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The underpotential deposition of bismuth and tellurium on cold rolled silver substrate by ECALE

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Abstract

Thin-layer electrochemical studies of the underpotential deposition (UPD) of Bi and Te on cold rolled silver substrate have been performed. Different approaches have been employed to investigate the influence of silver oxide film on Bi UPD. As a result, the precedent deposition of a little bismuth can effectively prevent silver from surface oxidation. The voltammetric analysis of underpotential shift demonstrates that the first Te UPD on Bi-covered Ag and Bi UPD on Te-covered Ag fit UPD dynamics mechanism. Thin film of bismuth telluride was formed using an automated flow deposition system, by alternately depositing Te and Bi. The electrochemical conditions necessary to form Bi_2Te_3 deposits of 50 cycles on cold rolled silver by ECALE are described here. X-ray diffraction indicated the deposits were Bi_2Te_3. EDX quantitative analysis gave the 2:3 stoichiometric ratio of Bi to Te, which is consistent with XRD result. Electron probe microanalysis of the deposits showed a worm-like network structure. The map of Te and Bi element indicated the distribution of both Te and Bi is homogeneous and locates the same sites, which is favorable to Te–Bi binary system. The composition analysis of structural expanded image also showed the approximately constant composition of Te:Bi $\approx$ 3:2 has taken place.

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

1. Introduction

Bismuth telluride belong to the class of VA–VIA binary chalcogenide compound semiconductor with a narrow optical energy band gap of 0.13 eV and a very high figure of merit [1–3]. These materials are widely used for thermoelectric and optoelectronic devices, for example in solid-state refrigeration, heat pumps, subminiature electronic devices, infrared sensors and high efficiency photovoltaic solar cells. Thin films of bismuth telluride and related compounds have already been elaborated by flash evaporation [4], co-evaporation [5], molecular beam epitaxy [6] and metal–organic chemical vapor deposition [7,8]. These methods are thermal and generally performed in vacuum. Atomic layer epitaxy (ALE) can form thin film by using surface limited reactions. Electrochemical atomic layer epitaxy (ECALE) [9–17] is the electrochemical analog of ALE. ECALE involves the alternated electrochemical deposition of elements to form a compound. Epitaxial deposition is achieved by using underpotential deposition (UPD) as the means to achieve surface chemistry-limited growth [18–22]. The phenomenon of UPD involves the deposition of an atomic layer of one element on a second, at a potential prior to (under) that needed to form deposits of the element on itself. The driving force is generally thermodynamic, involving the Gibbs energy of formation of a surface compound.

IIB–VIA compounds such as CdTe [9,10], CdS [11,12], and ZnSe [13] have been successfully formed by using ECALE, as well as IIIA–VA compound InAs [14], IIIA–VIA compound In_2Se_3 [15], IVA–VIA compound PbSe [16], VA–VIA compound Bi_2S_3 [17]. In our previous work, a first trial and preliminary result were reported on forming a Bi_2Te_3

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VA–VIA group compound film by ECALE [23–25]. As a follow-up in subsequent work, we report the electrodeposition of Bi_2Te_3 on cold rolled silver substrate at underpotential. The crystal structure of bismuth telluride is rhombohedral with the space group ($R3m$). Crystal structure of Bi_2Te_3 along the *XZ* plane shows the quintuple layer leaves of Te–Bi–Te–Bi–Te separated by a van der Waals gap. It is easy to cleave the crystals along the *c*-plane as the mechanical strength is weak. The weakness of the *c*-plane mechanical strength is a problem for fabrication of the thermoelements used in the micro-modules for optoelectronic telecommunications. This issue may be solved by forming a perfect in-plane alignment texture tape. It has been found that the perfect in-plane alignment texture tape was suitable to improve the mechanical properties and to reach high values of figure of merit [26]. Experiments have shown that the textured tape could originate from the epitaxial growth on texturing substrates [27]. It is also known that cold rolled silver can obtain a high level of biaxial texture [28]; it is thus a promising substrate for the second generation of optoelectronic telecommunication thermoelectric devices. In contrast to cold rolled silver, hot rolled silver is not a good choice. Hot rolling can occur the dynamic recrystallization during deformation whether the hot rolled temperature is high or low and cannot obtain some amount of texture component. In this letter, a biaxial alignment is achieved by deposition of the Bi_2Te_3 thin film directly on cold rolled silver by using ECALE and the effects of varying surface structure of silver substrates and electrochemical factors on the underpotential deposition processes is analyzed.

Since silver substrate oxidizes readily under lower pH condition, so we were interested in the range of pH over which it is possible to dissolve bismuth and tellurium, meanwhile not to disrupt the structure of the silver surface through the formation of a silver oxide layer. Tellurium is soluble as $HTeO_2{}^+$ in a narrow range at low pH ($-0.37 < pH < 1.93$) for a Te concentration of 0.1 mM according to the thermodynamic Eqs. (1) and (2) [29,30]:

$$Te^{4+} + 2H_2O \Leftrightarrow HTeO_2{}^+ + 3H^+$$

$$pH = -0.37 + 0.333 \log \frac{[HTeO_2{}^+]}{[Te^{4+}]} \qquad (1)$$

$$HTeO_2{}^+ \Leftrightarrow TeO_2 + H^+$$

$$pH = -2.07 - \log[HTeO_2{}^+] \qquad (2)$$

and also at high pH as $TeO_3{}^{2-}$ ($pH > 8.36$, Eq. (3) [29,30]):

$$TeO_2 + H_2O \Leftrightarrow TeO_3{}^{2-} + 2H^+$$

$$pH = 10.355 + 0.5 \log[TeO_3{}^{2-}] \qquad (3)$$

In the pH range of 1.93 to 8.36, tellurium precipitates as TeO_2. In order to dissolve tellurium, we used concentrated perchloride acid to dissolve 0.1 mM TeO_2, and then the solution was pH adjusted with ammonia to form a pH 8.5 solution of $HTeO_3{}^-$.

Bismuth is soluble as Bi^{3+}, but only for $pH < 2$ according to the thermodynamic Eq. (4) [29]:

$$Bi^{3+} + H_2O \Leftrightarrow BiOH^{2+} + 4H^+$$

$$pH = 2 + \log \frac{[BiOH^{2+}]}{[Bi^{3+}]} \qquad (4)$$

At higher pH ($pH > 4.98$) for a Bi concentration of 0.1 mM, bismuth precipitates as Bi_2O_3 (Eq. (5)):

$$2BiOH^{2+} + H_2O \Leftrightarrow Bi_2O_3 + 4H^+$$

$$pH = 2.98 - 0.5 \log[BiOH^{2+}] \qquad (5)$$

In the pH range of 2–4.98, bismuth is soluble as $BiOH^{2+}$. Therefore, in order to dissolve bismuth, it is necessary to work at a pH below 2.

2. Experimental

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 using 0.1 M $HClO_4$ as a supporting electrolyte, pH 1.5. Tellurium solutions were all 0.1 mM in TeO_2, and also used 0.1 M $HClO_4$ as a supporting electrolyte. The pH 8.5 Te solution was pH 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. The working electrodes were cold rolled silver (99.99%) substrates. The substrates were mirror-like polished mechanically and then annealed in a muffle furnace under vacuum for 30 min at 650 °C. Before depositions, the electrode was polished chemically for 5 s in a silver etch solution, which consisted of a mixture of 0.1 M CrO_3 + 0.1 M HCl. After polishing, the electrode was soaked first in concentrated ammonia for about 5 min, and then in concentrated sulfuric acid for about 20 min. Finally, it was rinsed thoroughly with water.

An automated deposition apparatus consisting of peristaltic pumps, valves, programmable logistic computer (PLC), electrochemical flow cell and potentiostat was used under the control of a computer. The electrolytic cavity was delimited by the working electrode and the 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 reference electrode, saturated calomel electrode (SCE), was positioned at the cavity outlet. Both the subminiature valve bank and the cell were developed by our group and were described in our previous work [23,24].

The deposit is annealed in Ar to convert precursor layers of the elements into the compounds in 200 °C. Deposit stoichiometric ratio was measured using Oxford Inca energy dispersive X-ray spectrophotometer (EDX). The XRD pattern was obtained with a Philips-PW 1710 X-ray diffractometer