Electrochemical and photoelectrochemical characterization of SnS photoabsorber films

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A B S T R A C T

A comparative study on the electrochemical and photoelectrochemical behavior of SnS thin-film electrode in acidic media was carried out to investigate the SnS-electrolyte interface reactions. The cycling voltammetry examinations were performed to characterize the oxidation and reduction reactions during electrochemical decomposition of the SnS layer in a background solution of 0.1 M H₂SO₄. It was observed the presence of passivating oxide-hydroxide layers on the surface on SnS films and studied dynamics of its formation. The corresponding interface reactions were discussed in details and compared with state-of-the-art in similar researches.

Photoelectrochemical measurements show that the decrease of photoactivity of SnS is caused mainly by tin hydroxide ultra-thin layer formation on the SnS surface. On the other hand, after electrochemical reduction of the passivating hydroxide layer the photoactivity increase is observed e.g. electrochemical oxidation at +1200 mV vs. SCE forms on the surface of SnS ultra-thin SnO layer and increases photoactivity almost 4 times. In this paper, special attention is paid to modification of SnS photoabsorber interface by the electrochemical treatment.

1. Introduction

In the last several years, as one of the most important candidate materials for the photovoltaic cell, SnS has attracted much attention. SnS has direct 1.2–1.5 eV [1] and indirect optical band gap of 1–1.2 eV [2], a high absorption coefficient α > 10⁴ cm⁻¹ [3] and a high carrier concentration and mobility (hole mobility ~ 90 cm² V⁻¹ s⁻¹) [4] that have made it a promising candidate for photovoltaic [5,6] and photoelectrochemical cell [7,8], Li ion battery anodes [9], electrochemical capacitors [10] and photodetectors [11].

Although tin sulphide is relatively chemically stable compound, the polycrystalline SnS surface can be hydrolyzed with formation of thin tin hydroxide top layer, which passivates the SnS surface in ambient conditions i.e. in presence of water vapors and oxygen [12].

The formation of some passivated film on the surface of semiconductor electrode could enhance excitation of photogenerated charged. Numerous surface treatments have been reported in an effort to tailor the physicochemical properties of the semiconductor–liquid interface, and in turn, the overall photoelectrochemical response [13].

The electrolyte/semiconductor contacts offer a number of unique opportunities for characterization of crystals and especially thin film structures. Transparent electrolyte contacts are used for photocurrent and capacitance spectroscopy or electrolyte electroreflectance measurements, which provide new knowledge into basic science of materials and processes. The semiconductive electrode immersing in liquid formed photosensitive junction, which is extremely abrupt and matched in the atomic scale, compared to a p–n or metal–semiconductor junction.

Photoelectrochemical studies on n-type SnS single crystals in contact with aqueous electrolytes containing various redox couples have been reported [14,15]. Under illumination, the electrode was unstable in both acidic and alkaline media and the photocurrents were mostly due to the decomposition of the semiconductor, which was attributed to the existence of surface states at the semiconductor/electrolyte interface consisting primarily of negatively charged surface sulphur atoms. Mishra et al. [16,17,18 and 19] discussed electrochemical behaviour of p-type SnS films on the basis of Pourbaix diagrams, by performing photoelectrochemical studies in aqueous electrolytes with various redox couples. The flat band location of the SnS surface was observed at 0.40 ± 0.05 V (SCE) regardless of the redox potential of the electrolyte [16]. Polarization curves of the SnS samples revealed partial rectification for cathodic current flow in the dark, establishing the SnS as p-type. The authors explained the incomplete rectification by formation of defects (e.g., grain boundaries) in the polycrystalline...
films.

The first part of this study has been to investigate the electrochemical behaviour of tin (II) sulfide in acidic media. The work was initiated to study the electrochemical and photoelectrochemical behaviour and evolution of the chemical composition, structure and electrical properties of the tin sulfide layer using potentiodynamic, galvanostatic and impedance techniques.

2. Experimental

2.1. Preparation of SnS film

Thin films of SnS were deposited onto FTO/glass substrates with the high-vacuum evaporation technique using BOC EDWARDS Auto 500 systems. The SnS films with the thickness of 0.5 μm were deposited at a constant substrate temperature (T_S) of 300 °C, with a deposition rate of 0.2 nm/s. The deposition was carried out in a vacuum chamber at a pressure of around 1×10⁻⁶ mbar with a deposition source-to-substrate distance of 25 cm. The deposition parameters and results of Raman, XRD and HRSEM studies of obtained SnS layers are represented in our previous paper [20].

2.2. Photo- and electrochemical measurements

The electrochemical, photoelectrochemical and impedance measurements were performed using a Gamry Reference 3000 potentiostat/galvanostat with a three electrode cell configuration: a working electrode glass/FTO/SnS, a platinum-wire counter electrode and a reference saturated calomel electrode (SCE). All electrochemical experiments have been done in 0.1 M H₂SO₄ background electrolyte (SCE). The open current potential value in the range ± 10 mV.

Before the electrochemical measurement, glass/FTO/SnS electrodes were immersed in the electrolyte for 20 min, in order to stabilize the open current potential value in the range ± 10 mV.

For the photo-electrochemical measurements, the glass/FTO/SnS electrodes were illuminated in electrochemical cell with a white light from LED lamp. The light intensity measured on the SnS interface was around 30 mW/cm².

3. Results and discussion

Although tin sulfide is relatively chemically stable compound, the polycrystalline SnS surface can be hydrolyzed with formation of thin tin hydroxide top layer, which passivates the SnS surface in ambient conditions i.e. in presence of water vapors and oxygen [15]. The simplified mechanism of hydroxide layer formation on the surface of the sulfide of metal with variable valence can be represented by the following schematic reaction:

\[ MS + xH_2O + 1/2xO_2 \rightarrow M_{1-x}S + xM(OH)_2, \]

where MS is a metal sulfide.

Usually, hydroxide layers are not formed uniformly over the surface of the sulfides of metals. It should be noted, that the surface composition of the sulfides of metals can be the metal deficient or sulfur-rich i.e. chemically variable and the presence of small, oxidized particles and particle interactions must be considered. [21]. The passivation of tin sulfide film is completed by the formation of SnO₂ from initially Sn(OH)₂, which has been reported by V. Brunetti in [22].

3.1. Electrochemical study of SnS in acidic solution

The cycling voltammetry examinations were performed to characterize the oxidation and reduction reactions during electrochemical decomposition of the SnS layer.

All electrochemical potentials (vs. SCE) of the reactions (below shown Eqs. 1–11) were calculated using data from the source [20,23] and given at pH =1 for concentration of dissolved species in the electrolyte of 10⁻⁷ mol·l⁻¹.

Fig. 1 shows the representative cyclic voltammogram of SnS electrode with potential sweep from 0 V (all the potentials are referred to SCE) to a maximum negative potential ~0.9 V (cathodic branch, curve a) and from 0 V to a maximum positive potential (anodic branch, curve b). These curves were measured with scan rate of 20 mVs⁻¹ in the potential range ~0.9 V - +1.5 V.

The shape of voltammetric curves in anodic branch and cathodic branch is not identical and depends dramatically on the potential sweep direction due to irreversible reaction on the surface of SnS electrode associated with formation of passivated/isolated tin hydroxide-oxide layers under anodic polarization.

The cathodic current peak C3 at potential ~0.7 V refers to a reduction of SnS and coincides with the peak C4 corresponded to hydrogen evolution by water splitting on the electrode surface.

The electrochemical reduction of SnS occurs with formation of metallic Sn⁰ surface layer and formation of H₂Sₐbs (Eq. (1)). The process is mainly reversible, the peak A1 observed at the reverse sweep potential increases with concentration of hydrogen sulfide at the electrode surface corresponds the formation of tin sulfides.

\[ SnS + 2H^+ + 2e = Sn^{0} + H_2S_{abs} \quad -0.70 \text{ V vs. SCE} \quad (1) \]

The oxidation peaks (A2 and A1) are very intensive for voltammogram started in cathodic direction (cathodic branch, curve a) and notably smoothed for voltammogram started in anodic direction (anodic branch, curve b). The reason for this electrochemical behavior is connected with anodic passivation by layer of tin oxide on the surface of SnS layer that decreases the rate of redox reactions on the SnS electrode surface.

Indeed, it is expected for the surface of bare tin sulfide electrode i.e. the surface of SnS is hydrated/oxidized step-by-step with forming of a thin tin hydroxide-oxide interface layer. The peak C1 corresponds to partial reduction of tin IV hydroxide/oxide layers at potential ~0.3 V (Eqs. 2–4).

\[ Sn(OH)_4 + 2H^+ + 2e = Sn(OH)_2 + 2H_2O \quad -0.21 \quad (2) \]

\[ Sn(OH)_4 + 2H^+ + 2e = SnO + 3H_2O \quad -0.22 \quad (3) \]

\[ SnO_2 + 2H^+ + 2e = SnO + 2H_2O \quad -0.28 \quad (4) \]

The reduction of tin oxide/hydroxide to metallic tin takes place under more negative potentials. Peaks C2 and A2 up to ~0.45 V correspond to redox reactions of different oxides and hydroxides of tin II formed on the surface of tin sulfide by reactions Eqs. 5–7. The redox potentials of the reactions are very close to each other, so it is difficult to distinguish.

\[ Sn(OH)_2 + 2H^+ + 2e = Sn^{0} + 2H_2O \quad -0.39 \quad (5) \]
The anodic excursion part exhibits active/passive transitions. The anodic (peak A2) current peak corresponds to the processes of oxidation of reduced tin and precipitation of tin II oxides on the electrode surface by Eqs. 5–7. There are followed by a passive region. Precipitation of tin oxides on surface blocks the active SnS surface sites and causes to its inactivation.

The oxidation potentials region involve a net anodic contribution (peaks A3, A4). The oxidation of tin II oxides is followed by the formation of tin IV oxides (peak A3) according to reverse reaction of Eq. (4).

The electrochemical oxidation of SnS in aqueous acidic electrolyte leads to the formation of tin oxides and sulfur on the surface of SnS electrode (Eqs. 8 and 9). Peak A4 corresponding to this route of oxidation is noticeable at anodic scanning at the potential of 0.4 V.

\[
\text{SnO} + 2\text{H}^+ + 2e^- = \text{Sn}^0 + \text{H}_2\text{O} \quad -0.41
\]

\[
\text{SnO}_2 + 4\text{H}^+ + 4e^- = \text{Sn}^0 + 2\text{H}_2\text{O} \quad -0.41
\]

Fig. 2a shows the shift of the reduction peaks depending on the initial potential of the scan. The peak C1 corresponding to the reduction of hydroxides of tin is shifted to more negative potentials with increasing of the initial positive potentials of scan. At the initial positive potential of 0.6 V amorphous upper Sn(OH)\text{2} and/or SnO layers are oxidized to form a more dense layer of SnO\text{2}.

A significant shift of oxidation potentials was detected for a scanning from a highly positive potential values (Fig. 2a, scanning curves of 0.6 V and 1 V). At these starting potentials, SnS is oxidized forming SnO and SnO\text{2} layers (Eqs. 8 and 9). Peak C2 corresponding to cathodic reduction of formed oxides shifts to more negative potentials region and increases intensity. All these processes might affect on the thickness growth of the SnO\text{X} film accompanying with a change of its crystalline properties [21,24]. Indeed, relatively thick passivating tin oxide film prevents reduction of SnS and therefore supression of the reverse anodic peaks A1 and A2 is observed. Since the reduction potentials of oxides and hydroxides of tin II and IV are very close (peak C1), it is possible that the peak C2 is responsible for reduction of SnS + 5H\text{2}O = SnO + 3SO\text{2}^- + 10H^+ + 8e^- + 0.43

\[
\text{SnS} + \text{H}_2\text{O} = \text{SnO}_2 + \text{SO}_\text{2}^- + 12\text{H}^+ + 10e^- + 0.38
\]

\[
\text{SnS} + 3\text{H}_2\text{O} = \text{SnO}_2 + \text{SO}_\text{2}^- + 10\text{H}^+ + 8e^- + 0.47
\]

The peak A6 corresponds to oxygen evolution at the anode up to 1.4 V.

Fig. 2b shows the shift of the reduction peaks depending on the initial potential of the scan. The peak C1 corresponding to the reduction of hydroxides of tin is shifted to more negative potentials with increasing of the initial positive potentials of scan. At the initial positive potential of 0.6 V amorphous upper Sn(OH)\text{2} and/or SnO layers are oxidized to form a more dense layer of SnO\text{2}.

The cycling voltammetry and photoelectrochemical (PEC) response of bare SnS thin film under chopping illumination in the electrolyte 0.1 H\text{2}SO\text{4} in the potential scan range from 0.1 V to –0.75 V is shown in Fig. 4a and b. The scanning started from the potential value of 0.1 V with following direction to negative potential of –0.75 V and reverse to 0.1 V with scan rate of 20 mV s\text{−1}. The forward scan is depicted by red curve, the reverse scan - by black curve. The PEC cell was illuminated by a pulsed white LED light with an intensity of 30 mW/ cm\text{2}.

During the cathodic examination, a small dark current flows through the surface following the expected behavior for a forward polarization of the p-type SnS (before the breakdown potential has been reached).

Under illumination, the anodic branch of the voltammogram remains practically unchanged but the cathodic current is highly increased. This is the expected result when taking into account the photo-oxidation of electrons-holes pairs in the p-type SnS semiconductor layer.

Small cathodic photocurrent growth was detected at potential more negative than –0.2 V and was accompanied with the onset of dark oxidation of SnS layer (peak C1, Fig. 1). The photocurrent increases with increasing of the cathodic polarization and reaches the local maximum at –0.4 V, followed by a plateau.

The significant fraction of the photocurrent is due to the reduction decomposition of water or the surface material according reaction Eqs. 2–4.
Also, the photocurrent increases at potentials more negative than −0.6 V, however the polarization at these potentials is associated with the dissolution of the SnS electrode and intensive evaluation of hydrogen, so the scan is complete before reaching the saturated photocurrent.

The reverse scan examination (red curve) shows the local photocurrent peak under potential −0.55 V, that corresponding to dissolution of reducted tin from surface (peak А2, Fig. 1). The increasing of photocurrent is possible due to a decrease of tin content on the SnS surface, which forms recombination centers for photogenerated charge carriers.

The photocurrent decreases until plateau at −0.4 V with subsequent decreasing of cathodic potentials. The main reason of decreasing of photocurrent could be formation of hydroxide/oxide passivating film on surface of SnS electrode as the result of reversible reactions Eqs. 5–7.

3.2.1. Modification of SnS surface by electrochemical treatments

It could be proposed, that the photocurrent of bare SnS films is strongly limited by the recombination of photogenerated charge carriers at the surface/electrolyte interface. Electrochemical treatment of a surface layer changes the SnS semiconductor surface environment and can modulate the response, including a shift in the onset potential.

A number of SnS films were treated by a process of surface conditioning in electrochemical cell prior to photo-electrochemical operation. It should be noted, that the selective electrochemical etching by cathodic reduction could remove surface impurities and/or oxide-hydroxide passivated layer from the surface of semiconductor SnS films.

3.2.1.1. Electrochemical oxidation of the surface. The oxidation effect of electrochemical treatment on the photocurrent response of SnS layer is shown in Fig. 5 (red curve). Here, SnS film was polarized under 1.2 V vs. SCE during 5 min in a 0.1 M H2SO4 background electrolyte.

As shown in Fig. 5, the bare SnS shows a weak PEC response. On the other hand, the electrochemically oxidized surface of SnS with top SnO layer significantly enhances the photocurrent response from −0.4 V to more negative applied potentials.

The photocurrent saturation value for anodized SnS film was detected at around −0.6 V (about 200 µA cm⁻²) that four times higher of saturated photocurrent value for bare SnS film at −0.35 V (about 50 µA cm⁻²).

The onset potential of the photocurrent, defined by the potential where the tangent of the photocurrent at the onset inflection point crosses the linear extrapolation of the exchange current observed before the photocurrent onset. The cathodic photocurrent density onsets of bare film (defined here as the potential where the photocurrent become negative) at ca. −0.1 V vs. SCE and slow and linear increase up to 0.4 V vs. SCE. (Fig. 6).

The photocurrent shows an onset potential for oxidized SnS film at about 0.3 V, a rapid increase to reach ca. 0.2 mA cm⁻² at −0.6 V and a saturation (photocurrent plateau) of 0.2 mA cm⁻² from −0.6 V. However, the observed photocurrent onset at −0.1 V vs. SCE is in a strong contrast to the flat band potential (Vfn) determined for this material (0.4 V vs. SCE as measured by the impedance spectroscopy for the SnS studied here (Fig. 7b)).

According to our assumption, thin upper SnOx layer can passivate charge carriers recombination on the surface of SnS electrode by preventing formation of the surface defect states and/or promote the desired chemical reaction by catalyzing faster charge transfer to the redox species. Indeed, both mechanisms enhance quantum efficiency for the water-splitting reaction, by reducing the charge-carrier losses at the electrode interface.

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3.2.1.2. Electrochemical reduction of the surface. The SnS films for this study has been kept for around 6 months in ambient condition under periodic lab illumination. The films have been examined by linear swept voltammetry under chopped white light illumination. It should be noted, that prepared SnS layers show relatively high dark current density and poor photocurrent response as shown before in Fig. 5.

The improvement of photoactivity of SnS film as a semiconductor electrode can be determined from the Mott–Schottky plots using the electrochemical impedance spectroscopy (EIS). The Mott–Schottky plots can be obtained by plotting the reciprocal of the capacitance (C) versus the applied voltage (E). At the relatively high frequency of 15 kHz, the equivalent circuit of a semiconductor/electrolyte interface can be simplified, and the E0 of a photoanode can be determined from the slope and intercept of the fitting line of its Mott–Schottky plot, using the Mott–Schottky equation [25]:

\[
\frac{1}{C^2} = \frac{2}{qD_0e\varepsilon}\left[ E - E_0 - \frac{kT}{q}\right]
\]

where \(k\) is Boltzmann constant, \(T\) is the absolute temperature, \(C\) is the capacitance of the space-charge of the film, \(e\) is the dielectric constant of the film, \(e_0\) is the permittivity of the vacuum, \(A\) is the surface area of the film (1 cm²), \(N_d\) is the charge density of the film, \(q\) is its electric charge, \(E\) is the applied voltage, and \(E_0\) is the flat-band potential of the film.

The Mott–Schottky characterization of electrolyte/SnS junctions was performed at 15 kHz in 0.1 M H₂SO₄ electrolyte and recorded with different polarizations. Fig. 7a shows the C⁻² vs. E plot obtained for bare SnS films at first and second electrode measurement routes. The slope of Mott–Schottky plots of SnS electrode is negative, which confirms p-type of conductivity of obtained SnS films. From the slope of the linear part of the curve in the range of 0.2 to −0.3 V vs. SCE the flat band potential value was found (around 0.4 V vs. SCE).

Certain abnormalities are observed: change of the slope and curve shift during experimental routine i.e. the slope of the second route is shifted vs. the position the first route because the capacitance of the depletion layer intensively increases due to electrochemical oxidation of the surface of SnS.

According to our assumption, the slope of the linear part of the curve in the range of −0.3 to −0.6 V vs. SCE corresponds to formation of layers of p-type SnO on the surface of SnS, and flat band potentials of passivating SnO film could be determined as −0.24 V vs. SCE (Fig. 7a). As noted, there is a correlation between the corrosion behavior of a chalcogenide minerals and the semiconductor properties of a passivating film [26,27].

In addition, the electrochemical polarization in acidic electrolyte at anodic potential range of +0.6 to +1.2 V vs. SCE was used to oxidize/passivate the surface of SnS electrode. Fig. 6b shows the Mott–Schottky plot obtained for oxidized SnS films. The flat band potential film can be graphically determined from the Mott–Schottky plot from linear parts of the curve in the range 0.1 < E < −0.3. After electrochemical oxidation, flat band potential of formed SnO layers shows the shift to negative potential range from −0.24 to −0.35 V vs. SCE (Fig. 7a and b).

4. Conclusions

The study of the electrochemical transformation of polycrystalline SnS thin-film surface in acidic media was performed. Obtained results showed that the electrochemical oxidation-reduction of SnS accompanies with series of the interface SnS/electrolyte reactions and the several intermediate species could be formed. The main features of SnS semiconductor electrochemistry has been discussed. Formation of the SnOx/Sn(OH)x thin layer on the surface of SnS has been confirmed by the electrochemical voltammetric and the impedance measurements.

Based on the electrochemical measurements, it was concluded that photocurrent of SnS films is strongly limited by the recombination of photogenerated charge carriers at the SnS electrode surface/electrolyte interface.

It was found, that the decrease of SnS photocurrent is caused mainly by tin hydroxide surface layer formation on the SnS surface. After electrochemical reduction of the passivating hydroxide layer an increase of photocurrent is observed. On the other hand, electrochemical oxidation at +1200 mV vs. SCE forms SnO layer on the surface of SnS. It was shown that SnO layer can passivate charge carriers recombination on the surface of SnS electrode and therefore promote the desired chemical reaction by catalyzing faster charge transfer to the redox species and increases photocurrent respond of SnS layers almost 4 times.

In general, electrochemical etching of the SnS layers can be potentially used to obtain desired properties of the SnS interface for various applications e.g. in photoelectrochemical cell, photoelectrocatalysis and solar cells.

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References