Journal of ELECTRONIC MATERIALS, Vol. 42, No. 6, 2013
DOI: 10.1007/s11664-013-2554-7

$Cu_2ZnSnSe_4$ Solar Cells with Absorbers Prepared by the Metallic Ink-Printing Method Using Nanosized Cu-Zn-Sn Pastes and Selenization

DONG-HAU KUO[1,2] and TZUNG-RU JAN[1]

1.—Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan. 2.—e-mail: dhkuo@mail.ntust.edu.tw

A large-grained $Cu_2ZnSnSe_4$ (CZTSe) absorber for solar cells was fabricated by the metallic ink-printing method and subsequent selenization at 600°C to 700°C with overpressures of two different selenium compounds and a step-heating procedure. The developed CZTSe grain size was confirmed as 8 μm to 20 μm. The second heating stage was helpful in inducing crystallization and was important for grain growth. For the nonvacuum approach, nanosized Cu, Zn, and Sn powders were chosen for preparing inks. Ceramic Al_2O_3 was used instead of glass to prevent the thermal decomposition of the substrate. A nanosized $Cu(In,Ga)Se_2$ layer was coated on a Mo electrode to provide a barrier to avoid direct contact of Cu, Zn, and Sn with Mo. The selenization under the combination of two selenide pellets played a crucial role in preparing the CZTSe absorber. The fabricated CZTSe solar cell device showed power conversion efficiency of 1.14%, open-circuit voltage of 130 mV, short-circuit current density of 33.1 mA/cm^2, and fill factor of 0.265.

Key words: $Cu_2ZnSnSe_4$, solar cells, ink printing

INTRODUCTION

Cu_2-II-IV-VI_4 quaternary compounds of $Cu_2ZnSnSe_4$ (CZTSe), Cu_2ZnSnS_4 (CZTS), and their solid solution (CZTSSe) with energy gaps of 1.0 eV to 1.5 eV and absorption coefficients of 10^4 cm^{-1} to 10^5 cm^{-1} are cost-effective materials for thin-film solar cells.[1,2] However, research efforts in Cu_2-II-IV-VI_4, in general, are far behind those in $Cu(In_{1-x}Ga_x)Se_2$.[3,4] Recently, rapid progress in earth-abundant Cu_2-II-IV-VI_4 solar cells with efficiencies of 8% to 10% has indicated that this system has great potential.[2,5–7]

The processes for Cu_2-II-IV-VI_4 solar cells include vacuum and nonvacuum methods. Based upon a vacuum method, Reppins et al.[8] demonstrated 9.15%-efficient cells with absorbers prepared by four-source co-evaporation. Katagiri et al.[9] obtained 6.7%-efficient cells by cosputtering with Cu, SnS, and ZnS targets, followed by sulfurization with H_2S at 580°C. CZTS solar cells with efficiency of 3% to 5% were also fabricated by sequential sputtering deposition of metallic films using multiple targets followed by selenization or sulfurization at high temperatures.[10,11] Using the nonvacuum method, Barkhouse et al.[5] reported high-efficiency (10.1%) CZTSSe cells made using a hydrazine solution and a nonvacuum method followed by an annealing process at 540°C. Redinger et al.[12] reacted an electroplated Cu/Zn stack with decomposed Sn and S(Se) vapors for fabrication of CZTSSe cells with 5.4% efficiency. We also reported enhanced grain growth with $SnSe_2$ to provide the Se vapor for selenization.[13] Other nonvacuum methods did not reach the expected efficiency.[14,15] Basically, the successful hydrazine solution method can leave Cu_2-II-IV-VI_4 films without organic residues, which would prevent good film crystallization. For vacuum- and nonvacuum-based Cu_2-II-IV-VI_4 solar cells, it is important to obtain samples with good crystallization, densification, and

(Received October 23, 2012; accepted February 28, 2013; published online April 4, 2013)