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Chapter 14

CHEMICAL PROCESS OF RECOVERING CYANIDE AS CYANIDE-BRIDGED Cu(II)-Co(III)/Fe(III) BIMETALLIC ASSEMBLIES FROM PREPARATION OF SEMICONDUCTORS FOR SOLAR CELLS

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ABSTRACT

Safe and recyclable procedures of dispose waste KCN solution were developed for fabrication of Cu(In,Ga)Se₂ (CIGS) solar cells. Since KCN treatment is commonly carried out on CIGS optical absorber layer to remove surplus Cu_{2-x}Se extra phases, the solution contains Cu-Se. Cyanide-bridged bimetallic assemblies have been widely investigated. Metal source of [M(CN)₆]ⁿ⁻ (M=Co(III) or Fe(III)) can be purchased and may be thermodynamically stable except for exchange reactions in solutions. Whereas [M'L₂]^{m+} moieties (L = bidentate ligands; M'=Cu(II)) are easy to occur dissociation of ligands in solutions. Preparations at surface of solutions of cations and anions give rise to precipitates of the resulting bimetallic assemblies easily. We have developed combination of several well-known chemical reactions <1> Formation of K₃[M^{III}(CN)₆] (M= Co, Fe) species under basic conditions, <2> Isolation of [CuL₂]₃[M(CN)₆]₂ precipitates in the solid states, and <3> Preparation of CdSe nano-particles to prevent from emitting HCN gas by keeping basic condition without bad ions at early steps. After checking orders treatment procedures and chemical reactions for model systems, we have tested and treated actual waste solutions containing cyanide and Cu²⁺ ions successfully. Since poisonous KCN solutions should be used carefully, chemistry must develop safe procedures for dispose waste solutions of KCN treatment.

INTRODUCTION

In recent years, demands for several types of solar cells as one of renewable energy are increasing to solve problems about deficiency of energy resources obtained from fossil fuel. Among them, Cu(In,Ga)Se₂ (CIGS) solar cells are expected to be a promising type and are developed for making commercial use. During making processes of materials for CIGS solar cells (namely multi-layers of [surface] transparent conducting oxide (TCO)/ZnO/CdS/CIGS/Mo/soda-lime glass (SLG) [substrate]), CIGS photo-absorbing layer tends to fabricate by selenization of Cu(In,Ga) precursors [1], or thermal deposition of several elements [2]. However, low resistance properties of Cu-Se leads to bad performance as solar cells. Therefore, to remove Cu-Se related extra phases, etching has been carried out using KCN solutions since KCN tends to etch only Cu-Se and not react with CIGS and Mo layer. Although using the minimum amount of KCN or some treatments such as diluted aqueous solutions, methanol, or crown-ethers methods are used, KCN is poisonous for both human beings and environment. Herein we propose new chemical process to collect poisonous cyanide, Cu²⁺, and Se²⁻ ions from waste solutions of the KCN treatment as useful inorganic materials such as bimetallic assemblies of molecule-based magnets and nano-particles of a semiconductor. In this study, we propose developing safe procedures for dispose waste solutions of KCN treatment and the way to recycle products derived from waste solutions of KCN treatment.

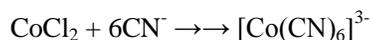
RESULTS AND DISCUSSION

Strategy for collecting some poisonous ions. Basic concept of the present chemical processes proposed is combination of well-known chemical reactions 1-3 for preparation of some inorganic materials.

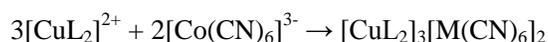
Collecting cyanide and Cu²⁺ ions. Cyanide-bridged bimetallic assemblies have been widely investigated [5, 6]. Metal source of [M(CN)₆]ⁿ⁻ can be purchased and may be thermodynamically stable except for exchange reactions in solutions. Whereas [MⁿL₂]^{m+} moieties (L = bidentate ligands) are easy to occur dissociation of ligands in solutions. Preparations at surface of solutions of cations and anions give rise to precipitates of the resulting bimetallic assemblies easily.

Collecting Se²⁻ ion. We have developed combination of several well-known chemical reactions to prevent from emitting HCN gas by keeping basic condition without bad ions at early steps. After checking orders treatment procedures and chemical reactions for model systems, we have tested and treated actual waste solutions containing cyanide, Cu²⁺ (as [CuL₂]₃[Co(CN)₆]₂·4H₂O) and Se²⁻ ions (as CdSe nano-particles) successfully.

<Reaction 1> Formation of K₃[M^{III}(CN)₆] (M= Co [5], Fe [6]) species under basic conditions.



<Reaction 2> Isolation of $[\text{CuL}_2]_3[\text{M}(\text{CN})_6]_2$ (M= Co [7], Fe [8], L=bidentate chelate amines such as *N*-ethylethylenediamine (N-Eten)) precipitates in the solid states.



<Reaction 3> Preparation of CdSe nano-particles [9].

Testing reaction conditions of KCN etching. At first, we tested optimized reaction conditions of KCN etching for an ideal system of multi-layered [surface] Cu-Se/Mo/SLG [substrate]. Cu-Se layer was obtained by selenization of Cu thin film using diethylselenide $[(\text{C}_2\text{H}_5)_2\text{Se}]$ [1, 10]. Figures 1 and 2 exhibit that optimized concentration and temperature conditions of KCN treatment are 5 wt% and 50 °C (323 K), respectively (The mol% denotes the amounts of the elements measured with an EDX). Considering industrial applications of a large scale, area dependence was also investigated. Figure 3 indicates that this KCN treatment can be carried out for Cu-Se layers less than 570 cm² effectively. In this way, these tests using model systems hereafter are carried out considering these optimized conditions for ideal experiments as a reference as follows:

Reaction 1. The best concentration of KCN solution is 3 wt% (among 1-7wt%) at room temperature for 1 min, which is gentle for CIGS thin films.

Reaction 2. Inert Co(III) ion (oxidized from labile Co(II) ion) was better than Fe(III) (Fe(II)). Co(II) was oxidized to Co(III) above 343 K for 20 min, which does not occur at room temperature. Acidic condition is forbidden because of HCN gas. Additionally, Low pH (among pH 9.0-12.0) is appropriate, because $\text{Cu}(\text{OH})_2$ is obtained at pH 12.0 .

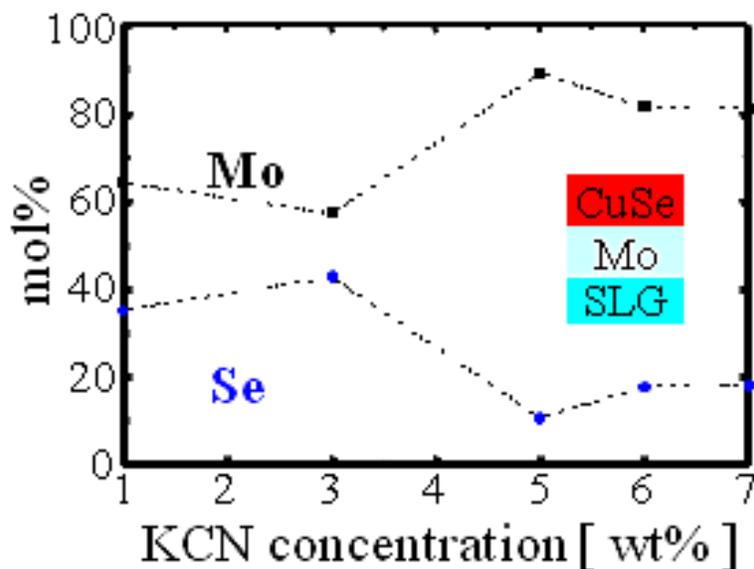


Figure 1. KCN concentration dependence of etching Cu-Se and Mo layers.

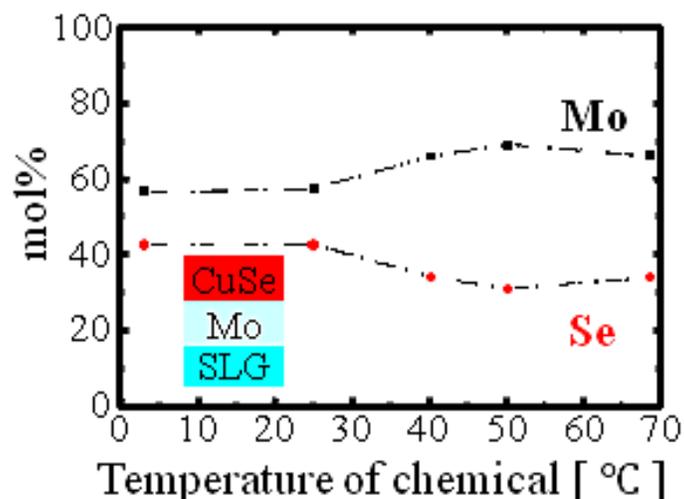


Figure 2. Temperature dependence of etching Cu-Se and Mo layers.

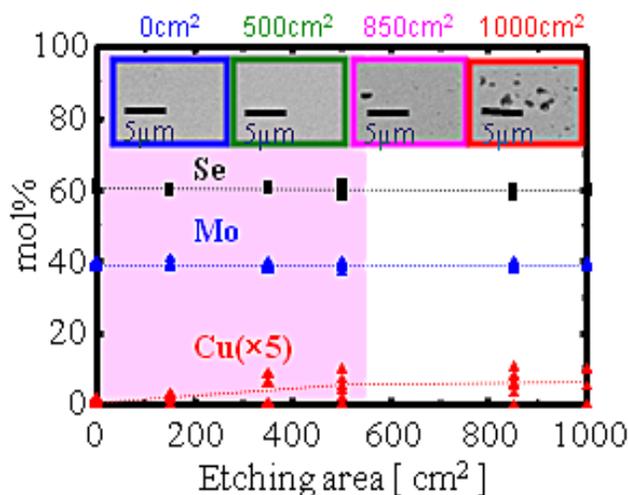


Figure 3. Area dependence of etching Cu-Se layers by KCN treatment.

Order of reactions for model systems. Secondly, we have compared the order of chemical reactions 1-3 for model systems. The results of removing cyanide ions by means of IR spectra were shown in Figures 4 and 5, which revealed that the order B was better process than the order A to prevent from obtaining Cu-Se precipitates again.

<Order A> Removing Se^{2-} , CN^- , and Cu^{2+} .

Given conditions (KCN 1.09 g, Cu-Se 0.2g, and CoCl_2 1.73 g) for model systems yielded $\text{K}_3[\text{Co}(\text{CN})_6]$ (1.233 g; 51.37 %) and black Cu-Se precipitates. Although CN^- could be removed, resolved Cu-Se precipitates were also obtained from the solutions again, which was confirmed as predominant XRD peaks at $2\theta = 28, 32, 41, 25, 51^\circ$.

<Order B> Removing Se^{2-} , Cu^{2+} , and CN^- .

Under the same conditions, $[\text{CuL}_2]^{2+}$, $\text{K}_3[\text{M}(\text{CN})_6]$, and CdSe precipitates could not be obtained properly in this order.

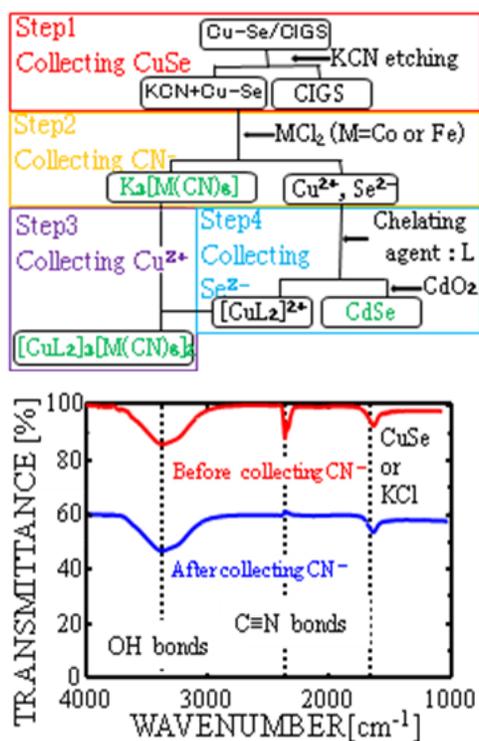


Figure 4. Scheme (up) and IR spectra (down) for a model system <order A>, the worse one.

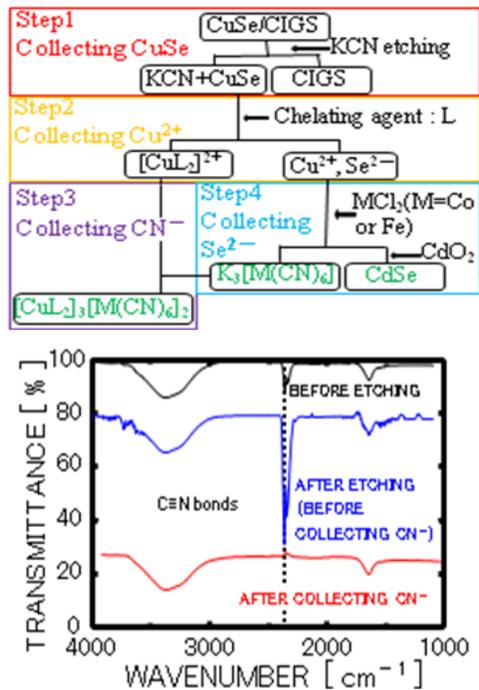


Figure 5. Scheme (up) and IR spectra (down) for a model system <order B>, the better one.

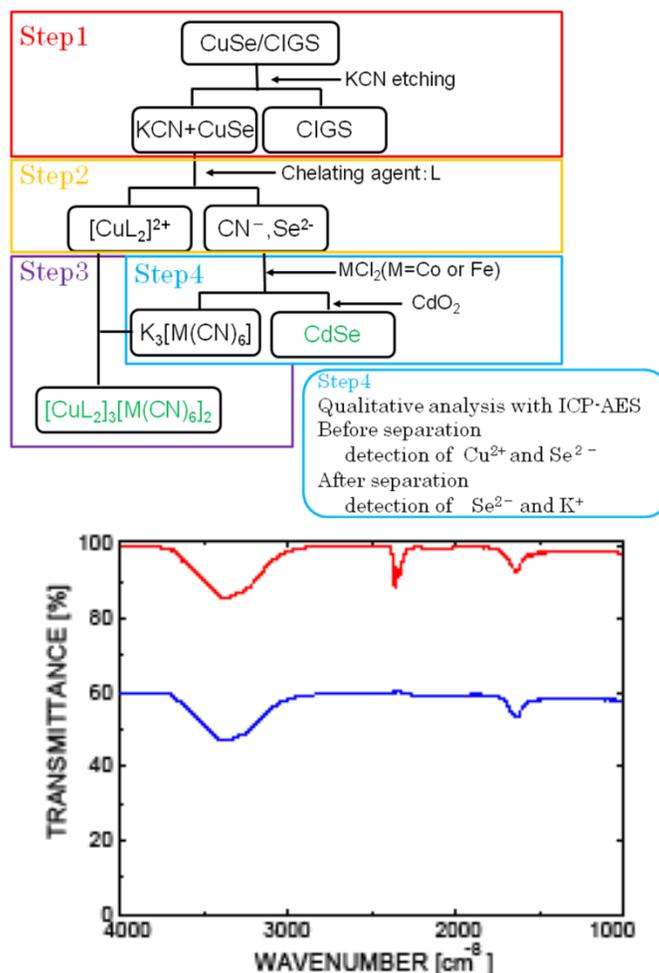


Figure 6. Scheme (up) and IR spectra (down) for actual samples before (up; red) and after (down; blue) collecting cyanide ion appearing a band around 2100 cm^{-1} .

Application for actual samples: Finally, we tried to apply the optimized chemical process to treat actual samples taken from preparation of CIGS semiconductor materials. As shown in Figure 6, the procedure of <order B> was employed with the following optimized treatments and conditions:

<Step 1> At 328 K (among 276-343 K), the concentration of KCN was determined to be 3 wt% (1.09 g in 35 mL water) to prevent from unstable remaining of Se^{2-} ions more than it (among 1-7 wt%).

<Step 2> 0.2 g of L was added to the waste solutions after Step 1.

<Step 3> Under pH 9-11, 1.8 g of CoCl_2 in 35 mL water at 343 K was added to the solution after Step 2 for 20 min to prevent from precipitating $\text{Cu}(\text{OH})_2$ more than pH 12. After that, producing $[\text{CuL}_2]_3[\text{Co}(\text{CN})_6]_2$ was confirmed with an IR spectrum.

<Step 4> Treatment of a Cd precursor and a Se precursor under N_2 at 543 K gave rise to CdSe nano-particles, which was confirmed by emission after UV (320 nm) light irradiation.

Removing cyanide ions and Cu^{2+} or Se^{2-} ions in the resulting solutions treated was confirmed by disappearing IR bands (Figure 6) and ICP-AES measurements, respectively.

CONCLUSION

In summary, we have successfully proposed new chemical processes to collecting poisonous ions emerging from waste KCN solutions during preparation of materials of CIGS solar cells. Testing various conditions and reactions, we have constructed chemical process to remove poisonous ions of waste water of KCN etching. We have prepared valuable inorganic materials, $[\text{Cu}(\text{N-Eten})_2]_3[\text{Co}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$ and CdSe nano-particles, from the waste solutions. We have successfully applied the method to actual KCN etching during preparation of a semiconductor. It could also be applied for practical samples. Although chemical decomposition of KCN is widely employed for treatments, the present method has advantages of not only precipitating cyanide ions similar to classical ways in a textbook on inorganic chemistry [11] but also recycling as some useful inorganic materials.

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