Structural and Photoelectrochemical Evaluation of Nanotextured Sn-Doped AgInS₂ Films Prepared by Spray Pyrolysis

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Spray pyrolysis was used to prepare films of AgInS₂ (AIS) with and without Sn as an extrinsic dopant. The photoelectrochemical performance of these films was evaluated after annealing under a N₂ or S atmosphere with different amounts of the Sn dopant. DFT was used to calculate the band structure of AIS and understand the role of Sn doping in the observed properties. All AIS films were n-type, and Sn was found to increase the photocurrent and carrier concentration of AIS with an optimum doping level of x = [Sn]/([Ag]+[In]) = 0.02, which gave a photocurrent of 4.85 mA cm⁻². Above this level, the Sn dopants were detrimental to the photoelectrochemical performance, likely a result of a self-compensating effect and the introduction of a deep acceptor level, which could act as a recombination site for photogenerated carriers.

Introduction

Since Fujishima and Honda[10] reported that under UV radiation TiO₂ can be used to split H₂O into H₂ and O₂, photoelectrochemical cells (PEC) that use semiconducting absorber materials have been investigated for solar energy-to-fuel applications. Currently, the most studied semiconducting materials for PECs have been oxides such as TiO₂, WO₃, and Fe₂O₃. However, these oxides have bandgaps > 2 eV, which limits their solar energy-to-H₂ efficiency. There has been much work on the incorporation of dopants to increase visible-light absorption in these oxide materials without the introduction of sites where the photogenerated carriers can recombine.[2-4] These issues related to light absorption and the transport of charge carriers are also relevant to researchers in the photovoltaic (PV) community. Among the most promising and successful thin-film PV materials are based on the Cu-chalcoprylate family, of which Cu(In,Ga)Se₂ solar cells demonstrate approximately 20% solar energy-to-electricity efficiency.[5,6] The high performance of chalcoprylate absorbers is attributed to several unique characteristics of the materials, which include a high absorption coefficient of 10⁵ cm⁻¹, a direct bandgap that is tunable based on its composition, high minority carrier diffusion distances, and a high tolerance for grain boundaries. However, chalcoprylates have very complex defect chemistries. Even ternary CuInS₂ (CIS) has 12 possible intrinsic defects (three vacancies, three interstitials, and six antisite defects), many of which have a very low defect-formation energy of approximately 1 eV.[8] As a result, there have been many studies that try to understand the effect of intrinsic defects, as well as extrinsic dopants, on the transport and photovoltaic properties of chalcoprylates.

Chalcoprylates have also been investigated in photoelectrochemical applications because of their aforementioned attractive material properties, particularly the ease of band gap tuning through the formation of solid solutions. For example, solid solutions of CuInS₂, AgInS₂, and/or ZnS,[6-11] as well as AgGa₁₋ₓJnₓS₂ alloys,[12] have been studied as slurry photo-

catalysts. Photocathodes of CuInS₂,[11] CuInSe₂,[14,15] Cu(In,Ga)Se₂,[13] Cu₂ZnSnS₄,[17,18] and CuGaSe₂[19] have also been studied, but their solar energy-to-H₂ efficiencies are limited by the small bandgaps of Cu-chalcoprylates and band-edge positions that require large external bias to achieve overall H₂O splitting.[19] Owing to the kinetic overpotentials for H₂O splitting, a bandgap of 1.8 eV is suitable[18,21] to obtain the maximum efficiency (solar energy-to-H₂) in a PEC (compared to an ideal bandgap of 1.4 eV for PVA). To this end, AgInS₂ (AIS) is attractive as a photoelectrode because of its bandgap of 1.8 eV. In contrast to CIS, which is commonly p-type because of intrinsic defects (namely, Cu vacancies),[22] AIS is almost always n-type, which is likely a result of donor levels from S vacancies.[23-24] Compared to n-type oxides, AIS has a more suitable bandgap and band-edge position for both H₂ and O₂ production. The implication for this is that a p/n-PEC that uses an n-type chalcoprylate can result in a higher maximum operating current density (which can be found by overlapping the individually tested current-voltage characteristics for the photocathode and photoanode and determining the intersection of the curves)[25] compared to an n-type oxide photoanode. However, the drawback is that sulfides are generally not stable to photocorrosion if used as photoanodes,[26,27] and thus the anodic reaction is typically the oxidation of sulfide- and sulfite-
based sacrificial reagents rather than that of H$_2$O. Nevertheless, recent reports have shown that atomic-layer-deposition (ALD) coatings of stable oxide materials such as TiO$_2$ can be used to impart remarkable stability to n-type Si$^{28,29}$ another photoanode suffering from photocorrosion, which suggests that coatings and other protection strategies may allow materials such as n-type AIS (n-AIS) to be relevant as photoanodes for H$_2$O oxidation. Thus, a better understanding of the photoelectrochemical properties of AIS and the effects of doping is needed.

This is particularly true considering that previous studies have shown that the properties of AIS are highly dependent on the method of synthesis. For example, AIS made by electrodeposition gave films with carrier concentrations of 10$^{15}$ cm$^{-3}$, whereas AIS made by sulfurization of Ag-In metal gave films with a resistivity of 10$^5$ $\Omega$cm and carrier concentrations of 10$^{12}$ cm$^{-3}$, and AIS synthesized by hot-wall epitaxy onto GaAs displayed carrier concentrations of 10$^{17}$ cm$^{-3}$. Other films synthesized by using spray pyrolysis yielded AIS with resistivities between 10$^5$–10$^3$ $\Omega$cm. Additionally, the reason for the n-type behavior of AIS, and the compositional and structural requirements to turn it into p-type, are not well understood. For example, p-AIS was synthesized by using co-evaporation with Ag/In ratios from 0.77 to 1.13, which suggests that AIS can be p-type in both Ag-rich and Ag-poor cases. This is different from CIS for which Cu vacancies promote p-type behavior. The role of extrinsic dopants in AIS is similarly not well understood. For instance, Sn is a dopant in n-type CIS$^{23,24}$; however, p-type AIS was also formed through doping with Sn$^{25,26}$. In most of the previous work related to AIS characterization, the properties were determined by using solid-state methods such as hot-probe, thermoelectric, or Hall measurements; the relevant photoelectrochemical measurements have not been performed for any of the p-AIS materials and have only recently been pursued for n-AIS and Ga-doped n-AIS.$^{21,39}$

Here, we report a systematic study on the effect of annealing conditions and Sn doping on the optical, electrical, and photoelectrochemical properties of AIS prepared by spray pyrolysis with the hope of shedding more light on the characteristics needed for high performance photoelectrodes. Compared to other methods to synthesize AgInS$_2$, such as hot-wall epitaxy,$^{40}$ chemical-bath deposition,$^{41}$ electrophoresis,$^{42}$ co-evaporation,$^{43}$ and sulfurization of metal films,$^{44}$ it is easy to obtain large-scale, high-quality films by using spray pyrolysis. The effect of annealing the deposited films under a N$_2$ or S atmosphere was investigated to control the crystallinity and understand the role of S vacancies on the AIS films. Sn was used as an extrinsic dopant because of the previously reported work on Sn-doped, p-type AIS.$^{27,38}$ Density functional theory (DFT) was also used to analyze the effect of Sn-doping in AIS.

Results and Discussion

XRD patterns of AgInS$_2$ films

Compared to other I–III–VI compounds, AIS can adopt an orthorhombic phase in addition to a tetragonal chalcopyrite phase, of which the chalcopyrite phase is stable to >620 °C and characterized by a bandgap of 1.86 eV compared to 1.96 eV for the orthorhombic phase.$^{42}$ Figure S1A shows the XRD patterns of films of undoped AIS as well as AIS with different amounts of Sn doping after spray pyrolysis onto glass substrates prior to annealing under N$_2$. The main peaks belong to the (112), (200), (220), and (312) planes of the chalcopyrite phase of AgInS$_2$ (ch-AIS). The (112) peak shows the strongest intensity, which indicates that spray pyrolysis could yield ch-AIS with good crystallinity. Smaller peaks that belong to the orthorhombic phase (o-AIS) were also present, and Ag$_2$S was observed in the undoped sample. These side products are likely to be present because the precursor solution was Ag-rich to compensate for the volatility of Ag.$^{31}$ Ag-rich precursor solutions also resulted in films with a predominant chalcopyrite structure in previous studies.$^{43}$ Samples synthesized at temperatures below 300 °C did not crystallize well or show good adhesion to the substrate after PEC testing. The amount of Sn doping was controlled through the ratio x = Sn/(Ag+$\text{In}$). Changing x from 0 to 0.08 did not change the presence of the ch-AIS peaks, although the increasing Sn concentration caused the Ag$_2$S peak to disappear and the o-AIS peaks to increase in intensity. This suggests that the presence of Sn can affect the structure of as-deposited AIS to favor the orthorhombic phase. After annealing the films under N$_2$, the ch-AIS (112) peak increased in intensity relative to the o-AIS peaks (Figure S1B). Deposition of the AIS films onto the fluorine-doped tin oxide (FTO) substrate showed similar XRD patterns, although the large reflections from FTO obscured the smaller peaks of o-AIS and Ag$_2$S (Figure 1). However, the peak intensities from o-AIS were significantly weaker for AIS films deposited on FTO compared to those on glass, which indicates a preference for ch-AIS formation over that of o-AIS on FTO.

In previous studies on Ga-doped AIS, the (112) peak was observed to shift towards lower diffraction angles with increasing Ga content, which indicates the substitution of Ga at In sites, which is expected from the ionic radii of 0.8 Å for In$^{3+}$ and 0.62 Å for Ga$^{3+}$. In contrast, the XRD pattern of Sn-doped AIS did not appear to have any peak shifts relative to the undoped AIS, which suggests that the Sn dopants did not occupy Ag or In sites.

Morphology and composition

The AIS films showed a wavy morphology textured with nanoparticles as small as 30–60 nm. The microstructure was not affected by Sn doping. Figure 1B shows an SEM image of Sn-doped AIS with x = 0.02 on FTO. Other reports of the use of spray pyrolysis to deposit AIS$^{27,31}$ did not achieve the same morphology, but had films that displayed more bulk characteristics. It is possible that this morphology is a result of the formation of small droplets of 110–120 µm in diameter from the atomization of the precursor solution during spraying. Spray deposition onto Mo-foil substrates led to films with similar morphologies (Figure S2). The nominal ratio for Sn doping was very similar to the actual amount of Sn determined by using energy dispersive X-ray spectroscopy (EDS) in conjunction with
nantechned Sn-Doped AgInS₂ Films

![Graph](image)

**Figure 1.** (A) XRD pattern for AIS films deposited by using spray pyrolysis onto FTO substrates (+: a-AIS, : ch-AIS, •: FTO) for x=(Sn)/(Ag+In) in which x is (i) 0, (ii) 0.02, (iii) 0.04, (iv) 0.06, and (v) 0.08. (B) SEM image of an AIS film, inset shows magnification.

<table>
<thead>
<tr>
<th>Nominal ratio</th>
<th>Actual ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>0.017</td>
</tr>
<tr>
<td>0.040</td>
<td>0.040</td>
</tr>
<tr>
<td>0.060</td>
<td>0.072</td>
</tr>
<tr>
<td>0.080</td>
<td>0.075</td>
</tr>
</tbody>
</table>

**Table 1.** Values of x=(Sn)/(Ag+In) in Sn-doped AIS determined by EDS.

SEM (Table 1). The compositions [wt% and at%] of the films determined by EDS are shown in Table S1.

**Optical characterization**

The transmission data for the AIS films with different amounts of Sn doping showed that about 50–60% of the light was transmitted for wavelengths > 700 nm (Figure S3A). The curvature of the transmitted light began to increase at 650 nm, which corresponds to the bandgap (E_g) of AIS. The transmittance was lowest for the undoped AIS sample and increased with Sn doping; the sample with x = 0.02 showed the highest transmittance of approximately 60%. This may reflect a change in the crystalline quality of the AIS films upon Sn doping. The films with x = 0.02 may show a lower density of native defects than the other Sn doping concentrations, which results in a higher transmittance²⁴.

The absorption characteristics of the AIS films and E_g were determined by using diffuse reflectance instead of transmission because of the surface roughness of the films. In the diffuse reflectance spectra (Figure S3B), other than the sharp decrease around E_g, the reflectance increased as the wavelength decreased below 500 nm. The direct bandgap was acquired from the linear extrapolation of the Tauc plot to the x axis (Figure 2A). There were some variations in the calculated E_g among samples with the same composition because of the surface roughness of the films. The thickness of the AIS films was approximately 350–500 nm. Bulk AIS is a direct bandgap semiconductor with E_g ≈ 1.8 eV. The AIS films showed direct bandgaps that range from 1.833 ± 0.004 eV for undoped AIS to 1.703 ± 0.133 eV for x = 0.08. The average E_g and root-mean-square deviation over three films for each composition are shown in Table 2. E_g was observed to increase for x = 0.02, but then decreased when x > 0.04. The increase in E_g with increas-
ing Sn doping from \( x = 0 \) to 0.04 could be a result of the increased presence of the higher \( E_g \) \( \alpha \)-AIS phase, as shown by XRD. Our DFT calculations also suggest that Sn doping could decrease the \( E_g \) of AIS, which could explain the decrease in \( E_g \) when \( x > 0.06 \). The absorption coefficients for the films were \( 10^2 \) cm\(^{-1}\) in the visible range, consistent with previous reports for AIS.\(^{464}\)

**Photoelectrochemical analysis**

The flatband potential (\( V_{bf} \)) corresponds to the applied voltage needed to flatten the bands, or remove the band bending, at the semiconductor-electrolyte interface. Determination of \( V_{bf} \) can identify the location of the Fermi level of the semiconductor. There are three methods to determine \( V_{bf} \): 1) the open circuit voltage upon illumination, 2) the photocurrent onset potential in linear sweep voltammetry (LSV) measurements, and 3) Mott–Schottky (M–S) analysis.\(^{465}\) All three of these measurements were performed for the AIS films with an electrolyte that contained Na$_2$SO$_4$ (0.25 M) and Na$_2$S (0.35 M, pH 13). Figure S4 shows the \( V_{bf} \) obtained from the illuminated open circuit voltage and photocurrent onset for AIS samples with different amounts of Sn doping annealed under \( N_2 \) or S after deposition. M–S analysis was performed only for AIS samples annealed under \( N_2 \).

All of the samples, even with Sn doping and annealing in S, displayed n-type behavior. This was evident from the change to negative potentials under illumination under open circuit conditions, by the positive slope of the M–S plots (Figure 2B), and by the photoanodic behavior (Figure 3), although there were variations in the \( V_{bf} \) values obtained. From the illuminated open circuit voltage measurements, \( V_{bf} \) became increasingly positive with larger amounts of Sn doping (Figure S4). However, the \( V_{bf} \) position acquired from M–S data decreased with larger amounts of doping. This may be because the light intensity used for the open circuit voltage measurements was not strong enough to flatten the bands near the electrolyte interface. M–S plots have also been shown to give \( V_{bf} \) values approximately 0.1 eV more positive than the photocurrent onset value, which may cause the discrepancy.\(^{466}\)

These data contradict the previous results obtained by Albor-Aguilera et al.,\(^{17,18}\) wherein p-type conduction, determined by using hot-probe methods, was observed with Sn doping in AIS. Moreover, the S annealing conditions used here were not effective to make the AIS films p-type. S annealing to fill S vacancies is a common strategy to prepare p-type chalcopyrites,\(^{42,47}\) but the conditions used here do not seem to be effective for producing p-type AIS films.

Determination of the carrier concentration from the slope of the M–S plots showed that the carrier concentration increased with Sn doping at \( x = 0.02 \), but then decreased with increasing Sn doping (Table 3). As suggested by the transmission data, this may reflect a difference in the defect density of the AIS films.

Annealing the spray-deposited samples was required to obtain the chalcopyrite structure, as discussed above. Annealing under a \( N_2 \) or S atmosphere had a notable effect on the photoelectrochemical performance. All of the AIS samples showed n-type photoanodic behavior. As the electrolyte contained Na$_2$SO$_4$ and Na$_2$S, which act as sacrificial hole scavengers, the anodic reactions are shown in the below [Eqs. (2)–(5)].\(^{49}\)

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**Table 2.** Average bandgap and standard deviation for AIS films with different ratios of Sn doping, for which \( x = [\text{Sn}]/[\text{Ag}]+[\text{In}] \).

<table>
<thead>
<tr>
<th>( x )</th>
<th>Average bandgap [eV]</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.833</td>
<td>0.004</td>
</tr>
<tr>
<td>0.02</td>
<td>1.876</td>
<td>0.063</td>
</tr>
<tr>
<td>0.04</td>
<td>1.919</td>
<td>0.030</td>
</tr>
<tr>
<td>0.06</td>
<td>1.746</td>
<td>0.027</td>
</tr>
<tr>
<td>0.08</td>
<td>1.703</td>
<td>0.131</td>
</tr>
</tbody>
</table>

**Table 3.** Flatband position \( V_{bf} \) and major carrier concentration \( N \) calculated from M–S analysis of AIS films with \( x = [\text{Sn}]/[\text{Ag}]+[\text{In}] \).

<table>
<thead>
<tr>
<th>( x )</th>
<th>( V_{bf} ) [V vs. Ag/AgCl]</th>
<th>( N ) ( \text{[pA cm}^{-2}\text{}], \text{Cm}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.897</td>
<td>1.43 \times 10^{19}</td>
</tr>
<tr>
<td>0.02</td>
<td>-0.982</td>
<td>4.66 \times 10^{19}</td>
</tr>
<tr>
<td>0.04</td>
<td>-1.000</td>
<td>4.17 \times 10^{19}</td>
</tr>
<tr>
<td>0.06</td>
<td>-1.005</td>
<td>2.88 \times 10^{19}</td>
</tr>
<tr>
<td>0.08</td>
<td>-1.046</td>
<td>2.68 \times 10^{19}</td>
</tr>
</tbody>
</table>
H₂O + e⁻ → 1/2 H₂ + OH⁻  

SO₄²⁻ + H₂O + 2H⁺ → H₂SO₄

2S²⁻ + 2H⁺ → S₂ 

S²⁻ + SO₄²⁻ → S₂O₃²⁻ + S²⁻ 

SO₄²⁻ + S²⁻ + 2H⁺ → S₂O₃²⁻ 

in which h⁺ indicates a photogenerated hole from AIS. The cathodic reaction was H₂O reduction by using the photogenerated electron (e⁻) to form H₂ on the Pt counter electrode [Eq. (1)].

LSV was used to evaluate the photoanodic performance of the AIS films (Figure 3). The highest photocurrents obtained at 0.5 V versus Ag/AgCl are listed in Figure 3C. For undoped AIS, the highest photocurrent was 1.4 mA cm⁻² (Figure 3C). Sn doping increased the photocurrent to 4.85 mA cm⁻² for x = 0.02 (Figure 3A), but the photocurrent dropped with increasing values of x, for which x = 0.08 gave very similar photocurrents to the undoped AIS for samples annealed under N₂.

Although annealing CIS in a S atmosphere can improve its conductivity and turn it into a p-type material, [22] AIS films treated under similar conditions remained n-type and showed lower photocurrents compared to those annealed under N₂, for which the highest photocurrent of approximately 2 mA cm⁻² was observed for x = 0.02 and 0.04 (Figure 3B and C). Previous studies on the room-temperature electrical properties of AIS found that AIS films annealed under a minimum S pressure had a resistivity five orders of magnitude lower than n-AIS films annealed under a maximum S pressure. [23] S annealing has also been shown to change AIS from n- to p-type, but the p-type films also had several orders of magnitude higher resistivity. [24] These observations, along with our PEC data, can be explained by the fact that S vacancies in AIS are donors [25, 26] and that S annealing can remove these donor levels, decrease the carrier density, increase the resistivity, and decrease the photocurrent.

The energy-band diagram of a semiconductor can be constructed by using Vₐ and the calculated bandgap. For n-type semiconductors, the conduction band edge is approximately 0.1–0.2 eV higher than the Vₐ value. [27] The Vₐ determined by M–S analysis was ~1.0 V versus SCE in the pH 13 electrolyte, and the bandgap was approximately 1.83 eV. Based on these conditions, the band edges for the conduction and valence bands for AIS are shown in Figure 4. The band edges for the commonly studied photoanodes TiO₂, WO₃, and Fe₂O₃ are also shown for comparison. [28] The band edges for AIS straddle the H₂ and O₂ redox potentials, which indicate that it is suitable for overall H₂O splitting without additional voltage bias, unlike WO₃ and Fe₂O₃. It also has a higher overpotential for H₂ evolution than TiO₂. However, as mentioned previously, sulfide semiconductors are not typically stable to photocorrosion. To confirm this, the stability of a Sn-doped AIS film with x = 0.02 was evaluated at 0 V versus Ag/AgCl in a Na₂SO₄ solution (0.5 M, pH 7) under chopped light. In this environment, the initial photocurrent was approximately 2.1 mA cm⁻², which decreased to approximately 1.2 mA cm⁻² at which it was stable for approximately 1 h (Figure 3D). After 1 h, the photocurrent remained at 50% of its original value. This result indicates that AIS may suffer from degradation without a sacrificial reagent or protective coating from photo-oxidative corrosion, similar to other sulfide materials. [24, 27]

DFT calculations

DFT calculations were performed to understand how the band structure of AIS changed after Sn doping and to better understand the location of the Sn dopants in the AIS structure. The previously observed p-type behavior in Sn-doped AIS was attributed to Sn located at S sites. [27] The dopant-formation energy for Sn to occupy a Ag, In, S, or interstitial site in AIS (Figure S5) was calculated for each of the different doping ratios used (Table 4). The results show that the Sn dopants prefer to occupy interstitial sites until high doping ratios (x = 0.125). Moreover, Sn in an S site is highly unfavorable.

To further investigate the Sn-doping effect, the electronic band structures and density of states (DOS) of pure AIS and Sn doped into an interstitial site in AIS for x = 0.031 and 0.125 were calculated (Figures 5, 6, and 7). The undoped AIS and Sn-doped AIS with x = 0.125 were calculated based on the AIS unit cell, whereas the x = 0.031 band diagram was predicted by using a 2x2x1 supercell. Therefore, the x = 0.031 case has a higher DOS and the energy levels form bands. The conduction band of pure AIS was found to be dominated by In 5s and S 3p orbitals, whereas the valence band is occupied by Ag 4d

<table>
<thead>
<tr>
<th>x</th>
<th>Site</th>
<th>Ag</th>
<th>In</th>
<th>S</th>
<th>Interstitial</th>
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<td>1.0</td>
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<td>1.0</td>
<td>1.9</td>
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</table>
and S 3p electrons. The addition of Sn into the interstitial sites resulted in the formation of three shallow donor levels and a deep acceptor level (Figure 5B). This deep acceptor level is composed of Sn 5p and S 3p orbitals for $x = 0.125$, whereas it is composed of Sn 5s and In 5s orbitals for $x = 0.031$. Close examination of the DOS near the region of the bandgap revealed that the conduction and valence band edges for pure AIS and Sn-doped AIS with $x = 0.031$ matched well (Figure 5A). However, the bandgap for $x = 0.125$ looks smaller, which indicates that higher Sn doping can reduce the bandgap of AIS, consistent with our experimental results (Table 2, Figure 2A). The DOS results also show that the deep acceptor level introduced by the Sn dopants increased proportionally with the amount of Sn and shifted towards the valence band for $x = 0.125$. This reflects the contribution from the S 3p orbital to the deep acceptor level.

We believe that the photocurrent data in Figure 3C can be explained as follows. The shallow donor levels introduced by the Sn dopants can result in an increase in the carrier concentration, consistent with the M–S results (Table 3), which can lead to higher photocurrents. However, at higher doping levels, the deep acceptor level is closer to the valence band, which increases the likelihood that the concentration of holes can be increased. This will cause the donor and acceptor levels to compensate each other, which decreases the major carrier concentration, consistent with the M–S analysis and photocurrent data. Such self-compensating effects have been observed in Sb-doped AIS in which the introduction of Sb allowed the preparation of AIS that is p-type but also highly resistive.\(^{44}\)

Moreover, it is well known that deep levels that are near the center of the bandgap can act as recombination centers and decrease the lifetime of carriers.\(^{49}\) As the DOS of the deep acceptor level increases with increased Sn doping, increased recombination can occur, which leads to lower photocurrents. This is consistent with our photocurrent data (Figure 3C) as well as the carrier concentrations derived from M–S analysis (Table 3).

Both the experimental and computational results show that small amounts of Sn doping into AIS can result in a higher photocurrent performance (for which $x = 0.02$ gave the highest value), although increasing the amount of dopant can be detrimental. However, even with the optimized amount of Sn dopant, the observed photocurrents were much lower than the theoretical maximum photocurrent of about 20 mAMcm\(^{-2}\) based on the 1.8 eV bandgap for AIS.\(^{45}\) This indicates that there may be other factors involved that can affect the photocatalytical performance such as surface states. Surface states have been found to play a large role in surface recombination in Cu-chalcocite pyrite photocathodes, in which negligible photocurrents are often observed if surface passivation through coating with another semiconductor or cocatalyst decoration is not used to improve charge separation\(^{11,12,46}\). Similar strategies may also be used for AIS and are currently under investigation.

**Conclusions**

Spray pyrolysis was successfully used to synthesize thin films of n-type AgIn\(_2\)S\(_4\) with a chalcopyrite structure. The properties and PEC performance of AIS were found to depend on both intrinsic defects and extrinsic dopants. Annealing under N\(_2\) resulted in higher photocurrents, likely a result of the formation (or maintenance) of S vacancies that act as donors. Sn doping at a ratio of 0.02 gave the highest photocurrent, but higher amounts of Sn resulted in decreased photocurrents and carrier concentrations. DFT results showed that Sn dopants likely occupy interstitial sites and that Sn introduced shallow donor levels and a deep acceptor level, of which the latter could act as a recombination site at higher Sn doping concentrations.

**Experimental Section**

Spray pyrolysis was used to prepare undoped and Sn-doped AgIn\(_2\)S\(_4\) thin films on FTO glass substrates as described in the literature.\(^{37,38}\) A solution of SC(NH\(_2\))\(_2\) (0.15 M, Sigma–Aldrich), CH\(_3\)COOAg (0.04 M, Reagent Plus, 99%, Sigma–Aldrich), and InCl\(_3\) (0.1 M, Sigma–Aldrich) was prepared in deionized water. CH\(_3\)COOAg and SC(NH\(_2\))\(_2\) were mixed first to form a dark brown solution to avoid precipitation. According to previous studies, Ag is more volatile than the other reagents, and the AIS chalcopyrite structure is favored when the sample is Ag rich.\(^{37,38}\) Thus, the Ag/In and S/In ratios used were 1.5 and 5, respectively. Excess S was needed owing to the volatility of SC(NH\(_2\))\(_2\) and SnCl\(_2\) (Sigma–Aldrich) was added into the solution according to the ratio $x = \text{[Sn]}/\text{[Ag] + [In]}$, which was varied from 0 to 0.08. After 10 min of stirring, absolute ethanol was added to the solution to promote solvent evaporation during the deposition. The substrates were cleaned by using ultrasonication in acetone, ethanol, and deionized water for 30 min each. After cleaning, the
FTO glass was fixed to a hot plate with a temperature of 300°C, as determined by using an IR camera. 
N₂ was used as the carrier gas at a pressure of 6×10⁻³ Pa. The spacing between the spray gun and 
the substrate was 25 cm. After deposition of the film, the sample was washed with ethanol. For annealing experiments, N₂ annealing 
was performed in a tube furnace at 375°C for 1 h, whereas S annealing was performed by adding S (250 mg, Sigma-Aldrich) and 
the samples to a steel autoclave sealed with a Cu O-ring gasket followed by heating in a box furnace at 400°C for 2 h. After S annealing, 
the sample was heated at 120°C for 10 min under N₂ to remove any excess S deposited on the surface. 

XRD characterization of the films was performed under monochromatic CuKα radiation (λ =1.5405 Å, Panalytical Xpert Pro). 
Field emission scanning electron microscopy (FSEM, FEI XL30) and EDS were performed to characterize the morphology and composition 
of the deposited films. To accurately determine the Sn concentration, EDS was performed on Sn-doped AIS films that were deposited 
on to glass substrates, not FTO. Optical transmission and diffuse reflectance were obtained by using a UV/Vis spectrometer (Perkin-Elmer Lambda 18) 
equipped with an integrating sphere over the wavelength range of 300 to 850 nm. The surface thickness was determined 
by using a profilometer (Dektak II). 

All photoelectrochemical tests were performed by using a potentiostat (Biologic VMP3) with the sample as the working electrode, Pt 
wire as the counter electrode, and a Ag/AgCl reference electrode. The electrolyte was prepared with deionized water and contained 
Na₂S (0.35 M) and Na₂SO₃ (0.25 M, pH 13) as sacrificial agents. A 450 W Xe lamp (Newport, model 69923) was used to provide an 
illumination of 100 mWcm⁻² intensity. The intensity of the illumination was measured by using a photometer (Thorlabs, Model S303). 
LSV was performed in the dark and under illumination from −1.0 to 0.5 V vs. Ag/AgCl. The photocurrents were evaluated by subtracting 
the dark current from the light current at 0.5 V vs. Ag/AgCl. To determine the flat-band voltage, illuminated open circuit measurements and M–S analysis were performed in an electrolyte 
that contained sacrificial reagents to compare to the photocurrent onset values obtained from LSV. M–S analysis was performed in the 
dark with a frequency of 10 Hz, AC amplitude of 25 mV, and voltage range of −0.9 to −0.6 V vs. Ag/AgCl. M–S analysis was also used 
to determine the free carrier concentration. Chronoamperometry was used to perform the stability test at 0 V vs. Ag/AgCl in a 
Na₂SO₃ (0.5 M) electrolyte. 

Computational methods 

DFT calculations were performed to study the Sn-doping effects in AIS by employing the VASP code [5,32]. The PBE functional [35] 
and projector-augmented wave (PAW) [34] potentials were used along with plane wave basis sets. The energy cutoff for the plane wave 
basis set was 300 eV. The total energy was converged to within 0.01 meV. The reciprocal space of the crystal was sampled at 6×6×6 
by using Monkhorst–Pack meshes. The Ag-4d and 4s; In-4d, 5s, 
and 5p; S-3s, and 3p; and Sn-4d, 5s, and 5p electrons were treated as valence electrons in the calculations. Based on these parameters, 
the tetragonal AgInS₂ (space group 42d) bulk crystal lattice constants were a = 5.937 Å and c = 11.456 Å, which are very close to 
the experimental values [54]. 

To dope AgInS₂ with Sn, there are generally four possible doping scenarios: the Sn atom could take a) 1 Ag site, b) 2 In sites, c) 3 Sn sites, 
or d) 2 interstitial sites. To change the doping rate of Sn, four different AgInS₂ simulation cells were studied: a) using the unit cell 
for a doping rate of x=0.125, b) using a 2x2x1 supercell for x=0.0625, c) using a 2x2x1 supercell for x=0.031, and d) using a 2x 
3x1 supercell for x=0.02. To identify which site the dopant Sn prefers, the dopant formation energy is defined as follows 
[Eq. (6)–(9)]:

For Sn in an Ag site:

\[ E_{\text{form}} = \left( E_{\text{AgInS}}-E_{\text{Ag}}-E_{\text{Sn}} \right) \]  

(6)

For Sn in an In site:

\[ E_{\text{form}} = \left( E_{\text{AgInS}}-E_{\text{Ag}}-E_{\text{Sn}} \right) \]  

(7)

For Sn in a S site:

\[ E_{\text{form}} = \left( E_{\text{AgInS}}+E_{\text{Sn}}-E_{\text{In}} \right) \]  

(8)

For Sn in an interstitial site:

\[ E_{\text{form}} = \left( E_{\text{AgInS}}-E_{\text{Ag}}-E_{\text{Sn}} \right) \]  

(9)

in which the m values 1, 2, 4, and 6 correspond to the unit cell, the 2x2x1 supercell, the 2x2x1 supercell, and the 2x 
3x1 supercell, respectively. 

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Tin best or tin pest? The role of Sn extrinsic dopants in chalcopyrite AgInS$_2$ is investigated to understand their effects on the optical, electronic, and photoelectrochemical properties of this promising photoanode material. We found that at low amounts, Sn increased the AgInS$_2$ carrier concentration and photocurrent, but was detrimental at higher dopant concentrations.