Journal of Electroanalytical Chemistry 713 (2014) 70–76

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Preparation of CdTe thin film by electrodeposition in butyl methyl imidazolium bath at 80 °C

K.R. Chauhan [a], Ian J. Burgess [b], Gap Soo Chang [c,*], I. Mukhopadhyay [a,*]

[a] School of Solar Energy, Pandit Deendayal Petroleum University, Gandhinagar 382007, Gujarat, India
[b] Department of Chemistry, University of Saskatchewan, Saskatoon, SK S7N 5C9, Canada
[c] Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, SK S7N 5E2, Canada

ARTICLE INFO

Article history:
Received 19 August 2013
Received in revised form 15 November 2013
Accepted 22 November 2013
Available online 1 December 2013

Keywords:
CdTe
Ionic liquid
Thin film
Photoelectrochemistry
Potentiostatic

ABSTRACT

CdTe thin films have been prepared on FTO substrates by eletrochemical deposition in a butyl methyl imidazolium chloride bath at 80°C potentiostatically at three different applied potentials. The electrodeposition process ensures the underpotential deposition of Cd on Te coated FTO substrate. CdTe thin film was grown at a relatively higher growth rate which resulted a typical thickness of 2.7 μm for a deposition time of 1 h at an applied deposition potential of −1.45 V. The XRD pattern indicates the formation of cubic CdTe phase with zincblende structure. The Cd to Te ratio of the film can be nicely tuned in the range of 0.8–2.27 by the selection of deposition potential. The film deposited at a potential of perfect stoichiometry (−1.45 V) shows interconnected clusters with an average size in the range of 40–100 nm. The formation of CdTe cubic phase is also ascertained by the microdomain Raman analysis. Hot probe analysis indicates the P-type behavior of the CdTe film. The band gap energy of the CdTe film is found as 1.44 eV from the UV–Vis measurements. A photoelectrochemical cell with the configuration: CdTe (0.5 cm^2) thin film |0.1 M K_2S_x(pH-9.2) |Pt (2 cm^2) has been constructed with the electrochemically deposited CdTe thin film. The photocurrent measurement under chopped light illumination shows an onset potential of 1 V (w.r.t. satd. Calomel) for cathodic photocurrent. The onset potential for the cathodic photo current generation has been complemented by the flat band potential of 0.93 V (w.r.t. satd. Calomel) from the Mott Schottky measurement in the same electrolyte.

1. Introduction

CdTe is one of the most promising candidates for the compound thin-film solar cells because of its near to ideal band gap of 1.45 eV [1] and higher absorption coefficient around 10^5 cm^{-1} [2–4]. Due to its high absorption coefficient, a micron thickness is required to absorb nearly the complete solar spectrum. The material continues to be attractive after the life cycle analysis study of CdTe modules by Fthenakis et al. [5] showing facts against the hypocrisy of a material to be hazardous and dangerous for the environment. CdTe is a versatile material even in terms of the route of fabrication and most popular growth methods are: close spaced sublimation, vapor transport deposition, and electrodeposition. In the search for low-cost alternatives to monocrystalline silicon, CdTe:CdS thin-film photovoltaic cells prepared by electrodeposition [6–17] are reaching the point where commercial exploitation is feasible. Historically, acidic aqueous sulfate solutions [18–22] at a pH in the range of 0–2 are usually employed for electrodeposition of CdTe, which suffers from lower deposition rate due to limited solubility of Te (IV) species in the acid bath which makes the control of stoichiometry difficult. To overcome this problem, many groups have tried alkaline solution at a pH of 10 and successful electrodeposition of CdTe has been demonstrated in ammonia-alkaline solutions containing Cd (II) and Te (IV) species [23]. As acid and alkaline solutions are hazardous and dangerous, an alternative to use non aqueous solutions has become popular, but the problem with the crystallinity of the film remained the major drawback as the resultant films were amorphous [24].

Over recent years, the concept of 'Green Solvents' has become popular among the researchers and room temperature ionic liquids (ILs) have gained a great interest especially in electrochemistry, catalysis, separations, and organic synthesis [25–30]. By definition, ILs are semi organic salts which solely consist of organic cations and organic or inorganic anions. ILs have extraordinary properties like very low vapor pressure, wide available electrochemical window, high ionic and electrical conductivity, high thermal and chemical stability which make them perfect substitutes for molecular solvents. ILs have opened up a new era for the electrodeposition

---

* Corresponding authors. Tel.: +91 9586864936; fax: +91 79 23275030 (I. Mukhopadhyay), Tel.: +1 306 966 2768; fax: +1 306 966 6400 (G.S. Chang).

E-mail addresses: khushbu.cphd10@sse.pdpu.ac.in (K.R. Chauhan), ian.burgess@usask.ca (I.J. Burgess), gapsoo.chang@usask.ca (G.S. Chang), indrajit.m@sse.pdpu.ac.in (I. Mukhopadhyay).

1572-6657/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jelechem.2013.11.032

of reactive elements such as Ge, Si, Ta, Nb and Li [30]; however examples of electrodeposition of semiconductors from IL are relatively fewer [31–34]. Electrochemistry on air stable 1-ethyl-3-methylimidazolium based IL is well studied for metal [35] as well as for semiconductor [36] deposition. Sun et al. [37] claimed a successful electrodeposition of stoichiometric CdTe only at temperature as high as 140 °C using the mentioned IL.

In this paper we have studied the electrodeposition of CdTe in air stable 1-butyl-3-methylimidazolium chloride IL at 80 °C. The optimum electrochemical growth conditions were established to obtain the stoichiometric CdTe thin film with a substantial growth rate (2.7 μm/h) for the first time at this temperature from an IL medium [12,38]. Detail structural and surface textural characterizations were carried out to establish a structure property correlation.

2. Experimental

2.1. Chemicals

The precursors cadmium chloride anhydrous (99%), tellurium dioxide (99%) and the solvent 1-butyl-3-methylimidazolium chloride (BMIM Cl^-) (99%) were purchased from Aldrich and used without further purifications.

2.2. Electrochemical set up

All the electrochemical experiments were performed using a potentiostat/galvanostat (HEKA PG 590). The three electrode arrangement of an electrochemical cell consists of FTO (15 Ω/□, 2.2 mm thick, Aldrich) of area 0.5 cm^2 as working electrode (WE), Platinum wire with effective surface area 2 cm^2 as counter electrode (CE) and platinum wire as quasi reference electrode. All the electrodes were ultrasonically cleaned by trichloroethylene (FTO)/acid (Pt metal), ethanol, acetone and DI water successively prior to each electrochemical experiment. A 1.5 ml vertical Teflon cell facilitating a horizontal growth was custom designed and utilized for the electrochemical synthesis. A digital PID controlled hot plate with ±2 °C accuracy was used to maintain a bath temperature at 80 °C. It is worth to mention that the ionic liquid exist well in liquid form only above 70 °C. Hence we tried electrodeposition of CdTe from such ionic liquid in the temperature range of 80–90 °C. The film with better stoichiometry and relatively good adhesion property was obtained at 80 °C. Electrodeposition was performed at a constant potential of −1.4, −1.45 and −1.5 V vs. platinum quasi reference electrode to find a potential that provides nearly perfect stoichiometry (PPS) for Cd:Te films. Unless mentioned otherwise all the potentials are cited with respect to Pt quasi reference electrode, which was standardized against reversible ferricenium/ferrocene (Fc+/Fc) couple. All potentials cited in the manuscript can be read as 200 mV positive with respect to Fc+/Fc couple.

2.3. Characterizations

The phase identification of the deposited films was done by XRD (Rigaku, RU 200) using Co Kα radiation (λ=1.79 Å). The microstructures of the deposited films were characterized by Raman microscopy (Renishaw 2000). The Raman spectra were recorded with an incident monochromatic radiation of 784 nm at incident energy of 10 mW. The interference of fluorescence to Raman signal was amicably avoided by photo bleaching the thin film samples for 10 min at 784 nm prior to acquiring the Raman spectra. Surface morphology and compositional analysis were done by SEM (JEOL 840A) equipped with EDS and AFM (PicoSPM). Optical measurements were performed using UV–VIS spectrophotometer (Agilent Cary 600 series).

2.4. Photoelectrochemical measurement

A single compartment photoelectrochemical cell of configuration CdTe (0.5 cm^2) thin film |0.1 M K_2S_x(pH-9.2)| Pt (2 cm^2) was constructed using electrodeposited CdTe thin film. A tungsten halogen lamp 12 V/125 W (50 mW/cm^2) was used as a white light source for the photocurrent measurements.

3. Results and discussion

3.1. Deposition of CdTe thin-film by electrochemical method

Typical cyclic voltammogram for the deposition of CdTe and its subsequent etching in basic IL, BMIM Cl^- at 80 °C is shown in Fig. 1. Three important cathodic peaks are observed besides the current loop at the extreme applied negative potential. The current hump C1 may be attributed to the starting of under potential deposition (UPD) of Te species on the FTO substrate (SI-Figure-1). The adsorption of Te^{4+} species on FTO under goes electron transfer gradually and finally peaking the maximum current at the second cathodic peak ‘C2’, which may be the Nernst equilibrium potential for Te^{4+} to Te conversion process. The third cathodic current peak ‘C3’ can be related to the reduction of Cd^{2+} to Cd on the Te coated FTO substrate based on the observations of independent experiments which is shown in SI-Figure-2. The current rise at the extreme negative potential attributes to the over-potential deposition of both Cd and Te species with three dimensional nucleation and growth of the CdTe which is observed in the form of a current loop. Contribution of reduction of Te to Te^{2-} species to the current rise at the extreme negative potential cannot be ruled out as well [37]. The anodic side shows two current peaks with a broad hump in the range of −1.25 to −0.5 V. While the peak ‘A1’ can be correlated with the stripping of elemental Cd and Te over the CdTe surface, the broad hump ‘A2’ may be attributed to the stripping out of CdTe layer in to the solution. The nature of the hump can be correlated to the dissolution of well formed homogeneous CdTe layer into the ionic liquid in a broad potential range. The anodic peak ‘A3’ can be attributed to the oxidation of Te^{2-} species in solution to the elemental Te. The assignment of ‘A3’ was confirmed from the cyclic voltammogram (SI-Figure-1) of Te^{4+} species in the same ionic liquid on FTO under identical experimental conditions. Assignments of the current peaks in the anodic and cathodic sides have been further confirmed by the observation of enhancement of current

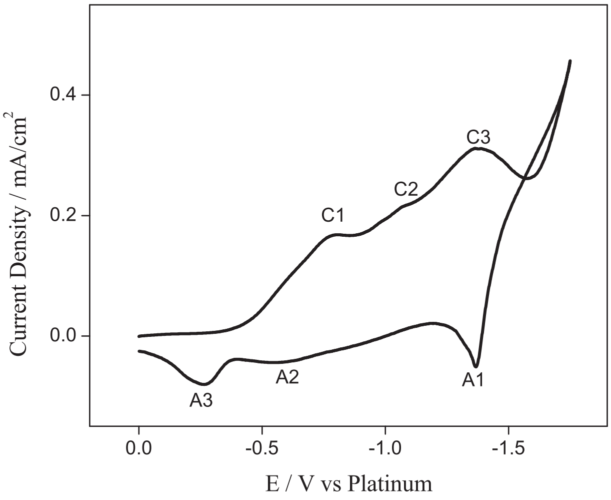

Fig. 1. Cyclic voltammogram for the Electrodeposition of CdTe from the bath containing 200 mM $CdCl_2$ and 5 mM TeO_2 in BMIM Cl^- IL at a sweep rate of 50 mV/s.