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Role of electrochemical process parameters on the electrodeposition of silicon from 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid

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ABSTRACT

The electrodeposition from Room Temperature Ionic Liquids (RTILs) has recently emerged as a low cost technique for the growth of group IV thin films or nanostructures giving some promising alternative to classical physical vapour or chemical vapour deposition techniques. As a relatively new field of research, only few studies exist describing the growth mechanism of electrodeposition from RTILs, especially for Si films. In the present work, Cyclic Voltammetry (CV), Electrochemical Quartz Crystal Microbalance (EQCM) and potentiostatic electrodeposition techniques have been used to study the role of the applied potential, the concentration of electroactive species, the temperature, and the use of organic additive on the electrodeposition of Si from 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid. The demonstrated investigation of the influence of these parameters on the purity and morphological features gives a better control over the growth of Si thin films and optimizes the technique to grow Si with structural properties suitable for specific applications.

1. Introduction

Silicon is one of the most important semiconductor materials used in various applications such as photovoltaic devices [1,2], batteries [3–5], biosensors [6–8] and other semiconductor devices [9,10]. Amorphous Si (a-Si) thin films are of great importance in different fields such as photovoltaics [11], Si based light emitters [12,13] and energy storage [14]. a-Si could be synthesized by different methods; gas-discharge by using high-temperature silane gas [15,16], chemical-vapour deposition [15,16], hot-wire deposition [17–19] and other physical-related techniques [12,20,21]. However, these techniques are mostly expensive and involve rigorous reaction conditions such as high temperature and high vacuum and the use of potentially dangerous gases such as silane. In order to overcome these difficulties, electrodeposition was proposed as a low cost and simple alternative for the synthesis of Si at ambient conditions. However, due to the limited electrochemical window of water and to the high reactivity of Si precursors with water, the electrodeposition of Si in aqueous electrolytes is limited.

In recent years, the electrodeposition of Si has been achieved using different non-aqueous electrolytic media such as molten salts [22–25], organic solvents [26–29] and ionic liquids [30–32]. Among these different solvents, deposition using ionic liquids is of particular interest because of their superior features in terms of electrochemical applications compared to other systems. RTILs generally have wide electrochemical windows which give them high electrochemical stability even under strongly reducing conditions, they are inherently conducting with negligible volatility and possess high thermal stability. Compared to molten salts, they do not require working at high temperature and compared to organic solvents, RTILs are also promising as a "greener" chemistry as some of them are already recyclable. Since the first report by Abedin et al. [30] on the electrodeposition of Si using 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid, researchers including our group have shown the successful deposition of pure Si or its alloys in the form of thin films or nanostructures using different ionic liquids [22,33–35]. In some of these studies, efforts have been made using STM [36] or EQCM [37] to obtain the in-situ characterizations of the Si deposits during the growth. However, because of the complex nature of the electrolytic

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medium, the relationship between the structural features and the electrochemical deposition parameters has not been extensively studied yet, which is of prime importance for the applications of such films. While in the aqueous electrolytic medium, the correlation between the electrochemical parameters and the structure of the deposits is already well understood, the complexity of RTILs based electrolytes induces differences in the growth process and makes it difficult to obtain such correlations. Therefore, a deeper understanding of the electrochemical mechanism and growth processes are absolutely necessary at this stage to characterize the Si thin films, in terms of purity, structure, morphology and homogeneity.

This study investigates the impact of three electrochemical process parameters, the applied potential, the concentration of electroactive species, and the temperature on the electrodeposition of Si in a specific RTIL, the 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, which has been proven in the literature to give pure Si deposits. Additionally, the role of acetonitrile as an additive on the electrodeposition of Si is also studied. The interest of the study is to provide a better understanding of the Si electrodeposition process in RTILs and to improve the material characteristics to optimize the growth of Si thin films for specific requirements.

2. Experimental

For the present study, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Py_{1,4}$[TFSI]) ionic liquid purchased from Solvionic was used as the solvent for electrodeposition. The purity of $Py_{1,4}$[TFSI] given by the suppliers is 99.99%. In order to reduce the water content, the ionic liquid was dried under vacuum at 110 °C for a minimum of 4 days. The drying of the ionic liquids was performed in an argon filled glove-box (Innovative Technology) with oxygen and moisture content below 1 ppm. Silicon tetrachloride (99.998%) purchased from Sigma Aldrich was used as the precursor for silicon. Anhydrous acetonitrile (99.98%) purchased from Sigma Aldrich was used as an additive.

All the electrochemical experiments were performed inside the argon filled glove-box using a three electrode based electrochemical cell. All the parts of the cell in contact with the electrolyte were thoroughly cleaned with Piranha solution (1:1 vol mixture of H_2O_2 and H_2SO_4) followed by washing with distilled water. Gold (Au) coated silicon (100) substrate was used as the working electrode for the deposition. Prior to use, the substrates were rinsed in acetone and then in ethanol in an ultrasonic bath for 10 min in order to reduce the surface contaminations. Platinum wire was used as the quasi-reference electrode which provides relatively stable electrode potentials for the present studies. A platinum wire was used as the counter electrode. Both the reference and counter electrodes were cleaned by rinsing in ethanol in an ultrasonic bath followed by refluxing in distilled water. The dried electrodes were then cleaned in a hydrogen flame to remove any organic impurities. After the electrodeposition, the substrates were cleaned by immersing in absolute ethanol solvent with multiple cycles of solvent changing, followed by rinsing with de-ionised water and dried before using the material for any characterizations.

All the electrochemical measurements were performed using a Voltalab PGZ 100 potentiostat/galvanostat controlled by Voltamaster 4 software. All the potential values cited in this article are measured with reference to the Pt quasi-reference electrode, unless specified. The heating of the electrolyte solution was achieved by using a Peltier system coupled with a Pt temperature sensor. The EQCM (Seiko EG&G QCA 922) system used 9 MHz AT-cut quartz crystal (0.2 cm^2) with Au coatings. The surface morphology of the deposited thin film was obtained by a Field Emission Scanning Electron Microscopy (FE-SEM Hitachi S-3400 N, or Leo Gemini). The chemical composition of the deposits was obtained by the Energy-Dispersive X-ray (EDX) spectroscopy coupled to the SEM. Analysis of the chemical composition was also performed by Secondary Ion Mass Spectroscopy (SIMS, Cameca IMS 7f). Raman spectroscopic (Jobin Yvon T64000) measurements were carried out to study the crystallinity of the deposits. Atomic force Microscopy (AFM) experiments were performed in tapping mode using a multimode V AFM from Brüker.

3. Results and discussion

Electrodeposition of Si requires the use of a solvent having a wide electrochemical window, as large as 5 V–6 V. To satisfy this requirement, the $Py_{1,4}$[TFSI] RTIL has been chosen for the present study as it is known to enable the deposition of Si [30]. Its theoretical electrochemical window is about *ca.* 6 V and its viscosity at room temperature is 78 cP. The CV of pure and dry $Py_{1,4}$[TFSI] ionic liquid is shown in Fig. 1 (Dashed red curve). The experimental electrochemical window of $Py_{1,4}$[TFSI] in our experimental conditions is estimated to be 5.5 V, and the cathodic reduction of $(Py_{1,4})^+$ cation starts at a potential of −3.2 V. The absence of any current on the forward or back scan (till the cathodic and anodic limits) demonstrates the lack of any electrochemically active impurities in the whole electrochemical window of the RTIL.

As inferred from our previous experiments and literature, a concentration of 0.1 M $SiCl_4$ for the precursor and a temperature of 50 °C for the deposition were chosen as reference parameters for Si deposition. The CV of 0.1 M $SiCl_4$ precursor in $Py_{1,4}$[TFSI] is displayed in Fig. 1 (black curve). The CV has been obtained at 50 °C at a sweep rate of 10 mV s^{-1}. On the CV, one peak (**C_1**) is observed around -1 V and two other peaks (**C_2** and **C_3**) appear in the range −2.0 V to −3.0 V on the forward scan. **C_1** is attributed to the reconstruction of the Au surface as it has already been observed [36]. This peak effectively disappears when the Au substrate is replaced by other substrates such as a highly doped silicon surface (cf. inset Fig. 1), confirming the correlation between the existence of **C_1** and the Au substrate. By polarizing the working electrode in the whole range from −2.0 V to −3.5 V, Si electrodeposition can be achieved. Therefore, both peaks **C_2** and **C_3** have been attributed to

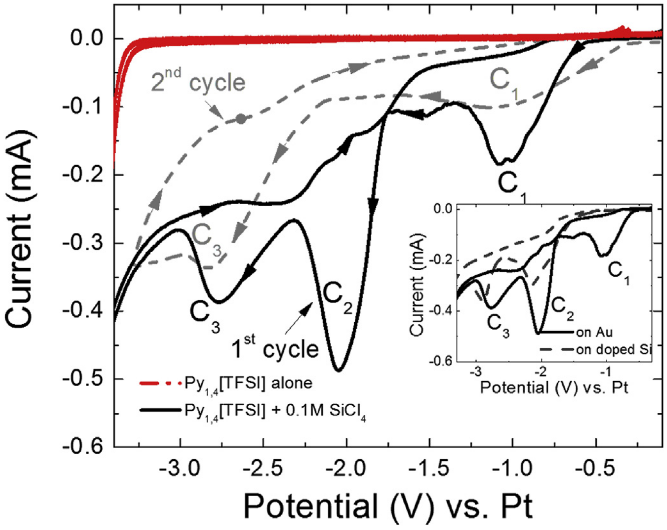

Fig. 1. Cyclic voltammograms of pure and dry $Py_{1,4}$[TFSI] and 0.1 M $SiCl_4$ in $Py_{1,4}$[TFSI] recorded on Au substrate at 50 °C with a scan rate of 10 mV s^{-1}. The inset displays a comparison of cyclic voltammograms of 0.1 M $SiCl_4$ in $Py_{1,4}$[TFSI] recorded at 50 °C with a scan rate of 10 mV s^{-1} on Au substrate and on highly doped Si substrate.