Int. J. Electrochem. Sci., 13 (**2018**) 8766 – 8774, doi: 10.20964/2018.09.51

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Preparation and Characterization of Electrochemically Deposited Silicon Films in Ionic Liquid from Polysilicon Byproduct $SiCl_4$

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Received: 12 May 2018 / *Accepted:* 2 July 2018 / *Published:* 5 August 2018

Silicon films were electrodeposited on a titanium plate by using a three-electrode system in a $SiCl_4$-based ionic liquid electrolyte ([BMIM]Tf_2N) under potentiostatic electrolysis conditions avoiding high temperature and a complex operation process. The microstructure of the deposited Si films was studied by Raman spectroscopy for varying deposition temperatures (room temperature, 35°C, 45°C, and 55°C) and electrolyte mass ratios ([BMIM]Tf_2N: propylene carbonate[PC]=1:1, 1:2, 1:3, 1:4). Raman spectra confirmed that the deposited Si films were in an amorphous state. The surface topography was studied by scanning electron microscopy (SEM). Results from Raman spectroscopy and SEM showed that films deposited at room temperature with a mass ratio of 1:3 show the best microstructure and surface topography. Energy dispersive X-ray spectroscopy was used to measure the Si elemental content. The optical and electrical properties of the as-deposited Si films were also investigated by varying the deposition time from 1h to 4h for an electrolyte mass ratio of 1:3 at room temperature. The results indicated that the films exhibit a relatively strong photoluminescence peak at a wavelength of approximately 1135nm and that the current-voltage curves for the Si/Ti junction show an evident rectifying behavior for a deposition time of 1h, which indicates that the deposited Si films have good electrical conductivity.

Keywords: $SiCl_4$, Electrochemical deposition, Ionic liquid, Photoluminescence, Electrical conductivity

1. INTRODUCTION

$SiCl_4$ is a main byproduct of polysilicon industries that can cause several environmental problems and harm human health [1]. An economic and environmentally safe technology needs to be

developed to utilize $SiCl_4$. Generally, two main approaches can be adopted when recycling $SiCl_4$. One approach is to use $SiCl_4$ as a raw material to produce chemicals, such as white carbon black, silicate ester, optical fiber, and organic Si [2]. Another approach is to directly convert $SiCl_4$ to $SiHCl_3$ [3, 4].

Electrochemical deposition of Si cannot be completed in aqueous solution because of the low electrochemical stability of water and low stability of Si halide sources in aqueous medium. Si can be well prepared from moisture-free organic solvents, such as tetrahydrofuran (THF) and acetonitrile [5]. However, these solvents are volatile and restrict the temperature window of the electrolyte. In addition, propylene carbonate organic solvent can be used as an electrolyte to deposit Si films, but the deposits contain impurities such as oxygen and chlorine [6, 7]. Given that non-aqueous electrolytes generally show poor conductivity, supporting electrolytes, which comprise salts or non-reactive ionic species, are generally added to improve ionic conductivity and maintain uniform current density. The most common supporting electrolytes used for electrochemical deposition of Si are based on tetraalkylammonium salts, such as tetramethylammonium chloride and tetraethylammonium chloride [8].

Ionic liquids are alternative solvents with wide electrochemical windows and low vapor pressures. Several studies of Si electrodeposition from $SiCl_4$ dissolved in ionic liquids have been conducted [9, 10]. Endres [11] was the first to report that Si can be well electrodeposited on the nanoscale at room temperature using the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide saturated with $SiCl_4$. Maldonad [12] found that crystalline Si was produced at low temperature by an electrochemical liquid–liquid–solid process in which an electrolyte system dissolved the $SiCl_4$. S. Zhang [13] reported an efficient method for preparing crystalline Si from $SiCl_4$ at a low temperature of 100 °C with an ionic liquid $[N_{4441}]$TFSI as the electrolyte. However, these previous studies did not illustrate the optical and electrical properties of the deposited Si film.

In the present work, thin Si films were prepared by a simple method to electro-reduce $SiCl_4$ with titanium plate as a substrate in ionic liquid at room temperature. The optical and electrical properties of the deposited Si film were studied. Photoluminescence (PL) spectra showed that the Si films can absorb infrared light, and the current-voltage (I-V) curve confirmed that the film has a good electrical property. Therefore, Si film has potential for application in devices, such as microelectronic devices and solar cells.

2. EXPERIMENT

2.1. Preparation of Si Films

$SiCl_4$ (analytical reagent) was purchased from Chengdu Aike Reagents Co., Ltd.; [BMIM]Tf_2N (1-butyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl]imide) was produced by Shanghai Cheng Jie Chemical Co., Ltd.

The electrodeposition behavior and electrochemical window of Si were investigated by using a single-chamber electrochemical cell with three electrodes. Ti plate was used as the working electrode

(99.99%, 10 mm × 10 mm × 1 mm). Pt wire (99.99%, 1 mm in diameter) was used as the counter electrode. Ag wire (99.99%, 0.5 mm in diameter) was used as the quasi-reference electrode. The working electrode (Ti plate) was first mechanically polished with 0.05 μm alumina to a mirror finish, ultrasonically washed in acetone for 10 min, immersed in ethanol for 10 min followed by deionized water, and then finally dried with a cold N_2 flow. Electrochemical measurements were performed on a CHI660 electrochemical workstation. After the experiment, the working electrode (Ti plate covered with deposit sediment) was stored in ethanol.

2.2. Measurements

The Raman spectra were obtained using an INVIA (514 nm wavelength, British Rennie Salt Company, Britain). Morphological images of the Si films were obtained by scanning electron microscopy (SEM) (Apollo 300, CamScan). The PL spectra of the Si films were acquired using laser excitation at a wavelength of 405 nm. The electrical property of Si films was confirmed by C-AFM (atomic force microscope, Dimension Edge, Bruker Corporation) in the contact mode using Pt-/Ir coated tips.

3. RESULTS AND DISCUSSION

3.1 Electrodeposition of Si films

To study the Si reduction in [BMIM]Tf_2N-PC-$SiCl_4$, a cyclic voltammogram for $SiCl_4$ reduction was performed on a Ti electrode in an electrolyte composed of [BMIM]Tf_2N with PC ([BMIM]Tf_2N:PC=1:3). The cyclic voltammetric response of $SiCl_4$ at room temperature is illustrated in Fig. 1. For the original electrolyte (Fig. 1(a)), the cyclic voltammogram showed a stable electrochemical window ranging from −3 to 3 V (vs. Ag QRE). For the saturated concentration of $SiCl_4$ in electrolyte solution, only one peak is shown in Fig. 1(b). The observed cathodic peak at -2.9 V (vs. Ag QRE) was attributed to the underpotential deposition of Si on the Ti electrode. This value is lower than that of Si on a Ti electrode in [BMIM]OTf-PC-$SiCl_4$ (-2.2V) [14], which may be attributed to the higher conductivity of [BMIM]OTf compared to [BMIM]Tf_2N [15].

Fig. 2 shows the current–time curve of the electrodeposition process with electrodeposition for 4 h. Generally, the formation and growth of Si crystals during electrodeposition can be divided into three parts [13]: fast nucleation and growth in the first 12 min (C1), crystal growth during the subsequent 2 h (C2), and an extended period of slow growth (C3), as shown in Fig. 5. In practice, the deposited Si shows lower conductivity compared to the metal electrode. As the electrodeposition process continues, the conductivity of the working electrode, which was covered with an increasing layer of cathode or anode product, will decrease, which makes the electron transfer complicated through the deposition process and prevents a continuous deposition reaction [16].

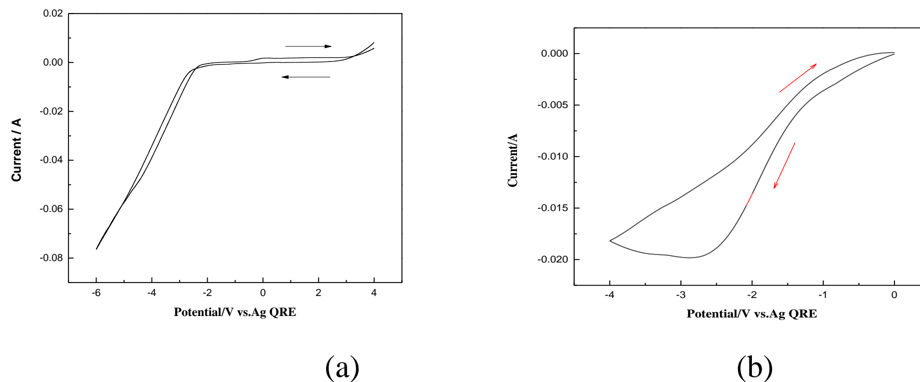


Figure 1. Cyclic voltammogram of $SiCl_4$ reduction on a Ti electrode in an electrolyte composed of [BMIM]Tf_2N with PC ([BMIM]Tf_2N:PC=1:3) at room temperature under N_2, using a scan rate of 0.05 V s^{-1} (a) Without $SiCl_4$; (b) Saturated concentration of $SiCl_4$ in electrolyte solution

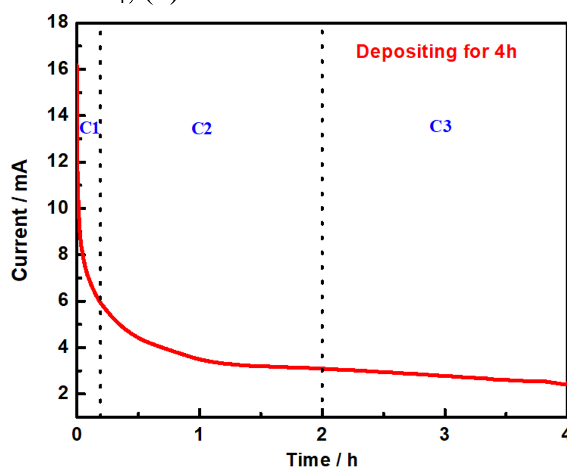


Figure 2. Current–time curve for the potentiostatic electrodeposition process at −2.9 V (vs. Ag QRE) for deposition for 4 h at room temperature.

3.2 Analysis of the microstructure, surface topography, and components of the electrodeposited Si films

Crystallographic analysis of the deposited Si was carried out by measurement of the Raman spectra, as shown in Fig. 3. Fig. 3(a) presents the Raman spectra of Si films deposited at four different temperatures (RT，35 °C，45 °C，55 °C) with the duration time of 1 h. Fig. 3(b) shows the Raman spectra of Si films prepared in electrolyte with varying electrolyte mass ratios [BMIM]TF_2N: PC = 1:1, 1:2, 1:3, 1:4）at room temperature with a duration time of 1 h. The Raman spectra of all of the specimens exhibited a broad peak at 640 cm^{-1}, which corresponds to the wagging modes of Si–H_2 and Si–H_3, indicating the presence of hydrogenated amorphous Si [17]. The weak silica peak at approximately 250 cm^{-1} was observed mainly because of surface oxidation incurred during the process of sample transfer [6]. The peak at approximately 150 cm^{-1} corresponds to the TA-like phonon mode for the a-Si or nc-Si network, which indicates formation of a Si thin film [18, 19].

As shown in Fig. 3, changing the temperature of the electrolyte and the electrolyte mass ratio has little effect on the structural properties of the electrodeposited Si film. The strongest Raman peak is found for the Si thin films prepared at room temperature with an electrolyte mass ratio [BMIM]Tf$_2$N: PC of 1:3, which indicates that the structure of the Si films prepared under these conditions is the most regular. Therefore, room temperature and an electrolyte mass ratio [BMIM]Tf$_2$N: PC of 1:3 is the most suitable for the preparation of a silicon thin film on a Ti plate using a three-electrode system in a SiCl$_4$-based ionic liquid electrolyte ([BMIM]Tf$_2$N).

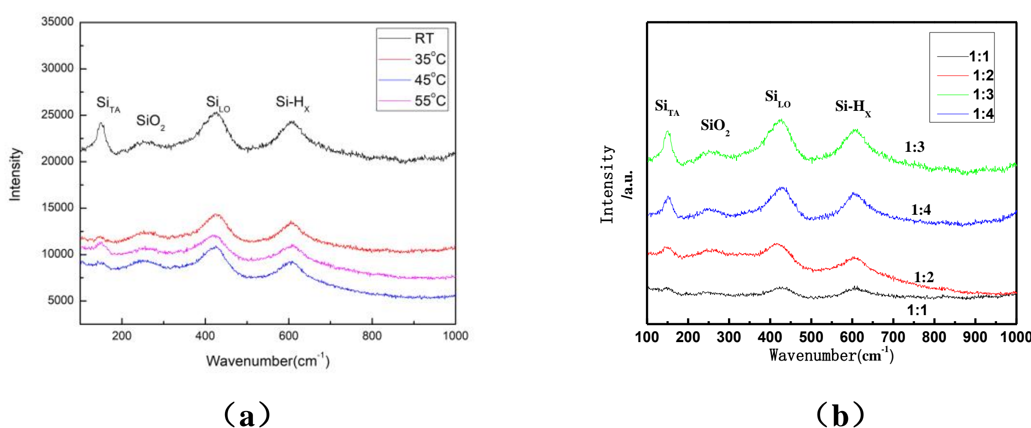
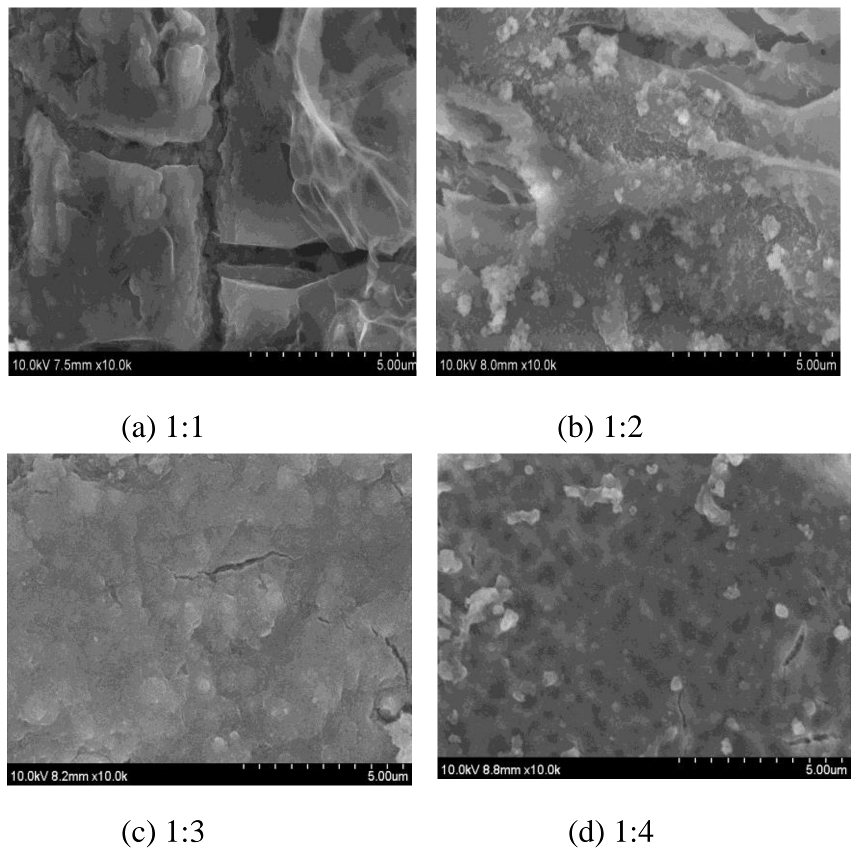


Figure 3. Raman spectra of the deposited Si films at −2.9 V (vs. Ag QRE) (a) Raman spectra of Si films prepared at different temperatures. (b) Raman spectra of Si films prepared in electrolyte with different mass ratios.

The SEM images of the deposited Si films on Ti plate at room temperature with different electrolyte mass ratios ([BMIM]Tf$_2$N: PC, (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4) are shown in Fig. 4.

SEM images show that the electrolyte mass ratio influences the morphology and quality of the deposited films. The film surface is rough and locally uniform with some large cracks observed when the electrolyte mass ratio is 1:1, as shown in Fig. 3(a). As the electrolyte mass ratio changed to 1:2, small nodes, due to the prominence of sediment where ions can discharge easily, appeared together with the cracks whose size became smaller, as shown in Fig. 3(b). As the electrolyte mass ratio changed to 1:3, the cracks on the surface became even smaller, and the Si film became denser and more uniform, as shown in Fig. 3(c). As the electron mass ratio continued to change to 1:4, several grid structures and particle accumulation appeared on the surface of the Si film, and the surface of the Si films became uneven. These results indicate that the optimal electrolyte mass ratio for deposition of a hydrogenated amorphous Si film is 1:3, which is consistent with the results of the Raman measurements.

Energy dispersive X-ray spectroscopy (EDS) was performed on the electrodeposited film with an electrolyte mass ratio [BMIM]TF$_2$N: PC of 1:3. The results are shown in Fig. 5. An analysis of the elements contained in the electrodeposited film is shown in Table 1.



(a) 1:1 (b) 1:2

(c) 1:3 (d) 1:4

Figure 4. SEM images of the Si films prepared in electrolyte with different mass ratios ([BMIM]TF_2N: PC) at room temperature (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4

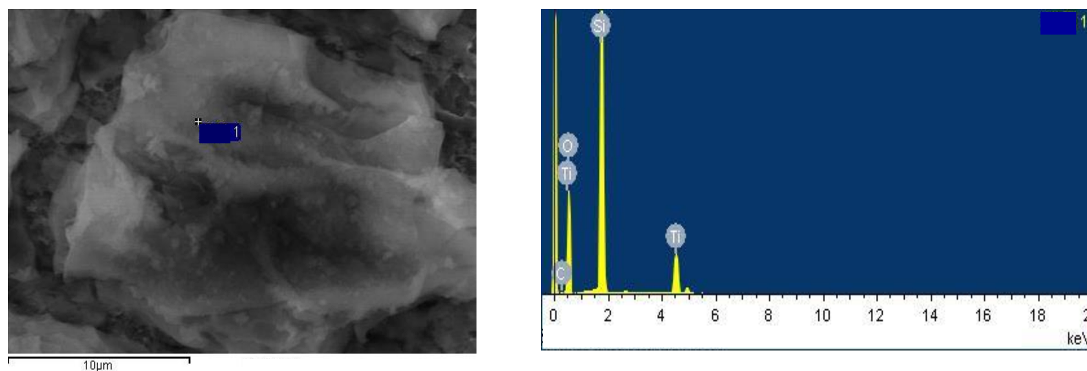


Figure 5. EDS of the electrodeposited film (mass ratio [BMIM]TF_2N: PC =1:3)

Table 1. Analysis of the elements in the electrodeposited film

Elements	Weight percentage (%)	Atom percentage (%)
C K	2.59	4.31
O K	53.91	67.38
Si K	34.46	24.53
Ti K	9.04	3.78

As shown in Fig. 5, the Si peak is stronger than the other peaks in the EDS energy spectrum, indicating that the Si elemental content is higher than that of the other elements, as shown in Table 1. This result confirmed that the product of electrodeposition is a Si film. The Ti peak is due to the substrate after the X-ray penetrated the specimen. The O element corresponds to the sample oxidation during or after deposition. The C element is attributed to impurities present in the solution.

In conclusion, the microstructure, surface topography, and purity of the deposited product show good results when an electrolyte mass ratio [BMIM]TF_2N: PC of 1:3 was used at room temperature.

3.3 Optical and electrical properties of Si films

The electro-reduction of $SiCl_4$ to Si to produce amorphous Si at the surface of a solid metal electrode has been reported in many papers [5, 7]. However, the optical and electrical properties of Si are the main characteristics that are useful for solar materials or other light-emission devices in which Si is usually required for the fabrication of a p–n junction or a cell. To demonstrate the possibility of application in solar cells or other light-emission devices, the optical property of electro-reduced Si films and the electrical properties of electro-reduced Si/Ti substrate junction were reported in this study.

The optical and the electrical properties of hydrogenated amorphous Si films of hydrogenated amorphous Si films prepared at room temperature with an electrolyte mass ratio of 1:3 were studied. The deposition time ranged from 1 h to 4 h.

The PL spectra of Si films deposited with duration times varying from 1 h to 4 h were measured at room temperature. The laser excitation wavelength was 405 nm. As shown in Fig. 6, the deposition electrolyte mass ratio was 1:3. All of the spectra exhibit a broad emission band ranging from 900 to 1400 nm, which can be attributed to the superposition of two absorption components: Si and SiO_2. The light-emission peak at approximately 1150 nm is due to the concentration of Si atoms and neutral oxygen vacancies [20]. When the deposition time is 1 h, the PL peak of the Si film is strongest. These results indicate that the electrodeposited Si films have a typical infrared absorption ranging from 900 to 1,400 cm^{-1}, which indicates potential application of this Si film in infrared light emission devices and solar cells.

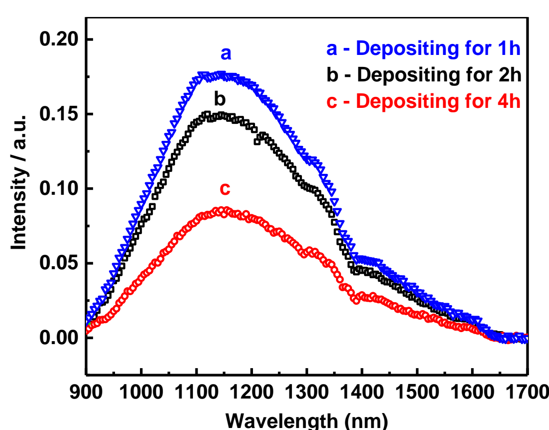
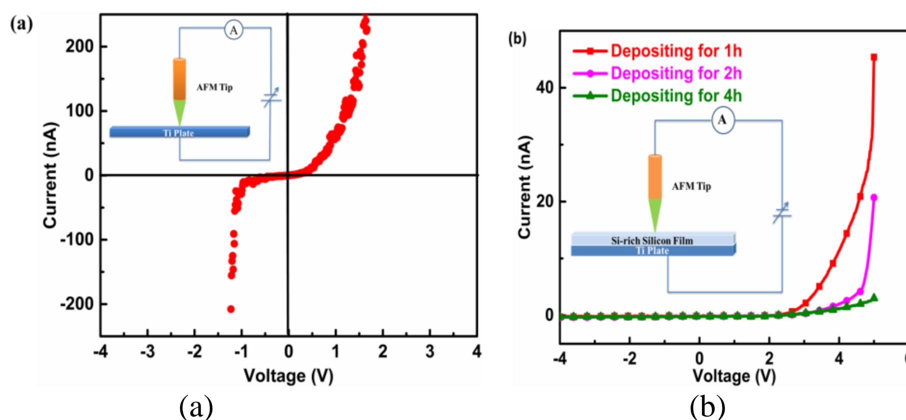


Figure 6. PL spectra of silicon films at different deposition times

The electrical properties of the Si films were measured by using C-AFM test mode, as shown in Fig. 7. The I-V curve was obtained by applying a bias directly to the sample with the AFM tip to avoid the tunneling effect between the AFM tip and the silicon film. Fig. 7(a) shows the I–V curve obtained for direct AFM tip contact on the Ti plate. The inset diagram presents a schematic of the AFM tip/Ti I–V testing. Fig. 7(b) shows the I-V curves for AFM tip contact on Si films deposited on Ti plate, which forms a Si/Ti junction. The inset diagram shows a schematic for the AFM tip/silicon film/Ti I-V testing.



(a) (b)

Figure 7. (a) Measured I-V curve for direct AFM tip contact on a titanium plate. (b) I-V curves obtained for the AFM tip on the Si/Ti junction with Si film deposition times of 1, 2, and 4 h.

When the AFM tip coated with Pt directly contacts the Ti substrate, the Ti/AFM tip contact is an ohmic contact. The I-V curve in Fig. 7(a) shows that the current and voltage maintain a linear relationship in the interval of −0.6 V to 0.6 V. However, when the voltage is greater than 0.6 V, the AFM tip/Ti plate contact breaks down, and the current increases sharply. The I-V curves of the AFM tip on the Si/Ti junction exhibit a rectifying behavior, as shown in Fig. 7(b). With increasing applied voltage, the current also increases, which suggests good electrical conductivity of the deposited Si/Ti junction. I–V curves were also measured for specimens prepared for 1, 2, and 4 h, and the results revealed that at an expected voltage, the current decreases as the deposition time increases. The main reason for this is that when the deposition time increases, the surface roughness of the Si film increases, which increases the resistance of the as-deposited films. The optimal current value indicates that the Si film prepared using a deposition of 1 h has the best surface (as shown in Fig. 7[b]), which is consistent with the SEM results.

4. CONCLUSION

Si was obtained by electrochemical deposition using $SiCl_4$ as the Si source at a cathodic potential of −2.9 V vs. Ag QRE on a Ti substrate using a PC-based electrolyte. Raman spectroscopy results revealed that the as-deposited films show a broad peak at 640 cm^{-1}, indicating amorphous Si: H films. SEM results showed that the film surface uniformity and smoothness are best for a deposition

time of 1 h, with a relatively strong PL peak obtained at approximately 1150 nm. Rectifying behavior for the I-V curves was obtained for the Si/Ti junction, which confirmed that the deposited Si films have good conductivity. These results indicate that the deposited silicon films have potential for application in infrared light-emission devices and Si solar cells.

ACKNOWLEDGMENTS
The authors would like to acknowledge financial support from the National Natural Science Foundation of China (No. 51474146), the Natural Science Foundation of Shanghai [No. 14ZR1416900], and Gaoyuan Discipline of Shanghai - Environmental Science and Engineering (Resource Recycling Science and Engineering). The authors would like to acknowledge the teachers from the Instrumental Analysis Research Centre of Shanghai University for help with the Raman experiment and XRD experiment. The authors are particularly grateful to teachers and classmates from the Solar Lab of Shanghai University and WEEE Research Center of Shanghai Polytechnic University for help in the scientific research work.

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