Relationship between the copper complexes condition in aqueous solution and its reduction potentials to synthesize CIGS alloy nano materials

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1. Introduction

Many researchers have vigorously studied to develop the low cost solar cells with high efficiency. Among the various solar cells, it is well known that CIGS ($Cu(In,Ga)Se_2$) type solar cell shows attractive performances, nevertheless it can be produced lower cost than Si solar cell. These CIGS type solar cell is synthesized by gas phase method. However, since vaporizing temperature of four elements is extremely different, productivity under the gas phase is relatively low, which read the large amount of waste of resources. Thus, to decreasing the cost of CIGS type solar cell, synthesis method with high recovery rate should be developed.

On the other hand, it is also well known that liquid phase reduction methods can be produced the nano materials with high recovery rate. Among the various liquid phase methods, we reported that well crystallized and uniform alloy nanoparticles, such as $Pd_{20}Te_7$, can be synthesized by restrict controlling the homogenization of metallic complexes in the aqueous solution which reading the control of reduction rate, under the room temperature [1]. However, ternary, or more, alloy nano materials with uniform structure can not be synthesized until now, because of difficulty of controlling these conditions.

Therefore, in this study, the relationship between copper and/or indium complex condition in the aqueous phase and its reduction potentials was evaluated.

2. Experimental

Amine-based and/or carboxyl-based complexing reagent, were used for the complex reagents. Condition of metallic complexes in the aqueous solution can be restricted to homogenized species by utilizing the theoretical calculation method using the critical stability constants. Detailed calculation procedure was summarized in Ref. 1. Reduction potential of Cu (and/or In) complexes was measured, and synthesized materials were analyzed by XRD.

3. Results and discussion

Figure 1 shows the results of calculation for the $Cu\text{-}NO_3\text{-}OH\text{-}$malic acid system (dissolution of $Cu(NO_3)_2$ and malic acid). The ratio of each species was Cu : NO_3 : malic acid =1 : 2 : 3. Horizontal and vertical axis shows the pH and abundance ratio (%), respectively. This calculation results indicated that copper complex was successfully restricted to $[(Cu^{2+})(mal)_2]$ at the pH range from 3 to 7, and to $[(Cu^{2+})(OH)_2(mal)_2]$ (c.a. 92.8%) at the pH range from 9 to 12. As the same manner, the condition which can restrict to single copper complex by using various complexing reagents was expected.

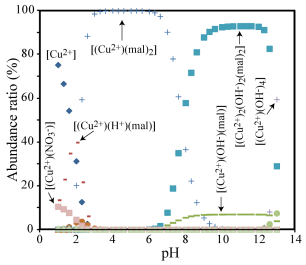

Fig.1 Result of calculation for $Cu\text{-}NO_3\text{-}OH$-malic acid system

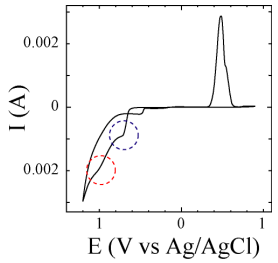

Fig.2 Result of cyclic voltammetry for $Cu\text{-}NO_3\text{-}OH$-malic acid system

Reduction potential was decided by using the results of cyclic voltammetry as shown in Fig.2 and XRD results of electrodeposited materials at corresponding potential.

4. Conclusion

It become clear that correlation between reduction potential and stability constants showed the linearly interaction. Moreover, it became apparent that, in order to synthesize CuIn alloy, amine-based complexing reagent which have large stability constants will be needed.

Acknowledgement

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References

[1] H. Takahashi, N. Konishi, H. Ohno, K. Takahashi, K. Asakura, A. Muramatsu, Applied Catalysis A: General 392, 80-85 (2011)