Electrodeposition of $Ni_3Bi_2Se_2$ Thin Semiconductor Films

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ABSTRACT: *The present contribution is devoted to the production of the Ni-Bi-Se thin films widely used in the field of electronics, electrotechnology, and computer technology. During the process, at first, the Bi-Se compound has been formed on the nickel electrode by electrochemical method, and then by thermal treatment of this compound at 673K, ternary compound $Ni_3Bi_2Se_2$ has been obtained. The results show that as the concentration of bismuth is increasing, its amount in deposited films increases regularly. The formation of the $Ni_3Bi_2Se_2$ compound was also confirmed by XRD results. The photochemical properties of the obtained compounds were investigated in the dark and light, constant current of 100 nA for 0-600 seconds. With the illumination of the dark samples, the potential shifts from a positive side to a negative side, this decrease indicates that obtained thin films are not only photosensitive, also have n-type conductivity.*

KEYWORDS: *$Ni_3Bi_2Se_2$; Electrodeposition; Chemical compounds; Thermoelectric materials.*

INTRODUCTION

Nowadays, the development of various fields of science and technology (microelectronics, computer technology, optoelectronics, etc.) is strongly associated with obtention, investigation of various properties, as well as application of thin-film coatings [1-6]. The structure of thin layers varies considerably depending on the condition of the deposited surface [7-8].

One of the most promising methods for the production of thin films is an electrochemical method [9]. The electrodeposition method has some advantages over other methods. So that, at low temperatures, using the electrolyte of various contents, it is possible to obtain stoichiometric compounds in the form of a thin layer and nanostructures with the required thickness on the complex and large surfaces in a short time. The use of this method doesn't require difficult devices and instruments. Moreover, parameters of the electrochemical deposition can be easily controlled, and this method is economically favorable. Therefore, the production of semiconductor chalcogenide thin films by electrodeposition is receiving much research attention due to the above-mentioned advantages.

As it is known, thin layers of bismuth, cadmium, stibium, and molybdenum with chalcogens are used in the manufacture of Thermo generators, thermoelectric devices, refrigerators, and photoelectric converters [10 - 19].

There are few literature references about the Ni-Bi-Se ternary system. Preparation of the binary and ternary compounds of this system has been performed by some authors [10, 11, 20-22].

Authors of [10, 11, 20-22] have synthesized the binary and ternary compounds NiSe, BiSe, NiBiSe and $Ni_3Bi_2Se_2$ that correspond to 1:1, 1:1:1 and 3:2:2 stoichiometric ratios, from the mixture of ethylene glycol, ethylenediamine, with additionally taken NaOH, Bi_2Se_3

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and $NiCl_2 \cdot 6H_2O$ compounds. The process was conducted in a slightly alkaline medium at 197^0C. When the synthesis process was carried out in an electrolyte in the absence of NaOH, at 190^0C, the NiBiSe compound corresponding to the 1: 1: 1 stoichiometry was formed.

Some polythermal sections of the Ni-Bi-Se system [20] were studied by DTA, XRD, microstructure analysis, and microhardness testing and its liquidus surface was constructed. The $NiBi_2Se_4$ and $Ni_3Bi_2Se_2$ compounds are formed by distectic reactions at 1088 and 980K, respectively. During the study, parkerite $Bi_2Ni_3S_2$ and other compounds similar to it were obtained by heating the pressed samples consisting of Ni, Bi, and Se powders in the vacuum quartz ampules for 6 hours at 1200^0C [21]. The study of the physical properties of these compounds has shown that the specific electrical resistance of both compounds is typical of metals up to 400 K. Measurements of specific resistance and specific thermal effects at low temperatures indicate that these compounds are highly conductive.

The authors of [22] have studied the crystal structure of the selenium-containing parenite – $Ni_3Bi_2Se_2$ compound using the XRD method and it was found that it crystallizes in a monoclinic system close to the lattice parameters of the parkerite – $Ni_3Bi_2S_2$.

Reviewed literature shows that preparation of the binary and ternary chalcogenides of bismuth as thin layers was not referred to as a research object and the study of Ni-Bi-Se ternary system has been mainly conducted by thermal methods. The main disadvantages of this method are its performance at high temperatures, obtaining samples as non-thin layers, and difficulties in controlling the process due to its realization in an isolated medium. Therefore, the present study is devoted to the foundation of the optimal conditions for the preparation of Ni-Bi-Se samples in the form of thin films, as well as the investigation of their opto-physical properties.

EXPERIMENTAL SECTION

The process for obtaining the Ni-Bi-Se system by the electrochemical method was as follows: initially, to prepare the electrolyte solution under study, a 1: 1 solution of citric acid in water was prepared, then the required amounts of $Bi(NO_3)_3 \cdot 5H_2O$ (analytical grade) and selenic acid (H_2SeO_3) were separately dissolved in citric acid solution.

The composition of the obtained electrolyte was $(4\times10^{-4}$- $2\times10^{-3})$M $Bi(NO_3)_3 \cdot 5H_2O$ + 5×10^{-2}M H_2SeO_3 + 5×10^{-3}M $C_6H_8O_7$. The electrochemical deposition on the Ni electrode in this electrolyte has been carried out by both galvanostatic and potentiostatic methods. The potentiostatic deposition process was monitored on a computer-equipped IVUMSTAT Electrochemical Interface potentiostat. In this case, a three-electrode electrochemical cell was used. Ni electrode with a surface area of 2 cm^2 was taken a s a working electrode. A silver-chloride (Ag/AgCl) electrode was used as a reference electrode, and a Pt plate with a surface area of 4 cm^2 was used as an auxiliary electrode.

Nickel electrodes before the experiment were corroded in a concentrated HNO_3 solution, then electrochemically polished in H_2SO_4, H_3PO_4, and citric acid (T=293-303K, i=50A/dm^2, τ=189s) solutions. Finally, nickel electrodes were washed with distilled water several times.

The phase composition of the obtained films was studied on D2 Phaser (CuK_α; Ni Filter) X-ray analyzer of Brucker Company.

The morphology, relief, and chemical composition of the deposited samples were investigated using a Carel Zeiss Sigma Scanning Electron Microscope (SEM).

ModuLight module has been used as a light source for photoelectrochemical studies. It is a specially designed programmable light source allowing exploration of photoelectric materials. The module is connected to a computer-equipped IviumStat XRe Electrochemical Interface potentiostat. ModuLight consists of 7 LED lamps with a wavelength of 460-740 nm**.** During operation, the LED can be selected programmatically. The sinewave generator of the potentiostat can then be used to modulate the light intensity of the LED with a frequency of 10 μHz to 2MHz.

Thermal treatments were carried out in a quartz furnace. The furnace consists of a heating device wrapped in an electric spiral on a quartz tube with a sharp end, tightly wrapped with asbestos rope and attached to a tripod. Depending on the values of the given electric current, it is possible to provide different temperatures in the furnace. The samples deposited on the Ni electrode were put in the porcelain crucible and the latter was placed in the furnace. A thin glass tube that fixed with a rubber stopper was intertwined on the wide side of the furnace and connected to the argon balloon through a plastic tube. To convert the atmosphere inside the furnace into an inert

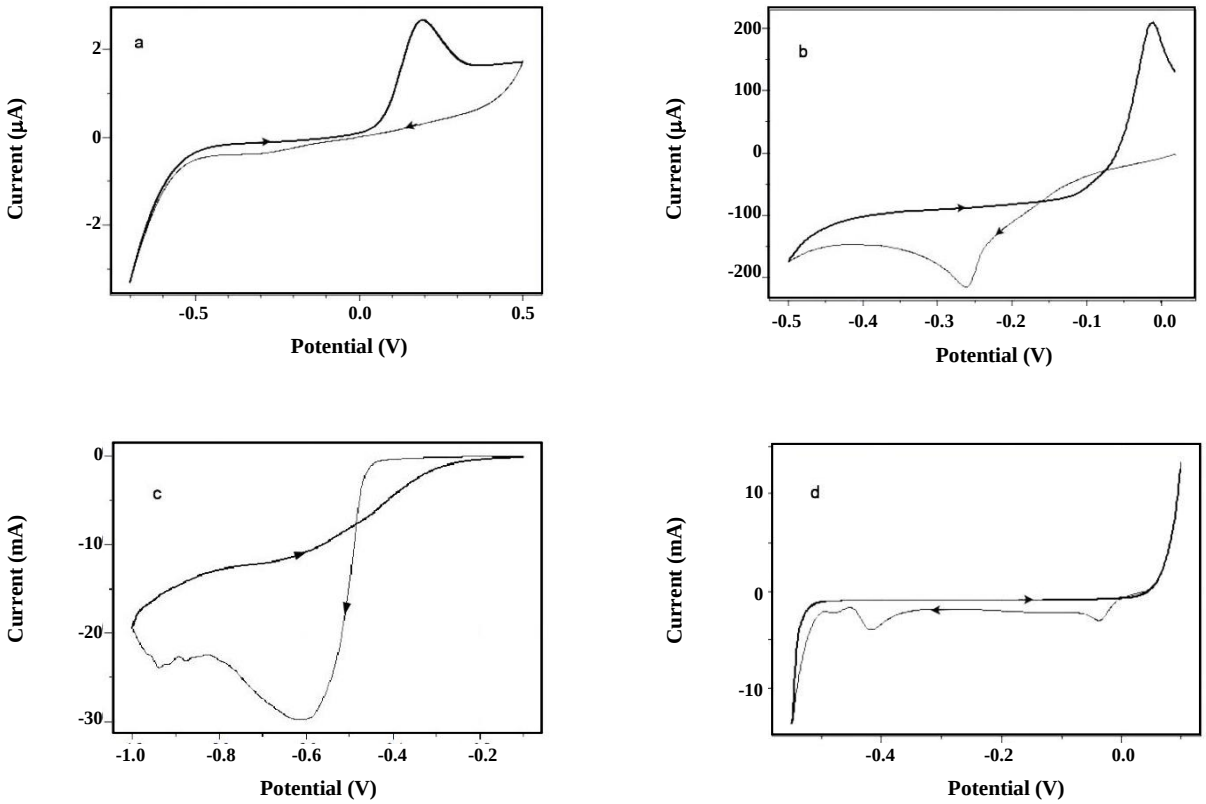

Fig. 1: The cyclic polarization curves of electroreduction of citrate acid, bismuth ions, selenide ions on the Ni electrode and co-electrodeposition of bismuth and selenium. Electrolyte (M): a) 5.2×10^{-3} $C_6H_8O_7$; b) 5×10^{-5} $Bi(NO_3)_3\cdot 5H_2O$ + 5.2×10^{-3} $C_6H_8O_7$; c) 5×10^{-2} H_2SeO_3 + 5.2×10^{-3} $C_6H_8O_7$; d) 5×10^{-5} $Bi(NO_3)_3\cdot 5H_2O$ + 5×10^{-2} H_2SeO_3 + 5.2×10^{-3} $C_6H_8O_7$; T=298 K, E_v= 0.02 V/s.

gas medium, the Argon balloon is opened and other gases inside the furnace are expelled from there. The gas-transfer tube is installed on the other sharp end of the furnace and the free end of the tube is immersed in a cup of water to observe the continual flow of Ar from the furnace and to prevent the air from entering the heater. The iridium-rhodium thermocouple was used to measure the temperature of the quartz furnace.

RESULTS AND DISCUSSION

In order to obtain the ternary compound in Ni-Bi-Se system by electrochemical method, a separate and co-deposition of Bi and Se from the above-mentioned electrolyte solution was carried out. For that, the electroreduction process of initial components was investigated separately.

Fig. 1 depicts the cyclic polarization curves of the electroreduction process of citrate acid, bismuth ions, selenite ions, and the joint deposition of bismuth and selenium on the Ni electrode. In reference to the background (Fig. 1 (a)), the electroreduction processes of the Bi ions and selenium ions occur in the potential regions of 0.0-(-0.5) V (Fig.1 (b)) and -0.4 – (-1.0) V (Fig.1 (c)), respectively. As can be seen from the curve (Fig.1 (d)) drawn at a potential interval of 0.1-(-0.55) V, several peaks were observed on the Ni electrode during co-electrodeposition.

In our opinion, the peak corresponding to the 0.0-(-0.06) V potential conforms to the deposition of bismuth ions; the electrode surface is coated with a gray layer within this potential range. Bismuth ions continue to deposit within -0.06-(-0.35) V in limiting current, whereas within (-0.35)-(-0.45) V potential interval Se^{2-} ions are deposited, after the potential value of -0.45 V, the Bi-Se film is formed combining the bismuth and selenium ions.

The process has been studied up to this potential because, after -0.55 V potential, the release of hydrogen was observed during electrodeposition of the Bi-Se films

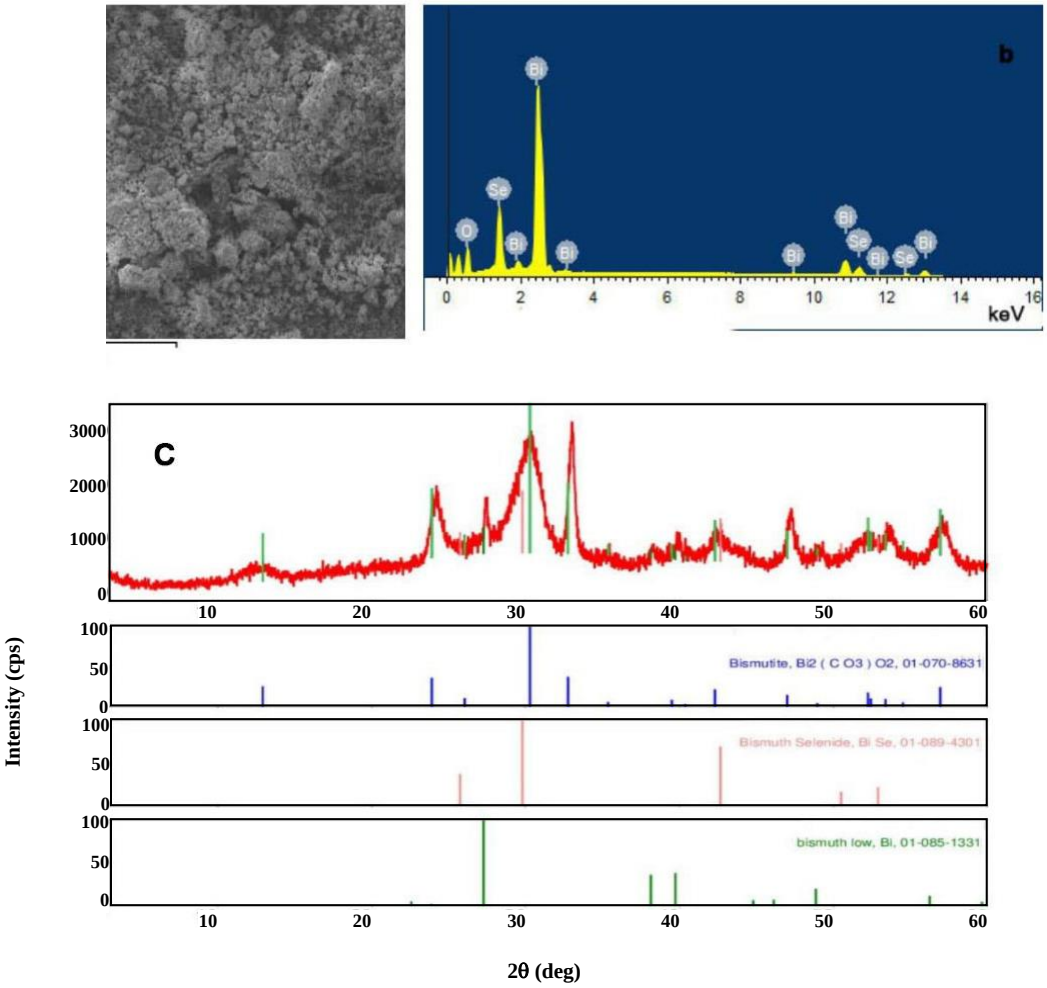

Fig. 2: The SEM (a), EDX (b), and XRD (c) results of Bi-Se films on the Ni electrode before thermal treatment.

on the Ni electrode. In comparison with the Pt electrode, the co-deposition process on Ni is much faster and the consumed current is higher than the one on Pt electrode (3.0×10^{-3} A on the Pt electrode, 1.35×10^{-2} A on the Ni electrode).

Deposits obtained by galvanostatic methods have been studied on the Ni electrode depending on the condition of electrodeposition and on the composition of an electrolyte. In this case, different samples were obtained with 5×10^{-5} - 5×10^{-4} M $Bi(NO_3)_3\cdot5H_2O$, 5×10^{-2} M H_2SeO_3 solutions and the solvent of a stable concentration (5×10^{-3} M $C_6H_8O_7$). Electrolysis was carried out at 298 K for 2 hours and a current density of 3-6 mA/cm^2 (Fig. 2).

As can be seen from the figure, only one Bi-Se layer is deposited on the Ni electrode from untreated samples. The EDX images (b) and XRD results (c) presented in Fig. 2 have not proved the formation of the ternary compound. The Bi-Se samples obtained on the Ni electrode were then thermally treated at 673K in an argon atmosphere. These results are also evident from the EDX (b) and X-ray (c) images shown in Fig. 3.

Obtained results show that the composition and quality of thin layers deposited by the galvanostatic method are different. As the concentration of bismuth in the electrolyte increases, its amount in deposited films increases as well. Above mentioned parameters also affect the sediment appearance (Table 1). A chemical compound of the three-component system - $Ni_3Bi_2Se_2$ was obtained after thermal processing (Fig. 3).

Formation of the ternary compound has been proved by the XRD and SEM analysis. These results are presented in Figs. 2 and 3, respectively.

Table 1: Experimental results of the preparation of Bi-Se thin semiconductor films on the Ni electrode. Current density - 4 mA/cm^2, the temperature of thermal annealing - 673K.

No	Electrolyte content, M		Mass fraction, %			The appearance of thin films
	$Bi(NO_3)_3 \cdot 5H_2O$	H_2SeO_3	Ni	Bi	Se	
1	5×10^{-5}	5×10^{-2}	24.3	54.5	21.2	Black, strong adhesive, evenly distributed, smooth
2	3×10^{-5}	5×10^{-2}	23.1	59.7	17.2	Black, strong adhesive, evenly distributed, smooth
3	1×10^{-4}	5×10^{-2}	15.6	66.3	14.1	Black, strong adhesive, evenly distributed, non-smooth
4	3×10^{-4}	5×10^{-2}	18.7	71.8	9.5	Brown, average adhesive, unevenly distributed, non-smooth
5	5×10^{-4}	5×10^{-2}	19.3	74.6	6.1	Black-brown, average adhesive, evenly distributed, non-smooth

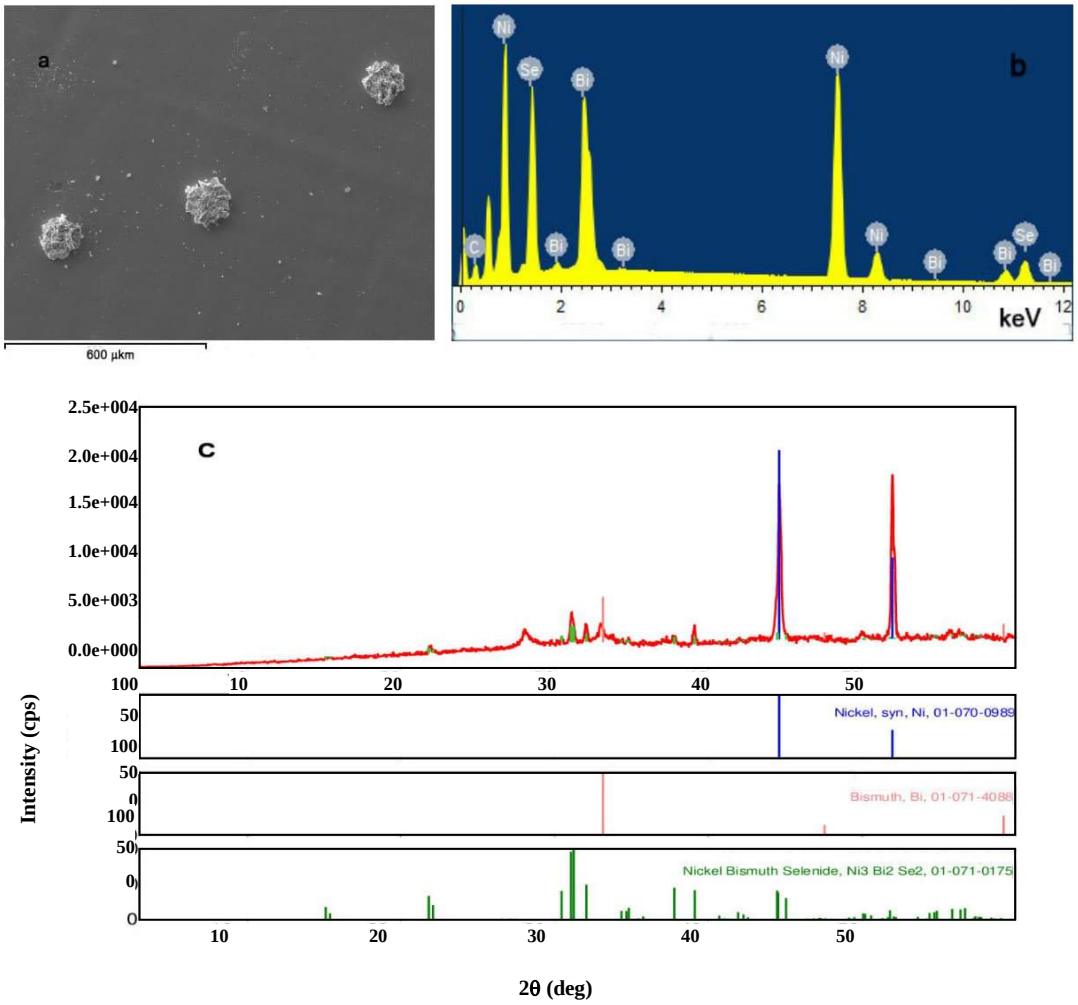

Fig. 3: The SEM (a), EDX (b), and X-ray (c) images of the obtained $Ni_3Bi_2Se_2$ compound after thermal treatment.

Table 2: The effect of current density on the formation of Bi-Se semiconductor thin films on the Ni electrode. Electrolyte (M): 5×10^{-5} $Bi(NO_3)_3\cdot5H_2O$ + 5×10^{-2} H_2SeO_3, T=298K.

No	Current density, mA/sm^2	Mass fraction, %		The appearence of thin films
		Bi	Se	
1	2	1.24	26.38	Black, evenly distributed, smooth, strong adhesion
2	3	69.7	17.2	Black, evenly distributed, smooth, strong adhesion
3	4	72.23	13.86	Black, evenly distributed, non-smooth, strong adhesion
4	5	65.81	23.57	Black-brown, unevenly distributed, smooth, average adhesion
5	6	76.4	16.19	Black-brown, unevenly distributed, non-smooth, weak adhesion

As can be seen from Table 1, an increase in the number of bismuth ions in an electrolyte has a significant effect on the change of stoichiometry in the deposited thin layers. The $Ni_3Bi_2Se_2$ ternary compound with maximum close to the stoichiometric composition is obtained when the concentration of ions is 5×10^{-5} M.

As it is known, one of the important factors influencing the electrodeposition process is the current density. From the results of the galvanostatic deposition investigated within 3-6 mA/cm^2 range, it can be concluded that crystalline thin films with strong adhesion to the electrode surface and evenly distributed on the surface are close to the stoichiometry and deposited at a rate of 3-4 mA/cm^2. Although the films have a good appearance at lower than 3 mA/cm^2, the stoichiometric composition is quite different. Within the 5-6 mA/cm^2 range, the appearance of the layers corresponds to stoichiometry, and their adhesions to the electrode partially deteriorate (Table 2).

As a continuation of the studies, the photoactivity of the obtained compounds was investigated by chronopotentiometric method. The chronopotentiometric study of Bi-Se samples deposited galvanostatically on a Ni electrode was carried out in the dark and light at a constant current of 100 nA within 0-600 sec. However, no change is observed in the investigated sample, as in the dark. That is, there is no displacement of current in any direction over time.

Fig. 4 demonstrates the chronopotentiometry curve of the $Ni_3Bi_2Se_2$ ternary compound obtained as a result of thermal treatment of Bi-Se samples at 673K and deposited onto the Ni electrode in the dark and light. Samples were exposed to a constant current of 100 nA for 0-600 seconds. With the illumination of the dark samples, the potential shifts from a positive side to a negative side, this decrease

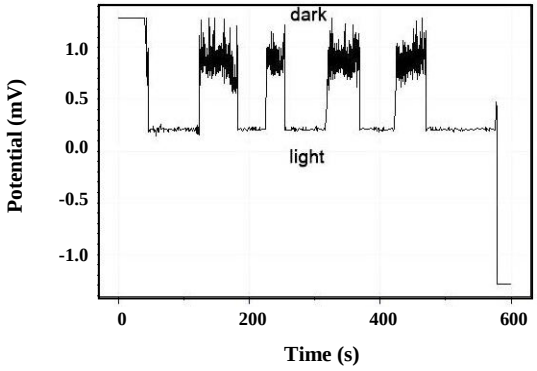

Fig. 4: The Chronopotentiometric corve of the Ni3Bi2Se2 Sample obtained atfer thermal treatment.

indicates that obtained thin films are not only photosensitive but also have n-type conductivity.

Thermoelectric properties of the $Ni_3Bi_2Se_2$ thin layers synthesized by electrochemical methods were determined by the width of the bandgap calculated based on the temperature dependence of specific electrical conductivity. Thus, the bandgap for the $Ni_3Bi_2Se_2$ thin layers is 0.352 eV, which indicates its thermoelectric properties.

CONCLUSIONS

As a result of the committed investigation, the electrodeposition of Bi-Se thin films has been carried out in an electrolyte of 5×10^{-5} $Bi(NO_3)_3 \cdot 5H_2O$ + 5×10^{-2} H_2SeO_3 + 5.2×10^{-3} $C_6H_8O_7$ composition, i_k = 3-4 mA/cm^2, at T= 298K. By thermal treatment of Bi-Se samples at 673K on Ni electrode, in an argon atmosphere, the $Ni_3Bi_2Se_2$ ternary compound was obtained by the galvanostatic method. Photoelectrochemical properties of the obtained compound were studied and it was determined that this is an n-type conductor with photosensitive properties.

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