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Department of Functional Materials Engineering		ID	099203
Name	Fariza binti Mohamad		

Advisor	Masanobu Izaki Seiji Yokoyama

Abstract

Title	Study on Electrochemical Preparation of Copper Oxides Semiconductor and the Diodes

(800 words)

Copper oxide semiconductors of p-Cu_2O and p-CuO has received broad attention as a candidate of the absorbing layer in the top layer of tandem cell with conversion efficiency of 40% and single photovoltaic cell, respectively. The conversion efficiency of oxide photovoltaic device was limited at 2.0 and 1.28% for Cu_2O/ZnO heterojunction prepared by the thermal oxidation and electrodeposition method, respectively. Electrodeposition is a well-known technique due to several advantages such as low-fabrication cost, low-temperature processing and possibility of large scale deposition. The improvement in the quality and purity is indispensable to overcome the obstacle laid in raising the efficiency close to the theoretical value. This study deals with the preparation of high quality and purity copper oxide semiconductor layers by heteroepitaxial electrodeposition followed by electrochemical construction of the heterojunction diode.

The heteroepitaxial electrodeposition of 2.0eV-(111)-p-Cu_2O films has been carried out and the effect of preparation temperature was investigated. The 1.52eV-visible light originated from the copper vacancies weakened with a decrease in the preparation temperature, and the emission of 2.0eV-visible light due to the recombination of phonon-assisted excitons could be observed for the Cu_2O film prepared at 298 K. The hole density related to the copper vacancies decreased and mobility increased with a decrease in the preparation temperature, and the maximum mobility of 21 $cm^2V^{-1}s^{-1}$ was obtained. The (111)-Cu_2O film is a promising candidate of absorbing layer in photovoltaic device due to the high quality.

The heteroepitaxial electrodeposition of 1.4eV-p-CuO layer with excellent photoactivity was carried out. Anodic electrodeposition-CuO film has been prepared in aqueous solution containing copper nitrate hydrate and ammonium nitrate. The (002)-oriented-CuO film possessed an excellent photoactivity of large photocurrent density and quick response compared to those for the randomly oriented-CuO film.

The construction of (111)-p-Cu_2O/(0001)-n-ZnO heterostructure was carried out using conventional electrodeposition method. There is a lattice relationship of (1x1)(111)<110>Cu_2O//(1x1)(0001)<1120>ZnO with the mismatch of 7.6%. Isolated hexagonal

columnar ZnO grains deposited at low cathodic current density, and the interface between the ZnO and Cu_2O films were clearly observed. The continuous (0001)-oriented-ZnO film was obtained at higher cathodic current density, but a metallic-Cu-intermediate layer was formed by reducing Cu_2O to Cu during the ZnO deposition. It was the reason for the reduction that the potential located in the Cu stable region not Cu_2O. The conventional electrodeposition was not viable for constructing the Cu_2O/ZnO heterostructure.

New light-assisted electrodeposition method was proposed to deposit the n-ZnO onto the p-Cu_2O for the construction of high quality and Cu-intermediate-layer-free heterojunction. The electrons needed for ZnO deposition were supplied by the irradiating light with the photon energy higher than bandgap energy of Cu_2O. We have revealed the light-assisted electrodeposition technique has allowed the formation of a continuous-(0001)-ZnO layer and the construction of highly oriented (0001)-ZnO/(111)-Cu_2O heterojunction with rectification feature. The structural, morphological, and optical characteristic was significantly improved.

The light intensity had a significant effect on the ZnO film deposition, and varied from 0, 4 to 33mWcm^{-2}. The high quality ZnO/Cu_2O heterostructure was obtained at a light intensity of 33mWcm^{-2}. Randomly oriented-ZnO grains were obtained at 4mWcm^{-2} and no deposition was observed without light irradiation. The metallic-Cu-intermediate-layer could not be traced between the ZnO and Cu_2O layers. The irradiated light plays a role in exciting the electrons from valence to conduction bands in p-Cu_2O and accelerated the ZnO deposition, resulting in the increase of ZnO amount with the light intensity. The ZnO films prepared with light irradiation emitted ultraviolet light due to the recombination of bound excitons at room temperature, and the intensity increased with an increase in the light intensity.

The electrochemical preparation of high quality 2.0eV-Cu_2O and 1.4eV-CuO and the diode construction with 3.3eV-n-ZnO semiconductor layer were investigated. The heteroepitaxial electrodeposition technique realized the preparation of (111)-Cu_2O layer with room-temperature band-edge emission and (002)-CuO layer with excellent photoactivity and is a powerful tool to improve the semiconductor quality. The conventional electrodeposition was not viable for stacking the n-ZnO on p-Cu_2O due to the reduction of the Cu_2O, resulting in the formation of ZnO/Cu/Cu_2O heterostructure. New light-assisted electrodeposition technique was proposed to construct the intermediate-Cu-layer-free-Cu_2O/ZnO heterostructure based on the thermodynamic consideration. The continuous-ZnO layer with room-temperature ultraviolet light emission due to the recombination of band exciton could be obtained at relatively high light intensity, and the light intensity strongly affected to the deposition and structure of the resultant ZnO layer. The Cu_2O/ZnO heterostructure prepared using the light-assisted electrodeposition showed a rectification feature.

The result demonstrated here will strongly contribute to the preparation of high quality oxide semiconductor and construction of the diode appropriate to the photovoltaic devices in electrochemical way.