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Templated growth of cadmium zinc telluride (CZT) nanowires using pulsed-potentials in hot non-aqueous solution

T. Gandhi, K.S. Raja, M. Misra *

Metallurgical and Materials Engineering, University of Nevada, Reno, NV 89557, USA

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Abstract

A single step non-aqueous electrodeposition of cadmium zinc telluride (CZT) nanowires on nanoporous TiO_2 substrate was investigated under pulsed-potential conditions. Propylene carbonate was used as the non-aqueous medium. Cyclic voltammogram studies were carried out to understand the growth mechanism of CZT. EDAX and XRD measurements indicated formation of a compound semiconductor with a stoichiometry of $Cd_{1-x}Zn_xTe$, where x varied between 0.04 and 0.2. Variation of the pulsed-cathodic potentials could modulate the composition of the CZT. More negative cathodic potentials resulted in increased Zn content. The nanowires showed an electronic band gap of about 1.6 eV. Mott-Schottky analyses indicated p-type semiconductor properties of both as-deposited and annealed CZT materials. Increase in Zn content increased the charge carrier density. Annealing of the deposits resulted in lower charge carrier densities, in the order of 10^{15} cm^{-3}.

Keywords: Nanowires; p-Type; CZT; Cyclic voltammogram; XRD

1. Introduction

Cadmium telluride (CdTe) and cadmium zinc telluride (CZT) compound semiconductors are used widely in infra-red (IR), X-ray and gamma ray radiation detection applications and in solar cell panels [1]. CZT is considered more advantageous than CdTe in radiation detection because of wider band gap and higher resistivity, which renders low noise level. Further, $Cd_{1-x}Zn_xTe$ with $x = 0.04$–0.07 finds application in infra-red detectors and solar cells [2]. In order to minimize the leakage current, room temperature radiation detector CZT materials are required to show very high resistivity, in the order of 10^{10} Ω cm. As a solar cell material the resistivity should be as low as possible [3]. The stoichiometry, low intrinsic charge carrier density and defect level at the band gaps control the resistivity of the CZT. Conventionally, CZT (typical composition $Cd_{0.9}Zn_{0.1}Te$) is manufactured as a single crystal using Bridgman technique [4]. The various other processes through which CZT can be produced are molecular beam epitaxy, vacuum deposition and electrodeposition. Among these processes electrodeposition is considered to be a cost effective route of fabricating large surface area compound semiconductors. Careful control of the electrochemical parameters could render CZT material with the required electronic properties [5].

Electrodeposition of CdTe [6–9] and ZnTe [9,10] in aqueous medium has been widely reported. In addition to the binary semiconductor materials, electrochemical deposition of ternary systems like CdZnSe and HgCdTe has been reported [11–14]. However, electrodeposited films in aqueous medium were reported to contain numerous micro cracks and pin holes due to concomitant hydrogen reduction [5]. Electrochemical deposition of CdTe using non-aqueous solution has been reported to result in monocrystalline and crack free thin films [5,15]. A single step electrodeposition of ternary systems such as CdHgTe using non-aqueous solution has been investigated [16]. Thin films of CdZnTe have been electrodeposited using both aqueous [17,18] and non-aqueous solutions [19]. However, the details of electrochemical conditions for achieving required stoichiometry are not readily available.

Recently, preparation of nanowires of compound semiconductors using electrochemical techniques has been reported by Zhao et al. [20]. These authors investigated the growth of nanowires of CdTe on porous alumina template. Theoretical studies [21] have predicted enhanced efficiencies for

* Corresponding author. Tel.: +1 775 784 1603; fax: +1 775 327 5059.
E-mail address: misra@unr.edu (M. Misra).

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one-dimensional systems (nanowires) as compared to two-dimensional systems (thin films), because of quantum confinement of electrons and holes. In addition to the desired one-dimensional electron transport properties of nanowires and large surface areas, nano-structured materials show superior physical (electronic), chemical, and mechanical properties as compared to their bulk counterparts [22]. Therefore, preparation of CdZnTe in the form of nanowire arrays could have great potentials for making large area detectors with minimized trap centers. This investigation reports single step electrochemical synthesis of nanowires of CdZnTe using a nanoporous TiO_2 template in non-aqueous solution.

2. Experimental procedures

2.1. Template preparation

The titanium dioxides used in our experiment were prepared by anodizing high purity titanium foils [23] (0.1 mm thick, 99.999 wt.% purity ESPI products). The surface area exposed for anodization was around 0.7 cm^2. The anodization was carried in a solution of 0.5 M phosphoric acid, 0.14 M sodium fluoride and pH of 2.0. Anodization was carried out at 20 V and 25 °C for about 45 min.

2.2. Sample fabrication

The non-aqueous medium used for deposition was propylene carbonate (PC). Propylene carbonate was chosen as a solvent because of its higher dielectric strength (65), higher dipole moment and charge acceptor number. Cyclic voltammogram (CV) studies were carried out to understand the growth mechanism's of CZT. Both platinum and anodized nanoporous TiO_2 were used as electrodes during cyclic voltammetry. The following electrolytes were used for cyclic voltammetry (CV) studies:

1. 25×10^{-3} M $NaClO_4$ in PC;
2. 5×10^{-3} M $CdCl_2 + 25 \times 10^{-3}$ M $NaClO_4$ in PC (referred as Cd solution);
3. 0.5×10^{-3} M $TeCl_4 + 25 \times 10^{-3}$ M $NaClO_4$ in PC (referred as Te solution);
4. 5×10^{-3} M $CdCl_2 + 0.5 \times 10^{-3}$ M $TeCl_4 + 25 \times 10^{-3}$ M $NaClO_4$ in PC (CdTe solution);
5. 5×10^{-3} M $CdCl_2 + 10 \times 10^{-3}$ M $ZnCl_2 + 0.5 \times 10^{-3}$ M $TeCl_4 + 25 \times 10^{-3}$ M $NaClO_4$ in PC (CdZnTe (CZT) solution);
6. 1, 10, 25×10^{-3} M $ZnCl_2 + 0.5 \times 10^{-3}$ M $TeCl_4 + 25 \times 10^{-3}$ M $NaClO_4$ in PC (Zn variance in ZnTe solution);
7. 5×10^{-3} M $ZnCl_2 + 1$–8×10^{-3} M $CdCl_2 + 0.5 \times 10^{-3}$ M $TeCl_4 + 25 \times 10^{-3}$ M $NaClO_4$ in PC (Cd variance in CdTe solution);
8. 5×10^{-3} M $ZnCl_2 + 5 \times 10^{-3}$ M $CdCl_2 + 0.1$, 0.5 and 1.0×10^{-3} M $TeCl_4 + 25 \times 10^{-3}$ M $NaClO_4$ in PC (CZT solution with Te variation).

Both the CV and pulsed-potential electrochemical deposition of CZT nanowires were carried out in a three-electrode cell at 95 ± 2 °C. CV tests were carried out using both Pt and nanoporous TiO_2 substrates at a potential sweep rate of 10 mV/s. About 5 cm^2 platinum foil in the shape of a flag was used as a counter electrode. A pure cadmium wire immersed in PC solution saturated with $CdCl_2$ and contained in fritted end glass tube acted as a reference electrode. Here after this reference electrode will be referred as a cadmium wire reference electrode. Anodized titanium dioxide sample was used as the template for nanowire growth. About 25×10^{-3} M $NaClO_4$ was used as the supporting electrolyte. All depositions were carried out in a controlled atmosphere inside a glove box (Labconco, Model 50600-00). Ultra high purity argon was used as the inert atmosphere. The oxygen and moisture contents of the glove box were controlled at low levels so that a pierced 25 W incandescent bulb could burn at least for an hour inside the glove box environment. Nanowires of CZT were deposited on the nanoporous TiO_2 template by pulsing the potentials. A typical pulsed-potentials cycle contained two cathodic, two anodic and one open circuit potential, as depicted in Fig. 1. All potentials were applied with respect to the cadmium reference electrode. Cathodic pulsed-potential used varied between −0.4 and −1.2 V and pulsed for 1 s. The anodic pulsed-potentials were kept constant in all the test runs. The two anodic potentials used were 0.3 V for 3 s and 0.7 V for 5 s. The deposition time was typically around 30 min. Potentials were applied using a computer controlled potentiostat (Schlumberger, Model: SI-1286, Farnborough, England) and Corrware software (Solartron). Once the depositions were done the samples were rinsed with anhydrous semiconductor grade methanol and dried in vacuum. The samples were then annealed at 350 °C in a CVD furnace in high purity argon atmosphere (200 cc/min) for 1 h. The annealed samples were cleaned with methanol and the samples were then characterized.

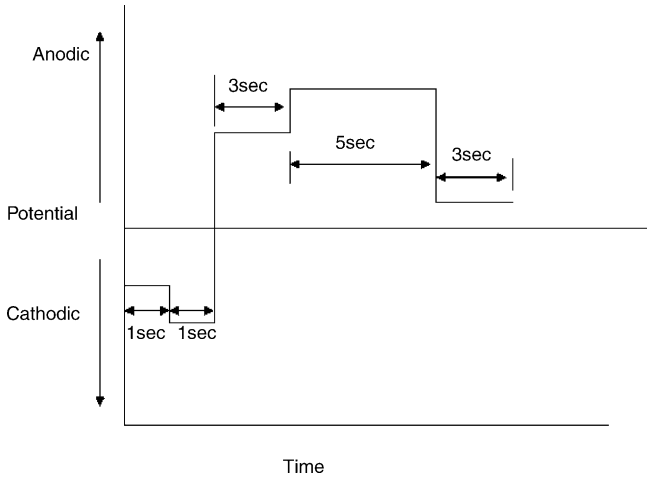

Fig. 1. Schematic showing the pulsing cycle used for the CZT deposition.

2.3. Sample characterization

Scanning electron microscopy (SEM) and glancing angle X-ray powder diffraction (XRD) measurements were used to