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Electrodeposition of Thin Lead–Tellurium Alloy Films from Fluoroborate Electrolyte

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Abstract—Electrodeposition of lead–tellurium alloys from a fluoroborate electrolyte was studied. Cyclic voltammetry was applied to determine the range of potentials of joint electrodeposition of Pb and Te to form PbTe on the cathode.

Lead telluride, and also solid solutions on its base in the form of thin films are widely used in various fields of semiconductor industry to fabricate thermoelectric transducers, thermoelements, and IR detectors [1].

Thin films of metal chalcogenides, including PbTe, are commonly obtained by vacuum evaporation [2]. This technique is labor-consuming, requires intricate equipment, and involves use of high temperature. Moreover, PbTe dissociates in evaporation into the components, which commonly leads to its fractional distillation and to deposition of compositionally inhomogeneous films. Therefore, the electrochemical technique has been frequently used recently for obtaining thin chalcogenide films [3, 4]. This method is distinguished by simplicity, low material expenditure, and possibility of easily controlling the composition and thickness of the layers obtained.

The first electrochemical syntheses of lead telluride were carried out in [5–7]. The syntheses were based on cathodic dissolution of tellurium and anodic dissolution of the metal whose telluride is being obtained. In the process, interaction between Te^{2-} and Pb^{2+} present in the electrolyte results in the formation of PbTe powder on the electrolyzer bottom.

In [8], thin layers of lead–tellurium alloy were obtained by cathodic deposition from a simple nitrate electrolyte containing $Pb(NO_3)_2$ and TeO_2. However, it is known [9] that high-quality cathodic deposits cannot be always obtained from simple electrolytes, especially in those cases when the standard potentials of the metals being codeposited are strongly different.

The standard potential of the $Te/[TeOOH]^+$ couple in acid media is $+0.551$ V, and that of the Pb/Pb^{2+} couple is -0.126 V. The difference of the standard potentials is 0.677 V.

To make closer the potentials of tellurium and lead deposition, such complex electrolytes were used in which tellurium forms more stable complex ions than lead. In this study, as such an electrolyte we used a fluoroborate lead-plating solution of the composition ($g\ l^{-1}$): $Pb(BF_4)_2$ 180, HBF_4 40, H_3BO_3 12.6 and joiner's glue 1.0 (electrolyte no. 1) [10]. In electrolyte no. 1, lead deposition occurs without any noticeable hindrance, whereas in fluorine-containing media, tellurium is present as a complex anion $[Te(OH)_2F_4]^{2-}$ [11], with $Te(OH)_2^{2+}$ ions formed in its dissociation directly involved in the cathodic discharge. According to [11], the discharge of $Te(OH)_2^{2+}$ ions occurs in stages, with each stage of formation of intermediates characterized by a certain equilibrium potential, which becomes more negative in reduction processes. This may also make closer the deposition potentials of tellurium and lead.

EXPERIMENTAL

The electrolysis was performed and polarization curves were measured in a poly(methyl methacrylate) cell. Platinum electrodes coated with tellurium, lead, and tellurium–lead alloy (up to 5 μm) served as cathodes, and platinum plate, as anode. The polarization curves were measured in the potentiodynamic mode at a potential sweep rate of 8 mV s^{-1} with a P-5827M potentiostat and a PDP4-003 self-recorder. As reference served saturated silver chloride electrode. The potentials measured were recalculated to the hydrogen scale. TeO_2 to be added to the lead-plating electrolyte was preliminarily dissolved in HF, since TeO_2 is in-

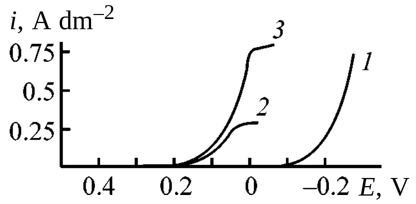

Fig. 1. Cathodic potentiodynamic polarization curves for deposition of (*1*) lead, (*2*) tellurium, and (*3*) lead–tellurium system, obtained in fluoroborate electrolytes of varied composition. (*i*) Current density and (*E*) potential; the same for Figs. 2 and 3. (*1*–*3*) Electrolyte nos. 1–3, respectively.

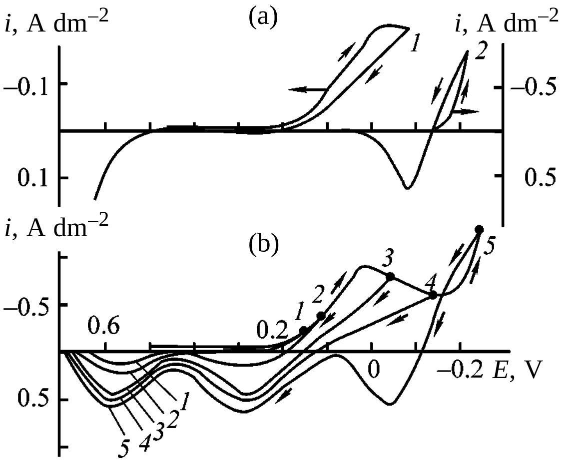

Fig. 2. Cyclic voltammograms of deposition and dissolution of (a) (*1*) tellurium and (*2*) lead and (b) (*1*–*5*) lead–tellurium system, obtained on a platinum electrode. Points *1*–*5* in the curves correspond to end potentials.

soluble in HBF_4. X-ray studies were carried out on a DRON diffractometer (CuK_α radiation). The content of tellurium in an alloy was determined gravimetrically [12], and that of lead, from the difference of masses of the cathodic deposit and tellurium. The cathodic deposits were also analyzed using a Cameca MS-46 X-ray fluorescence analyzer. The outward appearance of the deposits was assessed visually; the type of conduction was determined using a hot probe.

Figure 1 presents the cathodic potentiodynamic curves obtained in fluoroborate electrolytes of various compositions (g l^{-1}): electrolyte no. 2: HBF_4 40, H_3BO_3 12.6, joiner's glue 1.0, and TeO_2 1.0; electrolyte no. 3: $Pb(BF_4)_2$ 180, HBF_4 40, H_3BO_3 12.6, joiner's glue 1.0, and TeO_2 1.0. The stationary potential of Te in electrolyte no. 2 is 0.5 V; deposition of Te is accompanied by high polarization, the deposition overvoltage is 0.34 V at $i = 0.05$ A dm^{-2} (Fig. 1, curve *2*). The stationary potential of lead in electrolyte no. 1 is -0.12 V, and the deposition overvoltage at $i = 0.05$ A dm^{-2}, 0.04 V (Fig. 1, curve *1*).

The codeposition of tellurium and lead from electrolyte no. 3 (Fig. 1, curve *3*) occurs at more positive potentials than separate deposition of these metals, i.e., both the components are deposited into the alloy via depolarization. Such an arrangement of polarization curves is observed in those cases when codeposition of components is accompanied by formation of a compound or a solid solution at the cathode [9]. Thus, it may be assumed that codeposition of tellurium and lead at the cathode can be accompanied by formation of PbTe.

To confirm this assumption and determine the potentials at which tellurium and lead are codeposited, cyclic voltammograms were measured on platinum electrode. In this case, it could be expected that current peaks associated with oxidation of products formed during the cathodic half-cycle may appear in the curves of the anodic half-cycle.

As seen from Fig. 2a, deposition of tellurium on the platinum electrode onsets at a potential of 0.18 V (curve *1*), and that of lead, at -0.13 V (curve *2*). The anodic half-cycle of the voltammograms obtained for the individual components shows a single peak of anode current. The current peak is observed at 0.6 V for tellurium and at about -0.1 V for lead. The codeposition curve shows three peaks of anode current (Fig. 2b). The current peaks at 0.6 and -0.1 V are due to oxidation of, respectively, tellurium and lead. The current peak observed at a potential of about 0.3 V may be due to dissolution of PbTe by the reaction

$$PbTe \rightarrow Pb^{2+} + Te + 2e. \qquad (1)$$

The anodic half-cycle measured starting with a cathode potential of 0.15 V (Fig. 2b, curve *1*) shows only an anode current peak associated with oxidation of tellurium. Consequently, no codeposition of tellurium and lead occurs at the cathode up to a potential of 0.15 V, and elementary tellurium is the only cathodic product. Codeposition of tellurium and lead onsets at about 0.12 V, which is confirmed by the appearance in the anodic half-cycle (curve *2*) of a second anode current peak associated with PbTe dissolution. This is also confirmed by analysis of deposits obtained under potentiostatic conditions (see table).

The current in the PbTe dissolution peak mainly depends on the end potential, and increases when this potential is shifted to more negative values (curves *3*–*5*). In the anodic half-cycle curve measured on reaching the potential of lead deposition, a third current peak appears, associated with oxidation of lead as a separate phase (curve *5*). Deposits obtained at potentials more negative than –0.15 V are composed of PbTe and Pb.

It is interesting that, as soon as the platinum electrode is coated with tellurium and a certain potential is reached (0.12 V in the given case), codeposition of lead and tellurium occurs. Tellurium "stimulates" deposition of lead at more positive potentials; the depolarization for lead is –0.25 V.

A similar phenomenon was also observed in codeposition of bismuth and tellurium from a chloride–fluoride electrolyte [13]. This phenomenon is due to the tendency of tellurium to form Te^{2-}. It should be noted that, in contrast to ions of other metals, quadruply charged tellurium tends to undergo six-electron reduction [14] by the reaction

$$Te^{4+} + 6e = Te^{2-}. \quad (2)$$

According to [14], this reaction is possible even at current densities lower than the limiting diffusion current density, with the occurrence of reaction (2) being the more probable, the lower the concentration of quadruply charged ions in solution. In solutions with higher tellurium concentrations, the main energetically favorable cathodic process is the four-electron reduction of Te^{4+} to Te. At low tellurium concentrations in the electrolyte, the region of limiting diffusion current is reached fast. In this case, the four-electron process is hindered through depletion of the near-cathode layer of Te^{4+} ions, and conditions favorable for six-electron reduction are created. Under these conditions, tellurium deposited at the cathode may undergo cathodic dissolution by the reaction

$$Te + 2e = Te^{2-}. \quad (3)$$

Pb^{2+} ions adsorbed on the electrode surface or present in the near-cathode layer may readily interact with the negatively charged surface, and the mechanism of PbTe formation can be described by the scheme

$$Te(OH)_2^{2+} + 4e = Te + 2OH^-, \quad (4)$$

$$Te + 2e + Pb^{2+} = PbTe. \quad (5)$$

To obtain additional data on the influence exerted by tellurium on the codeposition of Te and Pb, voltammetric curves were measured on a tellurium-coated platinum electrode in electrolyte no. 1. The curves were obtained in the potential range from 0.4 to –0.2 V, which ruled out anodic dissolution of tellurium deposited onto platinum. As seen from Fig. 3, deposition of lead on Te(Pt) electrode occurs at more positive potentials than that on Te and Pt electrodes. A noticeable current is seen in the polarization curve at a potential of about 0.1 V (Fig. 3, curve *1*), in good agreement with the onset potential of codeposition of Te and Pb (Fig. 2b). This is indicated by an anode current peak at 0.3 V, corresponding to anodic dissolution of PbTe obtained in codeposition of Te and Pb. When the end potential is shifted to negative potentials, a limiting current region is observed, extending as far as the onset potential of lead deposition (curve *4*). In repeated cycles, the limiting current decreases (curves *2, 3*). The appearance of the limiting current may be due to either slow motion of charge carriers, i.e., the semiconducting properties of PbTe, or slow motion of tellurium or of lead ions across the PbTe film. At more negative potentials, lead is deposited as a separate phase. This is indicated by the appearance of an anode current peak at a potential of –0.12 V.

Composition and conduction type of films obtained in potentiostatic deposition from electrolyte no. 3. Electrolysis duration 60 min

Deposition potential, V	Phase composition* (Te content, wt %)	Type of conduction
0.1	PbTe, Te (55.6)	*p*
0.05	PbTe, Te (46.3)	*p*
0.00	PbTe, Te (40.2)	*p*
–0.5	PbTe, traces of Te (39.1)	*p*
–0.1	PbTe, traces of Te (38.9)	*p*
–0.15	PbTe, Pb, PbO_2, PbO (36.9)	*n*
–0.2	PbTe, Pb, PbO_2, PbO (30.2)	*n*

* Content of the components, found by chemical analysis.

Thus, in codeposition of tellurium and lead, the primary part in alloying is played by the tendency

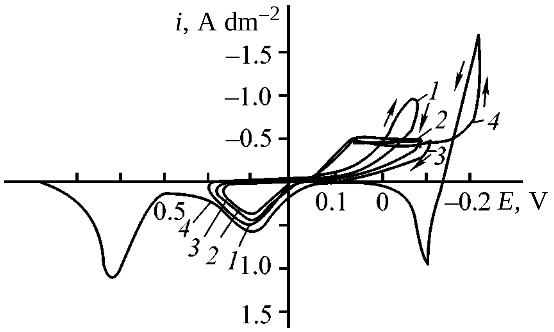

Fig. 3. Cyclic voltammograms obtained successively on a tellurium-coated platinum electrode in electrolyte no. 1. Potential sweep rate 40 mV s^{-1}.

of tellurium to undergo cathodic dissolution to form Te^{2-} ions. In this case, the depolarization in Te deposition into the alloy is associated with alloying (thermodynamic factor), and that in deposition of lead into the alloy, with the low overvoltage of lead deposition on tellurium (kinetic factor).

According to the results of X-ray phase analysis, films containing excess amount of tellurium and obtained at potentials more positive than -0.1 V are composed of two phases, PbTe and Te. The data obtained with a microprobe analyzer demonstrate that Te is mainly present in lower layers of the films (*p*-type conduction). The X-ray patterns of lead-rich films obtained at potentials more negative than -0.15 V contain, in addition to lines related to PbTe and Pb, also those associated with PbO and PbO_2 [15], with lead mainly present in upper layers of the films (*n*-type conduction). Films with composition very close to the compound PbTe are formed at potentials in the range $0.0-0.1$ V.

CONCLUSIONS

(1) In electrodeposition of the Pb–Te alloy from a fluoroborate electrolyte, both the components are deposited into the alloy with depolarization due to a thermodynamic factor in deposition of tellurium and to a kinetic factor in that of lead. The range of potentials at which Te and Pb are codeposited was determined.

(2) Tellurium-rich films have *p*-type conduction, and lead-rich films, *n*-type conduction.

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