Surface & Coatings Technology 231 (2013) 452–455

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

$CuInSe_2$ coatings prepared using solvothermal-synthesized $CuInSe_2$ particles

Chih-Hui Chang, Dillip Kumar Mishra, Jyh-Ming Ting *

Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan

ARTICLE INFO

Available online 25 August 2012

Keywords:
Films
Sintering
Electron microscopy
CuInSe2
Non-vacuum processes

ABSTRACT

$CuInSe_2$ (CIS) coatings were obtained on glass and Mo-coated glass substrates by sintering solvothermally synthesized CIS nanoparticles. This sintering was performed using a horizontal furnace in the presence of Se vapors. Sintering time, temperature, and heating rate were varied to study their effects on the resulting film characteristics. CuSe and In_2Se_3 were used as the sintering aid and for composition control, respectively. Two kinds of crucibles were used for sintering, one allowing the free escape of Se vapors and the other limiting the escape of Se vapors. It was found that the sintering is closely related to supply of the Se vapor to the samples while the Se supply depends on the sintering conditions and substrate type.

1. Introduction

CIGS thin film solar cells have exhibited a conversion efficiency as high as 20.3% [1]. CIS/CIGS coatings fabricated using vacuum processes often give smooth surfaces, larger grains, and higher conversion efficiencies to the cells [2], while non-vacuum processes provide the advantages of faster deposition, lower equipment costs, and large-area capability [3–5]. Non-vacuum processes generally include electrodeposition, chemical spray pyrolysis, and colloidal paste coating. In the colloidal paste coating process, a paste containing nanoparticles (NPs) are coated on substrates, followed by a sintering step to form absorber layers. The NPs are primarily elemental metals, metal alloys, metal oxides, or metal selenides [5–10]. On the other hand, some studies have investigated the use of pure CIS/CIGS NPs since they lead to better crystalline homogeneity and little or no volume change for resulting coatings, and resistance to oxidation [11]. Also, the use of toxic gas such as H_2Se, which is required for phase transformation and/or selenization during the sintering of elemental metals, metal alloys, metal oxides, or metal selenides, can be avoided.

However, the use of pure CIS/CIGS NPs is not without a problem. The use of cellulose binder leads to a significant amount of carbon residual in the resulting coatings [6]. Sintering of CIS/CIGS NPs at selenium vapor pressure less than 7.5 Torr gives not only porous coatings but also impurity residuals, such as In_2O_3 [12]. Also, soda-lime glass is the mostly used substrate which posts a limit in the sintering temperature. Therefore a sintering aid is often desirable. $CuTlSe_2$ and CuSe have been used as sintering aids during the sintering of $CuInSe_2$ particle layer [13,14]. However, thallium and its compounds are extremely toxic, and should be handled with great care. In the case of CuSe, without the presence of additional Se vapor, for example, Se powders, CuSe decomposes at 450 °C during sintering [14]:

$$2CuSe \rightarrow Cu_2Se + 1/2Se_2 \tag{1}$$

The high melting point of Cu_2Se prevents it from serving as a sintering aid. Furthermore, Cu-rich CIS coatings are often obtained due to the use of the aforementioned Cu-containing sintering aids [14] It is known that Cu-rich CIS absorber layers lead to lower bandgap, electrical resistivity, carrier concentration, and hole mobility [15]. Meanwhile, Cu_2Se was found in the sintered samples when CuSe was used as the sintering aid due to Reaction (1) [14].

In a previous study, we have developed a solvothermal method for the fabrication of pure CIS NPs [16]. In this study, we further show that the sintering of the solvothermally synthesized CIS NPs can be done without the use of any binder such that the aforementioned residual issue is avoided. Water was used as the binder in this study. During the sintering, CuSe was used as the sintering aid and In_2Se_3 as an additive. In_2Se_3 can react with Cu_2Se from Reaction (1) according to the following reaction [17].

$$Cu_2Se + In_2Se_3 \rightarrow 2CuInSe_2 \tag{2}$$

This allows a better compositional control by eliminating the formation of Cu_2Se as a residual. Meanwhile, the use of In_2Se_3 was expected to avoid the formation of Cu-rich CIS. The sintering was performed under a Se vapor pressure slightly higher than 1 atm. A high working pressure during sintering gives a larger average grain size and has been demonstrated even at pressure much less than 1 atm [12]. Also, the Se vapor is generated from a separate Se powder source but not mixed with CuSe, as reported previously [14]. Furthermore, we have shown that keeping Se vapors close to the sintering samples produces coatings with high densities and large grains.

---

* Corresponding author. Tel.: +886 6 2757575x62949; fax: +886 6 2385613.
E-mail address: jting@mail.ncku.edu.tw (J.-M. Ting).

0257-8972/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2012.08.038

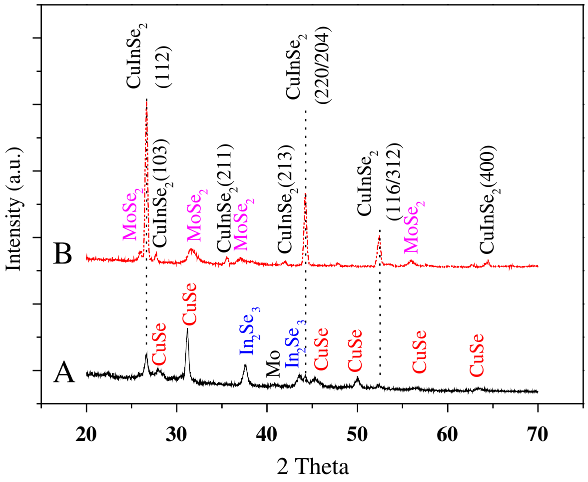

Fig. 1. XRD spectra of (A) a doctor-blade-coated CIS/CuSe/In2Se3 sample and (B) a one-stage sintered sample using the closed-type crucible. The sintering temperature, time, and heating rate are 580 °C, 60 min, and 20 °C/min, respectively.

2. Experimental

Crystalline and high purity CIS NPs were prepared using a solvothermal process as described earlier [16]. The obtained CIS NPs were then mixed with CuSe (99.5%, Alfa Aesar, melting point = 523 °C) and In_2Se_3 (99.99%, Alfa Aesar) by ball milling using alcohol as the medium. The CuSe was used as a sintering aid and the In_2Se_3 was included for the composition control. The molar ratio of CIS: CuSe:In_2Se_3 was pre-determined to be 1:3:1.5. Afterwards the ball-milled mixture was dried in air and then dispersed in de-ionized (DI) water to form a viscous liquid. Doctor blading was used to apply the viscous paste onto soda-lime glass or Mo-coated soda-lime glass substrates to form the precursor coatings. Precursor coating was then placed near a selenium powder loaded crucible for sintering. Two types of crucibles were used. One crucible, designated as open-type crucible, allows free escape of the Se vapor from the crucible during the sintering. The other crucible, designated as closed-type crucible, has a tight lid such that the escape of Se vapor is restricted or minimized. Sintering was performed in a horizontal single-zone quartz tube filled with flowing Ar. Both two- and single-stage sintering were performed. In the two-stage sintering, the specimen was first heated to 300 °C at a fixed heating rate of 10 °C/min, anticipating sufficient Se vapor generation (T_m for Se is 217 °C) and no sintering of the CIS powders at this temperature. After 10 min of dwell time, the specimen was then further heated at 2.5, 5, 10, and 20 °C/min to the sintering temperature to investigate the effects of heating rate. Both the open-type and closed-type crucibles were used in the two-stage sintering in order to examine the criticalness of keeping Se vapor near the sintering samples. A single-stage sintering was also performed using the closed-type crucible. Various sintering temperatures of 550, 560, 570, and 580 °C were

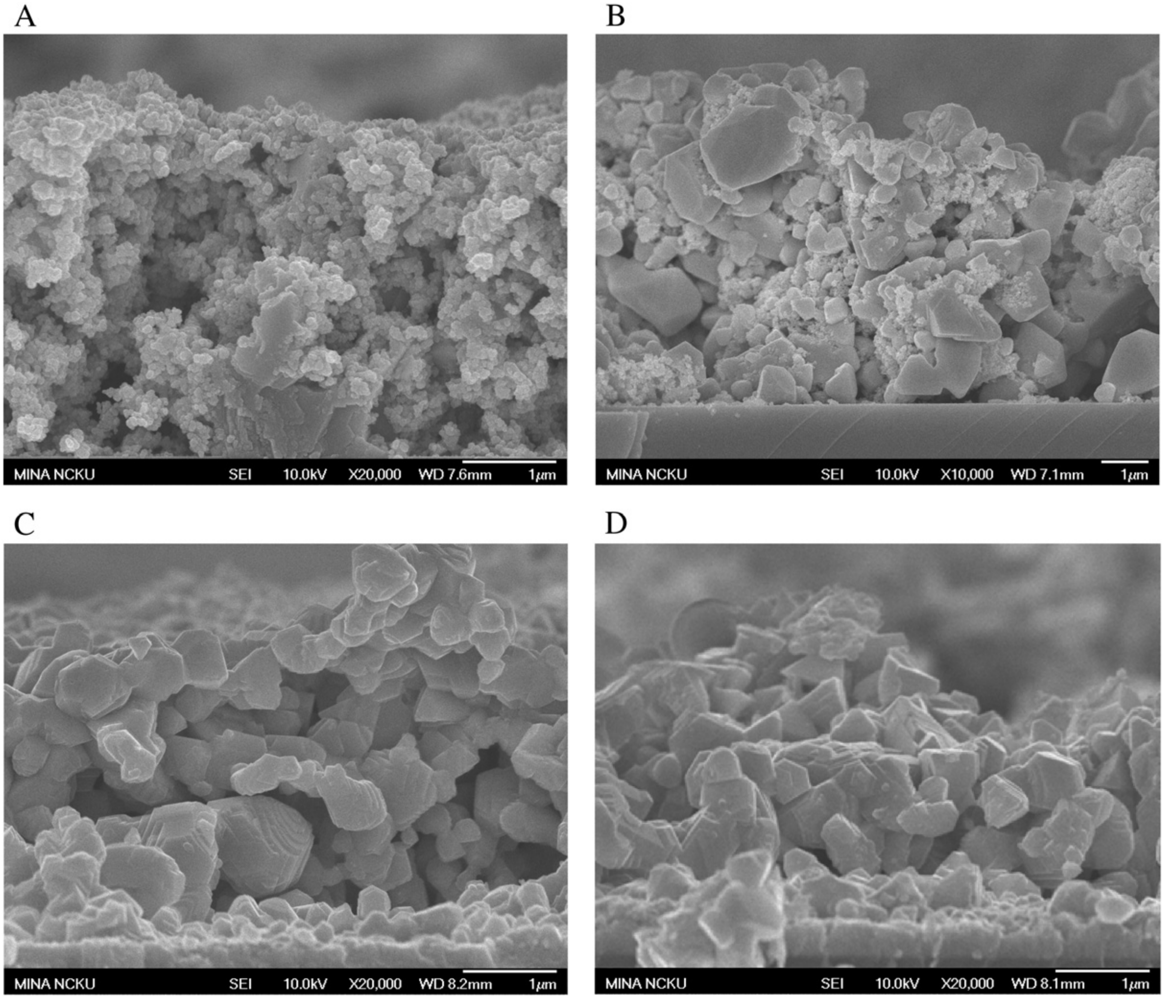

Fig. 2. Cross-sectional SEM morphologies of samples sintered in the open-type crucible using the two stage process at a heating rate of 10 °C/min and a sintering temperature of (A) 570 and (B) 560 °C for 120 min; in the closed-type crucible using two stage process at a heating rate of 10 °C/min and a temperature of (C) 550 and (D) 580 °C for 60 min.