SUMMARY OF THESIS

Low temperature fabrication of functional thin films of copper oxide and metallic copper *via* spray coating: Study on effective use of locally produced copper in Namibia

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In this study, a molecular precursor aqueous solution was prepared by typical chemical synthesis and electrochemical methods, and sprayed on a quartz glass substrate at 180°C in air using a simple airbrush. Then, photocatalytic cuprous oxide (Cu_2O) under visible light irradiation and conductive metallic copper (Cu) thin films were fabricated. The purpose of the study was to contribute to the industrialization of Namibian raw material through effective utilization of copper metal which is one of the Namibia's main mineral resource.

First, aqueous ammonia solution containing copper formate was sprayed onto a quartz glass substrate kept at 180°C in air to fabricate Cu_2O thin films with oxygen deficiency, which is an important factor for high photocatalytic activity. It was demonstrated that the oxygen deficient Cu_2O thin film efficiently achieved the discoloration of methyl orange (MO) aqueous solution under visible light irradiation from a fluorescent lamp (0.45 mW cm^{-2}). The the O-defect site was found in the Raman spectra of these photocatalytic active thin films. Next, a direct preparation method of Cu_2O precursor aqueous solution from metallic copper was developed using an electrochemical method. A *p*-type Cu_2O semiconductor thin film obtained by spraying coating an electrochemically prepared aqueous solution at 180°C in air was identical to that fabricated using solution from starting material of copper formate. Furthermore, it was found that by adding ethylenediamine-*N, N, N', N'*-tetraacetic acid (EDTA) into the electrochemically prepared aqueous solution result in a thin film of Cu single phase with the conductivity of the order 10^{-3} Ω cm *via* spray coating under same condition.

Heat treatment temperature of ca. 400°C and inert Ar gas were necessary for the formation of Cu_2O and Cu thin film by a conventional MPM. However, this study achieved their formation only by spraying corresponding molecular precursor aqueous solutions onto substrate at 180°C in air.

This study consists of 6 chapters. Chapter 1 outline and summarized research background. Chapter 2 described the principles of characterization techniques for precursor aqueous solution and thin films, reagents used in the experiments and the equipment used for the measurement. Chapter 3 summarizes the low temperature fabrication and photocatalytic activity of spay coated *p*-type Cu_2O thin films using chemically synthesized molecular precursor aqueous solutions. Chapter 4 describes the preparation of Cu_2O precursor aqueous solution by electrochemical method, and Chapter 5 describes the selective formation of Cu_2O and Cu thin film by spray coating electrochemically prepared molecular precursor aqueous solution. In chapter 6, the research was summarized, its future development was proposed and described. A summary of each chapter is given below.

CHAPTER 1: GENERAL INTRODUCTION

Thin films can impart various functions such as electrical, magnetic, and optical to the material surface. From the viewpoint of resource and energy saving, such functional thin film is very important for the sustainable development which satisfies the needs of both present and next generation. Methods for the formation of a functional thin film can be roughly divided into a gas or liquid phase in which a raw material of a gas or liquid phase reacts with a substrate. In a gas phase method, the film is formed in the high vacuum which is necessary to transform the raw material into the gas phase state. On the other hand, the liquid phase method enables the formation of functional thin films without vacuum. The liquid phase formation process of functional thin films is also important for sustainable development. The molecular precursor method (MPM) is a wet chemical process for the formation of thin films of various metal oxides, metal and phosphate compounds by coating a precursor solution in which a metal complex is dissolved onto substrate followed by heat-treatment. It is based on the design of metal complexes in precursor solutions with excellent stability, homogeneity, miscibility and high coatability, amongst its many practical advantages. The formation of various metal oxide, phosphate compounds, and metal thin films has been reported by coating a precursor solution onto substrate using a spin coating method. The formation of Cu_2O and metallic Cu thin film which are the main objective of this study has been previously reported. When fabricating these thin films by spin coating, volatile organic compounds (VOCs) are generally used as solvents. However, industrially, VOCs free solvents are desired because of the risk of ignition and adverse effects on human health and ecosystem associated with VOCs. From such viewpoint, the formation of Cu_2O and Cu thin films was attempted by preparing the molecular precursor aqueous solution and spraying it onto the substrate. Namibia is rich in resources such as diamond, uranium, gold, zinc, and copper. Copper in particular accounts for 50% of Namibia's annual export earnings. However, it is exported to foreign countries in its raw form for further processing into final products without being used in research and industrial fields inside the country. Therefore, it was considered that if functional thin films could be formed simply by using copper which is one of Namibia's rich natural resources, it will not only contribute to the sustainable development but also became an important asset to its value addition and industrialization in Namibia. In this study, Cu_2O precursor aqueous solution was prepared using metal salt as a starting material, and the formation of Cu_2O thin film at low temperature in air was achieved. In addition, a molecular precursor aqueous solution prepared from metallic copper plate using an electrochemical method was sprayed onto a substrate at 180°C in air to achieve the formation of a highly functional Cu_2O thin film and a conductive Cu thin film. The background and outline of these studies are summarized in Chapter 1.

CHAPTER 2: MATERIALS AND METHODOLOGY

Chapter 2, fully describes the preparation methods of precursor aqueous solution, the spray coating method for the preparation of thin films, the characterization and evaluation methods of formed thin films, and the measurement principles of measuring devices used under this study. The list of all chemical reagents, materials and equipment used is provided.

CHAPTER 3: Low Temperature Fabrication and Photocatalytic Activity of *p*-type Cu_2O Thin Films by Molecular Precursor Method

Single crystal of a *p*-type Cu_2O semiconductor has a band gap of about 1.9-2.3 eV. Cu_2O is one of the few *p*-type semiconductors among other oxides that absorbs visible light, therefore it is expected to be used as material for visible light-responsive photocatalysts and oxide solar cells. It is preference in those applications is due to its low toxicity, cost and minimum environmental loading. The fabrication of Cu_2O thin films by the conventional molecular precursor method has been achieved using alcohol-based system precursor solution such as ethanol. This is the first report on the formation of Cu_2O single phase thin film by liquid phase method *via* spray coating at 180°C in air. While even formation of *p*-type semiconductors by gas phase method shows some general difficulties. Previously, Cu_2O thin film was formed by heat treatment of precursor film coated and dried on substrate by spin coating method, at 350°C in argon gas atmosphere. In Chapter 3, we prepared a novel Cu_2O aqueous precursor solution, and examined whether it could form a thin film by spray coating it onto a substrate at 180°C in air. The photocatalytic activity of the formed thin film was examined under visible light irradiation. Specifically, the precursor aqueous solution were prepared in a diluted ammonia solution by dissolving Cu(II) formate and ammonium formate whose molar ratios to Cu(II) ion were 0, 2, 6 and 14. The aqueous precursor solution were sprayed onto a quartz glass substrate at 180°C in air using an airbrush to form thin films which adhered well to the substrate. The films formed were Cu_2O single phase, and their Hall effect measurements showed that both films were *p*-type semiconductors. It was found that the films became thicker and porous with increasing ammonium formate content in the aqueous precursor solution. The photocatalytic activity of the thin films was investigated by a discoloration test with visible light irradiation on the films immersed in methyl orange aqueous solution. In the cases of the molar ratios at 6 and 14, the Cu_2O thin films of 140 and 350 nm thickness respectively indicated a highly photocatalytic activity under visible-light irradiation of 0.45 mW cm^{-2}, and the pseudo-first-order rate constants of 0.056 and 0.087 min^{-1} were respectively obtained by tracing the discoloration of a methyl orange solution. The O-defect site was found in the Raman spectra of these photocatalytic thin films whose adhesion strength onto the quartz substrate were larger than 5.6 N.

CHAPTER 4: Preparation of aqueous Cu_2O precursor solution using electrochemical method

In Chapter 4, the direct preparation of Cu_2O precursor aqueous solution from metal copper plate was tried as a model of refined copper blister using electrochemical method. Concretely, ammonium formate aqueous solution was put into a glass vessel cell as an electrolytic solution, copper plates electrodes were immersed in electrolytic solution as both an anode and cathode, and a potential difference of 18 V was applied for 2 hours. The electrolytic solution changed from colorless to blue. However, precipitates thought to be copper hydroxide were formed in the solution. Additionally, two glass containers were connected through the partition of cellulose semipermeable membrane, ammonium formate aqueous solution and copper plate electrodes were placed in each glass container, and a potential difference of 18 V was applied. The aqueous solution in the anode glass vessel cell changed with time from colorless to blue, and no precipitation occurred. On the other hand, gas was generated from the copper plate without coloring the aqueous solution in the cathode glass vessel cell. The gas generated from the surface of cathode electrodes was identified as hydrogen. The absorption spectrum of the precursor aqueous solution obtained from the anode glass cell was in agreement with the absorption wavelength of the molecular precursor aqueous solution used in Chapter 3. Higher concentration of the Cu(II) complex was obtained in the precursor solution. Thus, an aqueous solution containing Cu(II) complex was obtained. The Cu_2O precursor aqueous solution, was prepared in one step by an electrochemical method using metallic copper.

CHAPTER 5: Selective Low Temperature Fabrication of Cu and Cu_2O Thin Films by Spray Application of Aqueous Solution Prepared by Electrochemical Method

The aqueous complex solution prepared in Chapter 4 was applied under the spray conditions of Chapter 3 to form a thin film. The formed thin films were Cu_2O single-phase *p*-type semiconductors identical to those formed in Chapter 3. On the other hand, ethylenediamine-N, N ', N' -tetraacetic acid (EDTA) was added to the same aqueous solution containing Cu(II) complex, and the resultant spray solution was sprayed under the same conditions to form a thin film. The resulting thin film was of a single-phase metallic Cu with a thickness of 170 nm, and its electrical resistivity was 8.9(2) × 10^{-3} Ω cm. Its adhesion strength to the quartz glass substrate showed 12(7) MPa. It was clarified that the fabricated conductive metallic Cu thin film could be selectively formed by the addition of EDTA to the aqueous solution containing Cu(II). Thus, we have developed a method to directly prepare precursor aqueous solution from metallic copper by electrochemical method. In addition, either by using electrochemically prepared precursor solution itself or that obtained by the simple method of adding EDTA to it, the selective thin film formation of Cu_2O semiconductor and metallic Cu could be achieved *via* spray coating at 180°C in the air.

CHAPTER 6: Summary and Future Developments

In this study, molecular precursor aqueous solution prepared using synthetic chemical method and electrochemical method will be sprayed on the quartz glass substrate at 180°C in air, to achieve the formation of high-performance Cu_2O thin film and conductive Cu thin film, respectively. In the future, the preparation of similar molecular precursor aqueous solution will be attempted using electrodes of crude copper mined and refined from Tsumeb mine in Namibia. The resultant solution will be used in the fabrication of catalytically active Cu_2O thin film by visible light and conductive Cu thin film. The fabricated films will not only be considered to be applicable material in energy devices such as thin film solar cells and flexible electronic devices, but also for application such as their formation of antibacterial materials for environmental purification and immobilized photocatalysts.

PUBLICATIONS FROM THE MAJOR RESULTS

1. Alina Uusiku, Hiroki Nagai, and Mitsunobu Sato ''Highly photo-reactive p-type Cu_2O thin films fabricated on a quartz glass substrate at 180°C in air, by spraying aqueous precursor solutions involving Cu(II) complexes.'', *Material Technology: Advanced Performance Materials"*, **00,** 1-12 (2019).

2. Alina Uusiku, Hiroki Nagai, and Mitsunobu Sato, ''Selective deposition of conductive Cu thin film at 180°C in air on a quartz glass substrate: Development of an aqueous spray solution using two-compartment electrolysis system.'', *Functional Material Letters"*, full length article (Manuscript accepted for publication, 2020).