別紙４－１（課程博士（英文））

Date of Submission（month day, year）：　January 07, 2019

Department Mechanical Engineering	Student ID Number	D 145108
Applicant's name	Pei Loon Khoo	

Supervisors	Masanobu Izaki
	Seiji Yokoyama

Abstract（Doctor）

Title of Thesis	Study on the Characteristics of Electrochemically Prepared Copper Oxide Photovoltaic Devices（電気化学的に形成した酸化銅光電変換素子の特性に関する研究）

Approx. 800 words

Solar cells, or photovoltaics (PV), which converts light into electricity using semiconductor materials, are proving to be essential and indispensable for a sustainable society. Numerous kinds of solar cells have been the focus of research interest of late, and thin solid films of metal oxide (MO) semiconductors, such as copper oxide based photovoltaics (PV) has always been considered a material suitable for the realization of low-cost solar cells. Cuprous Oxide (Cu_2O) and Cupric Oxide (CuO) are stable forms of copper oxides, at the same time being intrinsically p-type semiconductors with 2.1 eV and 1.4 eV respectively. Attractive points of these oxides originate from their non-toxicity, abundance, and low cost. Also, one main aspect of interest to be noted is the preparation process, which can be achieved by electrochemical preparation. Electrochemically-prepared ZnO/Cu_2O PV had been reported to achieve 1.28%, however, the theoretical limit is approximately 20% according to the Shockley-Queisser Efficiency Limit, based on the bandgap energy. The main objective of this research is to further investigate the limiting factors of the power conversion efficiency (PCE) of copper oxide based electrochemically-prepared photovoltaics and methods to further increase, based on close studies on the properties of its solid state physics.

In this thesis, in Chapter 1, the introduction, background, review, and purpose of this study are discussed. Latest climate researches are briefly concluded and the urgency of addressing global warming by switching to renewable energy, and the importance of solar energy is discussed. Metal Oxide (MO) PVs has the criteria of a high-potential candidate as cheap, and widespread. Among these MOs, copper oxides possess unique preferable properties such as ideal bandgap energies, at the same time being able to be fabricated by simple methods like the electrochemical preparation. It is then necessary to investigate the electrochemically-prepared copper oxides from its solid state physics. The definition of power conversion efficiency (PCE) is defined with proportional in relationship with the short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}) of a PV. However, the independent variables of preparations are wide and complex, and insufficient information calls for the detailed study of determining the affecting factor during preparations. Also, a strategy using multiple bandgaps (using both copper oxide) as the light-absorbing layer is discussed.

In Chapter 2, we report the fabrication of basic Cu_2O PV, and the successful increase in J_{SC} along with external quantum efficiency (EQE) and carrier mobility, by annealing in vacuum using a rapid thermal annealing. The optimum annealing temperature was found to be 423 K.

The effect of annealing during preparation is further studied in detail, which includes its microstructural, optical and electrical properties. The mechanism is discussed, and the elucidation of the mechanism concludes a contributing factor of an increased carrier mobility due to decreased scattering defects. Also, the relationship between the interface structure and V_{OC} is discussed.

In Chapter 3, we report the photovoltaic properties of basic CuO PV successfully fabricated by electrodeposition from a basic aqueous solution containing copper acetate hydrate and ammonia with highly resistive polysiloxane layer insertion as the buffer layer. This study indicates the ability of CuO to function as a PV, which validates the strategy of using both Cu_2O and CuO as the light absorbing layer to increase the light-absorption width.

In Chapter 4, we report the fabrication of directly stacked Cu_2O/CuO PV prepared by electrodeposition and annealing. A decrease in EQE due to the formation of nanopores and voids was observed. However, the EQE was studied in detail and showed an expansion of absorption width which originates from the charge collection of both the Cu_2O and CuO layer, with a two-way carrier transport. When a low reverse biased voltage was applied, the charge collection corresponding to the absorption edge originating from the CuO layer could be clearly observed due to improved carrier control. However, there is a necessity for an in-depth investigation into the energy states and the band alignment of the Cu-oxide PV.

Chapter 5 reports on the study of chemical and energy states, along with the band alignment study of the copper oxides. X-ray photoelectron spectroscopy evaluation was carried out in detail. Methods to accurately ascertain the type of oxides were explored which includes the Auger Parameter and the Wagner Plot. The band alignments were calculated based on the XPS results, and correspond to the results of the study in Chapter 4, explaining the two-way flow of carrier transport. An improved band alignment is proposed to further increase the PCE of the directly stacked Cu_2O/CuO PV.

In Chapter 6, the results obtained in this study are summarized. Limiting factors, such as scattering defects like grain boundaries and nanopores, the condition of heterointerfaces, and semiconductor qualities were identified. However, the viability of multi-bandgap Copper-based PV is proved based on these results as a sound strategy to further increase the PCE and a proposal to realize further improvement is discussed. The scientific knowledge obtained here will support further improvements in the electrochemically-prepared copper oxide based photoactive layers.