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Bi and Te thin films synthesized by galvanic displacement from acidic nitric baths

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ABSTRACT

Bismuth (Bi) and tellurium (Te) thin films were formed by galvanic displacement of different sacrificial iron group thin films [i.e. nickel (Ni), cobalt (Co) and iron (Fe)] where the formation was systematically investigated by monitoring the change of open circuit potential (OCP), surface morphology and microstructure. The surface morphologies and crystal structures of galvanically displaced Bi or Te thin films strongly depended on the type and thickness of the sacrificial materials. Continuous Bi thin films were successfully deposited with the sacrificial Co. However, dendrites and nanoplatelets were formed from the Ni and Fe thin films. Te thin films were synthesized with all the three sacrificial thin films. Chemical dissolution rate of the sacrificial thin films and mixed potential strongly influenced formation of Bi or Te thin films.

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1. Introduction

Bismuth (Bi) and tellurium (Te) are one of well-known materials used in thermoelectric devices, which convert thermal energy from temperature gradient into electrical energy (the Seebeck effect), or vice versa (the Peltier effect), without any moving parts [1]. Bi with a low melting point (271 °C) and a rhombohedral crystal structure has been extensively studied because of its unusual electronic properties; small effective electron mass $(0.001m_e)$, large carrier mean free path (\sim 100 nm at 300 K and \sim 400 μ m at 4 K), large Fermi wavelength $\lambda_{\rm F}$ (40 nm at room temperature), highly anisotropic Fermi surface, small band overlap (\sim 38 meV at 77 K) and low charge-carrier density [2,3]. Most of research works for Bi have been focused on fabrication methods, electronic properties, thermoelectric properties, and its applications. One- or two-dimensional Bi nanostructures (i.e. nanowires, nanotubes or thin films) have been recently used to investigate quantum confinement [2], finite-size effect [4], magnetoresistance (MR) effect [5,6], and thermoelectric effect [7] due to the potential applications in thermoelectric devices, photonics and optoelectronics. Several different methods such as electrodeposition [3,5], high-pressure

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E-mail addresses: dypark@hanbat.ac.kr (D.-Y. Park), myung@engr.ucr.edu (N.V. Myung). injection [8], evaporation or sputtering [9], electron-beam lithography [2], low-temperature hydrothermal reduction [10], room temperature aqueous chemical route [11], solvothermal method [12], and vapor-phase deposition technique [13] were used to synthesize these nanostructures.

Te with a p-type narrow band gap (direct band gap energy: 0.35 eV) and a highly anisotropic crystal structure has been studied because of several potential applications in high-efficiency photoconductors, thermoelectric and piezoelectric devices, electronic and optoelectronic devices [14,15]. Te exhibits several interesting chemical and physical properties such as catalytic activity, piezoelectricity, thermoelectricity, non-linear optical response, and photoconductivity [15,16]. Specially, trigonal tellurium (t-Te) shows a highly anisotropic crystal structure which consists of helical chains of covalently bonded Te atoms and is bound together through van der Waals interactions in a hexagonal lattice [14,16]. This anisotropic structure results in one-dimensional growth (e.g. nanowire, nanorod, nanobelt or nanotube) [16].

In addition, various functional materials can be synthesized using the reaction between tellurium and other elements (Bi [1], Cd [17], Pb [18–20] and Sb [21]). Most of research works for Te have been focused on synthesis of nanostructures and thin films by using the various techniques including refluxing [16], microwaveassisted synthesis [22], thermal decomposition [23], solvothermal or hydrothermal methods [24], biomolecule-assisted routes [25] and chemical vapor deposition [14,26].

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Bath compositions and operation conditions for galvanic displacement reactions to synthesize Bi and Te thin films.

Composition	Electrolyte	Temperature (°C)	Agitation
Bi	10 mM Bi ³⁺ + 1 M HNO ₃	RT	No
Te	10 mM HTeO ₂ ⁺ + 1 M HNO ₃	RT	No

Among different techniques to synthesize Bi, Te and its alloys, electrochemical processes such as electrodeposition, electroless (autocatalytic) deposition and galvanic displacement (also called as immersion plating or cementation) are considered as one of the promising processes due to several advantages over vacuum processes [27]. Galvanic displacement among other electrochemical methods can be considered as a simple and fast process to deposit Bi and Te thin films on the substrate and to tailor the morphology, crystal structure and composition by varying experimental conditions (e.g. sacrificial material, temperature, composition of electrolyte). Also, galvanic displacement can offer the advantage of selective deposition because reduction of metal ions in electrolyte is coupled with oxidation and dissolution of the sacrificial material on substrate. For example, galvanic displacement has been used to selectively deposit Cu and other metals onto Si for applications such as integrated circuits, microelectromechanical systems (MEMS), surface-enhanced Raman spectroscopy, catalysis and microchannel chemical reactors [28-30]. Recently, galvanic displacement has been utilized to deposit pure metals and binary alloys by several research groups [31–46] including noble (i.e. Au, Ag, Pt and Pd) [32–37] and less-noble (i.e. Ni, Cu and Pb) [38–42] metals. Xia and co-workers have also synthesized binary alloys including Au-Ag, Pd-Ag and Pt-Ag [43,44]. However, galvanic displacement has not

been utilized to synthesize less common metals and semiconducting materials, although extensive studies for Bi, Te and their alloys were investigated [1–7,14–16]. In our prior work, we demonstrated the feasibility of synthesizing of Bi_xTe_y nanotubes and thin films by galvanic displacement [45,46]. However, there is a lack of systematic studies on the formation of pure Bi and Te from sacrificial metals.

In this paper, we conducted systematic investigation to monitor the formation of Bi and Te by galvanic displacement of the sacrificial iron group metallic films (Fe, Co and Ni). Electrochemical technique such as open circuit potential (OCP) measurement was utilized to monitor the process. SEM and XRD were utilized to observe the surface morphology and microstructure.

2. Experimental

In order to synthesize Bi and Te thin films by galvanic displacement, three different sacrificial iron group (i.e. Ni, Co and Fe) thin films with approximately 3 μ m thickness were electrodeposited on Pt-coated Ti/SiO₂/Si substrates from chloride baths where the substrates consist of Pt(200 nm)/Ti(20 nm)/SiO₂(100 nm)/Si. Pt (platinum) and Ti (titanium) were formed on SiO₂/Si substrate by electron-beam evaporation process. Pt was used as a seed layer and Ti was used as an adhesion layer between Pt and SiO₂ layer. Electrodeposition was conducted using a Princeton Applied Research Potentiostat (VMP2) at current density of 5 mA cm⁻² and room temperature without stirring. Saturated calomel electrode (SCE) and Pt-coated Ti anode were used as a reference and a counter electrode, respectively. Electrolyte compositions and operation conditions for electrodeposition of the sacrificial thin films can be found elsewhere [46]. Calcium chloride was used as a supporting electrolyte



Fig. 1. Open circuit potential (OCP) as a function of galvanic reaction time; the sacrificial materials (Ni, Co and Fe) are immersed into nitric acid baths containing (a) 10 mM Bi³⁺, (b) initial stages of OCP curves in (a) within 3 min, (c) 10 mM HTeO₂⁺, and (d) initial stages of OCP curves in (c) within 5 min. Solid, dash, and dotted lines represent Fe, Ni, and Co, respectively.

and L-ascorbic acid was used to prevent oxidation of Fe^{2+} in the electrolyte for electrodeposition of Fe thin film. Solution pH was controlled to be 3 with HCl or NaOH.

For galvanic displacement, electrodeposited Ni, Co and Fe thin films were immersed into the bismuth or tellurium containing electrolytes for 1 h (or 3 h). Solution pH for galvanic displacement was fixed at 1. OCP during galvanic displacement reaction was measured in a three-electrode cell to monitor the effect of the sacrificial materials. Electrolyte compositions for galvanic displacement are listed in Table 1. Bismuth nitrate [Bi(NO₃)₃·5H₂O], tellurium oxide (TeO₂, 99.99%; Alfa Aesar) and nitric acid (HNO₃) were used to make the electrolytes for galvanic displacement. Concentrations of metal ion sources (Bi³⁺ for Bi thin film or HTeO₂⁺ for Te thin film) were fixed at 10 mM and HNO₃ at 1 M for comparison.

Surface morphology and film composition of the thin films obtained from electrodeposition and galvanic displacement were examined using a scanning electron microscope (SEM) (model: XL30-FEG, Phillips) and an energy-dispersive spectroscopy (EDS) (model: EDAX, Phoenix). An X-ray diffractometer (XRD) (model: D8 advance diffractometer, Bruker) with Cu K α radiation (operating at 40 kV) was used for the identification of the phase in the thin films. The conditions of XRD were a scanning range of 20–80° with 0.02° increments and a 0.5 s collection time per increment.

3. Results and discussion

Open circuit potentials (OCP) as a function of reaction time during galvanic displacement were measured to monitor the reactions between metal ions (Bi^{3+} and $HTeO_2^+$) in electrolytes and the sacrificial metal films (Ni, Co and Fe) as shown in Fig. 1. The sacrificial thin films are galvanically displaced to form Bi or Te thin films because there exists the difference of redox potentials between metal ions (Bi^{3+} or $HTeO_2^+$) in electrolyte and the sacrificial thin films (Ni, Co and Fe) as the following equations [1,20,45,47]:

 $Bi^{3+} + 3e^- \rightarrow Bi_{(s)} \qquad E^0 = 0.317 \,V \,vs \,SHE$ (1)

 $\text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e}^- \rightarrow \text{Te}_{(s)} + 2\text{H}_2\text{O}$ $E^0 = 0.551 \text{ V vs NHE}$ (2)

 $Ni^{2+} + 2e^- \rightarrow Ni_{(s)} \qquad E^0 = -0.257 V vs SHE$ (3)

 $Co^{2+} + 2e^- \rightarrow Co_{(s)} \qquad E^0 = -0.28 V vs SHE$ (4)

$$Fe^{2+} + 2e^- \rightarrow Fe_{(s)} \qquad E^0 = -0.44 \,V \,vs \,SHE$$
 (5)

Galvanic displacement occurs spontaneously because Bi or Te metals are more noble (easier to reduce) than the sacrificial materials (Ni, Co and Fe) [45]. Fig. 1(a) shows three OCP curves of Bi3+ ions for galvanic displacement with the sacrificial Ni, Co and Fe thin films during 60 min. It was observed in Fig. 1(b) that OCP curves started from negative potential values (-0.37 V for Fe < -0.15 V for Co < -0.07 V for Ni) at early initial stage of galvanic displacement reaction and the starting potential values in OCP curve were matched to the sequence of standard redox potential values (-0.44 V vs. SHE for Fe < -0.28 V vs. SHE for Co < -0.257 V vs. SHEfor Ni). The negative potential at the early initial stage in OCP curve may indicate the mixed potentials between reduction of Bi³⁺ in the electrolyte and oxidation of the sacrificial metal thin films. The driving force for galvanic displacement reaction is the difference of redox potentials between Bi³⁺ in the electrolyte and the sacrificial metal thin films [1,20,45]. After the early initial stage, OCP curve for the sacrificial Ni thin film leveled off without showing step I. However, OCP curve exhibited very short step I for the sacrificial Fe thin film and clear step I for the sacrificial Co thin film, respectively. Clear three steps were observed only for the sacrificial Co thin film and not for the sacrificial Ni and Fe thin films. Existence of step I during galvanic displacement reaction strongly depend on type of the sacrificial thin film. OCP curve sharply increase again (step II) as soon as the sacrificial thin film is completely covered by Bi thin film. After finishing galvanic displacement reaction, OCP curve reached to be another steady-state value at near OV vs SCE (step III). Reaction time for galvanic displacement with the sacrificial Co thin film was measured to be approximately 10 min and less than 1 min for the sacrificial Fe and Ni thin films. Absence of clear three steps in OCP curve for the sacrificial Ni thin films may be attributed to much slower dissolution rate of the sacrificial Ni layer than reduction rate of Bi³⁺ ions in the electrolyte. However, much faster dissolution rate of the sacrificial Fe layer than reduction rate of Bi³⁺ ions in the electrolyte is responsible for very short step I. Effects of extremely slow dissolution rate of the sacrificial Ni layer and very fast dissolution rate of the sacrificial Fe layer on formation of Bi thin film will be discussed further with SEM microscopic images in details. As the surface coverage of Bi or Te increased with the reduction of sacrificial film surface, it shifted the open circuit potential value toward more positive value during step II. After Bi thin films completely covered the surface, the potential reached a steady state mixed potential between Bi/Bi+3 and dissolved oxygen oxidation. Fig. 1(c) shows OCP curves of HTeO₂⁺ (with a concentration of 10 mM) ion with the sacrificial Ni, Co and Fe thin films for galvanic displacement during 60 min. Clear step I in OCP curve for all the sacrificial thin films (Co, Ni and Fe) were observed. Reaction time for galvanic displacement with the sacrificial Fe thin film was measured to be approximately 15 min. However, reaction times for the sacrificial Ni and Co thin films were measured to be greater than 60 min. From comparison of open circuit potential values at step III in OCP curves of Bi^{3+} [\sim -0.03 V for the sacrificial Ni, Co and Fe thin films in Fig. 1(a)] and HTeO₂⁺ [\sim 0.3 V for the sacrificial Fe, \sim 0 V for the sacrificial Ni, and $\sim -0.1 \text{ V}$ for the sacrificial Co thin films in Fig. 1(c) ions, it can be suggested that the sacrificial Ni and Co thin films were not completely displaced by Te during galvanic displacement reaction. In order to completely displace the sacrificial Ni, Co and Fe thin films with Bi or Te metals by galvanic displacement, surface morphologies during galvanic displacement reaction should be porous for metal ions $(Bi^{3+} \text{ or } HTeO_2^+)$ in the electrolyte to reach to the sacrificial layers. If the metal ions $(Bi^{3+} \text{ or } HTeO_2^+)$ in the electrolyte cannot reach and contact the sacrificial layers, galvanic displacement cannot be continued. This will be discussed further in Fig. 6. It was clearly observed that shape of OCP curve or potential value after finishing galvanic displacement reaction strongly depend on both type of the metal ion in the electrolyte and that of the sacrificial materials.

After finishing galvanic displacement reaction with the sacrificial metal thin films (Ni, Co and Fe) for 60 min, surface morphologies of galvanically synthesized Bi were observed using SEM, as shown in Fig. 2. Fig. 2(a) shows the surface morphology of electrodeposited sacrificial Ni thin film from chloride bath before galvanic displacement reaction [46]. Surface morphology of Bi galvanically synthesized with the electrodeposited Ni thin film exhibited several isolated particles [marked with red arrows in Fig. 2(b)], in the absence of uniform thin film. Needle-like shape surface in Fig. 2(a) and (b) comes from the electrodeposited Ni thin film. Those particles in Fig. 2(a) were verified to be Bi using EDS analysis. Therefore, it can be concluded that dissolution (oxidation) rate of the electrodeposited Ni thin film during galvanic displacement in nitric acid solution is extremely slow. On the other hand, surface morphology of the galvanically synthesized Bi thin film (Fig. 2(d)) with the electrodeposited Co thin film as a sacrificial thin film exhibits a granular structure with a polygon shape arrangement and somewhat similar to surface morphology of the electrodeposited Co thin film (Fig. 2(c)). EDS analysis confirm the formation of Bi thin film.

Three-micron thick electrodeposited Fe film had dense and uniform deposit (Fig. 2(e)). However, Bi thin film was not formed by galvanic displacement reaction (Fig. 2(f)). EDS also confirmed the finding which might be attributed to complete chemical dissolution



Fig. 2. Surface morphologies of sacrificial (a) Ni, (c) Co and (e) Fe thin films electrodeposited from chloride baths [46]. Surface morphologies of Bi thin films deposited by galvanic displacement reaction for 60 min with the sacrificial (b) Ni, (d) Co and (f) Fe thin films.

of Fe thin film prior to galvanic displacement. To further investigate the process, the effect of film thickness of Fe on the formation of Bi was conducted which will be discussed in later section. Also, only Bi particles were obtained using the sacrificial Ni thin film during galvanic displacement reaction. The exact mechanism leading to those phenomena in Fig. 2(b and f) has not yet been identified. It is obvious that formation of the galvanically synthesized Bi thin films with the sacrificial Ni, Co and Fe thin films strongly depend on type of the sacrificial thin films. From SEM observation in Fig. 2, it is clear that the galvanically synthesized Bi particles resulted from extremely slow dissolution rate of the sacrificial Ni thin films. Also, very fast dissolution rate of the sacrificial Fe thin films resulted in no formation of Bi thin film by galvanic displacement of thin Fe films (approx. 3 μ m).

Surface morphology of galvanically synthesized Te thin films with the sacrificial metal thin films (Ni, Co and Fe) for 60 min was observed using SEM, as shown in Fig. 3. Te thin films were successfully deposited with the three sacrificial thin films by galvanic displacement reaction. Te thin films deposited by galvanic displace-

ment with the electrodeposited Ni (Fig. 3(a)), Co (Fig. 3(b)) and Fe (Fig. 3(c)) thin films showed completely different surface morphology compared to the surface morphologies of the electrodeposited sacrificial Ni (Fig. 2(a)), Co (Fig. 2(c)), and Fe (Fig. 2(e)) thin films [46]. Surface morphology of the galvanically synthesized Te thin film with the electrodeposited Ni thin film exhibited a well-defined polygon shape as shown in Fig. 3(a). On the other hand, surface morphology of the galvanically synthesized Te thin film with the electrodeposited Co thin film in Fig. 3(b) showed a flower-like granular structure with very fine polygon shapes. Also, galvanically synthesized Te thin film with the electrodeposited Fe thin film had very fine polygon shape as shown in Fig. 3(c). It is clear that surface morphologies of galvanically synthesized Te thin films with the sacrificial Ni, Co and Fe thin films were not depended on those of the sacrificial thin films (Fig. 2(a) for Ni, Fig. 2(c) for Co and Fig. 2(e) for Fe).

Fig. 4 shows XRD patterns of Bi thin films deposited by galvanic displacement with the different sacrificial Ni, Co, and Fe thin films. Bi thin film was clearly formed by galvanic displacement only with



Fig. 3. Surface morphologies of galvanically displaced Te thin films with sacrificial (a) Ni, (b) Co and (c) Fe thin films.

the sacrificial Co thin films as shown in Fig. 4(b). Bi thin film in Fig. 4(b) exhibits a typical XRD pattern of Bi with a dominant (012) planes and a rhombohedral structure (JCPDS No. 05-0519). However, only a very weak peak of Bi was observed during galvanic displacement with the sacrificial Ni thin films as shown in Fig. 4(a). The weak Bi peak resulted from the formation of Bi particles instead of the formation of continuous Bi thin film. This XRD result is in good agreement with SEM observation of Bi particles in Fig. 2(b). Therefore, it is clear from SEM, EDS and XRD analyses that only some amounts of Bi particles with the sacrificial Ni thin film were deposited by galvanic displacement due to extremely slow dissolution rate of Ni thin films into the electrolyte and low mixed potential to drive the reaction. On the other hand, no peak for Bi from XRD

analysis of Fig. 4(c) was observed by galvanic displacement with the sacrificial Fe thin film. Further analysis was conducted using EDS because it is not clear whether Bi thin film was formed by galvanic displacement with the sacrificial Fe thin film, or not. Neither Bi nor Fe was not detected at all in EDS analysis. This result indicates that Bi thin film was not formed during galvanic displacement reaction with 3 μ m thick Fe thin film.

Fig. 5 shows XRD patterns of Te thin films obtained by galvanic displacement with the different sacrificial metals such as Ni (Fig. 5(a)), Co (Fig. 5(b)), and Fe (Fig. 5(c)). From XRD results, it is obvious that Te thin films were successfully synthesized by galvanic displacement with the sacrificial Ni and Co films, even with the sacrificial Fe thin film, compared to XRD results of Bi thin films (Fig. 4(a and c)). The galvanically synthesized Te thin films with the sacrificial Ni, Co and Fe thin films show a hexagonal structure (JCPDS No. 36-1452).

It is difficult to clearly observe total film thickness of the galvanically deposited Bi thin film using cross-sectional SEM image because of the formation of Bi particles instead of Bi thin film as shown in Fig. 2(b) and no formation of Bi thin film as shown in Fig. 2(f). Therefore, it is meaningless to compare thickness of Bi thin film obtained by galvanic displacement with the three different sacrificial thin films. However, Te thin films were successfully formed during galvanic displacement with the three different sacrificial thin films. Thicknesses of Te thin films galvanically synthesized from nitric acid baths for 60 min and the sacrificial Ni, Co and Fe thin films electrodeposited from chloride baths could be clearly observed using cross-sectional SEM image as shown in Figs. 6-8. Nickel thin film with a thickness of \sim 3 µm electrodeposited from chloride bath has a typical dimple structure (sponge-like structure) of ductile metal as shown in Fig. 6(a). After galvanic displacement for 60 min, Ni thin film was partially replaced by Te thin film with a polygon shape and thickness of Te thin film was measured to be \sim 0.8 μ m thick. Te thin film exhibited columnar growth (Fig. 6(b and c)). Columnar growth is commonly observed in the thin/thick films fabricated by other electrochemical processes such as electrodeposition [27,48] or electroless deposition [49–52]. Fig. 6(b) exhibits Te thin film with $\sim 0.8 \,\mu m$ thick after galvanic displacement reaction for 60 min with the sacrificial Ni thin film. The sacrificial Ni thin film with \sim 2.8 µm thick still remained as shown in Fig. 6(b). This result may come from much slower dissolution rate of the sacrificial Ni thin film compared to reduction rate of HTe₂O⁺ ion in nitric acid solution and is in good agreement with the result of OCP curve for the sacrificial Ni thin film (Fig. 1(c)). That is, OCP value for the galvanically deposited Te thin film with the sacrificial Ni thin film in Fig. 1(c) was measured to be -0.04 V and indicated that the sacrificial Ni thin film was partially displaced by galvanic displacement. Te thin film with ${\sim}0.8\,\mu\text{m}$ thick was formed by galvanic displacement the sacrificial Ni thin film for 1 h. After galvanic displacement reaction for 3 h, thickness of Te thin film was measured to be \sim 2.5 µm as shown in Fig. 6(c). It was observed that growth rate of Te thin film was linearly proportional to time of galvanic displacement reaction.

Fig. 7(a) shows the electrodeposited sacrificial Co thin film with \sim 3 µm thick. After galvanic displacement reaction with the sacrificial Co thin film for 1 h, thickness of Te thin film was \sim 1.8 µm thick as shown in Fig. 7(b). Te thin film was deposited galvanically in powdery form and showed very rough surface as shown in Fig. 7(d). After galvanic displacement for 1 h, significant amount of the sacrificial Co thin film in Fig. 7(b) still remained. This result may come from much slower dissolution rate of the sacrificial Co thin film compared to reduction rate of HTe₂O⁺ ion and is in good agreement with result of OCP curve for the sacrificial Co thin film (Fig. 1(c)).

On the other hand, cross-sectional SEM image for the electrodeposited Fe thin film with a thickness of \sim 3 µm is shown in Fig. 8(a).



Fig. 4. XRD patterns of the galvanically displaced Bi thin films with sacrificial (a) Ni, (b) Co and (c) Fe thin films. (S: substrate - Pt and Si).



Fig. 5. XRD patterns of galvanically displaced Te thin films with sacrificial (a) Ni, (b) Co, and (c) Fe thin films. (S: substrate - Pt and Si).



Fig. 6. Cross-sectional SEM images of Te thin films deposited with the sacrificial Ni thin film by galvanic displacement; (a) the sacrificial Ni thin films electrodeposited from chloride bath, (b) Te thin film deposited by galvanic displacement with the sacrificial Ni thin film for 1 h and (c) Te thin film deposited by galvanic displacement with the sacrificial Ni thin film for 3 h.



Fig. 7. Cross-sectional SEM images of Te thin films deposited with the sacrificial Co thin film by galvanic displacement; (a) the sacrificial Co thin films electrodeposited from chloride bath, (b) Te thin film deposited by galvanic displacement with the sacrificial Co thin film for 1 h, and (c) high magnification of Te thin film marked as region "A" in (b), (d) tilting top view of Te thin film in (b).



Fig. 8. Cross-sectional SEM images of Te thin films deposited with increasing thickness of the sacrificial Fe thin film by galvanic displacement; (a) the sacrificial Fe thin film $(3 \mu m \text{ thick})$ electrodeposited from chloride bath, (b) Te thin film deposited by galvanic displacement with the sacrificial Fe thin film $(3 \mu m \text{ thick})$ for 1 h, (c) tilted top view of Te thin film deposited by galvanic displacement with the sacrificial Fe thin film (10 μm thick) for 1 h, (e) tilted top view of Te thin film deposited by galvanic displacement with the sacrificial Fe thin film (10 μm thick) for 1 h, (e) tilted top view of Te thin film of (d), (f) Te thin film deposited by galvanic displacement with the sacrificial Fe thin film (10 μm thick) for 1 h, (e) tilted top view of Te thin film of (d), (f) Te thin film deposited by galvanic displacement with the sacrificial Fe thin film (10 μm thick) for 1 h, (e) tilted top view of Te thin film of (d), (f) Te thin film deposited by galvanic displacement with the sacrificial Fe thin film (20 μm thick) for 1 h, (g) top view of Te thin film in (f), and (h) XRD patterns of Te thin film for (d) and (f).

After galvanic displacement reaction for 1 h, Te thin films with triangular and spine-shape was formed. Thickness of Te thin film in Fig. 8(b) was measured to be ~0.4 μ m. Compared to the sacrificial Ni and Co layers, much faster dissolution rate of the sacrificial Fe thin film than reduction rate of HTe₂O⁺ ion in nitric acid solution

was observed. This result is in good agreement with the result of OCP curve for the sacrificial Fe thin film in Fig. 1(c); time to reach \sim 0.3 V, at which Te thin film was completely displaced by galvanic displacement reaction with the sacrificial Fe thin film, was \sim 15 min. Dissolution rates of the sacrificial Ni, Co, and Fe thin films in nitric



Fig. 9. Surface morphologies of galvanically displaced Bi from sacrificial Fe thin films with a thickness of (a) 10 μ m, low magnification. (b) 10 μ m, high magnification (c) 20 μ m, low magnification and (d) 20 μ m, high magnification for 1 h.

acid solution (pH 1 in this study) were measured to be in order of $Co \approx Ni < Fe$ from galvanic displacement reaction. Dissolution rate of the sacrificial layer may strongly depend on surface morphologies of Te deposited galvanically on the sacrificial layers at the initial stage of galvanic displacement; after covering initially the sacrificial layer by galvanic displacement, more porous surface of Te thin film on the sacrificial layer result in faster dissolution rate of the sacrificial layer. It was also observed that surface morphologies of Te thin films with both sacrificial Ni (Fig. 3(a) or Fig. 6(b)) and Co (Fig. 3(b) or Fig. 7(d)) layers were formed in more compact than that of Te with the sacrificial Fe layer (Fig. 3(c) or Fig. 8(b)). In order to investigate the influence of the sacrificial Fe layer thickness on surface morphology and thickness of Te thin film, thickness of the sacrificial Fe layer was changed from 3 to 10 and 20 μ m. Thicker and more compact Te thin films by galvanic displacement were formed with increasing thickness of the sacrificial Fe layer as shown in Fig. 8(b, d and f). From XRD analysis in Fig. 8(h), (101) peak (JCPDS No. 36-1452) was more clearly observed compared to XRD result in Fig. 5(c). Also, it can be suggest from XRD results that Te thin film may be very close to amorphous phase rather than crystalline phase.

To understand the effects of Fe layer thickness on the formation of Bi similar to Te, the thickness was varied from 3 to 10 and 20 μ m. Although Bi was not deposited from ~3 μ m thick Fe film (Fig. 2(f)), the dendrites and hexagonal nanoplatelets of Bi were deposited via galvanic displacement with increasing film thickness (Fig. 9). The morphology of the deposits was strongly influenced by the sacrificial film thickness where dendrites were observed with ~10 μ m thick Fe thin film [Fig. 9(a–b)]. Approximately 20 μ m thick Fe thin films led to the formation of hexagonal Bi nanoplatelets on the dendrites [Fig. 9(c–d)]. The X-ray diffraction patterns confirmed the formation of Bi with preferred orientation in (012) and (104) planes (JCPDS No. 05-0519) (Data not shown).

From OCP measurements (Fig. 1) and SEM results (Figs. 2 and 9 for Bi thin film, and Figs. 6-8 for Te thin films), it was obvious that the deposited thickness of galvanically synthesized Bi or Te thin films strongly depends on type of the sacrificial thin films. Also, it can be suggested that faster dissolution rate of the sacrificial Fe thin film than reduction rate of Bi ions in galvanic displacement for Bi thin film resulted in very short step I in OCP curve as shown in Fig. 1(a). Furthermore, extremely slow dissolution rate of the sacrificial Ni thin film may caused absence of step I in OCP curve. On the other hand, clear step I in OCP curve was observed in galvanic displacement of Te thin film due to relatively slow dissolution rate of the sacrificial Co and Ni than reduction rate of Te ions. Therefore, galvanic displacement reactions to fabricate Bi or Te thin films could be successfully monitored by OCP measurements. Also, it is clear from the observation of cross section morphologies that type of sacrificial materials has a strong influence on the structure of Te thin film. In other words, microstructure of the galvanically deposited thin film could be adjusted by the type of the sacrificial materials.

4. Conclusions

Bi and Te thin films were synthesized by galvanic displacement with three different types of the sacrificial thin films (Ni, Co and Fe). The sacrificial Ni, Co and Fe thin films were electrodeposited on Pt(nm)/Ti(nm)/SiO₂(nm)/Si substrate at room temperature without stirring. Galvanic displacement reactions to fabricate Bi and Te thin films could be successfully monitored by OCP measurements. It was clearly observed that a good agreement between OCP measurement, XRD analysis and SEM observation for the galvanically deposited Bi and Te thin films is existed. Surface morphologies and crystal structures of the as-synthesized thin films by galvanic displacement strongly depend on the type of the sacrificial materials.

Bi thin films were successfully deposited with the sacrificial Co thin films. However, only small amounts of Bi particles were deposited by galvanic displacement with the 3 µm thick sacrificial Ni thin films due to slow dissolution rate. Similar to nickel, Bi was not galvanically displaced on the 3 µm thick Fe thin films. By increasing the Fe film thickness, dendrites with hexagonal nanoplatelets of Bi were deposited.

Te thin films were successfully deposited using the sacrificial Ni, Co, and Fe thin films during galvanic displacement. Thicker sacrificial Fe films led to the formation of thicker and more compact of Te. Moreover, Te thin films exhibited different surface morphologies compared to the surface morphologies of the sacrificial thin films. The galvanically deposited Bi and Te thin films were successfully investigated using open circuit potential (OCP), surface morphology and microstructure.

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