

Thin Films of Copper (I) Iodide Doped with Iodine and Thiocyanate

Landewatte Ajith DeSilva, Joshua Harwell, Anne Gaquere-Parker, Unil A. G. Perera, and Kirthi Tennakone*

It is found that thiocyanate (SCN) is an alternative dopant that greatly stabilizes the p-type semiconducting properties of CuI. Thiocyanate doping can be achieved by a complete removal of the excess iodine and introduction of thiocyanate via suitable precursors at ambient temperature. A method of removal of iodine from CuI before casting films is described. The electrical and optical properties of thiocyanate-doped CuI thin films are also discussed.

1. Introduction

Copper (I) iodide in its ambient temperature stable phase γ -CuI is a p-type semiconductor of bandgap reported as ≈ 3.1 eV.^[1–6] The high hole mobility and ease of fabricating thin films by different techniques makes γ -CuI a rare example of a hole conducting optically transparent material, potentially valuable for opto-electronic applications.^[6–8] Copper (I) iodide has been adopted as the hole transport material in organic light emitting diodes^[9] dye-sensitized and perovskite cells,^[10–12] heterojunction diodes, and field-effect transistors.^[13–15]

The p-type semiconduction in γ -CuI depends on the presence of iodine in stoichiometric excess, when iodine acts as an electron acceptor generating holes in the valence band.^[16] The p-type electrical conductivity in iodine doped CuI is rather complex owing to volatility of iodine and dependence of conductivity on iodine concentration. In polycrystalline CuI films, excess iodine could partition between grain boundaries and the bulk. If an iodine-doped CuI film deposited on glass is heated to temperature as low as $\approx 100^\circ\text{C}$, a part of the excess iodine escapes changing the conductivity characteristics. Again, depending on temperature

and duration of storage varying amounts of iodine accumulate in the grain boundaries. Grain boundary iodine could act as surface dopant and the ionized donor (I^-) a hole trap. Furthermore, there is evidence that the morphology of CuI polycrystalline thin-films is affected by iodine doping.^[17,18] When iodine dopant concentration is increased, conductivity initially increases and begin decrease owing scattering and trapping by ionized donor I^- , located interstitially or at the grain boundaries. Recently it has been observed that at much higher iodine concentration γ -CuI turns into a degenerate semiconductor, reaching conductivity values above the optimum of the non-degenerate situation.^[7] Presumably because of the above features of iodine-doped CuI, the devices based on thin films of CuI do not remain stable. The first dye-sensitized solid-state solar cell was based on CuI as a hole collector.^[19] However, the stability of this device was poor, both short-circuit photocurrent and open-circuit voltage degraded with time when the cell was kept exposed to light. Again, these parameters of the cell were found decrease when the cell is stored in dark and measurements conducted subsequently. The early workers on dye-sensitized solid state solar cells also found that the cell stability can be improved by incorporation of thiocyanate ionic liquid into the CuI coating solution (solution in acetonitrile) and the effect was attributed to the function of SCN^- as a crystal growth inhibitor.^[20–22] The strong adsorption of SCN^- to CuI surface inhibits the growth of crystallite, enabling filling pores of the nanocrystalline TiO_2 film of the heterojunction n- TiO_2 /Dye/p-CuI. This article describes a fresh examination of the effect of thiocyanate on CuI, which reveals that thiocyanate (moiety SCN) acts a hole dopant in CuI, and being immobile unlike I is superior to the latter and found to stabilize p-type semiconduction. Thiocyanate p-type doping of CuI is achievable, provided the stoichiometrically excess iodine is almost completely eliminated before introducing SCN. The note also indicates an extremely simple procedure for removing excess iodine from CuI, describing methods of SCN doping and comparison of the electrical conductivity characteristics of I and SCN-doped iodine.

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2. Experimental Section

Commercial (Sigma), as well as laboratory made samples of CuI, were used to prepare thin films of CuI. Commercial CuI powder is almost always partly oxidized, oxidative degradation is aggravated by light and moisture. Oxidation results in liberation of iodine via reaction in Eq. (1).

Prof. L. A. DeSilva, J. Harwell
Department of Physics
University of West Georgia
Carrollton, GA 30118, USA

Prof. A. Gaquere-Parker
Department of Chemistry
University of West Georgia
Carrollton, GA 30118, USA

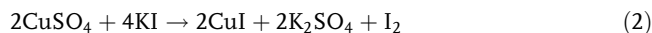
Prof. U. A. G. Perera, Prof. K. Tennakone
Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303, USA
E-mail: ktenna@yahoo.co.uk

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/pssa.201700520>.

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The following procedure was used to purify commercial CuI. The powder is dissolved in acetonitrile and centrifuged to sediment CuO and the decanted CuI solution is diluted with deionized water to precipitate CuI. CuI is filtered off, washed, and dried in vacuum or in a nitrogen atmosphere at 95 °C. CuI was prepared in the laboratory by mixing 1 M solution CuSO₄ with 1.8 M solution of KI. Copper (I) sulfate in excess of the stoichiometry of



which is needed to avoid dissolution of CuI in I⁻ aqueous solution.

The mixture is purged with sulfur dioxide to reduce iodine, CuI is separated by filtration and washed with sulfurous acid and deionized water. Samples of CuI prepared by above methods invariably contain iodine in excess to the stoichiometry of CuI. Excess iodine is estimated spectrophotometrically by measuring absorbance acetonitrile solution at 458 nm. A solution of CuI in acetonitrile devoid of excess copper is prepared by the following procedure. Copper filings (≈3 g) are added to CuI (≈6 g) dissolved in acetonitrile (≈20 ml) and the bottle closed after purging the solution with nitrogen. The bottle is intermittently agitated and the solution is decanted to another bottle which is stoppered after nitrogen purging. The sample is stored in the dark for 24 h. Before aliquots are withdrawn, solution is nitrogen-purged to prevent air entry. CuI films were cast on glass substrate by drop coating or by spin coating from a solution in acetonitrile. The average film thickness is determined by profilometry and the resistance at ambient temperature (18 °C) measured using a four-probe arrangement. Contacts were made by pressing strips of conducting glass (0.5 × 2 cm², ≈5 Ω sq⁻¹ surface resistance) with portion of the protruding edges silvered, as metallic contacts are corroded by CuI. The film resistivity is calculated from the film thickness. Iodine-doped CuI thin films were made by adding iodine to the coating solution or exposing iodine free films to iodine vapor in a closed container. In the latter method, the time variation of resistance was recorded. For doping CuI with thiocyanate, known quantities of KSCN or CuSCN were incorporated into the CuI solution and the films deposited by the previously described procedure. CuSCN is only sparingly soluble in acetonitrile, therefore, to determine the amount dissolved, the residue needs to be separated and weighed. Alternatively, in some experiments CuI films deposited on glass was wetted with a 1.2 × 10⁻³ M solution of KSCN in propan-2-ol and washed with propan-2-ol after a few hours. The presence of thiocyanate in doped samples were confirmed by extraction thiocyanate ion into NaOH and colorimetric estimation with Fe₂(SO₄)₃ solution.^[23] The transmission spectra of different films were obtained using Jasco 750 UV-Vis spectrometer and optical bandgaps were derived (estimated) from Tauc's plots.^[24] Bruker D8 Advance Instrument was used to obtain XRD data for different CuI samples using Cu Alpha radiation.

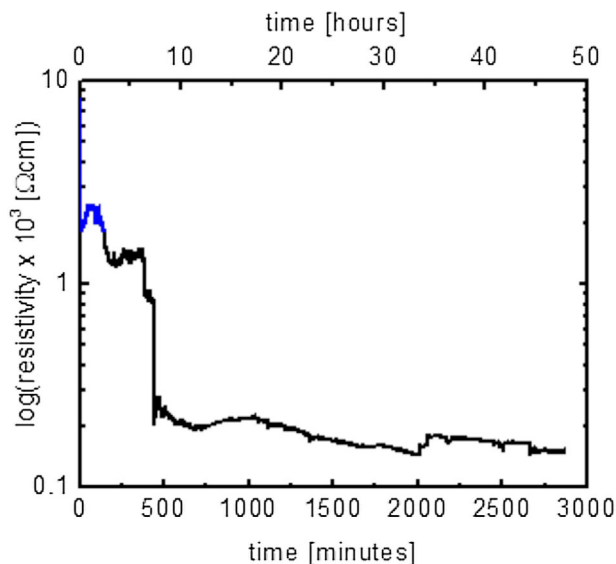


Figure 1. Time variation of resistivity of a CuI film cast from an iodine removed solution of CuI to which 60 mg of iodine is added (plotted in log scale).

3. Results and Discussion

CuI samples, purified from commercial samples or made in the laboratory by the procedure described in Section 2, contain some excess iodine and their resistivity values are in the range of 1.0×10^{-1} – 5.0×10^{-2} Ω cm. However, the resistivity of CuI films deposited from a solution in acetonitrile digested with copper filings is of the order 5×10^4 Ω cm. The digestion of CuI solution in acetonitrile effectively removes excess iodine converting it into CuI via the following reaction.



The excess iodine in commercial CuI was found to be ≈0.16 mol.% and the digestion with copper powder has reduced this to a value of less than 0.03 mol.%.

Figure 1 shows that time variation of the resistivity (plotted in log scale) of CuI film cast from an iodine removed solution of CuI to which 60 mg of iodine is added. The profile of the plot in

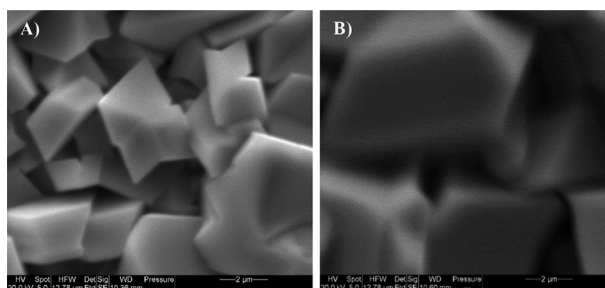


Figure 2. The SEM pictures of iodine removed (A) and iodine doped (B) CuI films fabricated from commercially available CuI.

Figure 1 has three distinct regions: 1) almost “instantaneous” drop in resistance by nearly one order of magnitude as the liquid evaporates; 2) a slow decrease in resistance for few hours followed by an nearly one order of magnitude sharp drop; 3) very slow decrease leading to an stabilized value. The observation can be understood as a process of iodine redistribution. As the solution evaporates, iodine segregates in the grain boundaries. Iodine in the grain boundaries acts as a surface dopant, injecting electrons to the CuI bulk and I^- residing on the surface. This explains the “instantaneous” drop in resistance as the film is formed. Iodine in the grain boundaries diffuse into the CuI lattice forming an interstitial donor impurity. Iodine in the grain boundaries will also diffuse to outside, as interstitial iodine concentration increases, the probability of trapping holes by I^- on the surface is greatly increased. When all the grain boundary iodine is lost to the outside, the resistance sharply drops. Unlike on the crystallite surface, interstitial iodine less prone to be lost by diffusion to outside and the resistance stabilizes. The SEM pictures of iodine removed and doped CuI films are shown in **Figure 2(A)**. Here, the crystal boundaries are distinctly clear, whereas the fuzziness in **Figure 2(B)** is an indication of iodine occupation in the grain boundaries.

The doping of a CuI film is faster when iodine is introduced in the vapor phase. **Figure 3** indicates the time variation of the resistance (plotted in log scale) of a CuI film in an air-filled enclosure saturated with iodine vapor at ambient temperature (18 °C). Here the resistance drops very rapidly by about three orders of magnitude and reach a stable value, indicating efficient interstitial doping without significant accumulation of iodine in the grain boundaries.

Just as in the case of iodine doping, thiocyanate doping was conducted by adding thiocyanate precursors (KSCN or CuSCN) to the excess iodine removed CuI solution in acetonitrile or repeated spreading of a solution of KSCN in propan-2-ol on CuI films heated to 105 °C. **Figure 4** shows that resistant variation with the dopant concentration in the two cases. It is seen that in the SCN-doped CuI sample, the time variation of resistivity is

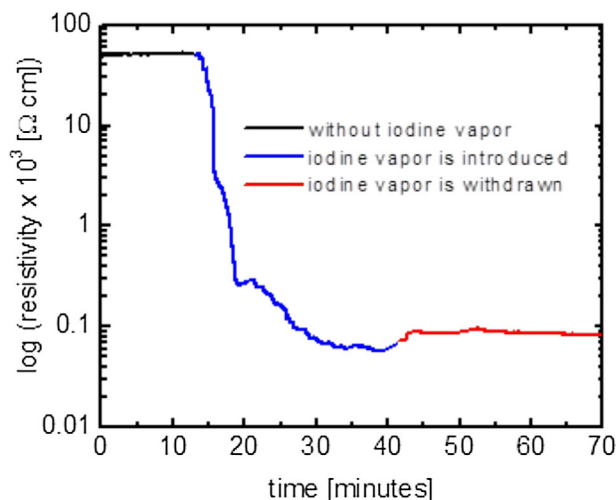


Figure 3. Time variation of the resistivity (plotted in log scale) of a CuI film in an air-filled enclosure saturated with iodine vapor at ambient temperature.

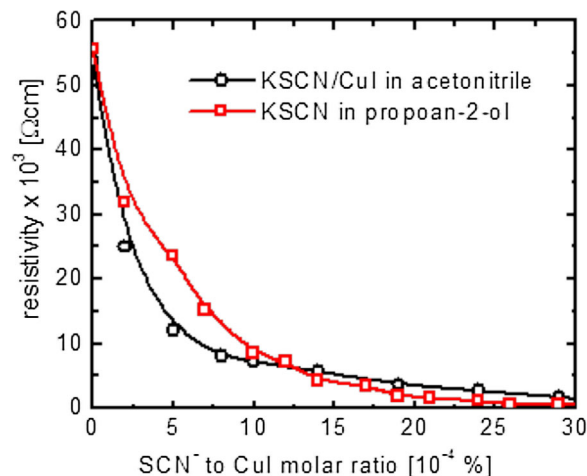


Figure 4. At ambient temperature, resistivity variation of a CuI film for different SCN^- molar ratios, doped by introducing KSCN into the coating solution of CuI in acetonitrile (circles) and doped by spreading a solution KSCN in proan-2-ol on CuI film (squares).

better stabilized compared to the surface doping sample. In the surface-doped sample, SCN may have not diffused into the bulk uniformly, whereas in SCN solution-doped sample, doping concentrations are uniform throughout the bulk.

The variation of the resistivities of SCN and I-doped films of CuI kept heated to 110 °C in air are plotted in **Figure 5**. It is seen in that the former sample, resistivity is more stabilized compared to the latter. The indication is that the dopant SCN is immobile, whereas at elevated temperatures, iodine tends to diffuses out of the bulk.

Figure 6 shows the XRD patterns for CuI thin films (a) iodine doping at ~0.16 mol.% and (b) iodine doping level reduced to <0.03 mol.%. It is revealed that the crystallinity is predominantly γ -CuI phase in both samples. The peak at $2\theta = 25.47^\circ$ indicates 111 orientation is the most stable. In the iodine-doped sample

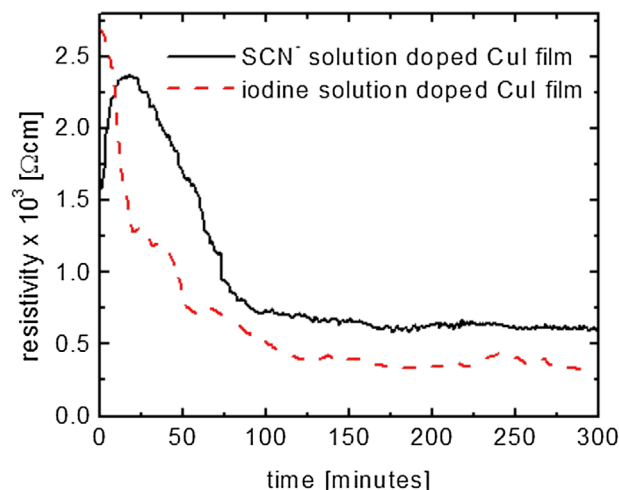


Figure 5. Time variation of the resistivity of a SCN solution doped CuI film at 110 °C (SCN^-/CuI molar ratio of 2.0×10^{-3}) (solid line) and of an iodine solution-doped film of CuI (excess iodine/CuI $\approx 0.1\%$ wt) (dashed line).

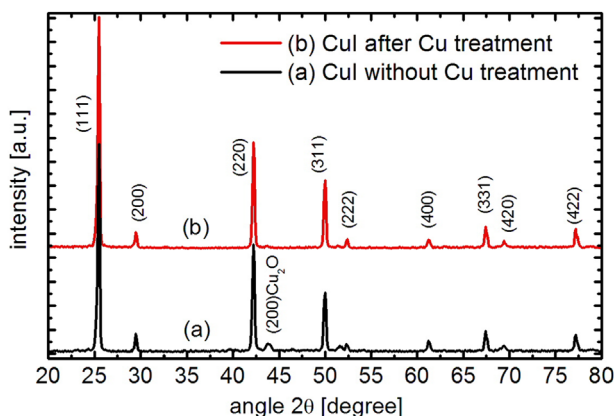


Figure 6. The XRD patterns for CuI thin films (a) excess iodine ≈ 0.16 mol.% (b) excess iodine < 0.03 mol.%.

(a), the peak at $2\theta = 43.85^\circ$ is identifiable as stable Cu_2O in (200) orientation. Clearly this peak is absent in the sample (b) where most iodine is eliminated by treating the CuI coating solution with metallic Cu. It appears that excess iodine enhances oxidation CuI, presumably via unavoidable contamination of oxygen and moisture.

Figure 7 shows the XRD patterns for SCN-doped CuI films. Here again, the crystallinity is predominantly γ phase. When the SCN doping level (SCN/CuI) exceeds 5×10^{-4} , two extra small peaks appearing at $2\theta = 26.78^\circ$ and $2\theta = 43.76^\circ$ corresponds to stable CuSCN in (101) and (241) orientations, respectively. The result suggests that SCN doping leads to a formation of some free CuSCN, possibly segregated at the grain boundaries. When the doping level is very low, the XRD signature for CuSCN disappears but the conductivity enhancement is still seen. When SCN-doped CuI is used to fabricate $\text{TiO}_2/\text{Dye}/\text{CuI}$ heterojunctions, excellent photo-response is observed indicating hole conduction.

Transmission spectrum of CuI thin films doped with SCN at different SCN/CuI molar ratio is given in the **Figure 8A**. The

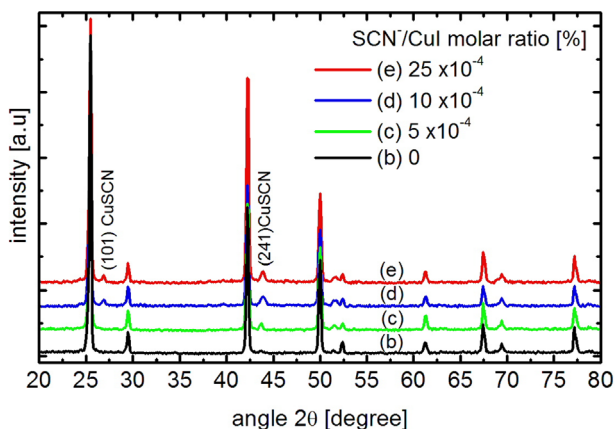


Figure 7. The XRD patterns for CuI thin films after excess iodine removal (b) and CuI films doping at different SCN⁻/CuI molar ratios for samples (c), (d), and (e).

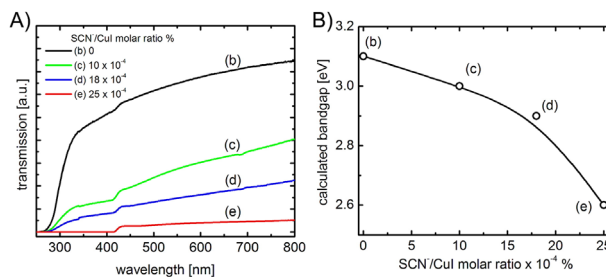


Figure 8. A) Transmission spectrum for CuI film after excess iodine removal (b) and for samples (c), (d), and (e) in which CuI films doped with different SCN⁻/CuI molar ratio. B) Bandgap variation of SCN⁻-doped CuI films at different SCN⁻/CuI molar concentration. Bandgap were obtained from Tauc's plot.

Table 1. Bandgap variation (determined from Tauc's plot) of CuI films with dopant concentration (SCN⁻/CuI molar ratio).

SCN ⁻ /CuI molar-doped ratio 10 ⁻⁴ %	Calculated bandgap (eV)
0	3.1
10	3.0
18	2.9
25	2.6

absorption coefficient a was calculated by using Beer–Lambert's law with the knowledge of the thickness d .

$$a = -\frac{1}{d} \ln(T) \quad (4)$$

where T is the transmission. The CuI is a direct bandgap semiconductor, the bandgap can be evaluated by plotting $(ah\nu)^2$ versus energy, which is the Tauc's plot.^[23] The bandgap variation which was derived from the Tauc's plots is given in Figure 8B. Bandgap values are given in **Table 1**. Just like in iodine bandgap is found to decrease with the increase of the dopant (SCN) concentration. As the XRD measurement reveals, SCN doping leads to formation of CuSCN at the grain boundaries and the loss in transmission seen in Figure 8A can be understood as scattering at the CuSCN-segregated grain boundaries. The apparent bandgap change in the visible region seems also to be associated with CuSCN segregation at the grain boundaries.^[25] The detailed elucidation of this effect requires further investigation.

4. Conclusions

The hole conductivity of γ -phase of CuI originates from stoichiometrically excess iodine. The present investigation shows that thiocyanate also acts as an effective p-dopant of CuI. Commercial and laboratory made CuI samples invariably contain excess iodine and a simple method is provided for the elimination of excess iodine from a solution of CuI in

acetonitrile. Thiocyanate doping can be carried out by introducing a thiocyanate precursor into the coating solution or spreading a precursor solution over thin-films of CuI. Unlike iodine, doped thiocyanate is immobile and is not lost during thermal processing or storage of CuI films. The investigation also revealed that excess iodine in CuI enhances the oxidation of CuI. As expected, thiocyanate-doped CuI exhibits higher thermal stability compared to iodine-doped films. As thiocyanate doping of CuI after iodine removal yields more stable films, experiments are underway to use the material as hole collectors in dye-sensitized solar cells and also determines hole mobilities in the films under different conditions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

copper iodide, hole conducting materials, thiocyanate doping, transparent semiconductors

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