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Evidence for an influence of anodic decomposition products of ionic liquids on the electrodeposition of Si_xGe_{1-x} semiconductor

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ABSTRACT

For the purpose of obtaining micrometer thick Si_xGe_{1-x} deposits, quite a long electrodeposition time was applied in ionic liquids containing $GeCl_4$ and $SiCl_4$. Surprisingly, it was observed that the deposit is dissolved with ongoing time, at room temperature, instead of getting thicker at a sufficiently negative electrode potential. The dissolution process was only observed in liquids with the bis(trifluoromethylsulfonyl)amide (TFSA) anion and not in liquids with the tris(pentafluoroethyl)trifluorophosphate (FAP) anion. Electrochemical and chemical experiments showed that the TFSA anion is subject to an anodic decomposition obviously promoted by the solutes $SiCl_4$ and $GeCl_4$. The decomposition products of the TFSA anion seem to oxidize the Si_xGe_{1-x} deposit chemically. These results, among others, show that the often reported superior chemical and electrochemical stability of some ionic liquids has to be handled with care: the stability limits can be significantly altered by e.g. the type of dissolved species.

1. Introduction

The electrochemical stability of pure ionic liquids is one of the key factors that make them promising solvents for electrodeposition processes and for batteries [1–5]. This has been proven by the amount of publications on the successful electrochemical deposition of several materials like metals and semiconductors from ionic liquids, which can otherwise not be deposited from aqueous solutions [1]. However, most of the published work focuses on the applications and the potential of ionic liquids in this field and little is known about the exact electrochemical behavior of them both at the cathode and the anode and how the solutes (electroactive species) exist in them. Moreover, it is not clear if these solutes can affect the electrochemical stability of ionic liquids, especially with time, or not.

A few studies showed that liquids with the bis(trifluoromethylsulfonyl)amide (TFSA) can decompose under cathodic conditions [6–9]. According to these studies, the TFSA anion is subject to cathodic decomposition especially in the presence of water [8,9]. Recently, it was reported by our group that the TFSA anion is surprisingly easily decomposed during the anodic dissolution of copper at 70 °C in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide [10]. The decomposition leads to a quantitative formation of CuF_2 in the reaction solution. The decomposition mechanism itself is not clear, but the formation of CuF_2 clearly shows that the TFSA anion (the only source of fluorine) is subject to an unexpected decomposition liberating F^- ions.

The present paper further supports these results by showing that the TFSA anion is decomposed even at room temperature during the electrodeposition of Si_xGe_{1-x} from different ionic liquids with the TFSA anion containing the solutes $SiCl_4$ and $GeCl_4$.

2. Experimental

The ionic liquids 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[Py_{1,4}]$TFSA), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]TFSA), 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide ([EMMIm]TFSA) and 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ($[Py_{1,4}]$FAP) were purchased in the highest available quality from Io-Li-Tec and Merck KGaA and used after drying under vacuum at 100 °C to water contents of below 2 ppm. $GeCl_4$ (99.9999%) and $SiCl_4$ (99.998%) were purchased from Alfa Aesar. The working electrode was Au (gold on glass), purchased from Arrandee™. In order to minimize possible surface contaminations, the substrate was carefully heated in a hydrogen flame prior to use. An Ag wire was used as a quasi-reference electrode, which gave in this work under the applied conditions a sufficiently stable electrode potential. A Pt-ring was used as a counter electrode. The electrochemical cell was made of Teflon and clamped over a Teflon-covered Viton O-ring onto the substrate yielding a geometric surface area of 0.3 cm^2. In order to avoid any contaminations, the Teflon cell and the O-ring were cleaned before use in a mixture of 50:50 vol.% of concentrated H_2SO_4 and H_2O_2 (35%) followed by refluxing in distilled water. A two-compartment electrochemical cell with a salt bridge filled with the ionic

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liquid was used, too, to separate the electrochemical reactions at the anode from the cathode compartment.

All electrochemical measurements were performed in an argon-filled glove box with water and oxygen contents of below 1 ppm (OMNI–LAB from Vacuum-Atmospheres) by using a VersaStat™ II (Princeton Applied Research) potentiostat/galvanostat controlled by powerCV software.

3. Results and discussion

The original aim of this work was to deposit ~10–20 μm thick Si_xGe_{1-x} films and to investigate the effect of different ionic liquids on the deposition process (deposit thickness, composition and morphology). In order to make deposits with such a thickness deposition times in the hours regime were applied. Surprisingly, it was observed that Si_xGe_{1-x} does not get thicker with time, in contrast it even dissolves with a long deposition time. This quite unexpected and interesting result raised our interest for this fundamental observation. For more information on the electrochemical behavior of $SiCl_4$ and/or $GeCl_4$ in ionic liquids, we refer to references [11,12].

Si_xGe_{1-x} was deposited on the Au electrode from the ionic liquid $[Py_{1,4}]$TFSA containing 0.1 M $SiCl_4$ and 0.1 M $GeCl_4$ by applying a potential of −2.9 V vs the Ag quasi reference electrode. It was confirmed in several experiments that the silver quasi reference electrode was quite stable. Thus, the effects described in this paper are not due to a shift in the reference electrode potential. After about 3 h of applying this potential, it was observed that in some areas the gold surface of the Si_xGe_{1-x}-covered gold electrode (Fig. 1) gets visible and becoming more significant within 5 h. Finally the deposit completely disappeared although a sufficiently cathodic electrode potential was applied which should ensure Si_xGe_{1-x} deposition. We observed that $GeCl_4$ can chemically oxidize the Si_xGe_{1-x} deposit. However, we can exclude this assumption as the applied potential is sufficiently negative to ensure the depletion of $GeCl_4$ and even $SiCl_4$ in the solution. In addition, the adhesion of Si_xGe_{1-x} on the gold surface is quite good. We have to assure that the ionic liquid itself leads to the dissolution. The question arises if the cation or the anion of the ionic liquid is responsible.

In order to answer this question, we utilized different ionic liquids with different cations and anions: first, we repeated the same experiment with [EMIm]TFSA. During the first 10–20 min of applying a potential of −1.9 V vs. Ag (due to thermodynamic reasons, Si_xGe_{1-x} deposition in [EMIm]TFSA occurs at less negative potentials than in $[Py_{1,4}]$TFSA, see references [11] and [12]), a Si_xGe_{1-x} deposit formed which was thicker than that from $[Py_{1,4}]$TFSA, after the same time. This is due to the viscosity difference of both liquids as we mentioned in a previous study [12]: the viscosity of [EMIm]TFSA is 27 mPa.s, while it is 60 mPa.s for $[Py_{1,4}]$TFSA [13]. But, after just 1 h the gold surface is recovered as shown in Fig. 2. Thus, the Si_xGe_{1-x} dissolution in [EMIm]TFSA is considerably faster than in $[Py_{1,4}]$TFSA. The enhanced dissolution might be attributed to either a chemical or a physical effect of the [EMIm] cation, or even both. From a chemical point of view, this cation has an acidic proton on the c2-position of the imidazolium ring. It was proposed that the reductive decomposition of the imidazolium cation proceeds initially via the reduction of ring protons, especially on the c2-position, to molecular hydrogen [14,15]. An enhanced cathodic stability of this cation was reported by capping the c2-position with an alkyl group like e.g. CH_3 [14]. Consequently, we used 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl) amide ([EMMIm]TFSA) for our experiment, which contains a CH_3 group instead of a proton on the c2-position. There was no significant difference in the dissolution rate as shown in Fig. 3. Therefore it is likely that the lower viscosity of [EMIm]TFSA (a physical participation) is responsible for the enhanced dissolution rate since a lower viscosity ensures a higher diffusion rate of the attacking species on the deposit. In addition, we cannot exclude a possible effect of interfacial layers of ionic liquids which are strongly dependent on the structure of the ions [16].

On the other hand, these experiments gave us hints that the TFSA anion seems to be responsible for the dissolution process. To confirm this assumption, the ionic liquid 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ($[Py_{1,4}]$FAP) was used for the deposition process. The electrochemical behavior of $SiCl_4$ and $GeCl_4$ in this liquid is presented in the cyclic voltammogram in Fig. 4: it is quite similar to that in the previous ionic liquids [11,12] but there are some reduction peaks in the back scan which are attributed to further deposition of Si and/or Si_xGe_{1-x}. However, for unknown reasons these reduction peaks do not always appear in the same manner and sometimes do not appear at all. For the deposition of Si_xGe_{1-x} from $[Py_{1,4}]$FAP, it was observed that after applying the same potential (−2.9 V) for even more than 20 h, the deposit does not dissolve as shown in Fig. 5. This leads to the conclusion that indeed the TFSA anion must be responsible for the dissolution of the deposit. But, does it dissolve chemically or electrochemically (through a decomposition reaction)? And, if electrochemically, does the TFSA anion decompose at the cathode or at the anode? To answer these questions the following experiments were performed: a thin film (roughly 0.5 μm) of Si_xGe_{1-x} was deposited from an equimolar solution (0.1 M) of $SiCl_4$ and $GeCl_4$ in [EMIm]TFSA (deposition potential is −1.9 V, deposition time is ~5 min), then the deposit was rinsed with pure [EMIm]TFSA for several times (inside the glove box) to remove traces of $SiCl_4$ and $GeCl_4$ and finally immersed in the pure liquid. No dissolution of the

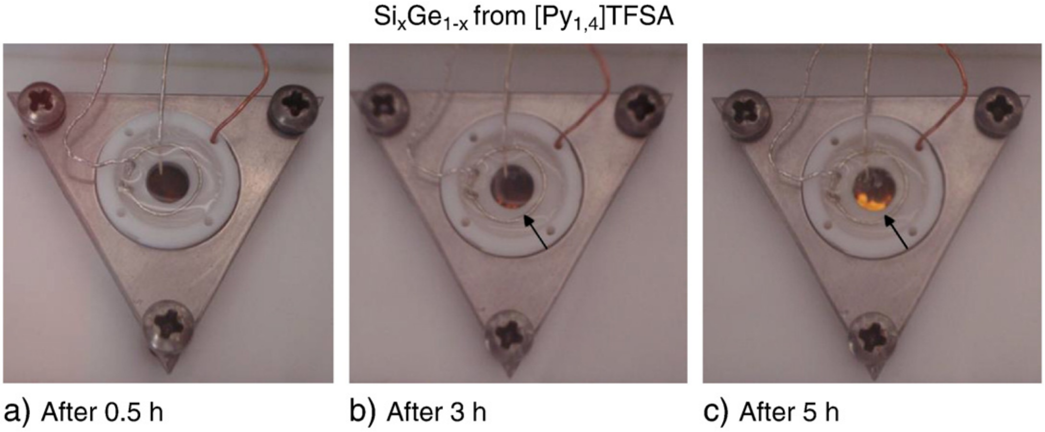

Fig. 1. Photographs of the electrochemical cell (inside the glove box) showing the Si_xGe_{1-x} deposit on Au substrate and its dissolution (see arrows) during applying the Si_xGe_{1-x} deposition potential of −2.9 V at 25 °C for: a) 0.5 h, b) 3 h, and c) 5 h. The reaction solution is $SiCl_4$:$GeCl_4$ (1:1 molar ratio) in $[Py_{1,4}]$TFSA.