Electrochimica Acta 55 (2010) 1072–1080

Contents lists available at ScienceDirect

Electrochimica Acta

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

Galvanic displacement of Bi_xTe_y thin films from sacrificial iron group thin films

Chong Hyun Chang[a], Youngwoo Rheem[a], Yong-Ho Choa[b], Deok-Yong Park[c,**], Nosang V. Myung[a,*]

[a] Department of Chemical and Environmental Engineering, University of California-Riverside, Riverside, CA 92521, USA
[b] Department of Fine Chemical Engineering, Hanyang University, Ansan, 426-791, Republic of Korea
[c] Department of Applied Materials Engineering, Hanbat National University, Daejeon, 305-719, Republic of Korea

ARTICLE INFO

Article history:
Received 21 May 2009
Received in revised form 1 September 2009
Accepted 26 September 2009
Available online 4 October 2009

Keywords:
Electrochemical process
Galvanic displacement
Bismuth telluride
Thin films
Thermoelectric materials
Semiconducting materials

ABSTRACT

Bi_xTe_y thin films synthesized by galvanic displacement were systematically investigated by observing open circuit potential (OCP), surface morphology, microstructure and film composition. Surface morphologies and crystal structures of synthesized Bi_xTe_y thin films were strongly depended on the type of the sacrificial materials (i.e., nickel (Ni), cobalt (Co) and iron (Fe)). Galvanically deposited Bi_xTe_y thin films from the sacrificial Ni and Co thin films exhibited Bi_2Te_3 intermetallic compounds and hierarchical structures with backbones and sub-branches. A linear relationship of deposited Bi content in Bi_xTe_y thin films as a function of $[Bi^{3+}]/[HTeO_2^+]$ ratio (within a range of less than 0.8) in the electrolyte was also observed. Surface morphologies of Bi_xTe_y thin films were altered with the film composition.

1. Introduction

Electrochemical techniques including electrodeposition, electroless (autocatalytic) deposition and galvanic displacement are widely used in printed circuit boards (PCB), semiconductor devices, integrated circuits, read/write heads, optical devices, sensors and other devices [1–3]. Electrodeposition is the process by which an ionized substance in liquid is deposited on an electrode (cathode) by the action of electricity (especially electrolysis). Alternatively, electroless routes such as electroless deposition and galvanic displacement differ from electrodeposition because both processes are conducted without the use of an external voltage or current [3]. In electroless deposition, the reduction of the metal ions in solution can be carried out through the oxidation of a chemical compound, known as a reducing agent, present in the solution itself. Galvanic displacement (sometimes referred to as immersion plating or cementation) takes place when the redox potential of a metal ion in solution is more positive than that of the sacrificial material on the substrate [3]. Galvanic displacement differs from electroless deposition because a reducing agent necessary in electroless deposition is not required. In galvanic displacement, the sacrificial material behaves as a reducing agent. Electroless deposition and galvanic displacement are commonly referred to as chemical processes rather than electrochemical processes because of the absence of an external power supply, although the mechanisms can be explained using their electrochemical redox potentials. Galvanic displacement has been used to synthesize hollow nanostructures and to selectively deposit Cu and other metals onto Si in many devices such as integrated circuits, microelectromechanical systems (MEMS), and microchannel chemical reactors [3–7]. In addition to semiconductor metallization and nanoporous transmetallation, galvanic displacement has recently been studied as an efficient fabrication method for thermoelectric materials [8–11].

Thermoelectric devices convert thermal energy from a thermal gradient into electrical energy (the Seebeck effect), or vice versa (the Peltier effect), without any actuating parts [12–14]. The $(Bi,Sb)_2(Te,Se)_3$-based thermoelectric materials has been investigated by many researchers because of various applications [12–25], which include microcoolers, power generation systems, infrared detectors, charge coupled device (CCD) cameras, laser diodes, microprocessors, thermocouples, blood analyzers, and portable picnic coolers. Among these thermoelectric materials, bismuth telluride (Bi_2Te_3) is considered one of the best materials for near room-temperature thermoelectric applications because of its superior ZT (the thermoelectric figure-of-merit) [12–14]. Bi_2Te_3 is a V2-VI3 compound semiconductor with narrow-band gap energy (0.11–0.15 eV at room-temperature). Also, n-type or p-type BiTe can be synthesized by slight modulation of the composition from its stoichiometric ratio [14].

* Corresponding author. Tel.: +1 951 827 7710; fax: +1 951 827 5696.
** Corresponding author. Tel.: +82 42 821 1278.
E-mail addresses: dypark@hanbat.ac.kr (D.-Y. Park), myung@engr.ucr.edu (N.V. Myung).

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.09.066

Table 1
Bath compositions and operation conditions for electrodeposition of the sacrificial Ni, Co and Fe thin films on $Pt/Ti/SiO_2/Si$ substrates.

Composition	Electrolyte	pH	Current density (mA cm^{-2})	Temperature (°C)	Agitation	Deposition rate ($\mu m\, h^{-1}$)
Ni	1 M $NiCl_2$ + 1 M $CaCl_2$	3	5	RT	No	5.45
Co	1 M $CoCl_2$ + 1 M $CaCl_2$	3	5	RT	No	6
Fe	1 M $FeCl_2$ + 1 M $CaCl_2$ + 0.03 M L-ascorbic acid	3	5	RT	No	7.2

Several different techniques including electrochemical processes (electrodeposition [12–14], galvanic displacement [11], electrochemical atomic layer epitaxy (ECALE) [26]) and vacuum processes (sputtering [27], evaporation [28,29], metal organic chemical vapor deposition (MOCVD) [30]) have been developed to synthesize Bi_xTe_y thin films. Among these methods, galvanic displacement is a simplistic and rapid deposition technique capable of tailoring surface morphology, crystal structure and composition by varying deposition conditions (e.g. sacrificial materials or compositions of electrolyte). Although extensive studies to synthesize thermoelectric BiTe alloys by other means have been conducted, the fabrication of BiTe alloys by galvanic displacement has not received significant attention, with previous work limited to synthesis of Bi_2Te_3 nanotubes [11].

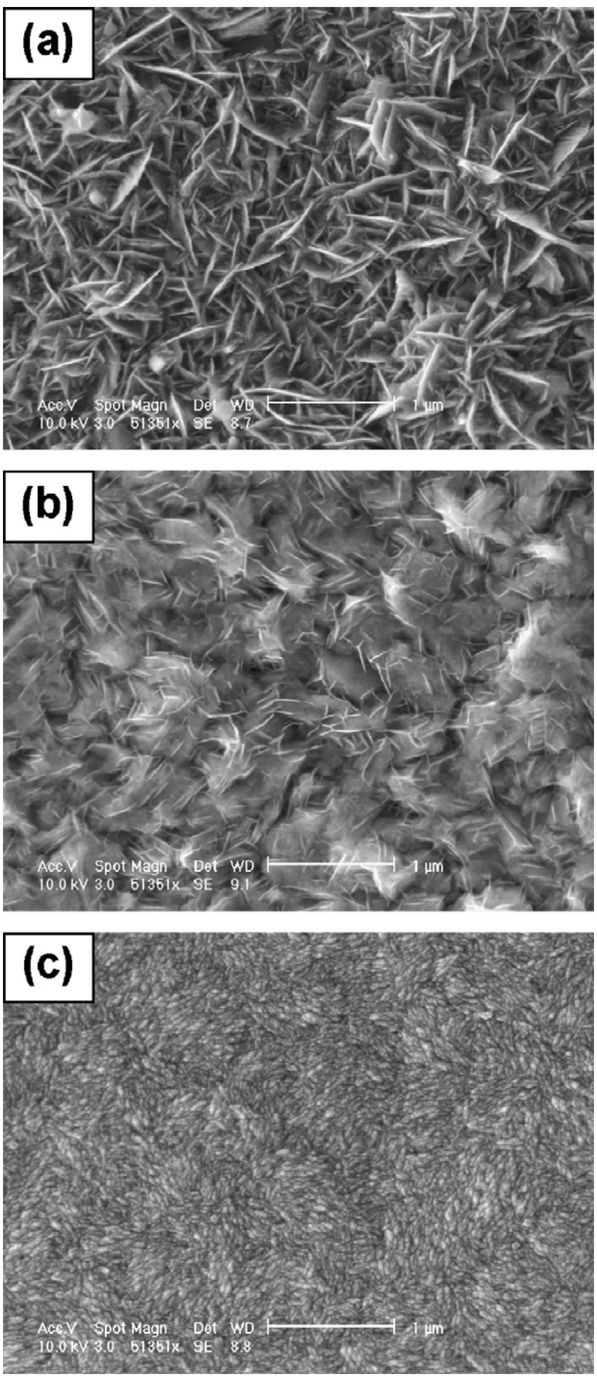

Fig. 1. Surface morphologies of the sacrificial thin films electrodeposited from chloride baths: (a) Ni, (b) Co, and (c) Fe.

In this paper, the synthesis of Bi_xTe_y thin films by galvanic displacement was systematically investigated. The electrolyte composition and sacrificial materials were varied. Several sacrificial metallic films (Fe, Co, and Ni) were electrodeposited on platinum-coated $Ti/SiO_2/Si$ substrates from chloride baths. Bi_xTe_y thin films were synthesized by galvanic displacement with these sacrificial thin films. Surface morphology, microstructure and composition of the galvanically deposited Bi_xTe_y thin films were studied and the growth mechanism was proposed.

2. Experimental

For electrodeposition and galvanic displacement reaction, the Pt(200 nm)/Ti(20 nm)/SiO_2(100 nm)/Si substrate was placed on a slide glass for mechanical support. The substrate was fixed using double-sided conductive copper tape (3 M, 1182a) for electrical contact during electrodeposition of the sacrificial layers. Pt (platinum) and Ti (titanium) were deposited on SiO_2/Si substrate by electron-beam evaporation process. Pt was used as a seed layer and Ti as an adhesion layer between Pt and SiO_2 layer. The entire sample including copper tape except an open area (1.0 cm^2) at the middle of the substrate was insulated using a red mylar insulting tape and Microstop (Pyramid Plastic, Inc.). Sacrificial Ni, Co and Fe thin films with a thickness of ∼3 µm were galvanostatically electrodeposited on the substrates from chloride baths. Table 1 lists bath compositions and operating conditions. Calcium chloride was used as a supporting electrolyte. L-ascorbic acid was added to prevent oxidation of Fe^{2+} in the electrolyte for electrodeposition of Fe thin films [31]. The solution pH was adjusted to 3.0 with HCl or NaOH. Electrodeposition was conducted using a Princeton Applied Research Potentiostat (VMP2) at current density of 5 mA cm^{-2} and room-temperature without stirring. A saturated calomel electrode (SCE) and platinum-coated titanium anode were used as a reference and a counter electrode, respectively.

Electrolyte compositions for galvanic displacement reactions are listed in Table 2. Bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$], tellurium oxide (TeO_2, 99.99%; Alfa Aesar) and nitric acid (HNO_3) were used to make the bath for galvanic displacement. The concentration of $HTeO_2{}^+$ was fixed at 10 mM with varying Bi^{3+} concentration from 2 to 20 mM to observe the dependence of solution $[Bi^{3+}]/[HTeO_2{}^+]$ ratio on film composition of Bi_xTe_y thin films. Nitric acid concentration was fixed at 1 M and solution pH was maintained at pH 1. Electrodeposited thin films were dipped into the displacement electrolytes for 60 min. Open circuit potential (OCP) during galvanic displacement were measured in a three-electrode cell to monitor the effects of different sacrificial materials in the electrolytes.

Surface morphology and film composition of thin films obtained from electrodeposition and galvanic displacement were examined