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Effect of potential on bismuth telluride thin film growth by electrochemical atomic layer epitaxy

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Abstract

In the present study, bismuth telluride compound thin film was grown by means of electrochemical atomic layer epitaxy (ECALE) with an automated thin layer flow cell deposition system. The dependence of the Bi and Te deposition potentials on Pt electrode was studied. Because developing a contact potential between the substrate and the growing semiconductor, the deposition potential adjustment is necessary for the first 30 or more cycles of each component. The dependence of the deposit as a function of the deposition potential adjustment slope has been investigated. The results show that an excess elemental Bi existed at a slope of -2 mV/p (p indicates per cycle), indicating that this is a lack of deposition at the potential. Single-phase Bi_2Te_3 compound could be obtained between -4 and -6 mV/p. Bi_2Te_3 and Bi_4Te_3 coexistence is observed at a slope of -10 mV/p. The EDS data indicates that the stoichiometry of compound is consistent with XRD result. SEM studies show that the deposits are inhomogeneous and have an micron sized particles morphology.

Keywords: ECALE; UPD; Bismuth telluride; Thermoelectric material; Thin film

1. Introduction

Bismuth telluride based compounds have attracted considerable interest as thermoelectric (TE) materials. These materials are widely used for Peltier coolers. The performance of thermoelectric devices depends on the figure of merit (ZT) of the material. Several possible approaches to enhancing ZT have been investigated [1–3]. In comparison with bulk TE materials, thin film TE materials offer tremendous scope for ZT enhancement. Meanwhile, thin films of bismuth telluride also can be applied to TE temperature controllers for subminiature electronic devices. In the formation of high quality thermoelectric devices, a number of thin film formation methodologies are used, including: molecular beam epitaxy (MBE) [4], chemical vapor deposition (CVD) [5,6], flash evaporation [7,8], co-evaporation [9,10], and sputtering [11]. In general, these methods are performed in vacuum and are thermal methods, achieving compound formation by heating the reactants and substrate.

Low temperature electrochemical deposition is desirable for avoiding heat-induced interdiffusion of adjacent layers in a structure, in addition, vacuum atmosphere is not longer a necessity. There are several methods presently used to form bismuth telluride compounds electrochemically, the most practical being codeposition [12,13]. The resulting deposits often require post-deposition annealing procedures, which negate the low temperature advantage of electrodeposition.

Atomic layer epitaxy (ALE), in general, is a thin film formation methodology where growth is controlled using surface limited reactions. Separate reactions are used for the atomic layers of each of the component elements, and these reactions are run in a cycle, with each cycle producing one ML of the compound. The thickness of the deposit is determined by the number of cycles performed. Electrochemical atomic layer epitaxy (ECALE) [14–26] is the electrochemical analog

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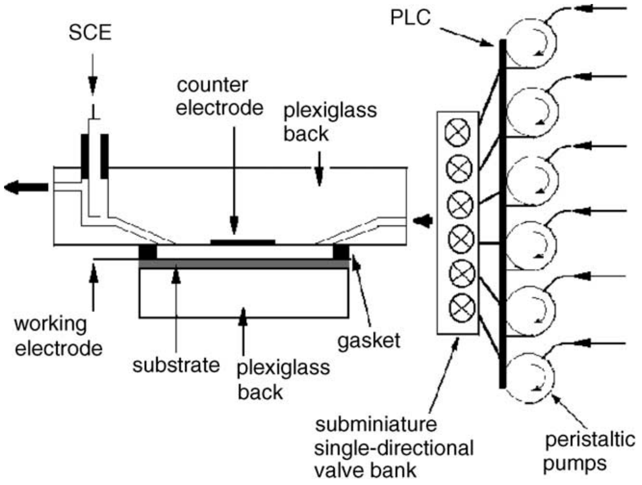

Fig. 1. The schematic drawing of an automated electrochemical thin-layer flow deposition reactor.

of ALE. Electrochemical surface limited reactions are generally referred to as underpotential deposition (UPD) [27–30]. Electrochemical ALE (EC-ALE) is the result of combining UPD with the principles of ALE to form a deposition cycle. ECALE cycles involve switching deposition solutions and potentials to form each component atomic layer. This is in marked contrast to codeposition, where a single solution is used to deposit all the elements, generally at a single potential. By using an ECALE cycle, the degrees of freedom in the deposition process are expanded. Variables in the cycle include the deposition potentials, the rinsing procedures, flow rates, deposition times, etc.

II–VI compounds such as CdTe [15–19], CdS [22–25,31], and ZnSe [20] have been successfully formed using by ECALE, as well as some III–V compounds: GaAs [32,33], InAs [34]. Recently Oznuluer has reported the kinetics and growth mechanism of VA–VIA compound Bi_2S_3 by ECALE [35]. Despite the element sulfur and tellurium belong to VIA family of periodic table, there are very significant differences for their electrochemical aspects. However, no work has been reported on the formation of bismuth telluride VA–VIA compound thin film by ECALE. In the present investigation, an automated computer controlled thin-layer electrochemical flow cell system is developed in this group (Fig. 1). The dependence of the Bi and Te deposition potentials on Pt electrode will be reported in this paper.

2. Experimental procedure

The deposition instrument consisting of peristaltic pumps, valves, programmable logistic computer (PLC), a flow cell and potentiostat was used under the control of a computer (Fig. 1). The electrochemical flow cell was similar to those described by Stickney work group [15]. However, some improvement were progressed by this group and described below. One involved the use of subminiature single-directional valve bank to avoid problems with mixture of solution each other via siphonal phenomena. The second approach involved the upturned flare of the channel at the inlet and outlet. The structure utilized the buoyancy to dislodge trapped bubbles automatically. The third approach was based on potential stabilization between the reference electrode and the working electrode. Here, the outlet stream of the cell was higher than the reference electrode underside. The structure ensured the reference electrode was contacted with solution adequately, rather than the outlet stream was level with the reference electrode underside, thereby potentially eliminated potential excursion. The cavity was defined by a Si(1 0 0) wafer substrate, coated with 1 μm of Pt by magnetic sputtering and an auxiliary electrode, a plate of Pt. These electrodes were held apart by a 5 mm-thick gasket, which defined a 0.7 cm × 3 cm rectangular opening. The plexiglass was transparent, allowing the deposition process to be followed visually. The reference electrode, saturated calomel electrode (SCE), was positioned at the cavity outlet.

Solutions were prepared with high purity reagents and twice-distilled water. All bismuth solutions consisted of 0.1 mM $Bi(NO_3)_3{\cdot}5H_2O$, and used 0.1 M $HClO_4$ as a supporting electrolyte, pH 1.5. Tellurium solutions were 0.1 mM in TeO_2, and also used 0.1 M $HClO_4$ as a supporting electrolyte. The pH 8.5 Te solutions were adjusted with ammonia. Various blank rinse solutions were also utilized, with a pH analogous to its respective deposition solution. All solutions were deaerated by blowing purified N_2 gas through and over the solution for 30 min. All experiments were performed at room temperature.

Energy dispersive spectroscope studies were performed using a Oxford Inca EDS. The XRD patterns were obtained with a Philips-PW 1710 X-ray diffractometer using Cu Kα radiation. SEM images were taken with a commercial instrument (Quanta 400)

3. Results and discussion

3.1. Electrochemical aspects of tellurium and bismuth

The curve shown in Fig. 2 is obtained from tellurium solution on the Pt substrate. The scan proceeded from right to left and resulted in two reduction peaks C1 and C2. Integration of this peak C1 corresponds to 0.4 ML Te coverage approximately, suggesting an apparently surface limited deposition. The UPD nature of this peak C1 is further supported by the fact that it disappears in the successive scans, in which only bulk TeO_2 reduction is observed (Fig. 3). Peak C2 corresponds to Te bulk deposition on the Pt substrate. The subsequent anodic stripping peaks A2 and A1 correspond to stripping of the Te bulk and Te UPD, respectively.

Due to the slower kinetics of Te reductive UPD on Pt, one method for forming the Te UPD layer involves first depositing a full aliquot of TeO_2 at −0.6 V, so that UPD and bulk Te result, followed by reduction of the bulk Te, forming soluble

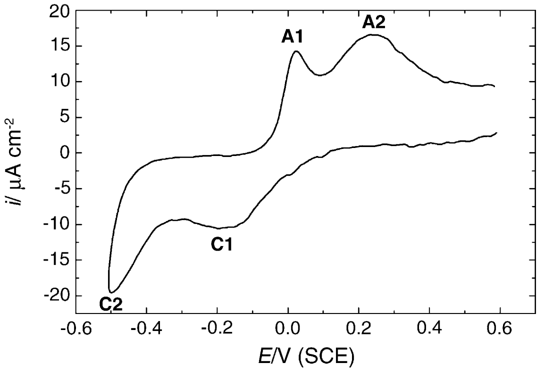

Fig. 2. Cyclic voltammogram of Te on Pt. The scanning rate is 10 mV/s.

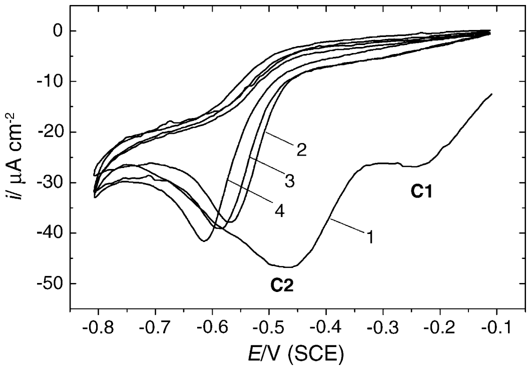

Fig. 3. Cyclic voltammograms of 0.1 mM TeO_2 in an ammonia buffer solution of pH 8.5 on Pt. The numeral indicates consecutive scans, from $E = -0.1$ to -0.8 V. The scanning rate is 10 mV/s.

H_2Te. This process is referred by Foresti and Stickney as oxidative Te UPD [18–20]:

$$\text{Te (UPD)} + \text{Te (bulk)} + H^+ + 2e \cdots \text{Te (UPD)} + HTe^- \quad (1)$$

Fig. 4 shows a cyclic voltammogram of a Pt electrode covered with overpotentially deposited Te (−0.6 V) in the pH 8.5 blank solution containing no Te redox system. The reduction peak C1 (−0.9 to −1.05 V) only involves the re-reduction process of bulk deposited Te. When the potential is scanned towards more negative values, the re-reduction process of Te (UPD) occurs giving a very narrow and sharp shape current peak C2.

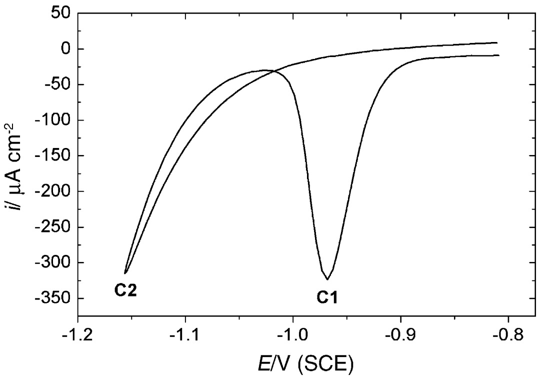

Fig. 4. Cyclic voltammogram of the bulk deposited Te reduction to Te^{2-} in an ammonia buffer solution of pH 8.5. The scanning rate is 10 mV/s.

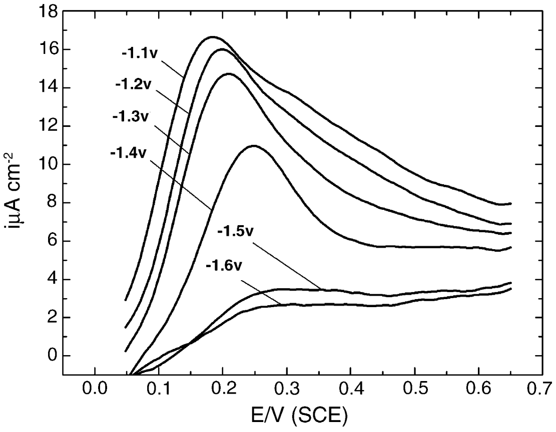

Fig. 5. Anodic potentiodynamic curves, obtained on the bulk deposited Te electrode in an ammonia buffer solution of pH 8.5. The electrode was polarized to the potential E (−1.1 V to −1.6 V) for 1.5 min, then the anodic potential scanning was performed from $E = 0.05$ to 0.65 V. The potential scanning rate was 10 mV/s.

Since the Te UPD layer is more strongly bound to Pt substrate and therefore it is expected to reduce at more negative potentials. It is clearly shown from the cyclic voltammograms recorded in the region of UPD stripping process after keeping the electrode at increasingly negative potentials (Fig. 5). Keeping the electrode at −1.1 to −1.3 V only occurs bulk deposited Te re-reduction. The underpotentially deposited Te, however, remains on the electrode, thus having an anodic striping peak of underpotential deposits in the region of UPD stripping process. As a matter of fact, the underpotentially deposited Te starts to be re-reduced at the potential of −1.4 V. Keeping the electrode at potentials as negative as −1.6 V causes complete re-reduction of the previously underpotential deposited Te, thus having no anodic stripping peak of underpotential deposits.

Fig. 6 shows the current–potential curves for different Bi concentration deposition and stripping on a Pt substrate. The

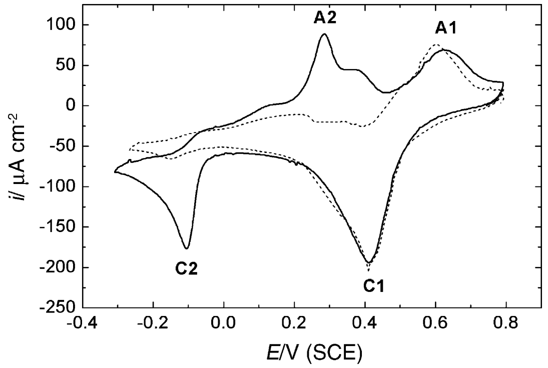

Fig. 6. Cyclic voltammograms of Bi on Pt obtained from 0.1 mM (dot line) and 0.4 mM (solid line) $Bi(NO_3)_3{\cdot}5H_2O$ in a prochloric acid solution. The scanning rate is 10 mV/s.

relatively broad cathodic peak between 0.5 and 0 V, labeled C1, and the stripping peak, labeled A1, are practically coincident, in despite of the concentration change. This suggested C1 and A1 to be conjugative deposition and stripping UPD peaks. In fact, because the UPD process is surface-limited, the charge involved in the UPD is independent of concentration: increasing concentration from 0.1 to 0.4 mM causes only the bulk redox process becomes more intensive. Fig. 6 shows a clear difference between cathodic and anodic charge, which labeled C2 and A2 for the concentration variety, corresponding to the bulk reduction and oxidation, respectively.

3.2. *ECALE film deposition*

Initial Bi potential of 0.2 V on Pt is selected, along with a Te potential equal to −0.6 V, for the first bismuth telluride program. Due to the low concentration of $HTeO_2^+$ and the slow kinetics for Te deposition, very little Te (bulk) formed. The $HTeO_2^+$ solution is then exchanged for a blank electrolyte solution, and a potential sufficiently negative (−1.1 V) to re-reduce Te (bulk), but not negative enough to re-reduce Te (UPD), is applied. The first cycle of the ECALE process for the deposition is schematized in Fig. 7. However, during the process of ECALE, using the potentials determined by cyclic voltammograms such as those shown in Fig. 7, for the deposition of elements on a Pt substrate, is a very simplistic approximation. The deposition charges decreased over the first few cycles if the potentials determined from Fig. 7 are used and kept constant during the ECALE process of the Bi–Te system. This is because the underpotentials for deposition of these elements on Pt are different from those for deposition on each other or on the compound. In the ECALE process of the Bi–Te binary system, the first Te deposition is essentially UPD of the element on the electrode. Then, the deposition of the Bi element occurs on a Te-covered Pt substrate and forms a monolayer of the compound. Foresti has suggested that this process is simply driven by the free energy change involved in the formation of the different chalcogenides [19]. That is, the underpotential depositions of Bi on Te-covered substrate should reflect the heat of formation of bismuth telluride. The more negative the heat of formation, the more positive the potential at which UPD occurs. Bi_2Te_3 is the least stable Bi chalcogenide, therefore, Bi UPD on Te-covered substrate should occur at less positive potentials. Moreover, once the adsorbed Te atoms present, interactions of Bi with the substrate become weaker than those involved in Bi_2Te_3 formation could shift the underpotential deposition towards more negative potentials. As a consequence, the potential 0.2 V chosen for deposition might become too positive to deposit a sufficient amount of Bi. Therefore, the Bi underpotentials for the first 30 cycles needed to adjustment gradually to lower, albeit in shorter and shorter steps, until maintain a steady state. This was also observed in ECALE of the CdTe system by Stickney and co-workers [15]. In fact, it must be stressed that bulk electrodeposition processes are scarcely influenced by the substrate. Thus, bulk Te reduction on a Bi-coated Pt electrode occurs at the same potentials as on the bare Pt electrode. After deposition of Te, it is a problem to shift the potential more positively for Bi deposition. If the Bi underpotentials drop for the first 30 cycles very small, the potential needed to shift back more positively for Bi deposition and some of the previously deposited Te would be stripped, though the Te UPD stripping potential could shift to a little positive position for the lower pH of Bi deposition. On the other hand, a large potential drop used for the first 30 cycles of Bi deposition will not result in loss of Te. However, if the potential drop too large bulk Bi deposits will occur. In the present study, potentials were not extensively optimized, however, to investigate the problems, such as described above, several potential drop which are adjustmented negatively each step for the first 30 cycles, are tried.

3.3. *Structure control and morphology of the compound growth*

Fig. 8 shows XRD patterns of 200-cycles electrodeposited compounds for different potential adjustment slopes of the

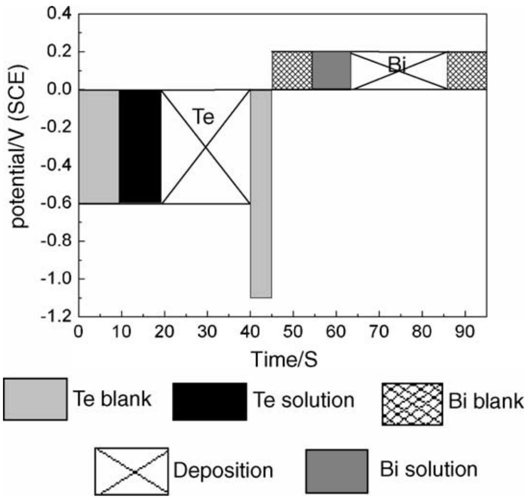

Fig. 7. Diagram of an ECALE cycle for Bi_2Te_3 formation.

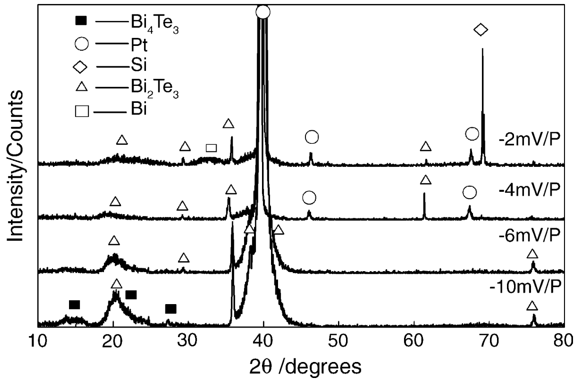

Fig. 8. X-ray pattern of 200-cycles electrodeposit on Pt for different potential adjustment slope of the first 30 cycles.

Table 1
The change in composition of thin films as a function of potential adjustment slope

Adjustment slope *X* (mV)	Bi (At.%)	Te (At.%)
−2	94.74	5.26
−4	42.51	57.49
−6	39.70	60.30
−10	49.60	50.40

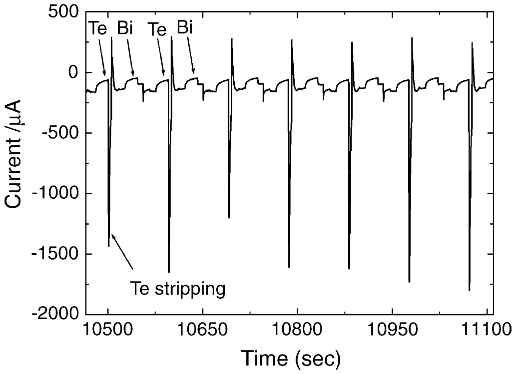

Fig. 9. Plots of the current involved in UPD of bismuth and tellurium alternately as a function of deposition time.

first 30 cycles. Peaks of Si and Pt are observed at a slope of −2 mV/p (p indicates per cycle), indicating that the coverage of electrodeposited thin film is low. It suggested this is a lack of deposition at the potential. Probably, as the above mentioned, this value, 0.2 V, corresponds to the deposition of Bi on Pt and had to be changed after the deposition of a Te layer. Increasing the negative slope from −2 to −4 mV/p, the XRD peak of Si disappears and the peaks of Pt weaken, along with the peaks of Bi_2Te_3 become more evident. It can be seen single-phase Bi_2Te_3 compound is obtained at a slope of −6 mV/p except the prominent substrate [1 1 1] reflection. Bi_2Te_3 and Bi_4Te_3 coexist with a further decrease of the slope to −10 mV/p.

Energy dispersive spectroscopy (EDS) is used as a preliminary diagnostic tool to study the compositions of the films. The variation in the composition of the films as a function

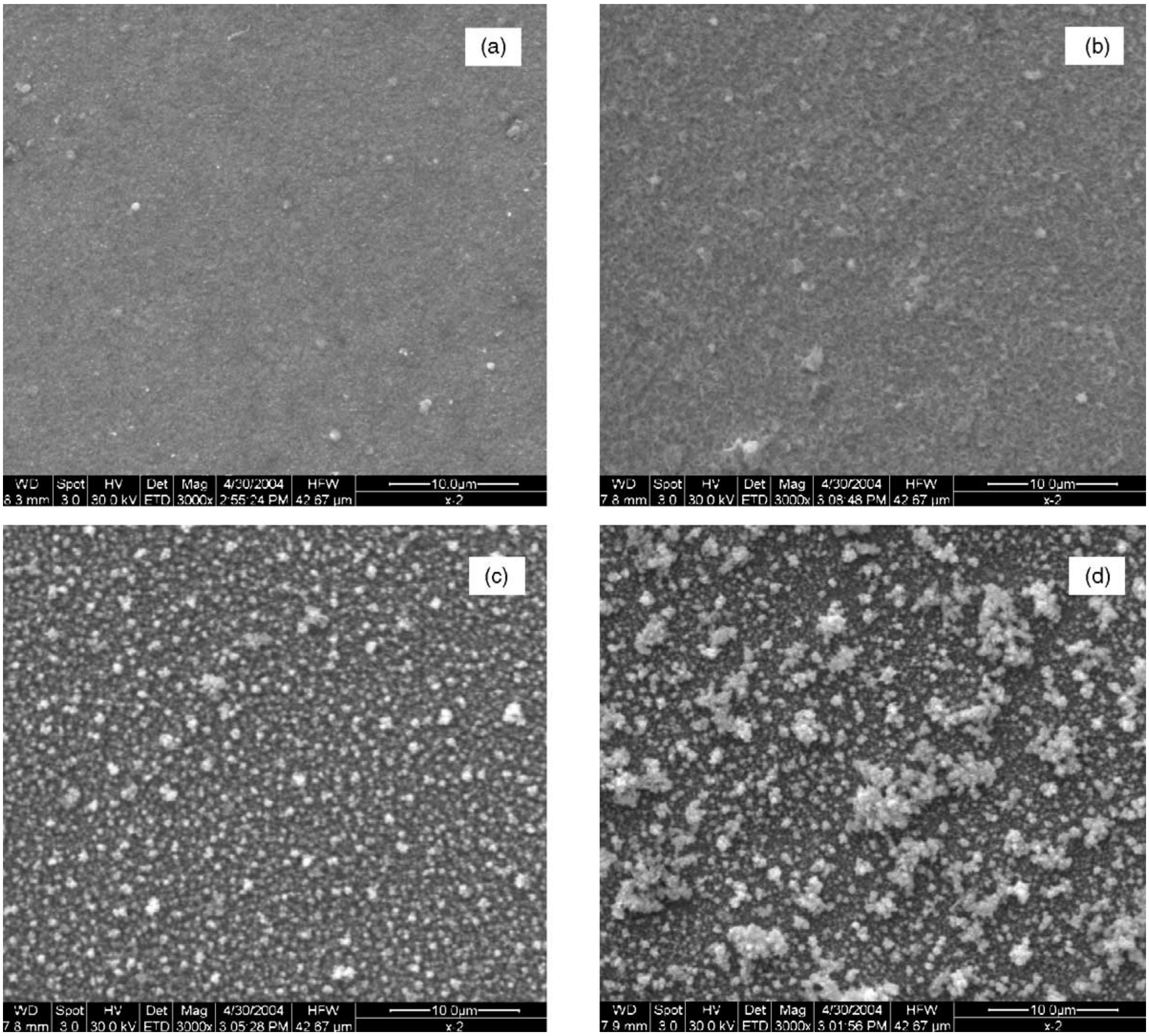

Fig. 10. SEM images of different examples: (a) naked substrate, (b) outlet of the flow cell, (c) center of the flow cell, (d) entrance of the flow cell.

of potential adjustment slope is summarized in Table 1. The compositions shown above are roughly 2:3 for Bi:Te when the slopes equal to −4 and −6 mV/p. Evident excess elemental Bi is observed at −2 mV/p. The evident Bi excess probably is due to a partial loss of Te in the Bi UPD process on the Te, where Te atomic layer, however, is not stable at 0.14 V, and will oxidatively strip from the surface under the positive potential conditions. The approximate 1:1 stoichiometric ratio for bismuth to tellurium at −10 mV/p suggested the Bi_2Te_3 and Bi_4Te_3 coexistence, which is consistent with XRD result.

In conclusion, the potential adjustment slope of −6 mV/p seems successful and feasible for the Bi_2Te_3 compound ECALE process. The current time traces for this procedure were shown in Fig. 9. Using the current time traces we can examine the deposition process for per step in real time and the current involved in each step is controlled. From integration of the currents for deposition, the Bi and Te coverages per cycle, from coulometry, averaged 0.6 ML of Te and 0.4 ML of Bi. The film prepared at −6 mV/p is examined by scanning electron microscopy (SEM). After 200 cycles, the deposited film shows an inhomogeneous distribution along the flow cell. Film grown at outlet of the flow cell is very smooth as seen by eye, like the naked substrate, and SEM image shows small, relatively monodispersed feature sizes, as shown in Fig. 10b. At center of the flow cell the film appear gray. Under the SEM the film shows a number of micron sized crystallites on the surface. However, the region appears smooth, and the crystals are stoichiometric (Fig. 10c). The film at entrance of the flow cell has rough morphology (Fig. 10d). As comparing, the naked substrate image, which has not any deposits, also shows in Fig. 10a. The inhomogeneous deposits are similar to that of the binary CdTe [15]. Stickney work group has suggested these results are related to the significant irreversibility for Te, which results in a not completely surface limited process. Given homogeneous conditions in the cell and the use of optimal potentials, high quality deposits can be formed. In future flow cells the 5 mm thick gasket has been limited to 0.8 mm thick, helping to establish laminar flow earlier in the flow channel. On the other hand, the presence of inhomogeneities also attributes to the poor quality of the substrate by magnetic sputtering, which is generally polycrystalline, and often accompany with some defects. Studies of bismuth telluride growth using ECALE on single crystal substrates are beginning, and should help to resolve the issue.

4. Conclusion

Preliminary study of the ECALE process of bismuth telluride thin film, and the electrochemical aspects are reported in this paper. The dependence of the deposit as a function of the potential adjustment slope used to deposit the first 30 atomic layers of Bi and Te is examined as well. XRD show the Bi_2Te_3 compound has been formed. The stoichiometric 2:3 ratio of Bi:Te, as expected for the formation of the compound, is confirmed by EDS. SEM studies indicate that the deposits are inhomogeneity, probably because the flow patterns within the cell have been developed, as well as it have correlated with defects in the substrates. It is evident that the cycles still need some optimization, however, it is also clear that EC-ALE can be used to grow Bi_2Te_3 with atomic layer control.

Works on optimizing the ECALE growth conditions for bismuth telluride are continuing. Different deposition conditions are tuning in order to further retard the growth of the films even further in order to improve the morphology and crystallinity of the films, and to control the composition more accurately.

Acknowledgements

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References

[1] J.Y. Yang, T. Aizawa, A. Yamamoto, T. Ohta, Mater. Chem. Phys. 70 (2001) 90.
[2] J.Y. Yang, T. Aizawa, A. Yamamoto, T. Ohta, Mater. Sci. Eng. B85 (2001) 34.
[3] J.Y. Yang, T. Aizawa, A. Yamamoto, T. Ohta, J. Alloys Compd. 312 (2000) 326.
[4] A. Boyer, E. Cisse’, Mater. Sci. Eng. B 113 (1992) 103.
[5] R. Venkatasubramanian, T. Colpitts, E. Watko, M. Lamvik, N. El-Masry, J. Crystal Growth 170 (1997) 817.
[6] A. Giani, A. Boulouz, F. Pascal-Delannoy, A. Foucaran, A. Boyer, Thin Solid Films 315 (1998) 99.
[7] A. Foucaran, A. Sackda, A. Giani, F. Pascal Delannoy, A. Boyer, Mater. Sci. Eng. B 52 (1998) 154.
[8] M. Stolzer, M. Stordeur, I. Stark, Proceedings of the 15th International Conference on Thermoelectrics, 1996.
[9] J. George, B. Pradeep, Solid State Commun. 56 (1) (1985) 117.
[10] H. Zou, D.M. Rowe, G. Min, J. Crystal Growth 222 (2001) 82.
[11] A. Heinrich, H. Griessmann, G. Behr, et al., Thin Solid Films 381 (2001) 287.
[12] Yuzuru Miyazaki, Tsuyoshi Kajitani, J. Crystal Growth 229 (2001) 542.
[13] M. Nedelcu, M. Sima, T. Visan, Tatiana Pascu, Izabela Franga, F. Craciunoiu, Proceedings of the 20th International Conference on Thermoelectrics, Beijing, China, 2001, p. 322.
[14] T.E. Lister, J.L. Stickney, Appl. Surf. Sci. 107 (1996) 153.
[15] B.H. Flowers Jr., T.L. Wade, J.W. Garvey, M. Lay, U. Happek, J.L. Stickney, J. Electroanal. Chem. 524 (2002) 273.
[16] K. Varazo, M.D. Lay, T.A. Sorenson, J.L. Stickney, J. Electroanal. Chem. 522 (2002) 104.
[17] L.B. Goetting, B.M. Huang, T.E. Lister, J.L. Stickney, Electrochim. Acta 40 (1995) 143.
[18] J.L. Stickney, in: D.M. Kolb, R. Alkire (Eds.), Advances in Electrochemical Science and Engineering, Wiley, Weinheim, 2002, p. 1.

[19] F. Forni, M. Innocenti, G. Pezzatini, M.L. Foresti, Electrochim. Acta 45 (2000) 3225.
[20] G. Pezzatini, S. Caporali, M. Innocenti, M.L. Foresti, J. Electroanal. Chem. 475 (1999) 164.
[21] T. Torimoto, A. Obayashi, S. Kuwabata, H. Yasuda, H. Mori, H. Yoneyama, Langmuir 16 (2000) 5820.
[22] B.W. Gregory, J.L. Stickney, J. Electroanal. Chem. 300 (1991) 543.
[23] M. Innocenti, G. Pezzatini, F. Forni, M.L. Foresti, J. Electrochem. Soc. 148 (2001) c357.
[24] A. Gichuhi, B.E. Boone, C. Shannon, Langmuir 15 (1999) 763.
[25] B.E. Boone, C. Shannon, J. Phys. Chem. 100 (1996) 9480.
[26] J.L. Stickney, T.L. Wade, B.H. Flowers Jr., R. Vaidyanathan, U. Happek, in: E. Gileadi, M. Urbakh (Eds.), Encyclopedia of Electrochemistry, Marcel Dekker, New York, 2002.
[27] R.R. Adzic, in: H. Gerishcher, C.W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, Wiley, New York, 1984, p. 159.
[28] E. Herrero, L.J. Buller, H.D. Abruna, Chem. Rev. 101 (2001) 1897.
[29] A.A. Gewirth, B.K. Niece, Chem. Rev. 97 (1997) 1129.
[30] D.M. Kolb, in: H. Gerischer, C.W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, Wiley, New York, 1978, p. 125.
[31] E.A. Streltsov, S.K. Poznyak, N.P. Osipovich, J. Electroanal. Chem. 518 (2002) 103.
[32] I. Villegas, J.L. Stickney, J. Electrochem. Soc. 139 (1992) 686.
[33] I. Villegas, J.L. Stickney, J. Vac. Sci. Technol. A 10 (1992) 3032.
[34] M. Innocenti, F. Forni, G. Pezzatini, R. Raiteri, F. Loglio, M.L. Foresti, J. Electroanal. Chem. 514 (2001) 75.
[35] T. Oznuluer, U. Demir, J. Electroanal. Chem. 529 (2002) 34.