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Abstract

論文内容の要旨 （博士）

Title of Thesis 博士学位論文名	Studies on the device structure of electrochemically prepared copper oxide photovoltaic devices.（電気化学的に形成した酸化銅太陽電池のデバイス構造に関する研究）

(Approx. 800 words)

(要旨 1,200 字程度)

Recently, the need for sustainable power generation has encouraged research into a variety of photovoltaic (PV) systems, which have the potential to cope with the global energy crisis in the future. Oxide thin film photovoltaic devices are promising for renewable energy applications due to their low material usage and inexpensive manufacturing potential. Cuprous oxide (Cu_2O) is a p-type semiconductor with the band-gap energy of 2.1 eV has received broad attention as a light-absorbing layer in a photovoltaic device, because of its non-toxicity, abundance, and theoretical conversion efficiency of 18%. The conversion efficiency of 6.1% has been reported for the AZO/Al-doped Ga_2O_3/Na-doped Cu_2O PV device prepared by the thermal oxidation of metallic Cu sheet in air followed by a pulse-laser deposition of Ga_2O_3 and AZO layers. In contrast, the electrodeposition process in aqueous solutions is a well-known technique due to several advantages such as low-fabrication cost, low temperature, ambient pressure processing, controllable film thickness, and possible large scale deposition. The conversion efficiency of 3.9% with Voc of 1.2 V has been reported for the AZO/Ga_2O_3/Cu_2O PV device prepared by electrodeposition of Cu_2O layer followed by an atomic layer deposition of AZO and Ga_2O_3 layers. The conversion efficiency, however, was limited at 1.28% for the randomly oriented super-straight type (SST) Cu_2O/ZnO PV device prepared by only electrodeposition.

Since, the power conversion efficiency is related to the generation of minority carrier inside the p-Cu_2O layer and the transportation of minority carrier from the p-Cu_2O layer to the interface to the n-ZnO layer, the improvement in the quality and purity of the Cu_2O layer as well as the heterointerface state including the interface area of the Cu_2O/ZnO heterojunction is important to increase the efficiency close to the theoretical value. There are two types of the Cu_2O PV device of super-straight type and substrate type PV device. The thermally-prepared Cu_2O PV device was specified as the substrate-type PV device, and the components of the n-ZnO, buffer such as Ga_2O_3 and transparent conductive window layers were stacked on the Cu_2O layer. The sunlight is introduced from the upper n-ZnO side. The electrochemically prepared Cu_2O PV device was specified as the super-straight type PV device, and the Cu_2O layer was stacked on the n-ZnO and transparent conductive window layer prepared on glass substrate. The sunlight was introduced from the lower glass substrate side.

In this thesis, I applied two device geometries and two buffer materials to overcome the low power conversion efficiency of Cu_2O-based PV devices. First, the super-straight type Cu_2O/Cl-doped ZnO PV

device was prepared by electrochemical reactions in aqueous solutions, and effects of the insertion of the ZnO-nanowires and highly resistive i-ZnO buffer layer on the photovoltaic performance was investigated by considering the energy state at the heterojunction. The insertion of ZnO-nanowires alternative to the continuous ZnO layer induced the increase in the short-circuit current density but the open-circuit voltage decreased, and the further insertion of i-ZnO layer under optimized condition gave the increase in both the Jsc and Voc due to the suppressing of the recombination loss at the interface. The insertion of highly resistive buffer layer at the heterointerface is an excellent tool to improve the photovoltaic performance.

Secondly, a photo-assisted electrodeposition technique was applied to stack the ZnO layer on the Cu_2O layer for fabricating substrate-type Cu_2O-PV device, and the growth mechanism is discussed by electrochemical investigations. An optimized ZnO layer is deposited onto highly oriented <111>-p-Cu_2O layer, showed a photovoltaic performance for the first time. Stacking the aluminum-doped ZnO (AZO) onto ZnO layer leads to increase in short-circuit current density. The AZO layer plays a role to take the carrier transported through n-ZnO layer from the Cu_2O layer out. And, the highly oriented (111)-Cu_2O layer exhibited a promising candidate of absorbing layer in PV device due to the increased in diffusion length.

Thirdly, a spin-coated TiO_2 intermediate layer is developed to mitigate the interfacial defect-assisted recombination at the ZnO/Cu_2O PV device. The TiO_2 layer thickness is controlled by sol concentration and spin coating speed. The insertion of TiO_2 intermediate layer decreases the recombination at the ZnO/Cu_2O interface to some extent, resulting in increase in the open-circuit voltage. Furthermore, topping the ZnO/TiO_2/Cu_2O PV device with AZO layer shows an increase in short-circuit current density due to the increased in carrier diffusion length.

Finally, I propose an optimized Cu_2O layer to overcome short minority carrier diffusion length in Cu_2O layer by stacking directly the AZO layer onto Cu_2O layer. The AZO layer acts as a carrier transporter to take out the minority carrier from the Cu_2O layer. The optimization of the AZO layer and Cu_2O layer thickness resulted in an improvement in the photovoltaic performance with maximum conversion efficiency is obtained due to the increased in carrier diffusion length. The results demonstrated here will strongly contribute to the improvement of the photovoltaic performance of oxide photovoltaic devices prepared by the electrochemical techniques.