contains small crystallites with sizes of approximately ≤50 nm. Quantum size effects have to expected at grain sizes below 5 nm in the case of silicon. The deposit can keep its dark appearance even under air, but sometimes, it is rapidly transformed into white powder, i.e., SiO$_2$. The EDX analysis gave as a result only gold from the substrate and silicon, but no detectable chlorine (Figure 7b). This proves that obviously elemental silicon was electrodeposited which can be subject to some oxidation under environmental conditions. In an experimentally challenging combined XPS/electrochemistry experiment under inert gas and ultrahigh vacuum, we could show that indeed elemental silicon is obtained which under the conditions of an inert gas glovebox is oxidized at the surface. These results will be published elsewhere.

The three-dimensional STM picture of Figure 8a shows the topography of a rough silicon layer with a thickness of 100 nm. The layer was electrodeposited at –1600 mV versus Fc/Fc$^+$ on HOPG, probed under potential control with the in situ STM. The thickness of the deposit was determined in situ from the z-position of piezo, which is a standard procedure in our laboratories. To show the semiconducting behavior of the deposited film, current–voltage tunneling spectroscopy was performed. It has already been shown by us that the I–V tunneling spectroscopy is a valuable technique for in situ characterization of electrodeposited semiconductors[49,50] and metals.

We could show via in situ I–V tunneling spectroscopy that germanium with layer thicknesses of ≥20 nm is semiconducting with a symmetric band gap of 0.7 ± 0.1 eV. On the other hand, we have found that very thin layers of germanium with thicknesses of several monolayers exhibit clearly metallic behavior.[49,50] Figure 8b shows an in situ current–voltage tunneling spectrum of the 100 nm thick silicon layer. The spectra are all over the surface of the same quality. As seen in the spectrum, a typical band gap of 1.0 ± 0.2 eV is observed. This value is quite similar to the value that we observed for hydrogen-terminated n-doped Si(111) in an ionic liquid.[51] The value of microcrystalline silicon in the bulk phase at room temperature is 1.1 eV. In light of these results, it can be concluded that elemental, intrinsic semiconducting silicon was electrodeposited from the employed ionic liquid as a thin layer. Our results on the deposition of silicon as an example for a semiconductor show that ionic liquids have the potential to deposit, due to wide electrochemical windows, elements which formerly were only accessible from organic solvents or molten salts. Variation of temperature and cation or anion effects in ionic liquids give more potential to tune deposit morphology than organic solvents or molten salts would give alone.

4. Conclusions

In this paper, we have presented and discussed some results of the electrodeposition of aluminum, tantalum, and silicon in ionic liquids. Our results show that uniform, adherent layers of Ta can be obtained in the ionic liquid [BMP]Tf$_2$N containing TaF$_5$ at 200 °C, under the right conditions. Nano- and microcrystalline aluminum are made in the ionic liquids [BMP]Tf$_2$N and [EMIm]Tf$_2$N, respectively. Moreover, well-adhering aluminum layers can be made on mild steel in chloroaluminate and [EMIm]Tf$_2$N ionic liquids after in situ electrochemical etching. Elemental semiconducting silicon is obtained in the ionic liquid [BMP]Tf$_2$N. It was also shown that a silicon layer with a thickness of 100 nm, electrodepoited in the ionic liquid [BMP]Tf$_2$N, exhibits a band gap of 1.0 ± 0.2 eV, indicating that semiconducting silicon was electrodeposited.

In this context, ionic liquids can be regarded as the missing link between aqueous/organic solvents and molten salts: they have the wide electrochemical windows of organic solvents like acetonitrile, but they are nonflammable and easy to dry. They consist of only ions like molten salts, but they are liquid at lower temperatures. Due to their wide thermal window of up to 400 °C, they are the thermal link between aqueous/organic solvents and molten salts. A benefit of ionic liquids, which is recognized only slowly, is the fact that there are not yet completely understood cation/anion effects which allow influencing deposit morphology and structure in electrochemically made materials. Such effects are practically unknown in aqueous/organic solvents and classic high-temperature molten salts.

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