THE ELECTRODEPOSITION OF GERMANIUM FROM AN IONIC LIQUID:
A MINI-REVIEW ON THE NANOSCALE PROCESSES

Frank Endres
Institute of Physical Chemistry
Universität Karlsruhe (TH)
D-76128 Karlsruhe, Germany

ABSTRACT

This mini-review summarizes some literature data on the electrodeposition of germanium from different media such as molten salts, organic solutions, water and, more recently, from air and water stable ionic liquids, on which the focus is set. In the latter systems in situ STM studies were performed to elucidate the processes during electrodeposition on the nanometer scale. The initial growth of Ge on Au(111) leads in the underpotential deposition regime to the growth of a rough monolayer of 300 pm in maximum height, which obviously shows surface alloying with the substrate. In the overpotential deposition regime stable and narrowly dispersed Ge nanoclusters as well as nanosized micrometer thick deposits can be obtained. A short outlook on the possible importance of ionic liquids for electrochemical nanotechnology is given.

INTRODUCTION

The electrodeposition of the elemental semiconductor germanium has not yet been widely investigated from low melting electrolytes. Winkler, who discovered germanium in 1886, reported in his two early publications about the electrosynthesis of a loosely adhering grayish deposit from basic aqueous solutions [1, 2]. In honor of his native country he called this new element “Germanium”. A certain shortcoming in these early studies was surely, that remarkable hydrogen evolution in aqueous solutions is a side reaction during electrodeposition of this element, thus leading to brittle deposits. Later on, this problem was circumvented by employing high temperature molten salts for electrowinning of the element, and a quality as high as 99.9 % for the obtained Ge was reported in literature [3].

Around 1950 several attempts were done to electrodeposit germanium from organic solutions, mainly based on glycoles [4, 5]. Furthermore, even aqueous solutions were employed for germanium electrodeposition studies [6, 7]. In all cases only low current efficiencies were reported, and the maximum thickness, that could be obtained, was in the hundred micrometer range. In the following years the interest in germanium electrodeposition decreased strongly, and only a few studies on this topic were performed. Systematic electrochemical studies like Cyclic Voltammetry, Potential Step Experiments or Impedance Spectroscopy are consequently almost completely missing.
Nevertheless, in recent years the interest in germanium has considerably increased, as it was discovered, that Ge clusters with dimensions of only a few nanometers show an interesting, size dependent photoluminescence around 1 eV. Furthermore, quantum size effects are present, as photoluminescence is shifted to higher energies with decreasing cluster size, and in contrast to the microcrystalline element, nanoscale Ge rather seems to be a direct semiconductor than an indirect one. The obvious direct optical transition of nanoscale Ge [8] makes nanosized germanium a promising material, for example for optical sensors. For nanoclusters with a thickness below 4 nm a transition from the cubic diamond structure to the tetragonal (ST-12) structure has been reported [9]. For these clusters a direct band gap of 1.47 eV was observed, and possible applications have also been discussed [10]. For comparison, microcrystalline germanium is an indirect semiconductor with a band gap of 0.67 eV at room temperature [11]. It should be mentioned here, that nanosized silicon shows size dependent photoluminescence, too, and there is a remarkable interest in "porous silicon" for several applications [12].

Almost all of the studies on germanium nanoclusters were performed on samples made under Ultrahigh Vacuum conditions like e.g. Molecular Beam Epitaxy. In the opinion of the author the requirement of UHV would complicate a possible future nanotechnological process to a certain extent. Therefore we were seeking a method how to make germanium by electrochemical means. In general, electrochemistry gives the unique chance to electrodeposit and -dissolve elements reproducibly, thus, such a process could become an interesting supplement to the well known UHV techniques. Furthermore, it is known, that the crystal size of electrochemically made deposits can be controlled by the overvoltage for the electrodeposition, as it is predicted by the Kelvin equation [13]. In aqueous solutions pulsed electrodeposition is well known to produce nanocrystalline metals with a narrow size distribution [14].

The air and water stable ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIm]+ PF$_6^-$) is well suited for the electrodeposition of germanium, as could be shown in several papers [15 – 17]. It has an electrochemical window of a little more than 4 Volt on Au(111), and it does not take up more than 2 mass-% of water at room temperature [18], furthermore it can be dried to water contents below 50 ppm. Therefore this liquid is well suited for studies on the electrodeposition of germanium from the hygroscopic germanium-(IV)-halides.

**ELECTROCHEMICAL WINDOW OF [BMIm]+ PF$_6^-$**

The Cyclic Voltammogram (CV) of pure [BMIm]$^+$ PF$_6^-$ is presented in Figure 1a with a scan rate of 1 mV/s [16]: in the dry state an electrochemical window of a little more than 4 Volt is obtained, and only capacitive currents flow between the anodic and the cathodic limit. In Figure 1b CV's were acquired with a scan rate of 100 mV/s. After passing the lower electrochemical limit of the liquid a clear reoxidation peak is observed at -600 mV vs. Pt-quasi-reference, which decreases in height with subsequent cycling. Furthermore, on passing the anodic limit, a slight reduction process is observed around +200 mV. If the electrode potential is held for 30 minutes at -3 Volt, one can visually observe that the gold substrate apparently loses its brightness, it gets rather mat and some small drops appear on the surface. After switching off the cell, the gold gets back its
original brightness within 30 minutes, and the ionic liquid only gets a little reddish upon this treatment: it is likely that [BMIm]⁺ reduction leads to [BMIm]ₓ oligomers. STM pictures in this potential range gave rise to a rapidly growing “deposit” on the surface without any structural features. It disappears completely from the surface as soon as the potentiostat is switched off.

![Graph showing CV's of [BMIm]⁺ PF₆⁻ on Au(111)](image)

**Figure 1.** CV’s of [BMIm]⁺ PF₆⁻ on Au(111) with different scan rates (a: 1 mV/s, b: 100 mV/s). The electrochemical window of the dry liquid is a little more than 4 Volt, only capacitive currents flow. Upon passing the anodic and cathodic limits oxidation and reduction products form which are in part electroactive. (From ref. 16 – Reproduced by permission of the PCCP Owner Societies)

At the anodic limit one can observe visually that the thin gold film can be completely electrodissolved if the potential is held at values more positive than +2.5 Volt for a sufficiently long time. Furthermore, STM pictures gave evidence, that the oxidation starts first at the steps of the gold terraces, with higher electrode potentials a pitting on the gold substrate sets in. Furthermore, *in situ* STM experiments showed that gold islands redeposit if the potential is switched back to values near the ocp after a potential step into the oxidation regime had been involved. We conclude therefore that the slight reduction peak around +200 mV is correlated with gold redeposition.

**ELECTRODEPOSITION OF Ge ON Au(111) FROM [BMIm]⁺ PF₆⁻ / GeI₄**

Figure 2 shows the CV of dry [BMIm]⁺ PF₆⁻ on Au(111) together with a CV of the liquid with c(GeI₄) ≈ 0.1 – 1 mmol/l. For comparison, the electrode potentials are
given with reference to the bulk deposition of Ge in this system. Several redox processes can be seen:

**Figure 2.** (a) CV of [BMIm]PF$_6$ on Au(111), as in Figure 1. (b) If Ge$_4$ is added, 5 redox processes are observed. $E_1$ is likely to be correlated with $I_2/I^{'}, E_2$ is correlated with gold step oxidation, at $E_3$ 250 pm high islands grow, at $E_5$ Ge bulk deposition sets in. $E_4$ could not be attributed without doubt to a definite surface process. With the exception of $E_3$ all peak currents show a linear dependence on the square root of scan rate, thus the processes are mainly diffusion controlled.

**Figure 3.** Upon a potential step from the open circuit potential to +500 mV vs. Ge (arrow, downscan) islands with an average height of 250 ± 20 pm grow that merge within a few minutes into a defect rich monolayer. (From ref. 15 – Reproduced by permission of the PCCP Owner Societies)
E₁ is probably correlated with I₂/T, E₂ is correlated with gold step oxidation, at E₃ 250 pm high islands grow, at E₅ Ge bulk deposition sets in. E₄ could not be attributed without doubt to a definite surface process. At E > 2 Volt vs. Ge gold oxidation is so fast, that the thin film is destroyed rapidly. With the exception of E₃ all peak currents show a linear dependence on the square root of scan rate, i.e. the processes are mainly diffusion controlled.

Figure 4: A Ge layer, that was electrodeposited at -1000 mV vs. Ge with retracted tip, shows a complicated annealing: within one hour the surface transforms into a terrace like structure with heights of 330 ± 30 pm. Within the limits of errors this is the value for Ge(111) bilayers.

Figure 3 shows an STM picture of an experiment, where at the arrow the electrode potential was set from the open circuit value to + 500 mV vs. Ge. On the upper part of the picture the typical gold steps of the substrate with an average height of 250 pm can be seen in acceptable quality, on the lower part of the picture, i.e. after the potential step had been involved, islands with an average height of 250 ± 20 pm start growing, and after a short oscillation of the feedback circuit the surface is probed in good quality. At this electrode potential the islands close rapidly to a defect rich monolayer. If the electrode potential is further reduced down to 0 Volt vs. Ge, only slight changes occur on the surface. As the tip disturbed the electrodeposition in the overpotential deposition regime, we retracted it by 50 μm, performed the deposition at -1 Volt vs. Ge and reapproached. The sequence of pictures in Figure 4 shows an experiment where the STM tip was reapproached 10 minutes after the electrodeposition had been performed. Initially a nanosized layer with a maximum thickness of 20 nm grows, where within about one hour
a certain annealing occurs. It leads to the transformation of the clusters into apparently well ordered terraces with an average height of 330 ± 30 pm. The theoretical value for Ge(111) bilayers in the cubic diamond structure is 328 pm, thus it is very likely that under the reported conditions Ge(111) bilayers were made electrochemically.

In order to exclude that this annealing was induced by the STM tip, the measurement was repeated under comparable conditions, but the reapproach was done one hour after the electrode potential had been set to -1 Volt vs. Ge. The result is shown in the upper 2/3 of Figure 5. Under these conditions, too, a terrace like structure with step heights of 330 ± 30 pm is obtained. It is remarkable that many defects can be found (arrows in Figure 5), whose depth can reach 1 nm.

![Figure 5. In the upper part of the *in situ* STM image at -1000 mV vs. Ge 330 ± 30 pm high Ge(111) bilayers are probed, a further growth does not seem to occur. The white arrows mark defects with depths of about 1 nm. At the black arrow the electrode potential was set to -500 mV vs. Ge: immediately wormlike nanostructures are formed on the surface with heights of not more than 1 nm. (From ref. 15 – Reproduced by permission of the PCCP Owner Societies)](image)

At the black arrow the electrode potential was set to -500 mV vs. Ge, and immediately wormlike nanostructures form on the surface. The heights of these structures do not exceed 1 nm. It is interesting that the partial oxidation started on the whole of the surface, and not preferentially at steps, as one can often observe in the initial oxidation of metals. If the electrode potential is again reduced to -1000 mV vs. Ge, these nanostructures heal in a complex annealing, and several surface processes can be
identified: besides electrodeposition of small Ge clusters also the electrodissolution of Ge islands is observed, furthermore pinch-off phenomena, which are most likely the result of periphery diffusion at the rims, occur. As a consequence the wormlike structures disappear within about 2 hours and a terrace like surface structure is recovered. Under these conditions the maximum film thickness was approximately between 12 and 16 nm. Interestingly, from the electrochemical measurements the Ge deposition seems to be irreversible, and under no circumstances a clear stripping peak was observed in the CV. Nevertheless the thin Germanium film disappears completely as soon as the potentiostat is switched off. It was found that a chemical oxidation of Ge by GeI₂ occurs, and it is likely that GeₓIᵧ species form. Such observations were also made in studies on Ge electrodeposition from organic solutions [4, 5]. A disadvantage of the system that is presented here, is, that micrometer thick Ge films, that are well suited for ex situ characterization, can not be made. Furthermore, stable nanoclusters obviously can not be obtained, rather a transformation of nanoclusters into Ge(111) bilayers occurs. The oxidation of the islands in the underpotential deposition regime could hardly be investigated because oxidation falls into a potential range where also gold oxidation sets in. Therefore, also other germanium halides were used to study the electrodeposition of germanium.

**ELECTRODEPOSITION OF Ge on Au(111) FROM [BMIm]⁺ PF₆⁻ / GeBr₄**

Figure 6 shows the CV of [BMIm]⁺ PF₆⁻, saturated with GeBr₄, with a scan rate of 1 mV/s. The CV is mainly determined by two irreversible mainly diffusion controlled reduction processes.

![Figure 6](image_url)

*Figure 6. CV of GeBr₄, saturated in [BMIm]⁺ PF₆⁻ with a scan rate of v = 1 mV/s: the first reduction process at E » +700 mV is mainly correlated with the reduction of Ge(IV) to Ge(II), at 0 Volt the electrodeposition of the Ge bulk phase begins. At electrode potentials E > +1 Volt strong gold oxidation sets in. (From ref. 19 – Reproduced by permission of the PCCP Owner Societies)*

Electrochemical Society Proceedings Volume 2002-19

683
The first reduction process with a minimum at about +700 mV vs. Ge is mainly correlated with the reduction of Ge(IV) to Ge(II), at 0 Volt bulk deposition of Ge begins. In some CV's (as shown in Figure 6) two peaks were observed for Ge bulk deposition, but the first one usually disappears already at v = 2 mV/s. It is possible that it is correlated with electrodeposition of Ge at defects. The peak currents of the two main reduction processes rise linearly with the square root of scan rate, thus the processes are mainly controlled by diffusion. At about -1 Volt vs. Ge reduction of [BMIm]+ begins. Typical Ge stripping peaks are not observed, as with Ge from GeE, chemical oxidation by GeBr₄ plays a role. At E > +1 Volt vs. Ge oxidation of gold begins at the rims of the terraces.

The in situ STM measurements on Au(111) under open circuit conditions showed reproducibly a rough, rather striped surface [19]. Upon rising the electrode potential the surface becomes smoother but also oxidation of gold at the rims sets in. Therefore, in the STM experiments, the electrode potential was always reduced from the open circuit potential to more negative values. In Figure 7 STM pictures of the surface at +200, +100, +50 and 0 mV vs. Ge are shown. Figure 7a shows the surface at +200 mV vs. Ge: the surface is completely covered with a thin Ge layer that rather shows metallic behaviour. In the in situ I/U tunnel spectrum for this layer no band gap is observed [19]. From GeCl₄ quite a similar thin layer is obtained. At +100 mV vs. Ge striped structures with heights between 300 and 500 pm grow (b), at +50 mV by lateral merging islands with widths between 50 and 80 nm and initial heights of about 1 nm (c, d) form. If the electrode potential is further reduced, these islands mainly grow vertically, and at E = -250 mV vs. Ge nanosized, several micrometer thick Ge films can be obtained.

Figure 7. a) shows a closed “UPD” layer of Ge on Au(111) at +200 mV vs. Ge, b) at +100 mV 300 – 500 pm high striped structures (arrows) grow, c) shows the surface at +50 mV vs. Ge: the striped structures seem to merge laterally and at 0 Volt vs. Ge islands with widths between 50 and 80 nm and initial heights in the nanometer range are formed (d). (From ref. 19 – Reproduced by permission of the PCCP Owner Societies)
In Figure 8 an approximately 200 nm thick Ge film is shown, together with I/U tunnel spectra:

Figure 8. a) at -250 mV vs. Ge an approximately 200 nm thick Ge film was deposited: several islands with heights of some nanometers rise above the surface. The I/U tunnel spectrum (b) of this layer shows intrinsic semiconducting behavior with a symmetric band gap of 0.7 ± 0.1 eV. This value is in good agreement with the literature value of 0.67 eV for the band gap of microcrystalline germanium at 300 K. On the pure gold surface under open circuit conditions metallic behavior is observed. The Faradaic currents of the retracted tip (see inset) do not exceed 3 nA. The peak is correlated with germanium electrodeposition on the tip. (From ref. 19 – Reproduced by permission of the PCCP Owner Societies)

Figure 9. Starting from the open circuit potential the CV of GeCl₄, saturated in 1-Butyl-3-methylimidazolium-hexafluorophosphate, shows 2 irreversible mainly diffusion controlled reduction processes on Au(111). The first peak with a minimum at +500 mV vs. Ge is mainly correlated with the reduction of Ge(IV) to Ge(II), the second one with the electrodeposition of germanium. At about -1 Volt vs. Ge reduction of the organic cation starts. The oxidation current between about +0.7 and +1.0 Volt is due to Ge electrooxidation, at E > 1.2 Volt oxidation of gold starts at the steps. (From ref. 20 – Reproduced by permission of the PCCP Owner Societies)
The I/U tunnel spectrum of this layer shows intrinsic semiconducting behaviour with a symmetric band gap of 0.7 ± 0.1 eV. Within the limits of errors this value is in good agreement with the band gap of 0.67 eV at 300 K for microcrystalline germanium. On the gold surface under open circuit conditions metallic behaviour is observed, for the "UPD" layer shown in Figure 7a the I/U tunnel spectrum is also metallic, but the apparent work functions seem to be remarkably higher. Ex situ XPS measurements prove doubtlessly that the topmost about 5 nanometers of thick layers consist of elemental germanium.

**ELECTRODEPOSITION OF Ge on Au(111) FROM [BMIm]+ PF6− / GeCl4**

Both with GeI4 and GeBr4 in a wider sense underpotential deposition was observed on Au(111). But in both cases the oxidation of these "UPD" layers could not be investigated reversibly, as their oxidation fell into a potential range where obviously gold oxidation also set in. With GeCl4, however, germanium electrodeposition could be well investigated reversibly both in the "UPD" and the OPD regime, and from the three systems investigated it shows the most reversible behaviour. In Figure 9 the cyclic voltammogram of GeCl4, saturated in 1-Butyl-3-methylimidazoliumhexafluorophosphate, is shown:

As with GeBr4 the CV is mainly determined by the Ge(IV)/Ge(II) process and by the electrodeposition of Ge at E < 0 Volt. At E > 1.2 Volt vs. Ge the oxidation of gold starts at the steps. In order to get an overview on the nanoscale processes, simultaneously with the STM scan a slow LSV scan (1 mV/s) was started at +1200 mV vs. Ge (1 mV/s) towards more negative electrode potentials. On the STM pictures the electrode potentials are given on the top and on the bottom, the values in between can be interpolated linearly. The result is shown in Figure 10:

In the upper part of Figure 10a the typical gold terraces with an average height of 250 pm can be well identified. At approximately +900 mV vs. Ge under these conditions the first Ge islands form (arrow in Figure 10 a). Further measurements [20] show that at +1000 mV vs. Ge the gold steps get decorated first, then, with further reduction of the electrode potential, at +950 mV vs. Ge 150 pm high islands are formed. At +750 mV vs. Ge 250 pm high islands deposit, that leave behind holes in the surface upon reoxidation, thus surface alloying plays a role. If the electrode potential is further reduced, at +300 mV vs. Ge a closed but rather rough layer with a maximum thickness of 300 pm forms on the electrode surface. Between +300 and 0 mV this layer hardly changes its shape, and at -50 mV vs. Ge the growth of Ge nanoclusters with widths between 10 and 40 nm and initial heights in the nanometer regime begins. By reducing the concentration of GeCl4 narrowly dispersed Ge nanoclusters on gold can also be obtained by electrodeposition [21].
Figure 10. These in situ STM pictures show an experiment, where together with a slow STM scan (450 sec per picture) a Linear Sweep Voltammetry scan with a scan rate of 1 mV/s was performed: beginning at +1200 mV vs. Ge, islands deposit on the surface at approximately +900 mV vs. Ge (arrow in (a)). Upon further reduction of the electrode potential (b and c) a closed layer forms and at -50 mV the growth of Ge nanoclusters starts. A typical height profile shows their shape. At the horizontal arrow in (c) the LSV scan was stopped, and the electrode potential was held at -50 mV vs. Ge: only a slow cluster growth is observed under these conditions (d). (From ref. 20 – Reproduced by permission of the PCCP Owner Societies)

SUMMARY AND OUTLOOK

The nanoscale electrodeposition of germanium on Au(111) from the ionic liquid 1-Butyl-3-methylimidazolium-hexafluorophosphate containing either GeI₄, GeBr₄ or GeCl₄ shows several common but also several differing characteristics. With all three germanium halides in a wider sense underpotential deposition is observed on Au(111), and before the bulk growth of germanium sets in, a completely closed layer with a maximum thickness of not more than 300 pm is deposited on the gold surface. The oxidation of this "UPD" layer could only be investigated reversibly with GeCl₄ as a solute, in the presence of GeBr₄ and GeI₄ its oxidation fell into a potential regime where
also the oxidation of the gold substrate started. The initial stages in the OPD regime could not be investigated with \textit{in situ} STM if GeI$_4$ was employed as a solute. From the experiments, that were done, it is likely that initially Ge nanoclusters form that transform on the time scale of about 1 hour into Ge(111) bilayers. A further disadvantage is, that with GeI$_4$ we did not get layers that were thicker than 100 nm, even with saturated solutions. With GeBr$_4$ such a transformation of clusters into bilayers was only observed in part, with GeCl$_4$ nanoclusters can be obtained that are stable for days, even during permanent probing \textit{in situ} with the STM tip. Both with GeBr$_4$ and with GeCl$_4$ micrometer thick, nanosized layers can be obtained at room temperature from saturated solutions.

Qualitative \textit{in situ} I/U-tunnel spectroscopy on Ge layers made from GeBr$_4$ and GeCl$_4$ show that the "UPD" layer shows rather a metallic behaviour, but the apparent tunnel barrier seems to be remarkably higher than that of the pure gold surface under similar conditions. On Au(111) a band gap of 0.7 ± 0.1 eV is observed for Ge layers and clusters with thicknesses of approximately 10 nm and more.

As a conclusion it can be summarized that germanium can be electrodeposited from ionic liquids in high quality. Nanoscale studies on semiconductor electrodeposition from ionic liquids are still at the beginning, and it can be expected that in near future systems will be available that also allow the electrodeposition of silicon and of less noble compound semiconductors, such as GaAs, GaSb and GaP. In general, nanosized semiconductors play an important role in basic research meanwhile [22], and in the opinion of the author electrodeposition from ionic liquids might become an important supplement in this research field.

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