Photoelectrochemical Deposition of SnSe Thin Films on a Se-Modified Polycrystalline Gold Substrate[†]

Sunyoung Ham, Seungun Choi,[‡] Yujin Chae,[‡] Woo Ju Lee,[‡] Ki-Jung Paeng, Whan-Gi Kim,[‡] and Noseung Myung[‡,*]

Department of Chemistry, Yonsei University, Wonju Campus, Wonju, Kangwondo 220-710, Korea
[‡]Department of Applied Chemistry, Konkuk University Chungju Campus, Chungju, Chungbuk 380-701, Korea
[*]E-mail: myung@kku.ac.kr
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Tin selenide (SnSe) has attracted attention of many researchers due to its many interesting electrical and optical properties such as high absorption coefficients, which are useful for optoelectronic applications in memory switching devices, solar cells and holographic reading systems.[1-5] Also, it is composed of earth abundant, cost-effective and environmentally benign elements.[1] Therefore, much effort has been devoted to the synthesis of SnSe thin films by a variety of methods like vacuum deposition,[4] chemical bath deposition,[6] electrodeposition[2,3,7] as well as electrochemical atomic layer epitaxy (ECALE).[8] Recently, Brutchey and co-workers reported that SnSe nanocrystals synthesized by a solution-phase route exhibited quantum confinement effects, showing band gap increase from the bulk value of 1.30 eV to 1.71 eV.[1] The increased band gap matches well with the visible region of the solar spectrum, which implies more efficient utilization of solar energy in that region.

Electrochemical deposition has been widely used for the synthesis of semiconductor thin films because this technique has several advantages such as simplicity, low cost, possibility of using irregular surfaces, and room temperature operation.[9] However, this technique is fraught with problems related to film composition which varies with experimental conditions such as electrodeposition potential.[10] To improve the purity of the films, a two step method has been developed.[11] This approach is based on the initial electrochemical modification of the substrate with Se (for example, in case of CdSe), followed by the reductive stripping of Se to Se^{2-} in Se(IV) free electrolytes dosed with Cd^{2+} ions to generate CdSe on the substrate. This approach has been successfully used to synthesis of iron sulfide,[12] cadmium selenide,[11] cadmium telluride,[13] and zinc telluride[14] films or particles. However, the two step approach cannot be employed for the synthesis of some semiconductor films such as SnSe since Sn^{2+} is reduced to Sn before pre-electrodeposited Se is reduced to Se^{2-}. In this *Note*, we describe for the first time photoelectrochemical deposition route for the synthesis of SnSe semiconductor thin films, which is based on the initial electrodeposition of Se on the substrate and subsequent photoexitation (photocorrosion) of Se to Se^{2-} in electrolytes containing Sn^{2+} ions to produce SnSe.

Experimental

Details of the electrochemical instrumentation and the electrochemical quartz crystal microgravimetry (EQCM) set-up are described elsewhere.[15] An EG&G Princeton Applied Research (PAR) 263A instrument equipped with Model M250/270 electrochemistry software and a Seiko EG&G Model QCA 917 were used for microgravimetry and voltammetry. A 9 MHz AT-cut gold-coated quartz crystal (geometric area, 0.2 cm^2), a Pt wire and a Ag/AgCl/3 M NaCl were used as a working electrode, counter electrode and reference electrode, respectively. All potentials below are quoted with respect to this reference electrode. Prior to the electrodeposition experiments, the cleanliness of the gold electrode was checked by cyclic voltammetry in 0.1 M H_2SO_4. The potential was cycled between −0.8 V and 0.7 V until the voltammetric and frequency signals were stable.

Tin(II) chloride dihydrate (purity 98%), selenium dioxide (purity 99+%), hydrochloric acid (purity 37%), sodium sulfate (purity 99+%), sulfuric acid (purity 98+%) were obtained from Aldrich. All chemicals were used as received.

A Müller Elektronik-Optik tungsten halogen lamp was used as the light source. The light intensity measured on the electrode surface with a Newport Model 70260 radiant power meter combined with a Model 70268 probe was ~100 mW/cm^2 in all the experiments described below. This value is uncorrected for cell reflection and electrolyte absorption losses. Film morphology and composition were obtained on a field emission scanning electron microscope (Hitachi S4800) equipped with an energy dispersive X-ray (EDX) analysis probe. The X-ray diffraction patterns (XRD) were obtained with a Philips XPERT-MPD instrument using a Cu Kα radiation source.

Results and Discussion

Figure 1(A) shows a combined cyclic voltammogram and simultaneous frequency changes in the dark for the Se-modified Au electrode in 0.1 M Na_2SO_4. For the preparation of a Se-modified Au electrode, −0.6 V was applied to the Au electrode for 300 s in 10 mM SeO_2 dissolved in a 0.1 M Na_2SO_4 solution. As shown in the figure, selenium stripping to Se^{2-} begins at ~ −0.7 V, which is manifest from the cathodic wave and frequency increase (mass decrease). During the returning scan, electrochemically reduced Se^{2-} is again oxidized to Se^0 from ~ −0.5 V,
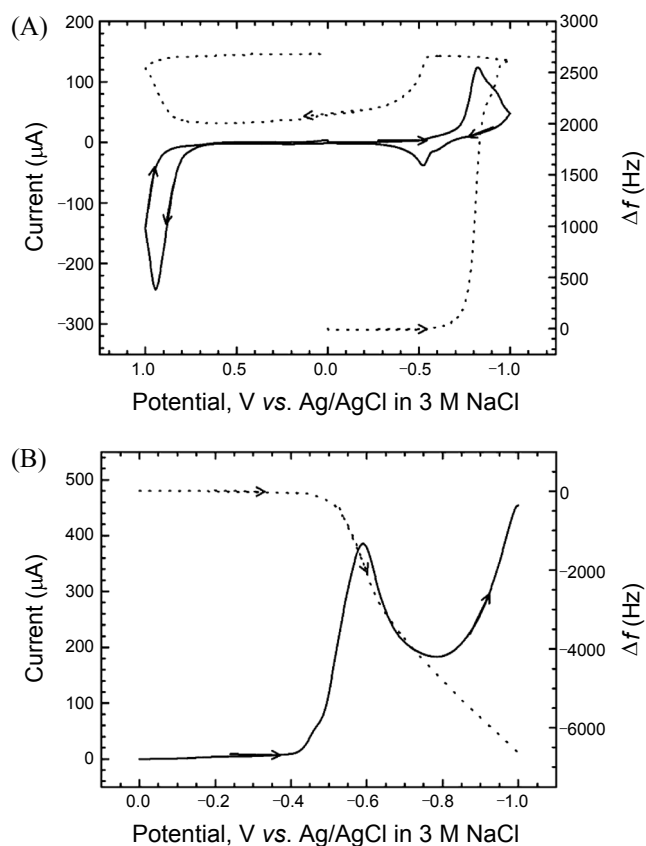

(A)

(B)

Figure 1. (A) Combined cyclic voltammogram (——) and the corresponding frequency changes (----) for the Se-modified Au electrode in 0.1 M Na_2SO_4. Se was pre-electrodeposited using a 0.1 M Na_2SO_4 electrolyte containing 10 mM SeO_2 at −0.6 V for 300 s. (B) Linear sweep voltammogram (——) and the corresponding frequency changes (----) in the dark for the Au electrode in 0.1 M HCl electrolyte containing 1 mM $SnCl_2$. Scan rate: 10 mV/s.
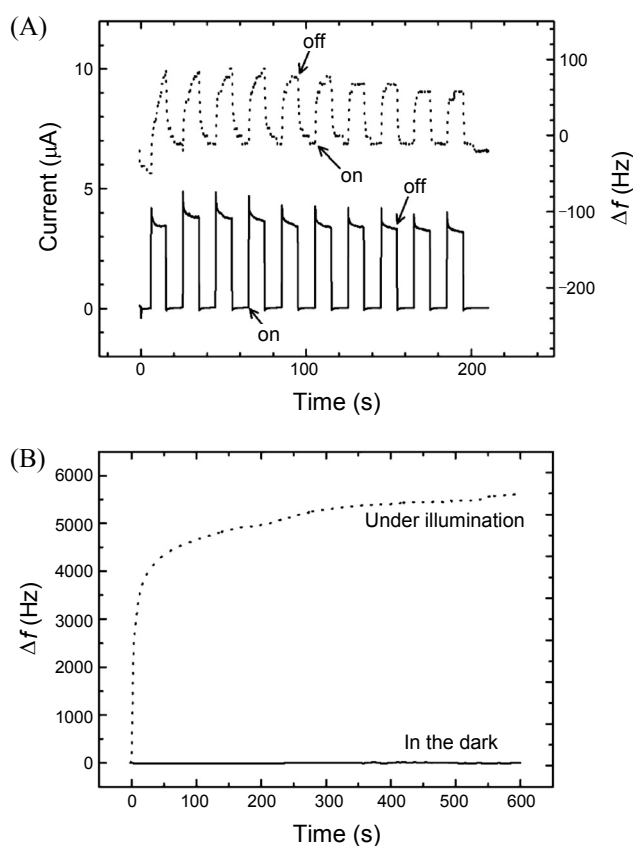
(A)

(B)

Figure 2. (A) Photocurrent transients (——) and corresponding EQCM frequency changes (----) at −0.3 V for the Se-modified Au electrode in 0.1 M Na_2SO_4 electrolyte. (B) Frequency changes for the Se-modified Au electrode at −0.3 V in 0.1 M Na_2SO_4 in the dark (——) and under illumination (----).

which is obvious from the mass increase and concomitant anodic wave. Another anodic wave and frequency increase at ~ +0.9 V can be assigned to the oxidation of Se to Se^{4+}. Note that no electrochemical reactions are shown between potentials for Se^{2-} oxidation to Se and Se oxidation to Se^{4+} in the dark.

Figure 1(B) demonstrates that the two step approach cannot be employed for the synthesis of SnSe semiconductor films. This figure contains data obtained from the linear sweep voltammogram and accompanied frequency changes for the Au electrode in 0.1 M HCl electrolyte containing 10 mM $SnCl_2$. From the mass increase and cathodic wave, it is evident that tin deposition begins at ~ −0.5 V. Two voltammograms in the Figure 1 clearly implies that a new approach is required for the electrochemical synthesis of SnSe thin films.

To demonstrate the photoelectrochemical deposition of SnSe thin films using a photocorrosion of Se, we investigated photoelectrochemical behavior of electrodeposited Se films. Well known is that selenium is a p-type semiconductor which shows cathodic photocurrent upon light illumination and produces Se^{2-} by photocorrosion.[11] Figure 2(A) shows photocurrent response and accompanied frequency changes of the Se-modified Au electrode in 0.1 M Na_2SO_4 electrolyte at −0.3 V. Again, Se was pre-electrodeposited on the Au electrode by holding the po-

tential at −0.6 V for 300 s in 10 mM SeO_2 dissolved in a 0.1 M Na_2SO_4 solution. The cathodic photocurrent generated when the light is switched on reveals that as deposited Se acts as a p-type semiconductor.[11] At the same time, frequency increase implies that the Se is photoelectrochemically reduced to Se^{2-} by the photocorrosion. Interestingly enough, electrode mass is increased when the light is switched off, showing that Se is electrodeposited on the Au electrode again. This can be understood since electrochemically generated Se^{2-} is oxidized at the potential of −0.3 V as seen in the Figure 1(A).

Next, Figure 2(B) demonstrates that Se can be completely reduced by the photocorrosion at a fixed potential of −0.3 V in 0.1 M HCl. Again, a Au electrode was pre-modified with Se by holding a potential at −0.6 V for 300 s in 0.1 M Na_2SO_4 electrolyte containing 10 mM of SeO_2. While no frequency changes are observed in the dark, frequency increase (mass decrease) by photocorrosion is complete within ~ 600 s upon light illumination on the selenium-modified Au electrode surface. The fact that Se is reduced to Se^{2-} by photocorrosion at the potential at which Sn^{2+} is not reduced to Sn reveals the possibility of the photoelectrochemical deposition of SnSe films.

Data in Figure 3(A) clearly demonstrate that SnSe can be synthesized when Se is reduced to Se^{2-} by photocorrosion in electrolyte dosed with Sn^{2+} ions. As shown in Figures 2(B) and 3(A), mass change is zero in the dark condition in both cases
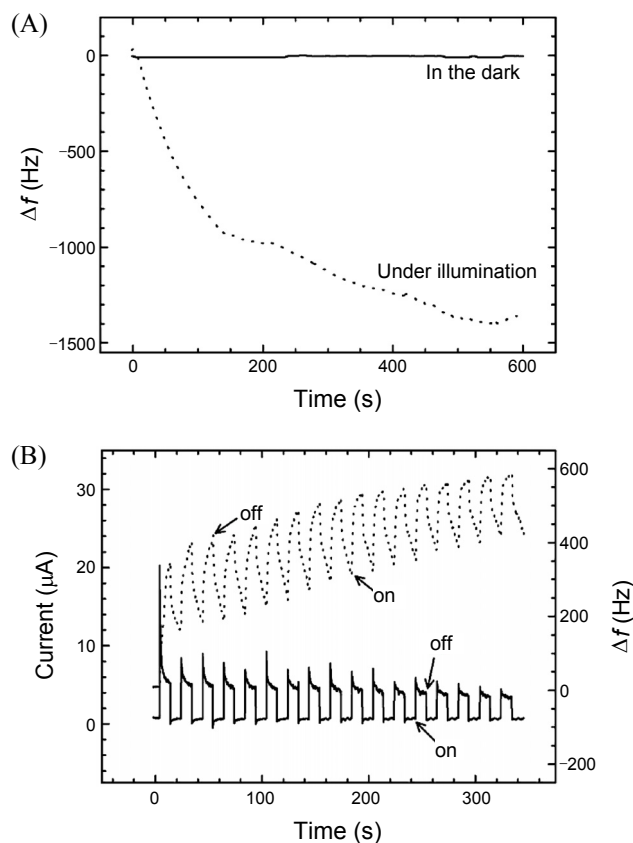
(A)

(B)

Figure 3. (A) Frequency changes for the Se-modified Au electrode at −0.3 V in 0.1 M HCl containing 1 mM of $SnCl_2$ in the dark (——) and under illumination (----). (B) Photocurrent transients (——) and corresponding EQCM frequency changes (----) for the SnSe-modified Au electrode at −0.3 V in 0.1 M Na_2SO_4 electrolyte. SnSe was photoelectrochemically synthesized using the conditions described in Figure 3(A) and excess Se was stripped by applying a fixed potential of −0.9 V for 600 s in 0.1 M Na_2SO_4.

when Sn^{2+} ions are either absent or present. However, on irradiation of the Se modified Au electrode at −0.3 V in 0.1 M HCl containing 1 mM of $SnCl_2$, frequency decreases quickly signaling mass gain by the reaction of Se^{2-} generated by photocorrosion with Sn^{2+} to produce SnSe films on the Au electrode surface:

Photocorrosion: $Se + 2e^- = Se^{2-}$

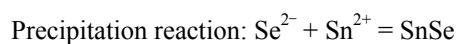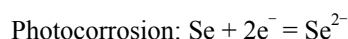Precipitation reaction: $Se^{2-} + Sn^{2+} = SnSe$

Figure 3(B) contains chronoamperometry and EQCM data obtained from the SnSe modified Au electrode at a fixed potential of −0.3 V in 0.1 M Na_2SO_4. Prior to the experiment in Figure 3(B), excess Se was cathodically removed by applying a fixed potential of −0.9 V in 0.1 M Na_2SO_4 blank electrolyte for 600 s. Again, photocurrent is cathodic, indicating that photoelectrochemically deposited SnSe film is p-type semiconductor.[5,16] The photocurrents are due to the SnSe since excess Se was cathodically removed prior to the photoelectrochemical experiment in Figure 3(B). As shown in the figure, frequency increases when the light is switched on and mass is regained with the light
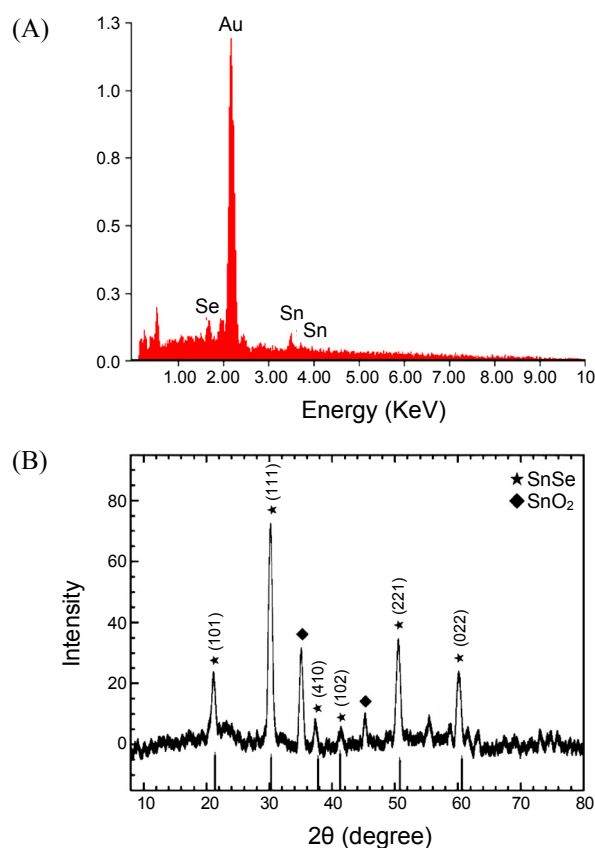
(A)

(B)

Figure 4. (A) EDX analysis of SnSe thin film. The excess Se was cathodically removed by the procedure in Figure 3(B). (B) The XRD pattern for the SnSe film annealed at 300 °C for 1 h in air.

switched off. Systematic change of frequency with light on-off cycles is consistent with the photocorrosion of SnSe to Sn + Se^{2-} with the light switched on and re-deposition of Se when the light is switched off since the potential is enough for the oxidation of Se^{2-} to Se. However, it is evident that not all Se^{2-} is oxidized to Se since the EQCM frequency does not attain its original level. Therefore, SnSe is photocorroded to Sn and Se^{2-}, resulting in increase of frequency and decrease of photocurrent as the light on-off cycles repeat. More efficient photoelectrolyte should be developed to suppress photocorrosion of SnSe films.

The successful synthesis of SnSe films is further demonstrated using EDX spectroscopy and XRD analysis. As shown in Figure 4(A), EDX analysis revealed that the SnSe films contained Sn and Se with a ratio of 1:1.1, in agreement with the stoichiometric composition of SnSe. Also, the XRD pattern for the SnSe films deposited on the ITO electrode by the photoelectrochemical approach shows diffraction lines at $2\theta = 21.395°$, $30.307°$, $38.131°$, $41.279°$, $50.722°$ and $60.650°$, which are in good agreement with the reported values for SnSe (JPCDS File No. 32-1382). The films were annealed at 300 °C for 1 h in air before the XRD measurement.

In summary, we demonstrated that SnSe thin films can be photoelectrochemically synthesized on the Se-modified Au electrode by employing photocorrosion of Se to Se^{2-} and precipitation reaction of Se^{2-} with Sn^{2+}. Thus synthesized SnSe acted as a p-type semiconductor with a stoichiometric ratio of

about 1:1.1 after stripping of excess Se. The approach described in this *Note* could be used for the synthesis of Se- or Te-containing semiconductor or thermoelectric materials such as SnTe, Sb_2Se_3 or Sb_2Te_3. Further studies on the synthesis of SnSe nanoparticles or nanostructured films by a PEC deposition approach, and applications to the fabrication of semiconductor sensitized solar cells using wide band gap semiconductors like ZnO and TiO_2 will be carried out in our laboratories.

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