

Electrodeposition of nanoscale silicon in a room temperature ionic liquid

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Abstract

In this letter we report for the first time that silicon can be well electrodeposited on the nanoscale in the room temperature ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide saturated with SiCl_4 . This liquid exhibits on highly oriented pyrolytic graphite (HOPG) an electrochemical window of 4 V, which is limited in the anodic regime by the degradation of HOPG, in the cathodic regime by the irreversible reduction of the organic cation. A silicon layer with a thickness of 100 nm exhibits a band gap of 1.0 ± 0.2 eV, which is shown by in situ current/voltage tunneling spectroscopy, indicating that semiconducting silicon was electrodeposited.

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1. Introduction

Silicon is one of the most important semiconductors as it is the basis of any computer chip. At room temperature silicon has an indirect band gap of 1.1 eV and the quantum efficiency of microcrystalline bulk silicon is in comparison to direct band gap compound semiconductors like GaAs, CdTe and other ones negligibly low. However, it was found that porous silicon made by wet etching of e.g. silicon wafers can show a high optical efficiency [1], although the mechanism of the photoemission is not yet fully understood. Furthermore, it was reported recently that silicon nanocrystals embedded in a SiO_2 matrix open an opportunity to develop a nanoscale silicon-based LASER [2]. There are numerous studies on the preparation of nanoscale silicon, and as one example among many other ones the ultra-high

vacuum electron-beam evaporation of silicon shall be mentioned here [3]. For an overview on the synthesis of semiconductor nanoparticles [4] shall be recommended here.

It has been known for a while now that semiconductors can also be made electrochemically [5] and there is a nice book on the electrochemistry of silicon and its oxide [6]. An electrochemical procedure is elegant as in comparison to ultra-high vacuum processes like, e.g. molecular beam epitaxy the experimental setup is less demanding. Electrochemistry is in general a valuable tool, as by variation of the parameters like overvoltage, current density and bath composition the structure and the size of the deposits can be influenced. Furthermore, in contrast to chemical procedures electrochemistry allows in principle to electrodeposit semiconductors on any conducting substrate. It has been shown by Stickney and coworkers [7] that electrochemical atomic layer epitaxy (ECALE) is a procedure by which compound semiconductors can be made layer by layer resulting in a quality of the deposits that is comparable to semiconductors made by the conventional physical methods. For silicon there were several approaches in the past to

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electrodeposit it in organic solvents [8–10], but the authors report about a disturbing effect by water that can hardly be avoided in organic solvents. Furthermore, there were studies on the electrodeposition of silicon in high temperature molten salts [11]. Recently, it was reported that silicon can also be electrodeposited in a low temperature molten salt [12]. In this study the authors employed 1-ethyl-3-methylimidazolium hexafluorosilicate and at 90 °C they could deposit a thin layer of silicon. However this film reacted with water to form SiO₂ so that the proof whether the deposited silicon species was elemental or even semiconducting is missing. It has been shown by us that ionic liquids are well suited for the electrodeposition of nanoscale semiconductors. At the example of germanium we could show with the in situ scanning tunneling microscope (STM) and with the in situ current/voltage tunneling spectroscopy that germanium with layer thicknesses of 20 nm and more is semiconducting with a symmetric band gap of 0.7 ± 0.1 eV [13,14]. Ionic liquids are by definition ionic melts with a melting point below 100 °C [15]. During the recent 5 years there has been a remarkable progress in the synthesis of ionic liquids, and there are already several companies on the market from which these new solvents can be purchased. Especially air and water stable ionic liquids have gained a great interest in the recent years, as depending on the liquid high ionic conductivities, negligible vapour pressures and wide electrochemical windows (up to 6 V) are obtained. These properties are very important for electrochemical studies, and it has been shown that it is possible to electrodeposit nanoscale light metals and semiconductors in them [16,17]. In this short paper we present for the first time that silicon can be electrodeposited in a room temperature ionic liquid. Furthermore, we show by the help of the in situ current/voltage tunneling spectroscopy that an electrodeposited around 100 nm thick film is semiconducting with a band gap of 1.0 ± 0.2 eV.

2. Experimental

The electrodeposition of silicon was investigated in the ionic liquid 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMP]Tf₂N) which was purchased from EMD. This ionic liquid is a good compromise between wide electrochemical window and acceptable viscosity of about 0.1 Pa s. The liquid was dried under vacuum over night at an elevated temperature to water contents below 3 ppm (by Karl–Fischer titration) and stored in an argon filled glove box with water and oxygen below 1 ppm (OMNI-LAB from Vacuum-Atmospheres). The ionic liquid was saturated with SiCl₄ (99.999%), which gives a concentration of about 1 mol/l. The working electrode was highly oriented pyrolytic graphite (HOPG) which was freshly

cleaved prior to use. Pt-wires were used as reference and counter electrodes, respectively. The electrochemical cell was made of polytetrafluoroethylene (Teflon) and clamped over a Teflon covered Viton o-ring onto the substrate, thus yielding a geometric surface area of 0.3 cm². All parts in contact with the solution were thoroughly cleaned in a mixture of 50/50 vol% H₂SO₄/H₂O₂ followed by refluxing in pyrogene free water (aqua destillata ad iniectionem) prior to use. The Pt electrodes were cleaned in a hydrogen diffusion flame before use. The electrode potential of the Pt-quasi reference was calibrated in several experiments vs. ferrocene/ferrocinium and it revealed sufficient stability during the experiments. The STM experiments were performed with in house built STM heads and scanners under inert gas conditions (H₂O and O₂ <1 ppm) with a Molecular Imaging Pico Scan 2500 STM controller in feedback mode. The STM experiments were performed in an air conditioned laboratory with $\Delta T < \pm 1$ °C. Usually the approach is done over night so that during the STM measurement a thermal equilibrium is obtained giving rise to a minimum of thermal drift. The electrochemical data were acquired with a PARSTAT 2263 potentiostat/galvanostat controlled by a PowerCV software. STM tips were prepared by electrochemical etching of tungsten wires (0.25 mm diameter) and electrophoretically coated with an electropaint from BASF (see e.g. [13,14]). During the STM experiments the electrode potential was controlled by the PicoStat from Molecular Imaging, and a liquid without ferrocene was used to exclude any side reaction with SiCl₄. For the current/voltage tunneling spectroscopy the tip was positioned on the site of interest and the tip voltage was varied between an upper and a lower limit. During this procedure the feedback is switched off by the software. The band gap of the silicon was determined from the dI/dU vs. U plot. In order to get a further insight into the deposit an SEM and EDX analysis were performed. For this purpose the ionic liquid with the silicon halide was replaced in the glove box by the pure liquid under potential control, the sample was washed with isopropanol and finally dried under vacuum. For the SEM and EDX measurements a high resolution field emission scanning electron microscope (Carl Zeiss DSM 982 Gemini) was utilized.

3. Results and discussion

Fig. 1 shows the cyclic voltammogram of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide on HOPG with the ferrocene/ferrocinium couple (curve 1) and with SiCl₄, without ferrocene, (curve 2). The liquid itself exhibits an electrochemical window of 4 V on HOPG. At the cathodic limit the irreversible reduction of the organic cation sets in which gives rise to a less defined deposit that can hardly be probed with the STM.

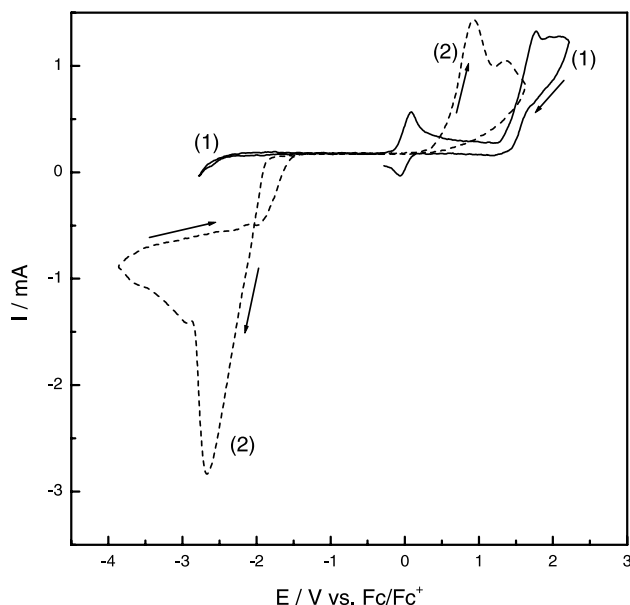


Fig. 1. Electrochemical window of [BMP]Tf₂N on HOPG with the ferrocene/ferrocinium couple. (2) Cyclic voltammogram of SiCl₄ saturated in the same ionic liquid. Scan rate each: 10 mV/s.

At the anodic limit a degradation of the HOPG surface occurs which starts at the steps of the basal planes finally leading to a hole formation in the surface. If the electrode potential is held for a sufficiently long time at 1700 mV and more vs. ferrocene/ferrocinium (Fc/Fc⁺) a massive degradation of HOPG is observed, making an STM probing almost impossible.

If the SiCl₄ saturated ionic liquid is investigated, a strong reduction current sets in at an electrode potential which is 600 mV positive from the cathodic decomposition limit of the liquid. The peak currents vary linearly with the square root of the scan rate indicating mainly diffusion control. After having passed the lower switching potential the anodic scan crosses the cathodic one at -2000 mV vs. Fc/Fc⁺ which is typical for nucleation, especially as the current passes zero in the anodic scan at an electrode potential which is more positive than in the cathodic scan. Approaching an electrode potential of +400 mV vs. Fc/Fc⁺ a strong oxidation current starts which is in part correlated to the SiCl₄ reduction process beginning at -1600 mV vs. Fc/Fc⁺ and in part correlated to HOPG oxidation as with SiCl₄ in the liquid a similar oxidation behaviour is observed if the scan is started towards positive potentials. Furthermore, a certain coevolution of chlorine cannot be excluded. As we also observed in other experiments the HOPG degradation seems to be favoured in the presence of halide. It shall be mentioned here that the irreversible reduction of the organic cation in the SiCl₄ containing liquid seems to be somewhat hindered. In some experiments we saw a second peak for the reduction of the cation at about -3000 mV vs. Fc/Fc⁺ (similar

to solvent decomposition on germanium in [18]), in some experiments we did not see a further peak at all or only a shoulder as here. Visual inspection of the surface upon passing the cathodic peak in the SiCl₄ containing liquid showed on gold and on platinum a black deposit, on HOPG it was only observed that the shining surface became mat when passing the reduction peak. As obviously an electrodeposition occurred we investigated the covered sample by high-resolution scanning electron microscopy, furthermore we performed an elemental analysis by electron dispersive X-ray scattering. As the deposit was only loosely adhering to the HOPG surface (obviously upon rinsing with isopropanole the deposit was washed away) we performed the deposition on a gold surface under comparable conditions, washed it under potential control with the pure ionic liquid and rinsed it in isopropanole prior to drying under vacuum. Fig. 2 shows a high-resolution SEM picture of that deposit. We find small crystallites with sizes between 50 and 200 nm, the layer itself has a thickness of a few hundred nanometers which was determined from several SEM pictures. It is worthy to mention that the deposit kept its dark appearance even under air. The EDX analysis gave as result only gold from the substrate and silicon, but no detectable chlorine (see Table 1). This proves that obviously elemental silicon was electrodeposited. However, a certain amount of chloride should be expected as electrodeposited silicon has, as germa-

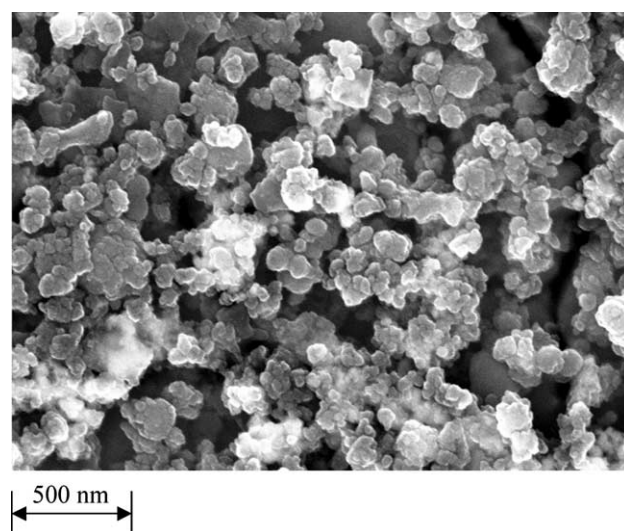


Fig. 2. SEM micrograph of electrodeposited silicon, made potentiostatically at -2700 mV vs. Fc/Fc⁺.

Table 1
EDX analysis of the surface of gold substrate after Si electrodeposition

Element	Weight %	Atomic %	Error %
Si	9.81	43.33	0.31
Au	90.68	56.67	4.87

nium [13,14], to be saturated at the surface. Most likely during ex situ handling this chloride was replaced. In order to get a further insight into the properties of the deposit we performed studies with the in situ STM. It was already shown by us that the STM is a valuable tool for the in situ characterization of electrodeposited semiconductors. In the case of germanium we could show that in an ionic liquid elemental germanium can be obtained which has at room temperature a band gap of 0.7 ± 0.1 eV for thicknesses of 20 nm and more [13,14]. Fig. 3(a) shows the STM picture of an about 100 nm thick silicon layer that was electrodeposited at -1600 mV vs. Fc/Fc^+ , probed under potential control with the in situ STM. The thickness of the deposit was determined in situ from the z-position of the piezo which is a good measure if thermal drift is minimal, as in our experiments. Its surface is smooth on the nanometer scale and its topography is similar to that one of a germanium layer of comparable thickness [13]. Fig. 3(b) shows an in situ current/voltage tunneling spectrum of HOPG (curve 1) and of the 100 nm thick silicon layer (curve 2). The spectra are all over the surface of the same quality. Whereas the tunneling spectrum of HOPG is – as expected – metallic, for the silicon deposit a typical band gap is observed. An evaluation of the band gap as mentioned in Section 2 gives a value of 1.0 ± 0.2 eV. This value is quite similar to the value that we observed

for hydrogen terminated n-doped Si(111) in an ionic liquid [19]. The value of microcrystalline silicon in the bulk phase at room temperature is 1.1 eV. In the light of these results we can conclude that elemental, intrinsic semiconducting silicon was electrodeposited from the employed ionic liquid. These results show how important ionic liquids are for the nanoscale electrodeposition of semiconductors, especially of those ones that cannot be electrodeposited in aqueous solutions like Si, Ge, GaAs and other ones. A detailed in situ STM study of silicon electrodeposition on different substrates is currently under progress in our laboratory.

4. Conclusion

We have shown in this short paper for the first time that silicon can be electrodeposited in the room temperature ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, due to its wide electrochemical window. SEM and EDX show that nanoscale silicon is obtained and that no chlorine is found in the deposit. In situ current/voltage tunneling spectroscopy reveals at room temperature a symmetrical band gap of 1.0 ± 0.2 eV which is typical for intrinsic elemental semiconducting silicon.

Acknowledgements

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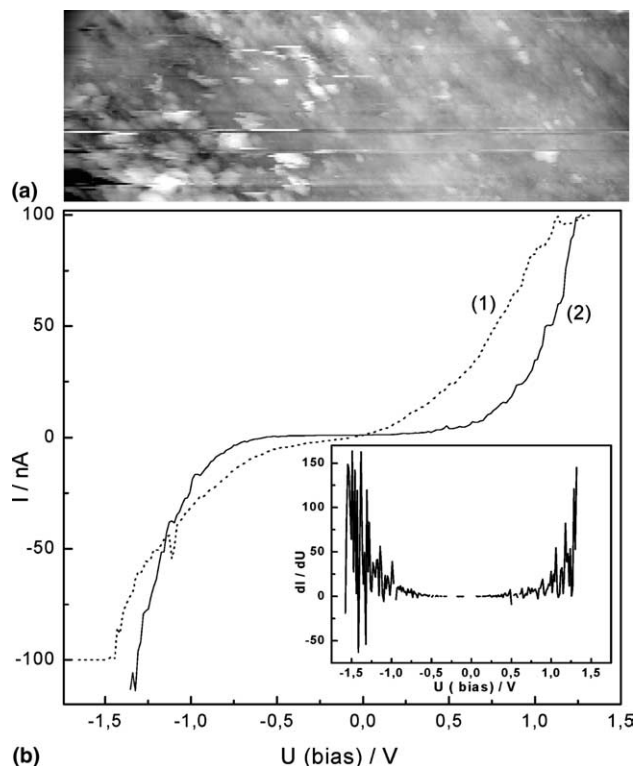


Fig. 3. In situ STM picture of an about 100 nm thick film (a) ($600 \text{ nm} \times 200 \text{ nm}$), in situ current/voltage tunneling spectra of HOPG (curve 1) and of the silicon electrodeposit (curve 2) on HOPG.

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