Form 3

Synopsis of Thesis

Title: Studies on Electrochemical Syntheses of Semiconductor Thin Films for Photovoltaic Applications
(太陽電池に用いる新規半導体薄膜の電気化学的合成に関する研究)

Name of Applicant Wilman Septina

In this study, we investigated fabrication of new photoabsorbers for photovoltaics, such as $Cu_2ZnSnSe_4$, Cu_2ZnSnS_4, $CuSbS_2$ and Cu_2O, by electrochemical deposition (electrodeposition) methods. These materials may replace conventional solar cell materials because they are composed of earth-abundant and safe elements and can be produced by low-cost processes.

Single-step electrodeposition from an acidic electrolyte containing Cu(II), Zn(II), Sn(IV), and Se(IV) species was investigated to synthesis $Cu_2ZnSnSe_4$ (CZTSe). The desired CZTSe film as the main phase was obtained at some selected applied potential ranges. Sulfurization of the as-deposited film at several temperatures under H_2S gas flow resulted in the formation of corresponding mixed compounds of CZTSe and Cu_2ZnSnS_4 (CZTS), *i.e.*, $Cu_2ZnSn(S,Se)_4$ (CZTSSe) with kesterite structure. However, photoelectrochemical measurements of the sulfurized films indicated insufficient quality of the films for photovoltaic application, most notably due to deviation from the ideal kesterite`s composition for solar cell application. To solve this problem, we employed sequential electrodeposition of Cu-Zn-Sn-Se and Cu-Sn-Se layers for fabrication of the CZTSe thin film. Annealing of the bilayer film under Se vapor formed a CZTSe thin film with an ideal composition for solar cell application. The solar cell with a device with the structure of glass/Mo/CZTSe/CdS/ZnO/Al:ZnO derived from thus-obtained CZTSe film exhibited a preliminary conversion efficiency of 1.1%.

We investigated the fabrication of CZTS and $CuSbS_2$ by electrochemical deposition from their metallic stacks. In both the cases, we investigated the effect of preheating to the electrochemically stacked layers of Cu/Sn/Zn and Cu/Sb before sulfurization process. When the CZTS film was fabricated without the 350-° C preheating, the film contained a secondary Cu_2SnS_3 phase and other impurities. The CZTS film also showed poor adhesion to the bottom molybdenum (Mo) substrate with many crevices and voids in the film. These structural failures of the CZTS film were significantly reduced when the metallic precursor was preheated at 350 ° C before sulfurization for 20 min. As expected from these properties, the solar

cell with an glass/Mo/CZTS/CdS/Al:ZnO structure derived from the 350 ° C preheated metallic precursor for 20 min showed the best conversion efficiency of 5.6%. Similarly, a $CuSbS_2$ film containing appreciable impurity components was obtained when the precursor metallic stack was heated monotonously from room temperature to 450 ° C in Ar then sulfurized at this temperature. The film showed poor adherence having many crevices; there were many appreciable pinholes at entire surface of the film. However, a $CuSbS_2$ film without including any impurity phases was obtained when the metallic precursor film was pretreated at 510 ° C in Ar for 60 min just before the sulfurization at 450 ° C. It was also clarified that the thus-obtained $CuSbS_2$ film showed good adhesion to the Mo/glass substrate and almost no notable pinholes. As expected from these structural analyses, the 510 ° C pretreated film worked as a relatively efficient absorber for the thin film solar cell with a glass/Mo/$CuSbS_2$/CdS/Al:ZnO structure: it gave a preliminary conversion efficiency of 3.1%.

Electrodeposition of Cu_2O was performed under potentiostatic control from an alkaline electrolyte solution (pH 12.5) containing copper (II) sulfate and lactic acid. The solar cells with a glass/FTO/Cu_2O/Al:ZnO structure were fabricated by sputtering an Al:ZnO film onto the Cu_2O film. We found that the morphologies and phase purities of the Cu_2O films are highly dependent on the electrodeposition potential; thus it strongly affects the photovoltaic properties. The highest efficiency of 0.603% was obtained with a Cu_2O film deposited at -0.6 V (vs. Ag/AgCl). In addition, we also investigated the feasibility of fabrication of a hybrid solar cell consisting of electrodeposited Cu_2O and spin-coated PCBM. The optimized solar cell showed overall power conversion efficiency of 0.095%.

様式7

論文審査の結果の要旨及び担当者

氏　名　（　Wilman Septina　）		
	（職）	氏　名
論文審査担当者	主 査　教 授　松村道雄 副 査　教 授　吉田 博 副 査　教 授　平井隆之 副 査　准教授　池田 茂	

論文審査の結果の要旨

低発電コストの太陽電池を開発することは、再生可能エネルギー利用拡大のために重要である。申請者は、その目的達成のために、低コストプロセスである電気化学的方法により$Cu_2ZnSnSe_4$(CZTSe)、Cu_2ZnSnS_4(CZTS)、$CuSbS_2$ 、Cu_2O薄膜を作製する方法を研究した。

Cu(II), Zn(II), Sn(IV), Se(IV)を含む水溶液から、１ステップで CZTSe薄膜を堆積するための条件を検討した。しかし、得られた薄膜の元素組成分析からは、Znが過剰であることが判明した。そこで、Cu-Zn-Sn-Se膜の堆積に続いて、Cu(II)、 Sn(IV)、 Se(IV)のみを含む水溶液からCu-Sn-Se膜を堆積させ、その上でSe雰囲気で熱処理を施した。その結果、量論比に近いCZTSeを得ることができ、ガラス/Mo/CZTSe/CdS/ZnO/Al:ZnO構造の太陽電池素子により1.1%の効率を得ることができた。

半導体の構成金属元素の各層を順次堆積させ、そののち硫化処理により半導体（CZTSおよび$CuSbS_2$）薄膜とする方法も検討した。この場合、基板との密着性が悪く良好な半導体薄膜を得ることができなかった。そこで、硫化する前に、金属層を加熱し合金化することを試みた。その後、硫化処理を行ったところ、良好な半導体薄膜が得られ、glass/Mo/CZTS/CdS/Al:ZnO構造の太陽電池素子により5.6%の効率を得ることができた。同様な処理によって得られた$CuSbS_2$薄膜を用いた太陽電池では、この半導体によるこれまでの最高効率である3.1%の効率を得た。

さらに、Cu2O薄膜の電気化学的堆積を検討し、得られた膜とZnO薄膜および有機ポリマーとの組み合わせにより太陽電池特性が得られることも確認した。

これらの結果は、太陽電池による発電コストの低減を実現する上での重要な知見となるものであり、博士（工学）の学位論文として価値のあるものと認める。