ARTICLE IN PRESS

Thin Solid Films xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

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

Characterization of the copper iodide hole-selective contact for silicon solar cell application

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ARTICLE INFO

Keywords:
Hole selective contact
Thermal evaporation
Copper iodide
Silicon solar cells
Passivation

ABSTRACT

Hole-selective contacts have been extensively studied in recent years due to their low-cost by low temperature processing (< 250 °C). The γ-copper (I) iodide (CuI) behaves as a p-type semiconductor with a zinc blende structure (cubic) and it has previously been studied as a hole-selective layer in organic solar cells, solid-state dye-sensitized solar cells. In this paper, CuI thin films with wide band gaps and large work functions were fabricated on n-type silicon substrates via a thermal evaporation technique. Changes to the structural, morphological and optical properties of CuI thin films based on different thicknesses (11 to 58 nm) were analyzed. X-ray diffraction patterns reveal that poly crystalline CuI thin films a have γ-phase with preferential growth in the (111) direction. Increases in the peak intensity for the (111) diffraction plane were observed in the thicker films. Generally, deposited CuI films exhibit triangular shapes with azimuthal orientation but these shapes disappeared as the film thickness was increased. Excellent electrical and optical properties were obtained at a CuI film thickness of 11 nm; measured values were 642 mV implied voltage, ~3.00 eV band gap energy, 5.68 eV work function value and 97.5% transmittance.

1. Introduction

The highest conversion efficiency for silicon heterojunction cell (SHJ) with interdigitated back contact technology have been recorded as 26.7% [1]. SHJ solar cells are generally fabricated by preparing a doped hydrogenated amorphous silicon [a-Si:H (n)/a-Si:H (p)] layer (for electron and hole collection) with a thin intrinsic hydrogenated amorphous silicon layer [a-Si:H (i)] for surface passivation [2]. The doped hydrogenated amorphous silicon layer is usually capped by indium tin oxide (ITO) on both sides for effective contact and to maximize incident light-coupling into the silicon substrate [3,4]. This is followed by deposition of a metal grid on the front side for external current collection [5]. This describes the simplest "standard" SHJ solar cell architecture. However, doped amorphous silicon layers suffer from optical losses associated with their narrow band gap of 1.7–1.8 eV combined with a strong absorption coefficient and high defect density [6–8]. It results in degradation of conversion efficiency and poor repeatability in SHJ solar cells. Instead of doped hydrogenated amorphous silicon, transition metal oxides have been suggested to solve these problems. High optical gains can be achieved by using a highly transparent and wide band gap semiconductor material such as molybdenum oxides (MoO_x) [9–15], vanadium oxides (VO_x) [10,13,15], tungsten oxides (WO_x) [10,13,16], rhenium oxides (ReO_x) [13], or lithium fluoride (LiF) [14]. These materials have distinctive p- or n-type characteristics and a wide range of work functions varying from 2 to 7 eV. These transition metal oxide (TMO) behave as hole-selective contacts (HSC) due to their electronic properties and large work function values ($\Phi_{TMO} > 5.0$ eV), which on Fermi level alignment with n-Si ($\Phi_{Si} \approx 4.2$ eV) induces a potential barrier (band bending) [10,15]. Charge selective contact devices by transition metal oxide still remained of unstable composition, therefore, more stable and effective materials should be investigated.

Among potential candidate materials, copper (I) iodide (CuI) with wide band gap of 3.1 eV has three crystalline phases: α (above 392 °C), β (between 350 and 395 °C) and γ (below 350) [17–21]. Among these, γ-CuI behaves as a HSC with a zinc blende structure (cubic) and has been studied as formed by several different techniques such as spin coating [19,22], electrochemical deposition [23], chemical bath deposition, solution methods [18,24,25], pulsed laser deposition [26,27], and thermal evaporation [17,28]. Based on previous research, pulsed laser deposition and thermal evaporation methods confer the most ideal properties to CuI thin films such as high transmittance and low resistivity [17,26–28]. In this work, CuI thin films as an HSC were thermally evaporated on n type silicon substrate and then, the structural,

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https://doi.org/10.1016/j.tsf.2018.04.040
Received 10 December 2017; Received in revised form 24 April 2018; Accepted 24 April 2018
0040-6090/ © 2018 Published by Elsevier B.V.

Please cite this article as: Joen, K., Thin Solid Films (2018), https://doi.org/10.1016/j.tsf.2018.04.040

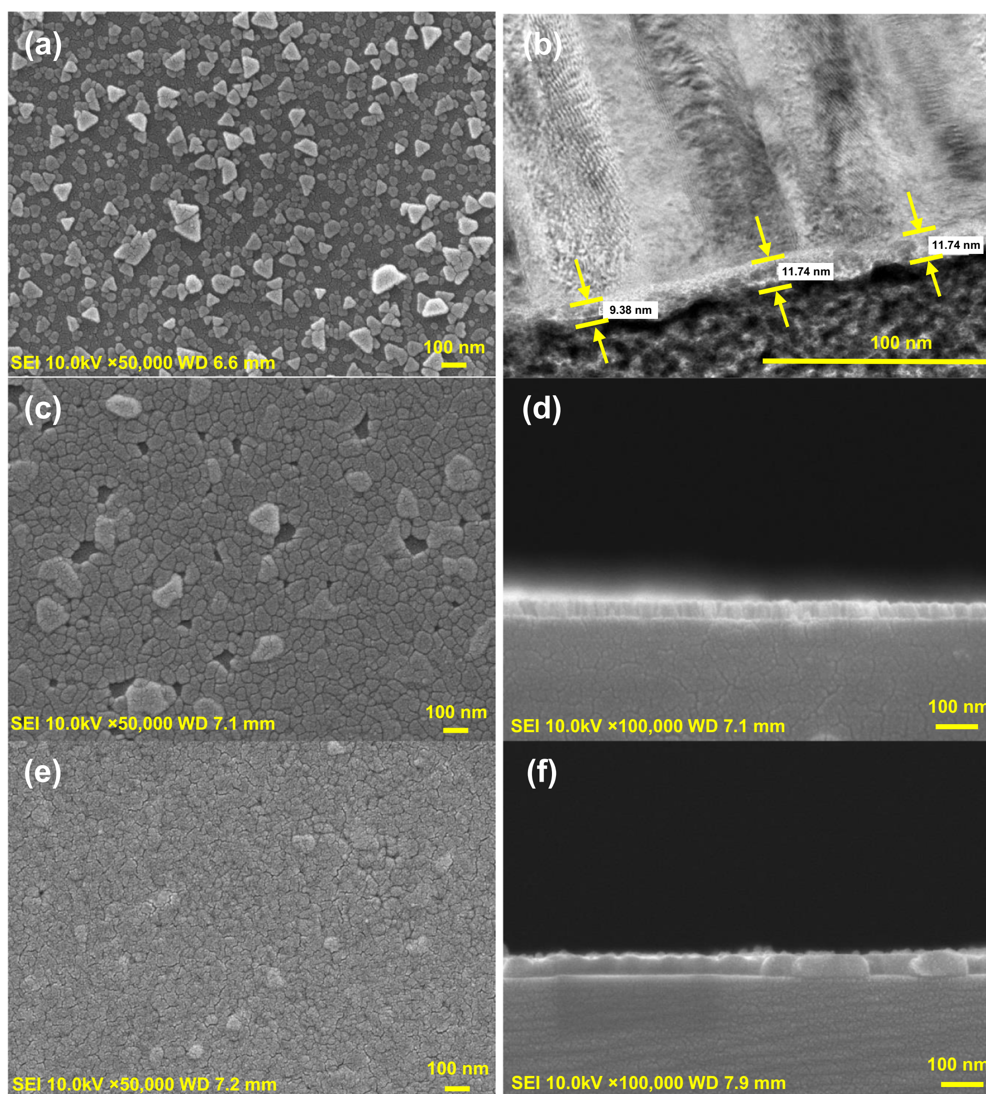

Fig. 1. Top views (a), (c), (e) and cross-sectional views (b) 11 nm, (d) 41 nm, (f) 58 nm of CuI thin films by FE-TEM and FE-SEM.

optical and electrical properties were specifically investigated.

2. Experimental details

The double-side polished float-zone Si wafers (~4 Ω cm, 100 orientation, 280 μm, n-type) were immersed in a standard RCA process solution (10 min) and 10% HF solution (1 min) to remove native SiO_2. The soda-lime glass substrates were ultrasonically cleaned for 15 min per step with acetone, ethyl alcohol, and deionized water, respectively. The CuI thin films were thermally evaporated on cleaned silicon wafer and glass substrate for measurement of the morphological properties, work function and optical properties. The CuI powder (Alfa Aesar, 99.998%) was installed in a tantalum boat and thermally evaporated with a deposition rate of < 0.2 Å/s under working pressure of $< 8 \times 10^{-4}$ Pa. Thickness of CuI films were controlled by increasing deposition time and varied from 11 to 58 nm. For the investigation of implied voltage (iV_{oc}), the cleaned Si wafers were etched in potassium hydroxide to obtain a random-pyramid surface texture and then, thin a-Si:H (i) films (~10 nm thick) deposited on front and rear side of wafer by plasma-enhanced chemical vapor deposition (PECVD) for surface passivation. CuI thin films were subsequently deposited on the samples.

The crystal structures of the deposited thin films were measured by high-resolution X-ray diffraction (XRD, X'pert PRO, Philips, Eindhoven, Netherlands) operated at 40 kV and 30 mA using Ni-filtered Cu K_a radiation [λ = 1.55056 Å]. The morphologies were observed by field emission transmission electron microscopy (FE-TEM, JEM-2100F, JOEL, Japan; sample preparation by focused ion beam method) at 200 kV and field emission scanning electron microscopy (FE-SEM, JSM-6701F, JOEL, Japan) at 10 kV. The FE-TEM sample preparation was performed following a standard focused ion beam (FIB) technique, and the thinning step of the sample was performed with decreasing beam current to reduce sample damage and improve sputtering of platinum target. Optical transmittance and work function of as-deposited films were obtained using ultraviolet visible spectroscopy (UV–Vis spectroscopy, V-670, Jasco, Japan) and ultraviolet photoelectron spectroscopy (UPS, Sigma probe, Thermo VG Scientific, USA) using a He I XUV source. The effective minority carrier lifetime (τ_{eff}) and iV_{oc} properties were obtained through transient photoconductance measurements (WCT-120, Sinton Instruments, USA).

3. Results and discussion

Fig. 1 show the FE-TEM and FE-SEM images of CuI thin films of increasing thickness. The surface morphologies of the CuI thin films observed clear variation with increasing film thickness. The CuI thin film thicknesses were ~11 nm (Fig. 1(b)), ~41 nm (Fig. 1(d)), and ~58 nm (Fig. 1(f)), respectively. The surface grain shapes were triangular type shown in Fig. 1(a), and in this case the growth was near the

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