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Additive-aided electrochemical deposition of bismuth telluride in a basic electrolyte

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Abstract: A new basic electrolyte with two cationic plating additives, polydiaminourea and polyaminosulfone, was investigated for the electrochemical deposition of the bismuth telluride film on a nickel-plated copper foil. Tellurium starts to deposit at a higher potential (−0.35 V) than bismuth (−0.5 V) in this electrolyte. The tellurium-to-bismuth ratio increases while the deposition potential declines from −1 to −1.25 V, indicating a kinetically quicker bismuth deposition at higher potentials. The as-deposited film features good adhesion to the substrate and smooth morphology, and has a nearly amorphous crystal structure disclosed by X-ray diffraction patterns.

Keywords: thin films; thermoelectric materials; electrochemical deposition; bismuth telluride; basic electrolyte

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1. Introduction

Thermoelectricity can be used for the direct conversion between heat and electricity *via* semiconductors. Bi_2Te_3-based thermoelectric materials are the best thermoelectric semiconductors near room temperature. Compared with various processes to obtain Bi_2Te_3-based thermoelectric materials, such as the conventional Bridgman method, molecular beam epitaxy (MBE) [1], pulsed laser deposition (PLD) [2], hydrothermal method [3], electro-chemical atomic layer epitaxy (ECALE) [4], magnetron sputtering [5], and powder metallurgy [6], electro-chemical-deposition (ECD) [7] features cost-effective, high-throughput, and nanostructure feasibility [8].

ECD has been successful in depositing films of Bi-Te binaries [9-14] and Bi-Se-Te or Bi-Sb-Te ternaries [15-19] in acidic electrolyte. However, the lack of thermoelectric performance tests is common in earlier literatures on ECD [8], partially due to the poor film morphology. Moreover, an ideal morphological property forms an indispensable prerequisite for practical thermoelectric application. Pulsed electro deposition [20-21] has already been studied to improve the film morphology, as to reduce surface roughness and eliminate porous structure. ECD in basic electrolyte is another option, though rarely reported [22-23]. The co-deposition of bismuth and tellurium is feasible in basic electrolyte as implied in a previous study [7]. Basic electrolyte avoids the corrosivity of the acidic solution residue, and brings a delicate crystallite structure as well. Considering that additives are widely used in the plating industry to obtain desired coating quality, here a different basic electrolyte was first reported, in which two cationic polymers, polydiaminourea (PUB, CAS: 68555-36-2) and polyaminosulfone (PAS), were added to grow a bismuth telluride film. The influence of additives on the crystal structure was also a major interest in this work, as crystal structure had an intimate relation with the film thermoelectric performance as disclosed in recent researches [24].

2. Experimental

The experiments were conducted in a three-electrode cell with 600-mL capacity. A graphite rod served as the auxil-

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iary electrode, which was separated with the electrolyte by saturated potassium chloride bridge. The working electrode is a special-shaped piece of copper foil of ~50 μm in thickness, stuck to the glass chip with wax. It was degreased *via* electrolyzing in the 0.1 M NaOH solution, then potentiostatically plated with nickel in a Watt bath for 5 min at 303 K, −1.1 V *vs.* saturated calomel electrode (SCE), to block reactions between copper and tellurium [22]. It was then activated for 5 min in 1 M HNO_3 before deposition. An SCE served as the reference electrode. All the electrodes were mounted on a custom acrylic rack. The electrolyte temperature was kept at 303 K by heating and was stirred with a magnetic stirrer.

The electrolyte composition is shown in Table 1. PUB and PAS were supplied by Wuhan Fengfan Chemical Co. Ltd.

Table 1. Electrolyte composition **($g·L^{-1}$, $mol·L^{-1}$)**

TeO_2	$Bi(NO_3)_3·5H_2O$	Triethanolamide (TEA)	NaOH	PUB (60wt% Diaminourea polymer)	PAS (50wt% polyaminosulfone)
1.920, 0.012	0.970, 0.002	2.390, 0.016	2.500, 0.0625	0.800	0.800

The cyclic voltammograph (CV) of relative solutions was drawn *via* a potentiostat (DJS-292, Shanghai), at a constant scanning rate of 32 mV/s and an electrolyte temperature of 303 K. The cathode was masked with the self-adhesive tape to leave a deposition area of 2.6 cm×(1-1.5) cm. The film was deposited under potentiostatic control at 303 K for 15 min, then rinsed in turn with water and ethanol, and dried in hot air.

The film composition was determined by energy dispersive X-ray spectroscopy (Horiba 7593-H mounted on a field emission microscope (FEM) of Hitachi S4800), calibrated with polished pure Bi_2Te_3. The M-lines of bismuth and L-lines of tellurium were chosen for quantification. The as-deposited film was analyzed and averaged at three points. The crystal structure was characterized by X-ray diffraction (Rigaku-D/MAX-2550PC, λ=0.154056 nm).

3. Results and discussion

3.1. cyclic voltammograph and the film composition

The electrochemical reactions during the film deposition on the cathode are expressed as below:

$$TeO_3^{2-}+3H_2O+4e^-\rightarrow Te+6OH^- \quad (1)$$

$$Bi^{3+}+3e^-\rightarrow Bi \quad (2)$$

In Fig. 1(a), bismuth starts to deposit at −0.5 V. This potential remains unchanged after PUB and PAS are added as shown in Fig. 1(b). In Fig. 1(c), tellurium starts to deposit at −0.3 V. This potential has little change when PUB and PAS are added as shown in Fig. 1(d). The peak around −0.35 V indicates the deposition of tellurium aided by PUB and PAS.

The alloy deposition starts from −0.3 V as shown in Fig. 2. It's slightly higher than that of TeO_3^{2-}, and the co-deposition occurs under −1.0 V as shown in Fig. 2. The x value in Bi_2Te_x rises gradually to more than 3 at −1.15 V as shown in Fig. 3. Thus, bismuth is kinetically quicker than tellurium to deposit in this basic electrolyte. The negative charge of TeO_3^{2-} slows down its adhesion on the cathode surface. Besides, a possible reduction of Bi^{3+} by atomic Te^0 increases the bismuth content:

$$4Bi^{3+}+3Te^0+18OH^-\rightarrow 3TeO_3^{2-}+4Bi+9H_2O \quad (3)$$

One proof of this mechanism is that, at −1.1 V when 0.002 M Bi^{3+} was added to the solution the same as in Fig. 1(d), the cathodic current rose from 7.6 to 11.4 mA, *i.e.* a 50% increase, and resulted in a Bi to Te stoichiometry of 2:2.55. If there was no reduction of extra Bi^{3+} by Te^0, the stoichiometry should be 2:3 exactly.

3.2. Morphology and crystal structure

The bismuth telluride film deposited in this work displays smooth appearance, good adhesion to the substrate, and flexible mechanical property, as shown in Fig. 4. In Fig. 5, the normally strongest peak of lattice plane [015] is weak in Bi_2Te_x films where x ranges from 0.59 to 3.45. TeO_3^{2-} ions can have ionic bonding with PUB and PAS molecules due to their reversed charges. This bonding together with the strong adhesion of PUB and PAS to the cathode increases the TeO_3^{2-} concentration near the cathode surface, and enables tellurium atoms to enter the film in a quick and different way during the deposition. Therefore, it is reasonable to attribute the crystal structure evolution to the active interference of additives during the crystal growth. The near room temperature electrolyte also helps to preserve such a thermodynamically-unstable structure. The relation between this near-amorphous structure and film thermoelectric performance needs to be disclosed in further research.

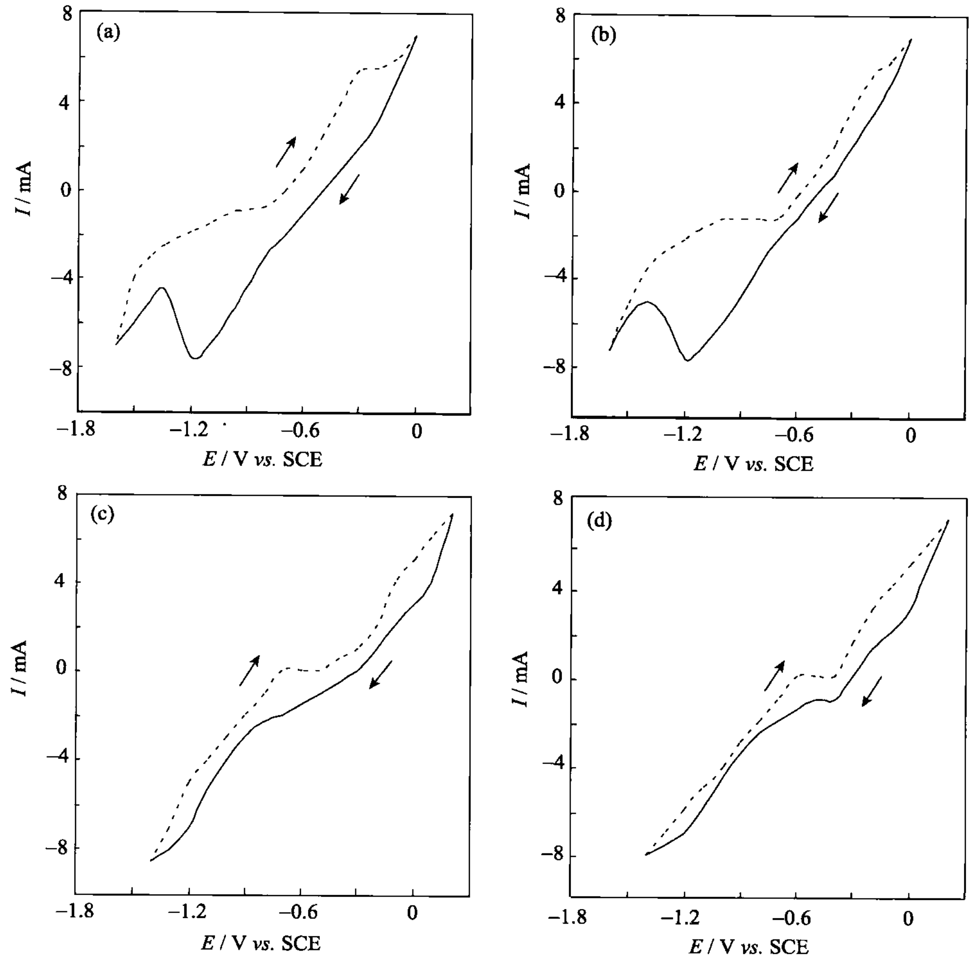

Fig. 1. **Cyclic voltammographs of solutions containing 0.002 M Bi^{3+} (a, b) and 0.012 M [TeO_3^{2-}] (c, d) ([NaOH]=0.0625 M and [TEA]=0.016 M for (a)-(d); PUB (0.800 g·L^{-1}) and PAS (0.800 g·L^{-1}) are added in (b) and (d); scan rate: 32 mV/s; solution temperature: 303 K; cathodic scan: the solid line; anodic scan: dotted line; scanning range: 0 to −1.6 V for (a) and (b), 0.2 to −1.4 V for (c) and (d)).**

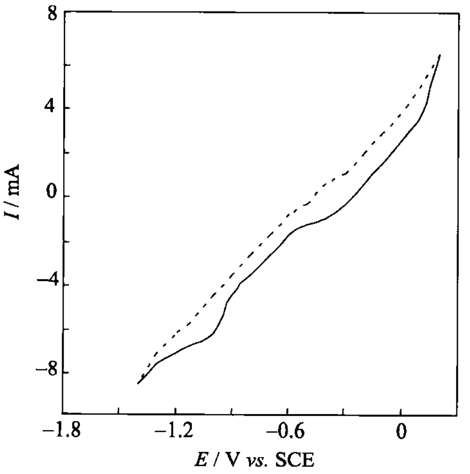

Fig. 2. **Cyclic voltammograph of the binary deposition solution with the composition listed in Table 1 (scan rate: 32 mV/s; solution temperature: 303 K; cathodic scan: solid line; anodic scan: dotted line; scanning range: 0.2 to −1.4 V).**

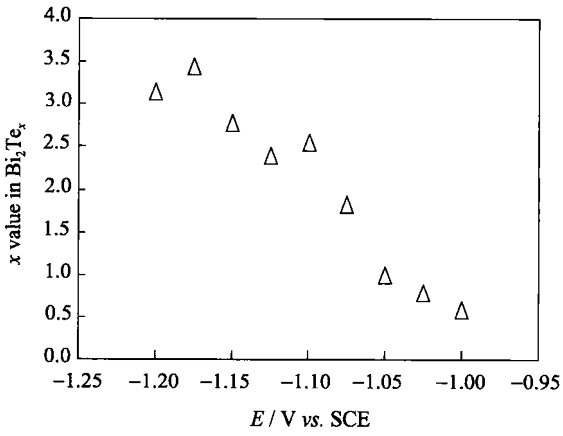

Fig. 3. **Potential dependence of the Bi_2Te_x film stoichiometry, [Bi^{3+}] = 0.002 M and [TeO_3^{2-}] =0.012 M (all the films are deposited potentiostatically for 15 min at 303 K; the film thickness is more than 3 μm according to Faraday's Law assumed a 100% current efficiency).**

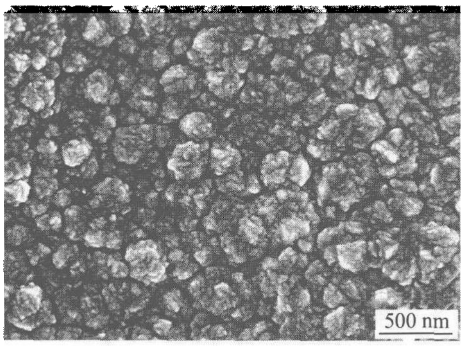

Fig. 4. SEM image of the as-deposited $Bi_2Te_{3.45}$ film.

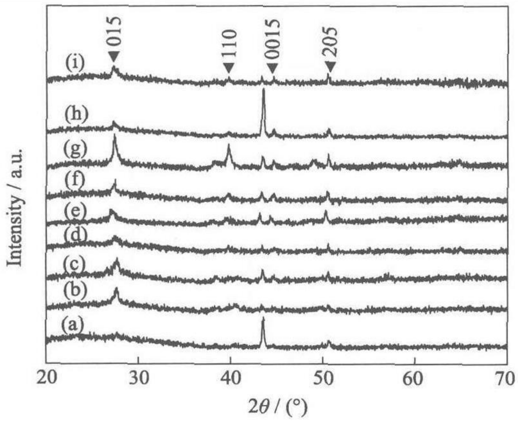

Fig. 5. XRD patterns of the as-deposited Bi_2Te_x film: (a) x=3.14; (b) x=3.45 ; (c) x=2.78; (d) x=2.39; (e) x=2.55; (f) x=1.82; (g) x=0.99; (h) x=0.79; (i) x=0.59 (the lattice plane marked comes from Bi_2Te_3 (PDF: 150863); the intensity of Cu [111] reflection around 43.5° varies between the samples due to the different film thicknesses).

4. Conclusion

With the help of polydiaminourea and polyaminosulfone, the bismuth telluride film can be readily deposited in a basic electrolyte. The additives studied in this work help to realize the continuous film growth, ideal film quality, and a near-amorphous crystal structure. Other Bi_2Te_3-based or Sb_2Te_3-based ternary films, such as Bi/Se/Te, Bi/Sb/Te ternary alloy films can be deposited in a similar electrolyte. The additive-related crystal structure can be a favorable option to improve the material thermoelectric performance.

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