ELECTRODEPOSITION OF NANOSCALE METALS AND SEMICONDUCTORS IN IONIC LIQUIDS

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ABSTRACT

Ionic liquids have been used to make nanoscale semiconductors like germanium and silicon as well as nanocrystalline aluminium. For the semiconductors air and water stable ionic liquids were used, whereas for electrodeposition of aluminum $\text{AlCl}_3$ based ionic liquids were employed in this approach. The electropolymerization of benzene in a room temperature ionic liquid is shortly presented.

INTRODUCTION

Nanoscale materials are of great importance for present and future technological applications. It is known in the case of semiconductors that quantum confinement is observed if grain sizes in the range of a few nanometers are obtained. Similar to the particle in a box problem the band gap of semiconductors rises if the particle size decreases (1). As a consequence the light emission of semiconductor nanoparticles shows a blue shift with decreasing particle size. It is an interesting aim to vary the wave length of a LASER by simple variation of the particle size. Semiconductor quantum dots on a variety of substrates might be of interest for quantum dot based LASERs (2). Almost all of the semiconductor nanoparticles were made in the past by chemical synthesis or by ultra high vacuum deposition, e.g. by molecular beam epitaxy. An electrochemical process would be highly interesting due to its versatility.

It is well known for metals that their hardness increases with decreasing size of the individual grain size. The reason is that with decreasing grain size the number of atoms in grain boundaries and triple junctions rises, where the crystallographic parameters are different from the bulk phase (3). As a consequence the hardness of a material can be increased strongly. For nickel, which is one of the best investigated nano­metals, it has been known for a while that nano-nickel with grain sizes of 10 nm is at least a factor of 5 harder than the microcrystalline metal. Electrodeposition has proved to be a versatile method to make nanocrystalline metals.

Polymers like polypyrrole, polyphenylene, polythiophene and their derivatives can be conductive for electrons and ions if they are partly oxidized (4). If they are fully reduced, on the other hand, the conductivity is negligible. With successive oxidation a rising electronic conductivity is obtained. Nowadays such conducting polymers are already used for the construction of organic light emitting diodes (5), where the typical thickness of the conducting polymer is only 100 – 300 nm. It was shown in the past that
with poly(para)phenylene blue light emitting diodes can be made (6).

Ionic liquids are a meanwhile well known class of solvents that are solely based on cations and anions. Besides the huge interest in organic and technical chemistry these liquids are very promising for electrochemical purposes. In contrast to the limited electrochemical window of water, which at room temperature is only a little more than 1.2 Volt, electrochemical windows of more than 6 Volt can be obtained with ionic liquids. Furthermore they can easily be dried to water contents below 1 ppm. It could be shown that these extraordinary properties make them ideal solvents for the electrodeposition of nanoscale semiconductors and metals (7, 8).

In this short contribution some insight into recent activities in Clausthal shall be given.

EXPERIMENTAL

Materials

All preparations (with the exception of the metathesis reaction) and electrochemical measurements were performed in an argon filled glove box (Omnilab from Vacuum Atmospheres) with water and oxygen concentrations below 1 ppm.

Preparation of the ionic liquids. 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm]PF$_6$ was made in a metathesis reaction at room temperature from [BMIm]Cl and NaPF$_6$ in an aqueous routine. The ionic liquid separated from the aqueous phase. The liquid was washed several times with high purity water before molecular sieve was added to remove the main amount of water. The liquid was filtered off and carefully pre-dried under vacuum and stirring at slightly elevated temperature. After several hours the temperature was increased to 100 Celsius and held over night. In the resulting liquid no traces of water could be detected on microcrystalline platinum electrochemically. Such a thorough drying is necessary to avoid decomposition of the PF$_6$.

AlCl$_3$ was purchased from FLUKA. For the AlCl$_3$ based liquids 1-ethyl-3-methylimidazolium chloride was mixed carefully with AlCl$_3$ to give the ionic liquid. 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide [BMP]TFSI and 1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [HMIm]FAP were purchased from EMD in the highest available quality. They were further dried under vacuum at 130 Celsius prior to use.

Preparation of the liquids for electrodeposition. For the electrodeposition of germanium GeCl$_4$ was dissolved in [BMIm]PF$_6$ up to saturation and to 0.001 mol/l, respectively. For silicon electrodeposition SiCl$_4$ was dissolved in [BMP]TFSI in a concentration of 1 mol/l. For Al electrodeposition [BMIm]Cl and AlCl$_3$ were mixed in a molar ratio of 45/55. For the electropolymerization of benzene it was dissolved in a concentration of 0.2 mol/l in [HMIm]FAP.
Measurements

Electrochemical Measurements. All electrochemical measurements were performed in a classical 3 electrode cell in an argon filled glove box, water and oxygen below 1 ppm. A PAR Versastat II or a PAR 2263 were used for the electrochemical measurements. The employed electrodes are given at the respective examples.

STM and STS measurements. The in situ STM experiments were performed with a Molecular Imaging PicoScan 2500 STM/AFM controller with in house built STM heads. These STM heads allow long term STM experiments under inertgas conditions with water and oxygen concentrations comparable to the quality of a glove box. The assembled STM head was put on a vibration damped table in an air conditioned laboratory with a temperature of 22 ± 1 Celsius.

RESULTS AND DISCUSSION

Fig. 1 a shows the electrochemical window of [BMIm]PF$_6$ on Au(111) with a scan rate of 1 mV/s. At the anodic limit the gold substrate starts to be oxidized whereas at the cathodic limit an irreversible reduction of the organic cation sets in. Between these 2 limits mainly capacitive currents flow. If GeCl$_4$ is added up to saturation, 2 reduction peaks and several oxidation peaks are observed (fig. 1 b).

![Figure 1](https://example.com/figure1.png)

Figure 1. (a) Electrochemical window of [BMIm]PF$_6$ on Au(111), (b) cyclic voltammogram of [BMIm]PF$_6$ saturated with GeCl$_4$ on Au(111). v = 1 mV/s

As was demonstrated elsewhere (9) the oxidation peaks are correlated with the surface oxidation of gold, whereas the reduction peaks are correlated with the redox processes Ge(IV)/Ge(II) and Ge(II)/Ge, respectively. Furthermore between the open circuit potential and +300 mV vs. Ge an underpotential deposition layer of about 300 pm
in thickness forms. It is important to mention here that in the cyclic voltammogram there is no evidence for the electrodeposition of a UPD layer.

In order to study the band gap of the deposited germanium as a function of thickness we deposited germanium in a liquid that contained GeCl₄ in a concentration of approximately 0.001 mol/l. Interestingly the growth was very slow and stable germanium nanoclusters were obtained that showed a relatively narrow size distribution. Fig. 2a shows such a surface, probed in situ by the STM tip.

Figure 2: (a) in situ STM picture of germanium nanoclusters with heights between 0.5 and 10 nm, (b) dependence of the measured band gap (by tunneling spectroscopy) as a function of particle thickness.

Fig. 2b shows the variation of the band gap as a function of the cluster thickness. In contrast to the expected increase of the band gap with decreasing height we observed a decrease of the band gap. Besides electronic interactions of the germanium nanoclusters with the metallic gold substrate there are some hints for a transition between well ordered bulk germanium to an amorphous phase with decreasing thickness.

Although the electrochemical window of imidazolium based ionic liquids is wide enough to make germanium by electrochemical means these liquids fail for the electrodeposition of silicon. It can be deposited, in our experience, however, the decomposition of the organic cation disturbs local probe measurements strongly. Therefore we selected [BMP]TFSI for the electrodeposition of silicon, which has an approximately 400 mV wider electrochemical window in the cathodic regime. For this purpose SiCl₄ was dissolved in a concentration of 1 mol/l in the respective liquid. Fig. 3 shows the cyclic voltammogram of SiCl₄ in [BMP]TFSI on highly oriented pyrolytic graphite (HOPG). In the anodic regime the disintegration of HOPG in the presence of halide is observed, in the cathodic regime we observe a great reduction peak followed by a shoulder. The first reduction peak is due to silicon electrodeposition, the shoulder is due to the irreversible reduction of the organic cation on the silicon surface. As demonstrated elsewhere (10) elemental analysis of the deposit only gives gold from the substrate, silicon and a little amount of chloride which has to be expected for electrochemically grown silicon. In order to investigate if the deposited silicon is semiconducting we deposited an approximately 100 nm thick layer on HOPG and acquired its tunneling spectrum at several sites on the surface.
Figure 3: cyclic voltammogram of Si electrodeposition on HOPG in [BMP]TFSI, c(SiCl₄) = 1 mol/l, v = 10 mV/s

Figure 4: upper part: in situ STM picture of approximately 100 nm thick silicon on HOPG, lower part: tunneling spectra of HOPG (dashed line) and of the 100 nm thick silicon layer
Fig. 4 (upper part) shows the surface of such a layer, which does not show characteristic features. Fig. 4 (lower part) shows the tunneling spectra of HOPG, which is metallic, and of the 100 nm thick silicon layer. There is a clear band gap for the silicon spectrum and its evaluation gives as result a value of 1.0 ± 0.2 eV. At room temperature for silicon a value of 1.1 eV has to be expected. These results show that the novel air and water stable ionic liquids are well suited to electrodeposit even such reactive elements like silicon.

![100 nm TEM image](image)

Figure 5: TEM picture of electrochemically made nanocrystalline aluminum, particle size distribution, determined by Warren-Averbach analysis

884 Electrochemical Society Proceedings Volume 2004-24
As was mentioned above nanocrystalline metals show in comparison to the microcrystalline ones improved hardness. Aluminum is an important metal for light weight construction, however, it is very difficult to make it nanocrystalline by methods like ball milling, gas phase condensation and others. On the other hand it is well known that ionic liquids are well suited to the electrodeposition of aluminum. Early results showed that the initial electrodeposition of Al in [BMIm]Cl/AlCl₃ leads to nanocrystals (11). Therefore we tried to make aluminium nanocrystalline by electrochemical deposition. In AlCl₃ based ionic liquids with additives like nicotinic acid we finally succeeded in making Al deposits with grain sizes down to 10 nm (12).

Fig. 5 shows a typical TEM picture and the respective particle size distribution. Preliminary measurements on the hardness of these nano-Al deposits show a hardness which is a factor of 2 – 3 higher than that one for a microcrystalline reference sample. As will be shown elsewhere the novel air and water stable ionic liquids are even better suited to the electrodeposition of Al than the established AlCl₃ based ones and there is some evidence that nanocrystalline aluminium can be made without any additive (13).

Finally, we would like to demonstrate shortly that the novel air and water stable ionic liquids are also well suited to the electrodeposition of conducting polymers. As shown in the introduction conducting polymers are important for the construction of organic light emitting diodes. It was shown in the past that with poly(para)phenylene blue OLEDs can be made (6). It is known that benzene can be electropolymerized, however, solvents like 18 molar H₂SO₄ or HF/SbF₅ are by far not easy to handle. Our aim was therefore to investigate if the novel ionic liquids are suited to the electropolymerization of benzene (see also (14)). For this purpose we selected [HIm]FAP which has not only a wide electrochemical window but also a high solubility for benzene. Fig. 6 shows a cyclic voltammogram on platinum in [HIm]FAP which contains benzene in a concentration of 0.2 mol/l. At an electrode potential of 1800 mV in this system the electropolymerization of benzene sets in, giving rise to a black deposit. Simultaneously the polymer is partly oxidized upon incorporation of anions.

Figure 6: Electropolymerization of benzene in [HIm]FAP on polycrystalline platinum, v = 10 mV/s. 5 successive cycles are shown
As will be shown elsewhere (15) at maximum oxidation 3 - 4 benzene rings carry one positive charge which is compensated by an anion of the ionic liquid. In the reduction branch of the cyclic voltammogram in fig. 6 a cathodic current is observed which rises from cycle to cycle. This is due to the reduction of the polymer whose amount rises from cycle to cycle in the polymerization regime. The anodic peak current is due to the partial oxidation of the formerly reduced polymer. From the cyclic voltammetry it can be concluded that benzene is easily electropolymerized in the ionic liquid giving rise to a well electroactive conducting polyphenylene. Fig. 7 exhibits a high resolution SEM picture of the polymer in its oxidized state. As can be seen there are some structural features that approach the nano-regime. The electropolymerization in ionic liquids is not only one order of magnitude easier than in the conventional solvents, also a strongly enhanced chemical and electrochemical reversibility and stability of the deposits in ionic liquids is conventionally observed.

Figure 7: SEM picture of electrochemically made polyphenylene

CONCLUSIONS

We have demonstrated in this short review that ionic liquids are ideally suited to the electrodeposition of nanoscale materials. Their wide electrochemical windows and the ease to make them water free open up ways to make reactive elements on the nanoscale. We could show that in situ STM and tunneling spectroscopy measurements on the nanoscale are possible. Germanium and silicon can be electrodeposited as intrinsic semiconductors. Furthermore, aluminum can be made as nanocrystalline bulk deposits with improved materials properties with respect to microcrystalline reference samples. On the other hand ionic liquids also seem to be ideally suited to the electrodeposition of conducting polymers, which are of great importance e.g. for organic light emitting diodes.
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