Chalcogenide Letters Vol. 9, No. 10, October 2012, p. 403 - 411

CHARACTERIZATION AND CORROSION BEHAVIOR OF BiTeSe THIN FILMS GROWN BY ELECTRODEPOSITION FROM CHOLINE CHLORIDE – OXALIC ACID IONIC LIQUID

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The paper presents preliminary results regarding the morphology, chemical composition and corrosion behavior of BiTeSe films prepared from a new ionic liquid bath containing choline chloride and oxalic acid. SEM images of BiTeSe films grown on copper substrate at 60 ^{0}C at two different cathodic overpotentials have shown different morphologies. EDX results indicated different chemical compositions; it was found for Bi and Te similar content in the film as in the bath, whereas Se content varied to a significant extent with the applied overpotential. In the corrosion tests, potentiodynamic polarization (Tafel plot) allowed to estimate the corrosion parameters. Electrochemical impedance spectroscopy was also applied and evidenced a gradual diminishing of polarization resistance by increasing anodic polarization.

(Received September 27, 2012; Accepted October 10, 2012)

Keywords: Ionic liquid; Semiconductor electrodeposition; Bismuth telluroselenide; Choline chloride – oxalic acid eutectic

1. Introduction

Studies about the characterization and chemical stability of semiconductor compounds of bismuth with tellurium (bismuth telluride), with selenium (bismuth selenide) and with both tellurium and selenium (bismuth telluroselenide or selenotelluride) have relevance for a wide range of applications, especially for thermoelectricity, solar cells, photoelectrochemical devices, micromechanical systems, optical filters, optical recording materials, superionic materials and sensor and laser materials. It is well known that BiTeSe with $Bi_2Te_{3-y}Se_y$ (y=0.3) composition is the best n-type semiconductor material for the use in thermoelectric devices at room temperature [1]. In the manufacturing of a high-quality thermoelectric device, several procedures of film formation were employed, including molecular beam epitaxy, chemical vapor deposition, sputtering etc. Electrodeposition is an attractive route for obtaining thin BiTeSe films because it offers several advantages and primarily low cost [2-11].

Recently, we have reported electrodeposition of some tellurium containing semiconductors from ionic liquids based on choline chloride (2-hydroxy-ethyl-trimethyl ammonium chloride, **ChCl)**; eutectic mixtures of ChCl with urea [12,13], malonic acid [14] and ethylene glycol [15] were used as supporting electrolyte in the bath. Our studies confirmed that these ionic liquids have low toxicity and are readily biodegradable; furthermore, they are easy to prepare and cheap and therefore they hold promises for electrodeposition applications on a larger scale. This paper is a preliminary report about the characterization and corrosion behavior of BiTeSe thin films prepared from an eutectic mixture of ChCl with oxalic acid (**OxA**). In order to study the above, we have synthesized BiTeSe films by electrochemical deposition on copper

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substrate in different operating conditions. This study is justified because the new generation of coolers and thermoelectrical power generators as micro-modules [1] has high packing density of film legs whose performances depend to a great extent on the contact resistances with metal pads. These devices can work frequently in aggressive media, especially as converters for energy harvesting in coolers and heat recovery from automobile exhausts and may be corroded if they are polarized during their work.

2. Experimental details

BiTeSe film samples were prepared at 60 ^{0}C under potentiostatic control on copper sheets from ionic liquid consisting in an eutectic of choline chloride and oxalic acid as supporting electrolyte. The bath containing ionic liquid was prepared as a mixture (ChCl-OxA 1:1 mole ratio) of choline chloride (99%) with oxalic acid dihydrate, both reagents being purchased from Aldrich. The binary mixture was heated at above 90 ^{0}C for 30 min until homogeneous colourless ionic liquid is formed. $BiCl_3$ (Aldrich), TeO_2 (Alfa Aesar) and SeO_2 (Alfa Aesar) were used as precursors for dissolved ionic species of bismuth, tellurium and selenium. The molarities were calculated using a density value of 1.2122 gcm^{-3} determined in our laboratory at working temperature (60 ^{0}C). Details about electrodeposition were described elsewhere [16].

Table 1 presents the operating conditions for obtaining BiTeSe films. Because the current density varied during deposition of BiTeSe films, we have included in Table 1 the electrical charge consumed, from which (using Faraday law) a thickness about 1-2 μm may be estimated.

Table 1. Working conditions during preparation of BiTeSe films deposited onto copper sheets using ChCl-OxA (1:1) based ionic liquid. Temperature: 60 ^{0}C.

Bath	Sample	Stationary potential, V *vs.* Ag ref.	Controlled potential, V *vs.* Ag ref.	Electrolysis time, min	Electrical charge consumption, mCcm^{-2}
ChCl-Ox.A (1:1) +10 mM Bi^{3+} + 5 mM Te^{4+} + 5 mM Se^{4+}	BiTeSe-I	-0.260	-0.35	120	1.5
	BiTeSe-II	-0.260	-0.42	60	1.3

For morphological and compositional characterization of deposited films, a scanning electron microscope QUANTA INSPECT F, equipped with field emission gun (1.2 nm resolution) and with an energy dispersive spectroscope (EDX, MnK resolution at 133 eV), was employed.

A special designed three-electrode set-up was constructed for the corrosion study. The working electrode was placed horizontally at the bottom of the cell and sealed with an O-ring rubber leaving a constant area of 0.636 cm^2 exposed to corrosion attack. Opposite to the working electrode, a platinum coiled wire (with large area) was used as auxiliary electrode and the reference electrode was a conventional Ag/AgCl electrode (Metrohm) filled with 3M KCl electrolyte. The aggressive medium consisted in a 0.5 M NaCl aqueous solution. A SP150 BioLogic Sci. Instr. potentiostat provided with a frequency response analyzer was used for electrochemical tests of corrosion at room temperature. Current-potential polarization curves in potentiodynamic conditions (3 mVs^{-1} scan rate) were carried out starting from 150 mV more negative than stabilized open-circuit potential and scanning up to +1.5 V anodic limit. Electrochemical impedance spectroscopy (EIS) measurements were performed using the same equipment. EIS spectra were collected in the frequency range of 100 kHz to 50 mHz with various values of anodic polarization superposed to a.c. signal of 10 mV.

3. Results and discussion

3.1. Morphological and compositional characterization

In order to get information about the behaviour and stability of BiTeSe thin films deposited on copper substrate, measurements of their morphological properties and chemical composition were carried out. We presents here the results of SEM microscopy and EDX chemical analysis for evaluation of two as-deposited BiTeSe films (Table 1) obtained with potentiostatic control from choline chloride - oxalic acid mixture as ionic liquid electrolyte.

Micrograph images of BiTeSe films are presented comparatively in Figures 1 and 2. The micrographs show the effect of change in the cathodic polarization for film deposition, *i.e.* modifications in film morphology although the electrical charge consumption has almost the same values.

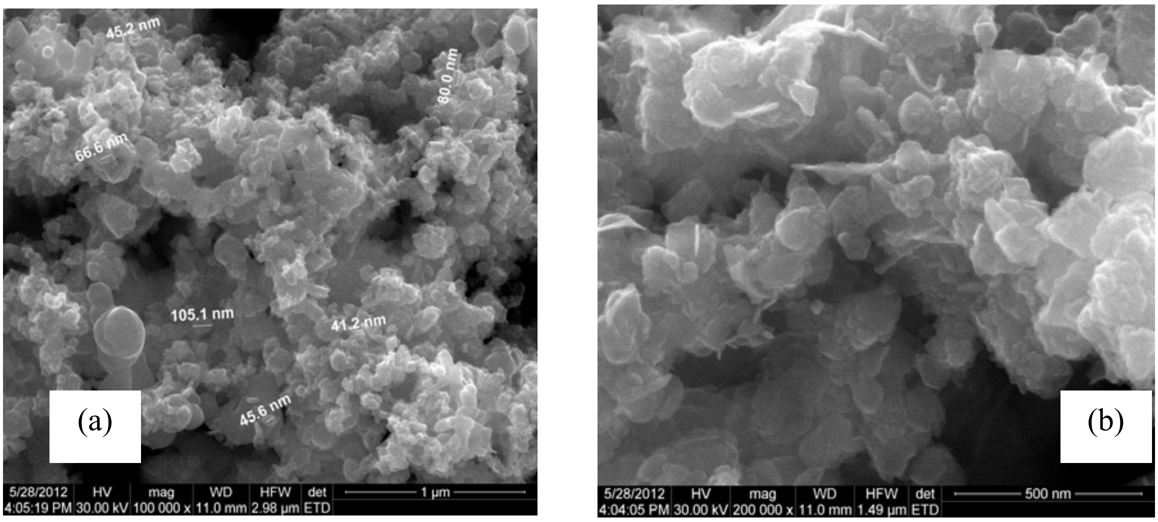

Fig. 1. SEM images for deposition of BiTeSe compound after 120 min electrolysis at 60 ^{0}C and -0.35 V potential polarization on Cu substrate in ChCl-OxA mixture containing: cBi = 10 mM, cTe = 5 mM, cSe = 5 mM. Magnification: (a) ×100000; (b) ×200000

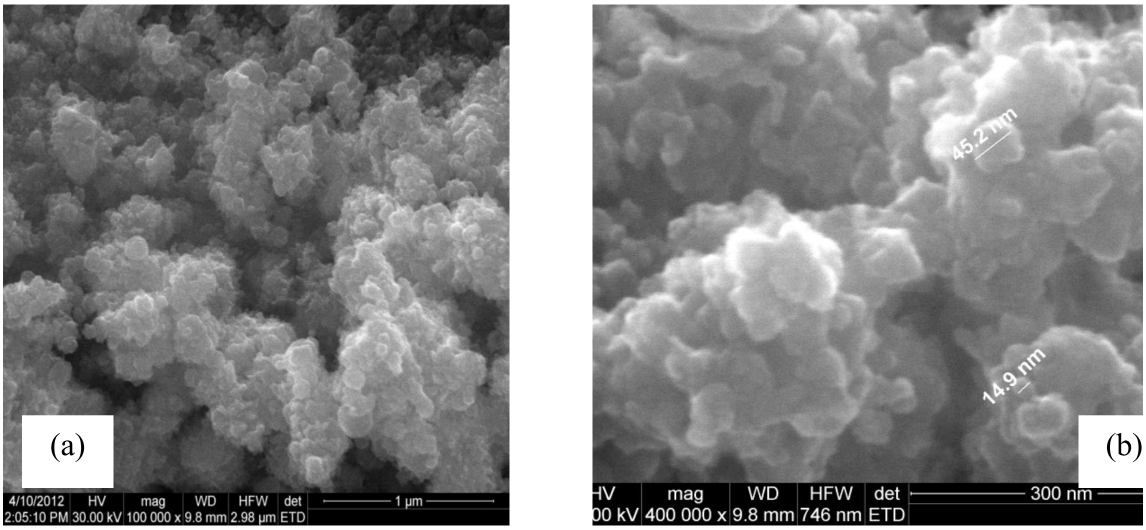

Fig. 2. SEM images for deposition of BiTeSe compound after 60 min electrolysis at 60 ^{0}C and -0.42 V potential polarization on Cu substrate in ChCl-OxA mixture containing: cBi = 10 mM, cTe = 5 mM, cSe = 5 mM. Magnification: (a) ×100000; (b) ×400000

The structure of both BiTeSe deposits is coarser, with irregular crystallites having sharpened corners and aggregated as rhombohedral formations with each other, proving a 3D growth. All images indicate clearly the porous surface morphology. However, SEM images in Figures 1 show for film electrodeposited at -0.35 V a morphology of finer aggregates but with grains having 40-105 nm size. In contrast, images in Figures 2 (film deposited at -0.42 V) show a surface covered by more compact granular structure, respectively with larger aggregates of grains having 15-45 nm dimensions. More dense film in Figs. 2 is certainly explained by larger cathodic polarization although the deposition time is shortened. The results demonstrate that the crystalline state and compactity of film are affected by shifting negatively the deposition potential. Depending on the deposition process parameters, it is possible to occur some cracks and rifts because of the copper surface uncovered yet.

The EDX results of composition of the BiTeSe samples are listed in Table 2.

Table 2. EDX results of chemical composition of BiTeSe films deposited on copper.
Bath: ChCl-OxA (1:1) ionic liquid + 10 mM Bi^{3+} + 5 mM Te^{4+} + 5 mM Se^{4+}

Element	Film deposited 2 hours at -0.35 V vs. Ag ref. (sample I)		Film deposited 1 hour at -0.42 V vs. Ag ref. (sample II)	
	wt.%	at.%	wt.%	at.%
Bi L	9.62	3.19	12.95	3.92
Te L	2.59	1.40	3.69	1.83
Se K	1.87	1.64	1.11	0.89
Cu K	85.93	93.76	78.37	78.01
O K	-	-	3.88	15.35

It is worth to mention that the significant amount of copper detected is due to very high energy of X-rays used by EDX technique, for instance in comparison to XPS (X-ray photoelectron spectroscopy). Because X-rays penetrate easily within the analysed very thin films, they reach to copper substrate, thus explaining the high Cu percentages in EDX spectra. It is therefore necessary for a correct interpretation to remove the copper content in the data of Table 2. In these cases we obtained for sample II a maximum 18 wt% content for oxygen, a value which may be provided either from oxidated surface of copper before electrolysis or from oxides (of Bi, Te, Se) deposited electrochemically together with the corresponding pure elements.

Quantitatively, taking into account the atomic weight of component elements, the following chemical compositions (in at%) of BiTeSe films were obtained:

- for film deposited 2 hours at -0.35 V, Bi:Te:Se atomic ratio is: **48 : 25 : 27**;
- for film deposited 1 hour at -0.42 V, Bi:Te:Se atomic ratio is: **58 : 28 : 14**.

From thermoelectrical point of view, the optimum Bi:Te:Se atomic ratio in films should be **40 : 54 : 6** [5,6]. Both BiTeSe samples do not fulfill the requirements of a good thermoelectric material. Thus, the sample I is closer to the optimum content of Bi than sample II, but the sample II is much closer than sample I regarding the optimum Te:Se ratio.

It is worth to notice that the atomic percentages of Bi and Te elements in the sample I (48 at.% Bi, 25 at.% Te) are almost equally with their concentration ratio in the bath (50 at.% Bi^{3+}, 25 at.% Te^{4+}). However, the atomic percentage of Se element in the sample II (14 at.% Se) is dramatically decreased regarding the Se^{4+} content in the bath (25 at.% Se^{4+}). It can be concluded that Se element is comparatively difficult to be deposited on copper substrate than on other electrodes (gold, platinum), probably owing to a weak adsorption onto copper surface of precursor ions (Se^{4+} or $HSeO_2^+$). In general, we consider that during the deposition of BiTeSe films, both microstructure and chemical composition varied to a significant extent with the bath composition, applied overpotential and corresponding current density, so the optimum operating regime is in a very narrow range.

3.2. Corrosion behaviour of BiTeSe film studied by Potentiodynamic Polarization and Electrochemical Impedance Spectroscopy

In this section we present only the results of corrosion tests for BiTeSe film (sample I) deposited 2 hours at -0.35 V. In the potentiodynamic polarization study with the BiTeSe film surface in contact with 0.5 M NaCl aqueous solution, typical Tafel plots are obtained. We mention that we took into account that prolonged anodic polarization might give rise to some changes at the surface (roughness modification, presence of adsorbed species, *etc.*); thus, we have avoided these effects by first plotting the cathodic branch and continuing with the anodic one. Fig. 3 presents, as an example, a potentiodynamic polarization curve recorded in semilogarithmic coordinates (Tafel curve).

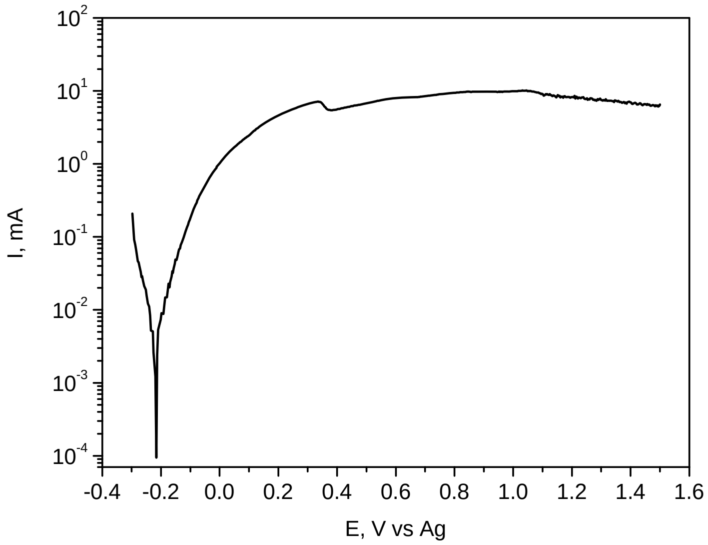

Fig. 3. The semilogarithmic polarization plot (Tafel) for BiTeSe film (sample I) in 0.5 M NaCl solution at room temperature. Surface area: 0.636 cm^2.

The cathodic reaction in the very negative polarization domain corresponds certainly to the beginning of hydrogen evolution. The anodic branch of polarization curve is the most important thing related to the corrosion resistance in the aggressive medium. As can be seen from Fig. 3 the resulted current after its minimum value (at corrosion potential) increases in the active portion of the curve, up to +0.35 V; in this part an intensive dissolution of film components is carried out, most likely the dissolution of bismuth which is expected to be the most electronegative element comparing to tellurium and selenium. It follows a small current decrease (up to +0.38 V) that is reproducible in all experiments and this can be attributed to a very short-time passivation of the surface. A temporary passivation may be due to corrosion products adsorbed on the electrode surface and this effect was also observed in non-aqueous media [17]. With more positive applied potential, the anodic current is restored and remains almost constantly having even a tendency of decrease in the region up to +1.5 V polarization. This means that a stationary state is reached, in which the rates of adsorption and desorption of corrosion products are equal; as a consequence, the corrosion rate is stationary or may decrease slowly if the adsorption prevails. However, we observed finally, at more positive than +1.6 V potential (not shown in Figure), a continuous increase of current that would be most likely due to oxidation of Cl^- ions present in NaCl solution.

The corrosion parameters were determined on the basis of current-potential characteristics in the Tafel region, using the specialized soft of BioLogic equipment, and they are listed in Table 3. Values of the corrosion potential (E_{corr}) and corrosion current (i_{corr}) were determined at the intercept of extrapolated linear parts (Tafel lines) of polarization curve. Also, the values of Tafel slopes (anodic and cathodic) were estimated. The value of polarization resistance (R_p) was obtained from a potential domain ± 40 mV *vs.* E_{corr}, where a linear polarization is considered.

Table 3. The corrosion data for BiTeSe film (sample I) in 0.5 M NaCl aqueous solution obtained from polarization curve.

Tafel domain				**Rp**, Ωcm^2 from linear polarization
i$_{\mathbf{corr}}$, μAcm^{-2}	**E**$_{\mathbf{corr}}$, V *vs.* Ag/AgCl	Tafel slopes, mVdec^{-1}		
		b$_{\mathbf{a}}$	**b**$_{\mathbf{c}}$	
6.48	-0.224	73.8	48.3	1522

EIS measurements were also carried out in other series of experiments using sample I. Nyquist and Bode spectra recorded for BiTeSe film in NaCl aqueous medium by polarizing the electrode at various anodic overpotentials were reproducible for several portions of the sample studied. Figures 4 show typical curves regarding the variation of film impedance in the active domain of anodic polarization, *i.e.* up to 400 mV anodic overpotential. As can be seen, Nyquist spectra (curves 1,2 in Fig. 4a) for overpotentials where significant increase of current is recorded on Tafel curve exhibit a single semicircle which is indicative of a single time-constant which is attributed to dissolution process. The semicircle diameter corresponds to polarization resistance (that is inversely proportional to the corrosion current). At more anodic polarization (curves 3-5) the semicircles with gradual diminished diameter are followed by a straight line displaying an angle of about 45^0 to the real impedance axis, which is characteristic for a diffusive layer consisting in corrosion products. This confirms the findings from potentiodynamic polarization curve interpreted as a competitive adsorption/desorption process of corrosion products that makes for the layer to be easily penetrated. However, we observed for those Nyquist curves at more positive polarization (an example is curve 6 in Fig. 4b) only a single semicircle which has a tendency of worm shape indicating more complex dissolution processes with participation of products with various chemical nature (oxide, hydroxide species of Bi, Te or Se and even of Cu substrate). Bode spectra (Fig. 4c) show the same series of gradual modifications: the phase angle decreases from value of -45^0 (which is typical for a process with diffusive control) to almost -5^0 and less, and the impedance modulus |Z| decreases also and may reach even values close to 1 Ωcm^2.

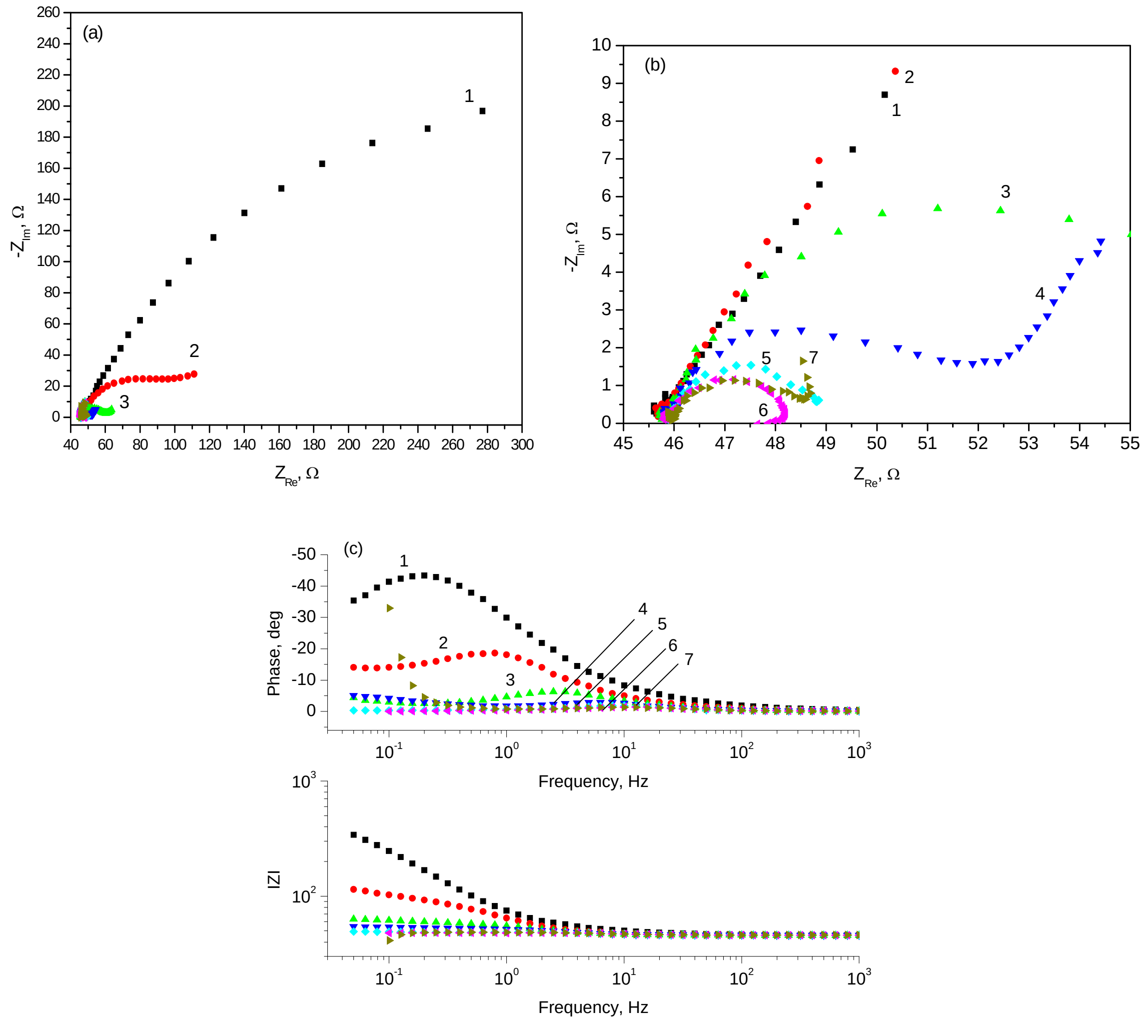

Fig. 4. EIS plots for BiTeSe film (sample I) in 0.5 M NaCl solution, polarized at various anodic overpotentials: (1) 100 mV; (2) 150 mV; (3) 200 mV; (4) 250 mV; (5) 300 mV; (6) 350 mV; (7) 400 mV. (a,b) Nyquist spectra; (c) Bode spectra. Surface area: 0.636cm^2

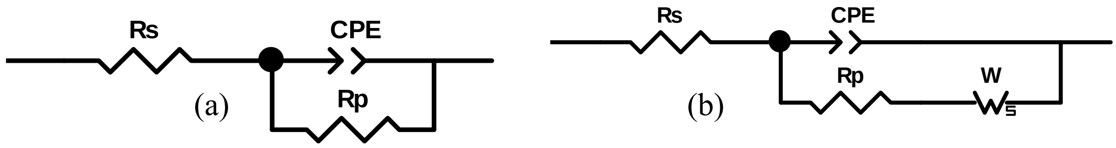

Fig. 5. Equivalent electrical circuits for anodization of BiTeSe film during EIS experiments:Rs –ohmic resistance of solution; CPE – constant phase element substituting an ideal double layer capacitance; Rp – polarization resistance; W – Warburg impedance for diffusion processes.

The results of impedance measurements performed on BiTeSe film at various anodic potentials were fitted by the use of equivalent electrical circuits and ZView 2.90c software. Figure 5a shows the simple Randles circuit taken firstly as model for electrode/electrolyte interface. The circuit consists in a combination of solution ohmic resistance (Rs) in series with a parallel circuit which contains the polarization resistance (Rp) in parallel with a constant phase element (CPE). This constant phase element has as components CPE-T as a pure capacitance of electrochemical double layer and CPE-P as an exponent (P=1 for pure capacitance). The alternative equivalent circuit shown in Fig. 5b contains an additional element W which is called Warburg impedance for diffusion processes. Its components (W-R, W-T and W-P) have significance of ohmic resistance, capacitance and its exponent, respectively.

Table 4. The fitting EIS data for BiTeSe film polarized in 0.5 M NaCl aqueous solution; the equivalent circuit from Fig. 5a was used, except for anodic overpotentials in 200-300 mV range.

Circuit parameter	Values at various anodic overpotentials						
	100mV	150mV	200mV*	250mV*	300mV*	350mV	400 mV
Rs, Ωcm^2	29.2	28.8	29.1	29.2	29.1	29.1	29.2
CPE-T, μFcm^{-2}	8717	14980	11087	11280	13514	10060	18716
CPE-P	0.76	0.72	0.90	0.92	0.90	0.98	0.85
Rp, Ωcm^2	389.0	53.3	8.6	3.9	1.9	1.5	1.8
W-R, Ωcm^2	-	-	4.1	13.2	0.3	-	-
W-T, Fcm^{-2}	-	-	4.0	12.1	1.9	-	-
W-P	-	-	0.53	0.66	0.64	-	-

*For these data (curves 3-5 from Fig. 4) the equivalent circuit from Fig. 5b is applied.

The values of the best fitting are listed in Table 4. The validation of fitting procedure is proved by low standard deviations of parameters, by equal values (28.8-29.2 Ωcm^2) of solution resistance across all experiments and values relatively close to each other for all other circuit parameters. An exception is the descending series of Rp values, that starts from corrosion potential (Rp = 1522 Ωcm^2, see Table 3) and continues to 389.0 Ωcm^2, 53.3 Ωcm^2 and so on, proving that the intensity of BiTeSe dissolution is increased gradually.

On the whole, we consider that the interpretation of impedance variation of BiTeSe film measured at different anodic overpotentials is consistent to the above described dissolution mechanism where the Tafel curve is interpreted.

4. Conclusions

Regarding film morphologies, SEM images showed that BiTeSe film electrodeposited at low cathodic overpotentials (around 100 mV overpotential) has finer aggregates but with higher size grains. In contrast, the films electrodeposited at more negative potentials (as the case of film deposited at -0.42 V) may change the morphology; the surface is covered by granular structure more compact although larger aggregates of grains with small dimensions are detected.

From EDX spectra the following chemical compositions (in at%) of BiTeSe films were obtained: (1) Bi:Te:Se atomic ratio of **48 : 25 : 27** for film deposited 2 hours at -0.35 V; (2) Bi:Te:Se atomic ratio of **58 : 28 : 14** for film deposited 1 hour at -0.42 V.

On polarization Tafel curve an active dissolution of films was found in the first anodic polarization domain (500 mV overpotential) followed by a stationary state where the anodic current remains almost constantly having even a decrease tendency. EIS measurements have revealed a descending series of polarization resistance, that starts from corrosion potential and continues up to the highest anodic polarization. The results obtained by both electrochemical techniques used for corrosion tests are in good agreement.

Acknowledgement

The support of the European Social Fund through POSDRU/88/1.5/S/60203 Project is acknowledged by the first author.

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