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# Review—Solution Processing of CIGSe Solar Cells Using Simple Thiol-Amine Solvents Mixture: A Review

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Recent results demonstrate the potential of thiol-amine binary solvents to prepare highly efficient thin-film chalcopyrite photovoltaic devices. The power of these solvent mixtures lies in their ability to dissolve a large variety of metal and metal chalcogenide precursors and their ease of application in low-temperature solution-based deposition techniques. This review recounts the early reports that revealed the flexibility and broad ability of the thiol-amine solvent system, and the chemistry behind these solvents. Next, the resulting CIGSe films PV devices fabricated using amine-thiol solution processing techniques are being introduced and analyzed in detail. Finally, Current challenges, as well as prospects for effective technology implementation, were discussed.

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Copper indium gallium selenide (Cu(In,Ga)$Se_2$ or CIGSe) thin film is one of the most attractive photovoltaic (PV) absorber materials. CIGSe has been well-studied and regarded as the next-generation solar cells due to its high absorption coefficient, favorable bandgap, outstanding photoelectric properties, and stability against photodegradation.[1–3] With the impressive progression made in recent years, CIGSe recorded cell efficiencies up to 22.9%,[4,5] which is the highest efficiency for thin-film solar cells.

The high-efficiency CIGSe absorber layer is conventionally fabricated using vacuum deposition techniques. The use of such methods requires high-cost equipment, which is the major obstacle for manufacturing processes.[6,7] Atmospheric solution-based deposition of semiconducting materials offers an attractive alternative to traditional vacuum deposition methods due to lower raw materials used and equipment prices, large-area production throughput, and better compatibility with flexible substrates and roll-to-roll fabrication processes.[8,9]

Solution deposition of the CIGSe absorber layer involves the application of two sequential steps: the formation of a homogeneous molecular precursor solution containing dissolved metal precursor, followed by deposition at relatively low temperatures using one of the coating techniques. In the later step, appropriate thermal treatment is applied to evaporate the solvent, eliminate impurities, and facilitate pure phase crystalline growth.[10–13] The problem with this technique is most chalcogenide sources, especially selenide (Se) and sulfur (S), are insoluble in common solvents, as the dissolution process requires solvents to efficiently overcome the strong covalent bonds that make up these structures.[14,15]

In 2004,[16] for the first time, Mitzi and co-workers at IBM used hydrazine in the presence of excess Se or S to dissolve bulk metal chalcogenides. The hydrazine solvent was successfully extended to the CIGSe absorber layer fabrication.[10,14,17,18] With a hydrazine-based slurry, a record power conversion efficiency of 17.3% for CIGSe solar cells was achieved.[11] Although the hydrazine-based device recorded the highest non-vacuum conversion efficiencies, it is difficult to commercialize due to its high toxicity and carcinogenic nature.[18–21]

With the aim of replacing hydrazine, less toxic and environmentally benign solvents have been adopted, such as dimethyl sulfoxide (DMSO) and thiourea,[22] thioacetic acid,[23] and butyldithiocarbamic acid.[24] Although some of these solvent systems have successfully produced relatively efficient CIGSe solar cells, none of the systems have higher efficiency than those from the hydrazine system. Unfortunately, the films produced using those free hydrazine solutions are either porous or have a fine-grained layer over Mo back contact, which limits the additional improvement of the device performance. Moreover, the precursor preparation is relatively complicated, and heat treatment is also required for dissolution. Furthermore, the solvents used are limited to deposit a few metal chalcogenides. Therefore, it is difficult to extend this precursor method to other metal chalcogenide systems.[13,25,26]

Although vacuum deposition technique is applied to fabricate high-efficiency CIGSe solar cells, the approach cannot guarantee cost reduction in continuous mass production because vacuum-based deposition techniques often require sophisticated deposition equipment and high initial investment. The demand for low-cost, high-throughput mass production has been pushing the research focus progressively toward less expensive, non-vacuum, and simple solution-based deposition approaches. The most successful pure solution approach to date in terms of the recorded CIGSe solar cell power conversion efficiency of 17.3% is the hydrazine-based technique. Despite the high efficiency of these hydrazine-based CIGSe solar cells, the toxic, explosive, and carcinogenic nature of the hydrazine product makes this process difficult at the industrial scale. To fully realize the advantages of solution-based deposition technique, alternative stable, non-toxic, environmentally friendly, and scalable production of precursor solutions or inks should be used to fabricate high-quality CIGSe absorber layer. The issues mentioned motivate more research efforts on real solvents that can dissolve and recover chalcogenide effectively and safely.

Subsequently, the process is extended to thiol-amine solvent mixtures, which can dissolve several precursors that could not be commonly dissolved previously. This new approach is promising for thin-film deposition using coating techniques. During annealing, most organic species are recovered without leaving undesirable impurities. The clean deposition approach and simple preparation of the precursor solution make this route extremely attractive from a manufacturing perspective. This paper aims to review previous reports regarding the flexibility and broad solvent ability of the thiol-amine solvent system and to analyze the fabricated CIGSe PV devices using these solutions.

## Thiol-Amine Solvents

Agrawal et al. introduced thiol-amine binary mixtures as hydrazine alternative solvents for the solution deposition process. They defined the term ‘alkahest ‘or “thiol-amine solvents” as a mixture of at least one type of amines (monoamines or diamines) and at least

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one type of thiols (monothiols or dithiols), which can effectively dissolve different types of metal sources and chalcogens.[27]

The use of thiol-amine solvents started in 2012. Liu et al.[28] demonstrated a new Se precursor for semiconductor nanocrystals applications by dissolving Se powder in a mixture of alkylthiols and oleylamine. The novelty of this method is that Se powder cannot be dissolved in amines or thiols alone but the powder dissolves in their mixture at room temperature. The color of the resultant Se solution was clear dark red, and the solution could be recovered by slow oxidation in the air to precipitate elemental selenium. Thus, this homogeneous solution has been successfully applied to synthesize high-quality Se nanomaterial thin-film.

Webber and Brutchey presented a binary solvent mixture composed of ethanedithiol (EDT) and ethylenediamine (EN).[29] The EDT/EN mixture with the ratio of 1:10 (vol:vol) could dissolve and recover nine bulk $M_2X_3$ chalcogenide materials at room temperature and ambient pressure. It was noticed that heating at higher than room temperature accelerated the formation of homogeneous solutions. Also, the stirring process facilitated dissolution. The resultant solutions were optically transparent and stable at room temperature. A photograph of the nine solutions is shown in Fig. 1. A subsequent work[30] determined that the same binary solvent could effectively dissolve elemental grey selenium and tellurium at the same conditions. Notably, the solubility of elemental Se in thiol-amine solvents is exceptionally high compared to the solubility reported in other solvents.[31]

The recovery of the dissolved precursors as a solid is the most influential step on the quality of the deposited chalcogenide materials. To identify the recovery temperatures for the thiol-amine precursor solution, thermal gravimetric analysis (TGA) was performed in the cases of elemental selenium,[30] sulfides, and selenides,[29] as depicted in Fig. 2.

The availability of these mixtures to dissolve and decompose inorganic semiconductor materials offers a new free-hydrazine route for chalcogenide thin-film deposition. Building off this idea, EDT/EN solvent was used to deposit high quality and nearly stoichiometric SnS thin film.[32] According to scanning electron microscopy (SEM), the thin films were free of cracks or pinholes. The calculated indirect and direct bandgap s of the recovered material were in good agreement with the reported values. The as-deposited films exhibited p-type behavior, which is optimal for solar cell applications. These results confirmed that the thiol-amine based inks are ideal for solution processing high-quality chalcogenide thin films.

In order to expand the choice of starting materials for thiol-amine solution formulation, alkahest solvents have been reported to be capable of dissolving 10 inexpensive bulk oxides ($Cu_2O$, ZnO, $GeO_2$, $As_2O_3$, $Ag_2O$, CdO, SnO, $Sb_2O_3$, PbO, and $Bi_2O_3$) under ambient conditions.[33] These dissolved oxides can be directly recovered to the corresponding sulfides as thiol itself is considered as the sulfur source in the solution. Also, the dissolved oxides can be mixed with chalcogens (i.e., Se and Te) to produce inks that yield crystalline Se or telluride (Te) after deposition. Almost at the same time, Lin et al.[34] reported that the thiol-amine mixture could effectively dissolve and recover a large number of metal chalcogenides, including $Cu_2S$, $Cu_2Se$, $In_2S_3$, $In_2Se_3$, CdS, and others. Later, the thiol-amine solvent mixtures were used to dissolve elemental Cu, Zn, In, Ga, In, Mg, Fe, Co, Ni, and Mn.[35]

The EDT/EN solvent is not the only thiol-amine mixture that can be utilized to formulate chalcogenide inks; various combinations of (mono or di/thiols) with (mono or di/amines) can be used. Brutcheys' group found that the identity of the used thiol in the starting precursor solution could affect the thin-film recovered phase.[29] In a similar manner, Agrawal's group demonstrated the dissolution of metals, metal chalcogenides, metal acetates, metal acetylacetonate, and halide salts in (EDT)/monoamines mixtures. Once more, they noticed that the deposited crystalline phase was influenced by the starting solvents and the precursors used.[36,37] Therefore, the recovery of the desired chalcogenide material requires careful selection of the suitable thiol-amine mixture. For example, elements and metal chalcogenides cannot dissolve in monoamine-monothiol or diamine-monothiol mixtures, whereas most of the metal salts can dissolve in any thiol-amine mixture.[38]

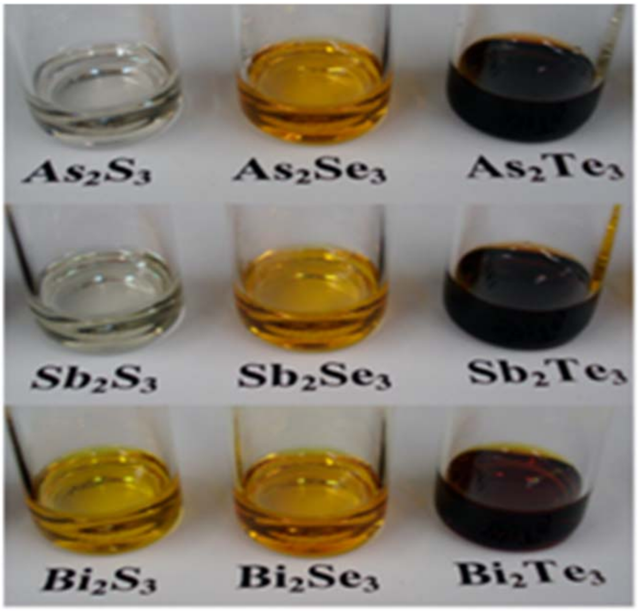

**Figure 1.** A Photograph of dilute solutions of nine $M_2X_3$ chalcogenide semiconductors in a (1:10 v/v) EDT/EN mixture.[29]

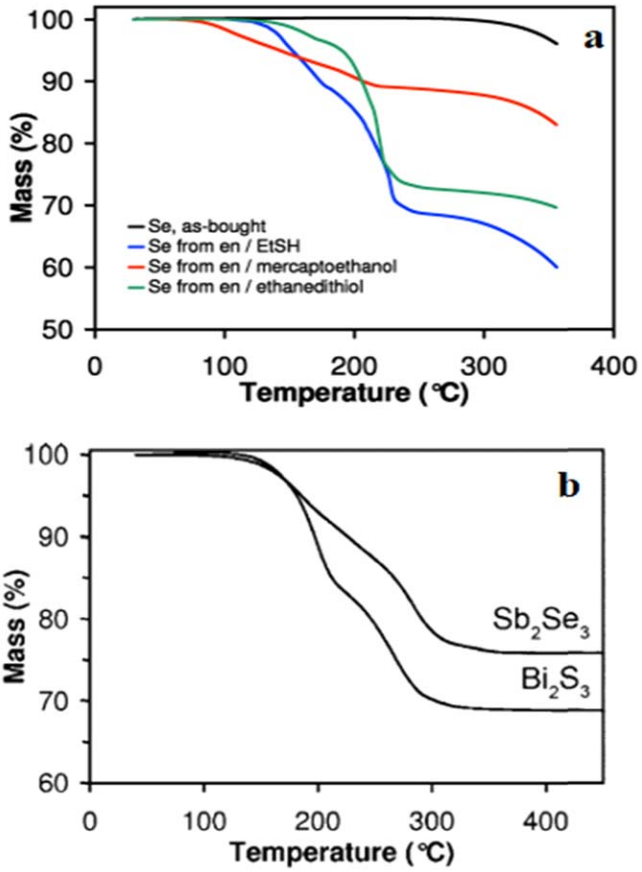

**Figure 2.** TGA data of the solid precursors obtained by pre-drying of (a) elemental selenium. solutions in different thiol-amine solvents[30] (b) $Sb_2Se_3$ and $Bi_2S_3$ dissolved EDT/EN solvent.[29] (In a nitrogen atmosphere at 125 ° C).

$$\begin{aligned}
&\textbf{(1)}\quad 2R_1 - SH \rightarrow R_1 - S - S - R_1 + 2H^+ + 2e^- \\
&\textbf{(2)}\quad Se_8 + 2e^- \rightarrow Se_8^{2-} \\
&\textbf{(3)}\quad 2R_2 - NH_2 + 2H^+ \rightarrow 2R_2 - NH_3^+ \\
&\textbf{(4)}\quad Se_8^{2-} + 2R_2 - NH_3^+ \rightarrow (Se_8^{2-})(R_2 - NH_3^+)_2
\end{aligned}$$

**Figure 3.** Proposed reaction mechanism of selenium dissolution in thiol/amine Mixture.[40]

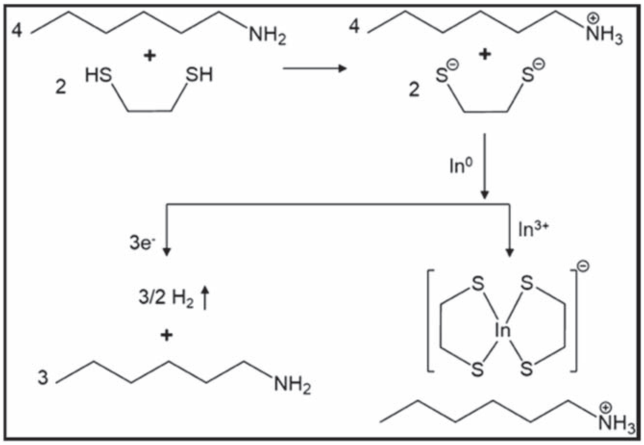

**Figure 4.** Proposed dissolution mechanism for (In) Metal in thiol-amine Solution mixture.[42]

***The chemistry of the thiol-amine solvent system.***—Although thiol-amine mixtures have shown great promise for chalcogenide thin-film solution processing, a few studies have been dedicated to investigating the chemistry behind this solvent system. It is worth noting that understanding the dissolution mechanisms and nature of the formed complexes is required to optimize the deposition parameters and identify the precursors and solvents that can be chosen to obtain high-quality chalcogenides films.

The use of thiols and amines combinations dates back to 1967 for the dissolution of bulk S.[39] In the proposed dissolution mechanism, the amine deprotonates the thiol, and the resulting thiolate anion opens 8-sulfur ring by a nucleophilic attack. The work reported by Webber et al.[29] showed that adding thiol in excess amine, approximately 10:1 vol:vol amine-to-thiol ratio, resulted in a remarkable dissolution ability. The electrolytic conductivity was observed to increase about 15,000 times, and the resistance decreased from 2.04 MΩ to 136 Ω, thus suggesting extensive ion formation. The stoichiometry of $(ENH^+)_2(EDT^{-2})(EN)$ was identified with the lattice stabilized by hydrogen bonding formed by amine and thiol groups. The N–H···S hydrogen bonding is an essential contributor to the dissolving of metal chalcogenides.

The dissolution of elemental chalcogenides in thiol/EN solvent mixtures was studied to identify the chemical nature of the solution. The dissolution of Se or Te was initiated by the transfer of protons from the thiol to amine. The partial thiol deprotonation was supported by the loss of the signal for the sulfhydryl proton in the $1^H$ NMR spectrum and the significantly reduced intensity of the S–H signal in the Raman spectrum of the thiol-amine mixture compared to the pure thiol.[30] In another study, the dissolved Se in oleylamine/alkylthiol mixture was studied by gas chromatography-mass spectrometry (GCMS). Through GCMS analysis, the presence of diethyldisulfide and elemental Se in the solution was observed with no appearance of organoselenium formation.[40] The previous results suggesting the mechanism for Se dissolution in the thiol/amine mixture are shown in Fig. 3.

Detailed analysis was performed to identify the species formed upon the dissolution of copper halide in the thiol-amine solvent.[41] CuCl and $CuCl_2$ precursors dissolved in n-butylamine/1-propanethiol mixtures were studied. The complexes detected in the solutions included copper thiolate complexes along with various ammonium chloride adducts, and no copper amine complexes were observed. Copper was found in its +1 oxidation state. These results suggested that the dissolution started by thiol deprotonation, followed by the coordination of thiolate anions with copper cations.

Recently, the structure and dissolution of Cu and In metal complexes formed in monoamine/dithiol solvents were examined.[42] Several characterization techniques were used to analyze these solutions, and then the overall reaction mechanisms of Cu and In in hexylamine/EDT mixture were proposed. It was found that the metal dissolution generated hydrogen ($H_2$) gas during oxidation. The metal oxidized to an average of $Cu^{+1}$ and $In^{+3}$ cations, thus forming bis(1,2-ethanedithiolate)indium(III) in the case of indium dissolution and high nuclearity Cu(I) thiolate clusters (number of Cu atoms = 2−8 in the molecule). The proposed reaction for In is shown in Fig. 4.

Despite the efforts exerted to investigate the chemistry and dissolution mechanisms of thiol-amine solvents, much remains unknown, especially the identity of the complexes formed in different thiol-amine combinations and how these complexes variations affect the quality of the deposited chalcogenide films. Furthermore, the safety and handling requirements during the thin-film deposition process should be inspected. Attempts must continue to expand the knowledge and optimize this promising solution-based technique to produce high-quality thin films.

***Thin-film deposition using thiol-amine solvents.***—Thin-film solution deposition involves two steps: the preparation of a homogeneous precursor solution, in which thiol-amine mixtures provide

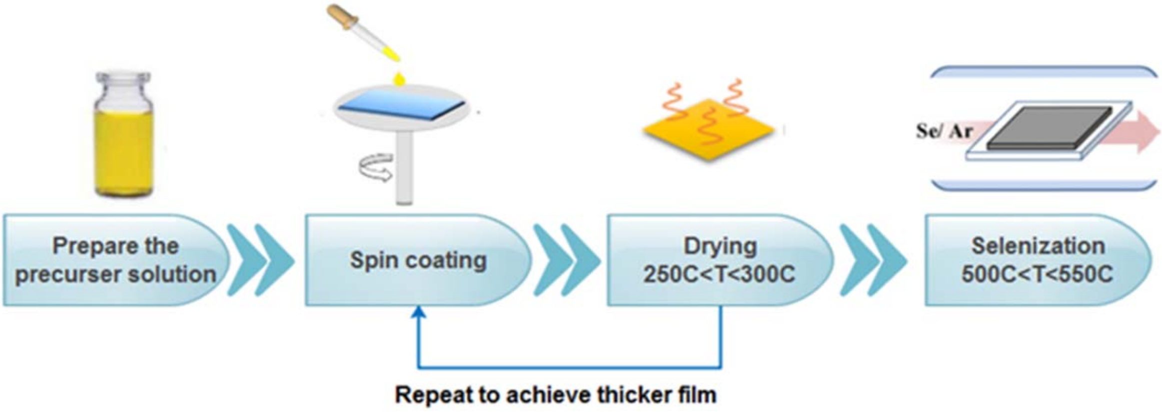

**Figure 5.** Schematic diagram of the sequential method used to fabricate CIGSe start with spin coating processes followed by annealing and, finally, selenization step.

many possible precursor choices for the formation of chalcogenide inks.[27,29,30,33–36] The precursor solution is then deposited by one of the coating techniques, such as spin or spray coating, doctor blading, inkjet printing, and roll-to-roll printing. Thiol-amine based thin films are commonly deposited using a similar process that starts with coating the precursor solution onto a substrate. Then, the prepared film is dried at intermediate temperature (250°C–350°C) to remove the solvent residual. The coating and sintering steps are repeated several times to achieve the desired thickness. Finally, post-selenization treatment is performed at temperatures of approximately 450 °C–600 °C in Se atmosphere.[43–45] Figure 5 shows the sequential spin-coating steps for CIGSe absorber layer deposition.

Selenization is the most crucial step to transform coated raw films into good uniformity, high-quality, single-phase CIGSe films with improved crystal size suitable for solar cells. Usually, the as-prepared film contains densely-packed amorphous colloidal particles. During selenization, sulfur leaves the film and is replaced by Se from vapor, hence producing a low or free sulfur film content. The replacement of sulfur by Se improves crystallization and eliminates void space.[46–48] The process also enlarges grain size, which effectively decreases grain boundary concentration, potentially boosts carrier mobility, reduces the chance of electron-hole recombination, and subsequently increases current generation.[49–51]

The next section discusses the development of a molecular-based approach for CIGSe PV devices using the thiol-amine solvent combination. Table I summarizes the recent PV performance of processed CIGSe thin-film devices fabricated using the thiol-amine route.

***CIGSe thiol-amine-based solar cells.***—The first thiol-amine solution-processed CIGSe solar cell was reported by Zhao et al.[52] EDT/EN mixture was used to dissolve elemental Cu, In, Ga, and Se at 60 °C together, then the solution was stirred for several hours until a clear homogeneous solution was formed. The CIGSe absorber layer solution was spin-coated onto the Mo-SLG substrate, followed by annealing in an argon atmosphere at 350 °C. The coating/annealing steps were repeated until 1–2 $\mu$m film thickness was obtained. Finally, the annealed films were selenized in a graphite box containing Se pellets in a tubular furnace at 550 °C. These CIGSe thin films were then integrated into a typical SLG/Mo/CIGSe/CdS/i-ZnO/ITO/Al PV device. After selenization, the X-ray diffraction (XRD) peaks became stronger and narrower, resulting from the increase of crystallite size. The SEM image demonstrated that the selenized CIGSe absorber showed a double-layer structure of about 600 nm large-grains layer at the top and 600 nm layer of smaller grains at the back. The reason for the formation of the layered structure referred to carbon residuals observed by energy-dispersive X-ray spectroscopy (EDX). A significant drop in the external quantum efficiency (EQE) spectrum was observed in the near-infrared range, mainly due to the fine-grained layer. The solar cell yielded an efficiency of 9.5%. The J-V curve and the EQE spectrum of the performing cell are shown in Fig. 6.

Subsequent work has been done to reduce the fine-grained layer to a large extent by optimizing the post-selenization step conditions.[53] CIGSSe ink was prepared by dissolving several bulk chalcogenides ($Cu_2S$, $In_2Se_3$, Ga, and Se) in EDT/EN (vol:vol of 1:10). The selenization step was conducted by a rapid thermal selenization process (RTP) furnace using a round graphite box. A larger grain size was obtained, and the fine-grained layer was effectively eliminated when using the RTP furnace instead of a tubular furnace, and a round graphite box instead of a rectangular graphite box. The conversion efficiency improved to 11.75%. The PV performance was mainly limited by the low $V_{oc}$ of 596 mV resulting from the relatively high bandgap ($E_g$ = 1.17 eV),[58–60] which was higher than the optimum bandgap value ($E_g$ = 1.14 eV),[61,62] and higher than the champion bandgap value ($E_g$ = 1.13 eV) of the CIGSe device.[4,63]

Agrawal's group[37] prepared individual solutions of $Cu_2Se$, $In(OAc)_3$, $Ga(acac)_3$, and Se in a mixture of dithiol-monoamine solvent. Then, the four solutions were mixed in appropriate ratios to produce CIGSe precursor ink, which was then directly spin-coated onto a glass substrate. After thermal annealing and selenization, an ultra-thin (520 nm) CIGSe layer was achieved with an efficiency of 10.3% with a relatively low $J_{sc}$ value of 29.4 mA cm$^{-2}$ and 1.16 eV bandgap. In the effort of increasing the absorber layer thickness to improve the PV performance, the researcher faced three difficulties: (a) the formation of sandwiched fine-grained layer upon selenization, (b) the porosity of the selenized films, and (c) copper loss from the annealed films during the subsequent spinning steps. Optimizing the experimental results suggested that either longer annealing time or higher annealing temperature during spin coating resulted in larger grains and more copper being incorporated into the lattice. Also, soaking the annealed films in the molecular precursor ink for 10 min, followed by drying at 300 °C after each coating step, prevented the formation of a fine-grained layer. After optimization, a 1.1 $\mu$m thicker film with very thin (<100 nm) fine-grained layer was detected, and an efficiency of 12.2% with a composition of $Cu_{0.9}In_{0.7}Ga_{0.3}Se_{2.05}$ was achieved.

Recently, CIGSe solar cells were prepared using $Cu_2S$, $In_2Se_3$, Ga, and Se dissolved in the EDT/EN solvent mixture.[56] The main improvement over the previous device with 12.2% efficiency is the construction of Ga grading composition profile of the CIGSe absorber layer, i.e., using higher GGI ([Ga]/([Ga] + [In]) ratios toward both the back and front contact and lower Ga content ("notch region") close to the front surface. It is well known that the Ga gradient is an effective technique for improving charge collection and maximizing solar spectrum absorption.[12,64–66] The precursor solution was prepared with different GGI ratios (10%, 30%, 35%, and 50%) and then deposited in different Ga gradient profiles to determine the optimal location and depth of the notch. The highest performing cell demonstrated improved efficiency of 13.12% and relatively high $V_{oc}$ and $J_{sc}$, and optimal bandgap value of 1.14 eV.

Thiol-amine based chalcopyrite absorber layer was deposited using the spin coating technique, in addition to the spraying pyrolysis method being utilized.[54,67] About 1−1.5 $\mu$m thick $CuIn(S,Se)_2$ (CISSe) absorber layer was deposited by spraying mixtures of $Cu_2S$ and $In_2S_3$ dissolved in EDT/EN at 310 °C in the air onto Mo coated glass to yield CIS precursor films, which were then transformed to dense large-grained crystalline CISSe film of approximately 600 nm thick after selenization. It was determined that using an RTP oven during selenization produced a thinner $MoSe_2$ layer and improved the electrical contact at the Mo/CISSe interface compared to the selenization process using a tube furnace. The solar cell device with the configuration of IZO/ZTO/CdS/CISS/Mo/glass achieved the conversion efficiency up to 8%, $V_{oc}$ of 452 mV, $J_{sc}$ of 31.4 mA cm$^{-2}$, FF of 56%, and a bandgap of 1.03 eV. The performance of this device is comparable to a similar hydrazine-based low sulfur content CISSe with 10.7% efficiency.[17]

Arnou et al. attempted to improve the sprayed device performance.[55] Specifically, increasing the bandgap by gallium incorporation. The CIGSe absorber layer was prepared by individually dissolving $In_2S_3$, $Cu_2S$, and (Ga + Se) in EDT/EN and stirred all night. Inks with different Ga contents were used. The characterization of selenized films by XRD indicated that a pure chalcopyrite phase was achieved, and the EQE spectra showed systematic red-shifted emission as the Ga content increased. The efficiency of the incorporated PV devices reached 9.8% for a graded bandgap of 20%–30% GGI content and higher bandgap as expected. The later improvement achieved a champion efficiency of 12.0% for the same device by implementing N/Mo back-contact barrier to suppress $MoSe_2$ formation at the Mo/CIGSe interface during high-temperature selenization.[68,69] The sputtered nitride Mo barrier layer significantly reduced $MoSe_2$ formation and consequently improved the stability and quality of the CIGSe absorber.[57,67]

On the other hand, to address difficulties related to the corrosivity and toxicity of thiol-amine solvents, a new solution approach was introduced using metal thiolate salts formed in the thiol-amine solvent. Firstly, metal thiolate salts were isolated by evaporating the

**Table I. Photovoltaic performance of processed CIGSe thin-film devices fabricated using thiol-amine approaches.**

| Absorber Material | CIGSe | CIGSe | CIGSe | CISe | CIGSSe | CIGSe | CIGSSe |
|---|---|---|---|---|---|---|---|
| Precursors | Cu, In, Ga, Se | $Cu_2S$, $In_2Se_3$, Ga, Se | $Cu_2Se$, $In(OAc)_3$, $Ga(acac)_3$, Se. | $Cu_2S$, $In_2S_3$. | $In_2S_3$, $Cu_2S$, Ga,Se | $In_2S_3$, Cu2S, Ga,Se | $In_2S_3$, $Cu_2S$, Ga,Se |
| Solvent component, vol:vol ratio | EDT+EN, 1:10 | EDT+EN, 1:10 | EDT+HA, 1:10 | EDT+EN, 1:10 | EDT+EN, 1:10 | EDT+EN, 1:10 | EDT+EN, 1:10 |
| Dissolution Conditions (temperature/stirring time) | 60/Few hours. | 70/12 hours | RT/overnight. | RT/overnight. | RT/overnight. | 70/overnight. | RT/overnight. |
| Deposition Technique/annealing condition°C. | Spin coating/350 | Spin coating/350 | Spin coating/325 | Spray Pyrolysis/310 | Spray pyrolysis/310 | Spin coating/350 | Spray pyrolysis/310 |
| Power conversion efficiency ($\eta$%) | 9.5 | 11.8 | 12.2 | 8 | 9.8 | 13.12 | 12.05 |
| open-circuit voltage Voc (mV) | 528 | 596 | 560 | 452 | 528 | 585 | 622 |
| short circuit current density Jsc ($mAcm^{-2}$) | 26.64 | 28.25 | 33.3 | 31.4 | 30.7 | 31.75 | 28.67 |
| Fill factor FF% | 67.5 | 69.8 | 65.4 | 56.2 | 60.2 | 70.6 | 67.53 |
| bandgap energy Eg (ev) | 1.17 | 1.17 | 1.17 | 1.03 | 1.15 | 1.14 | 1.17 |
| Ref. | 52 | 53 | 37 | 54 | 55 | 56 | 57 |

HA = hexylamine, EDT = ethanedithiol, EN = ethanolamine, RT = room temperature.

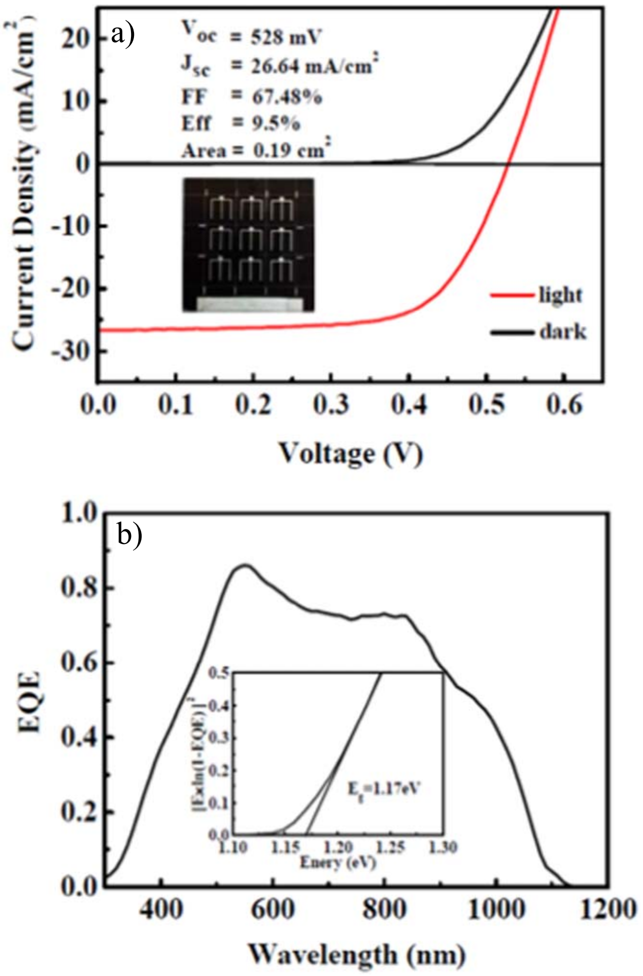

**Figure 6.** (a) J-V curves measured in the dark and under AM1.5 G illumination (b) The EQE in the outside curve, inside is the bandgap determined from the EQE curve.[52]

thiol-amine solvent, and then these isolated thiolates were redissolved in several harmless solvents. Among various solvents used for thiolate dissolution, DMSO gave higher solubility for metal thiolates. A CISSe PV device using DMSO-thiolates complexes with an efficiency of 9.03% was demonstrated. This approach can be widely generalized for the fabrication of chalcopyrite thin-film devices.[42]

Despite the similarities between hydrazine and thiol-amine dissolution methods in terms of their wide-ranging solvent power with low volatilization temperature and the ability to recover into uniform chalcopyrite thin films, solar cells fabricated using hydrazine pure solvent exhibit higher *Jsc*, FF, *Voc* and final conversion efficiency than thiol-amine solution-based devices. The lower overall performance of the thiol-amine device may be attributed to charge recombination occurring at the fine-grained layer remaining after selenization, which is not observed in the hydrazine based device. The average thickness of the fully crystalline large-grain in thiol-amine absorber layer is less than 1 $\mu$m, which is relatively thin compared to 1–2 $\mu$m layer in hydrazine-based devices,[10,14,17,18] Unfortunately, as discussed previously, working with hydrazine presents safety and practicality issue that may make this method prohibitive to scale. For comparison, Fig. 7 shows the J-V curves with the corresponding SEM cross-section images of spin-coated CIGSe absorbers for exemplary hydrazine devise (with 15.2% efficiency),[10] and for the champion thiol amine-based device of graded bandgap deposition.[56]

***Challenges and prospects for thiol-amine based CIGSe solar cells.***—In this brief review, the fundamental aspects of thiol-amine mixture processing approach for CIGSe thin-film deposition are strategically discussed. Although the efficiency of thiol-amine solution-based CIGSe solar cells has been dramatically improved in recent years, there are still some challenges limiting CIGSe PV devices toward high efficiency, which can be summarized as follows:

- When trying to grow a thicker absorber layer (> 1 $\mu$m) with coarsened grains, a thick fine-grained layer rich in selenium and carbon is often generated upon selenization, which actively lowers the device fill factor. It is necessary to control solvent composition and optimize annealing conditions in order to improve the growth mechanisms and minimize the fine-grained layer.[53,55]
- A significant elemental reduction is noticed in the thiol-amine deposition process for Cu and other inorganic elements during spin-coating deposition. Therefore, a detailed study about the chemistry of thiol-amine solvents and the nature of the formed complexes is required to identify suitable metal precursors to obtain high-quality chalcogenide films.[70]
- During high-temperature long-term selenization, a thick $MoSe_2$ interface layer formed between CIGSe and Mo, which deteriorates the electrical properties of the solar cells. Rapid heating treatment was previously applied to achieve a thinner layer of $MoSe_2$. However, the $MoS_2$ layer still formed at high selenization temperature. The introduction of a thin barrier layer into the Mo back-contact layer can be carried out to control Se diffusion and $MoSe_2$ growth, and also to reduce Cu migration at the back contact. Although many investigations have been conducted on applying diffusion barriers such as ZnO, Ag, TiN, Mo-N, and $MoO_2$, only molybdenum nitride is used as a barrier in thiol-amine devices.[69]
- Extrinsic or intrinsic alkali incorporation techniques have been used to improve electronic properties and enhance the grain growth of the CIGSe absorber layer. For improving thiol-amine PV device performance, alkali dopants can be supplied by dissolving alkali compounds directly into the precursor solution.[71–73]
- Thiol-amine solvents introduce an advantage to dissolve chalcogen precursor materials in the presence of excess chalcogenide directly in the starting solution. Based on this advantage, post-selenization processes that require sophisticated instrumentation can be avoided, and a clean annealing process can be sufficient to produce high-quality absorbers by providing a proper amount of chalcogenide in the starting solution.[13,21]
- Thiol-amine organic mixtures are considered a promising alternative to high-toxic hydrazine solutions. The application of these solutions can avoid critical synthesis steps and handling limitations of hydrazine-based process. However, many thiols are toxic and have strong odor. Further studies are needed to extend the use of molecular inks for processing, in which thiols are replaced with a more environmentally friendly solvent.[42]

To date, the efficiency of thiol-amine based CIGSe solar cells has reached 13.12% at the laboratory scale, compared to 17.3% for hydrazine CIGSe and 22.9% for vacuum-based solar cell. It is hoped that this review will provide a comprehensive understanding of the deposition and performance of thiol-amine solvent-based CIGSe solar cells as a lot of work needs to be done.

## Conclusions

Thiol-amine mixtures offer various advantages, hence making the mixtures a very general solvent system for metal chalcogenide chemistry. In addition to its low toxicity compared to hydrazine, thiol-amine solvents can dissolve various materials in different thiol/amine combinations, therefore providing several routes to chalcopyrite thin-film deposition. Several research groups have used these solvent mixtures for the deposition of CIGSe absorber layer. Thiol-amine based CIGSe PV devices result in a near-ideal bandgap,

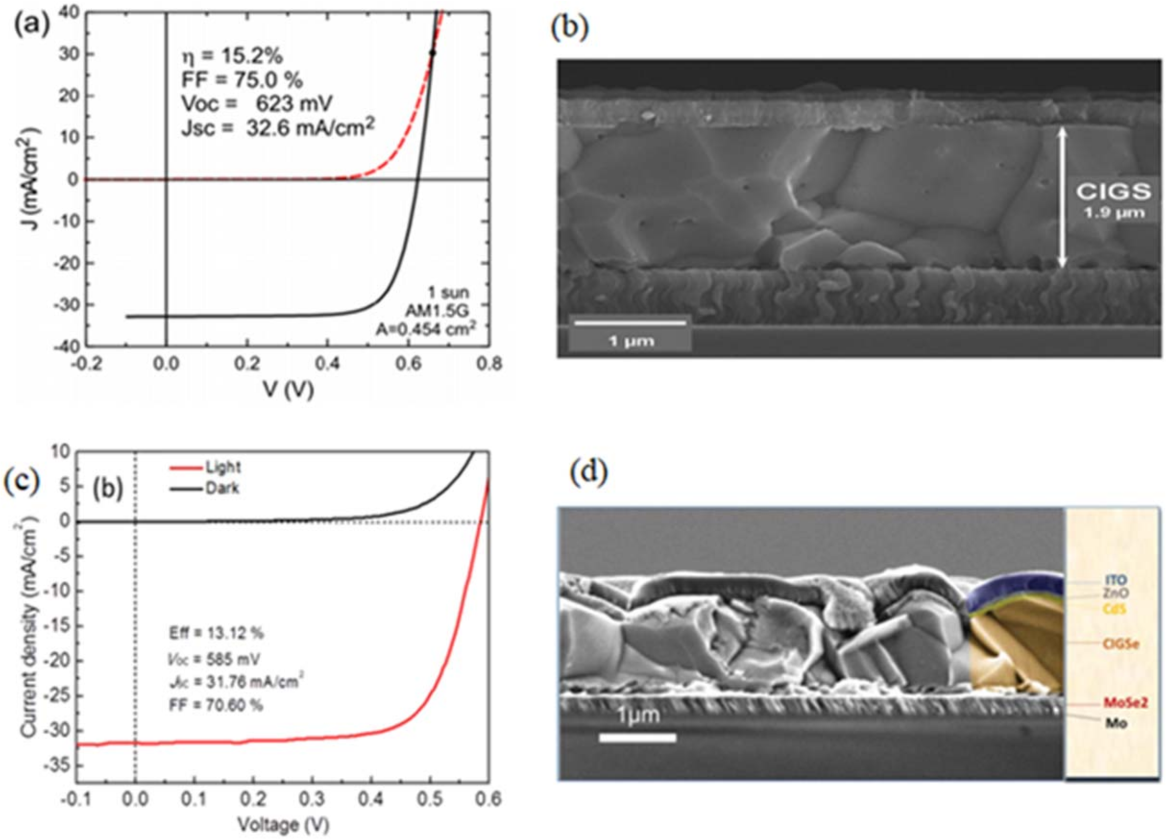

**Figure 7.** (a) J-V curve, and (b) cross-sectional image of exemplary hydrazine processed absorbers.[10] (c) J-V curve, and (d) cross-sectional image of the champion thiol amine-based device.[56]

promising electronic properties for the absorber layer, and competent conversion efficiencies up to 13.12%.

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