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THE ELECTRODEPOSITION OF GALLIUM SELENIDE

Abstract. The electrochemical deposition of gallium selenide on a glassy carbon electrode from sulphate electrolytes at a constant potential was carried out. The cyclic voltammetric curves of the glassy carbon electrode in two different electrolytes were studied: sulfuric acid and citrate buffer solution containing gallium and selenium ions. The influence of change in the concentration of gallium ions and the deposition potential on the composition of the resulting precipitate is studied. Increasing of the gallium ions concentration from $6\cdot10^{-3}$ to $1\cdot10^{-1}$ M at a constant concentration of selenium ions $2\cdot10^{-3}$ M in the electrolyte leads to an increase in the gallium content in the deposit composition. It is established that in order to obtain the stoichiometric composition of the film, the content of gallium (III) ions in the electrolyte must be many times higher than the content of selenium (IV) ions. The results of elemental analysis of the precipitate confirmed that a film of gallium selenide with a content of 26.7 at% gallium was obtained at a ratio of the concentration of gallium ions and selenium of 50: 1 in the sulphate electrolyte at a potential of -0.8 V. Investigation of the morphology of the surface showed that a uniform coating of the surface of the glassy carbon electrode is achieved at potentials of -0.8 and -0.9 V. X-ray phase analysis confirmed the presence of the Ga_2Se_3 phase in the resulting films.

Keywords: gallium selenide, electrodeposition, voltamperometry.

Introduction. Semiconductor compounds of the III-VI group have attracted great attention of researchers thanks to their suitable structural and optical properties for the application in photoelectronic converters [1]. This group includes gallium monoselenide, GaSe which has hexagonal structure with an optical width of band gap of 2.1 eV and contains Se-Ga-Ga-Se layers and gallium diselenide, Ga_2Se_3, which has a cubic structure with 1.8-2.6 eV width of band gap [2, 3] and crystallizes in α-and β-structural modifications. In Ga_2Se_3 structure, one third of cationic centers is free and the structure of compound is, therefore, defective. In turn, the defective compound is used in optoelectronic devices for the passivation of heterogeneous compounds, for switching of the memory of light-emitting diodes [4], in combination with GaP substrate [5]. There is a set of methods to obtain gallium selenide. They are the chemical deposition from a vapor phase (CVD) [6], chemical transfer of vapor in vacuum [7], vapor-phase epitaxy [8], heterovalent reaction of V-VI exchange [9], thermal evaporation [10] and molecular beam epitaxy [11, 12]. The most well-known Stokbarger-Bridgmen method [13] of obtaining gallium selenide monocrystals, Ga_2Se_3 is the synthesis at the directed crystallization when a quartz ampoule with the material is stretched in a special furnace and heated to 1473 K with the subsequent slow decrease in temperature. This method requires high purity of materials, and high vacuum and temperature.

Thin Ga_2Se_3 films can be obtained by the zol-gel technique at a crystal formation temperature [14]. Compared to the above-described method, the electrodeposition method from aqueous solutions to obtain thin films on conductive substrates has a number of advantages and is an inexpensive method making it possible to control thickness, morphology and structure of film during deposition 15-17]. In this work, the conditions of gallium selenide electrodeposition on a glassy carbon electrode at a constant potential have been studied.

Methods of study. Voltammetric measurements on a disk glassy carbon electrode with 0.07 cm^2 surface and gallium selenide electrodeposition on flat glassy carbon plates of 1.0 cm^2 area were carried out in a three-electrode thermostatted glassy cell using a silver-chlorine reference electrode and a platinum counter electrode.

Before the experiment, the electrodes were treated with fine abrasive 2000 paper, washed with distilled water and dried in the open air. The sulfate electrolyte with pH = 2.2 (0.45 M Na_2SO_4 + 0.05 MH_2SO_4) and the citrate buffer electrolyte with electrolyte pH = 2.92 were used as background electrolytes. The latter was prepared from 39.3 ml 0.1 M sodium citrate and 60.7 ml 0.1 M HCl. The solutions of gallium and selenium salts (analytically pure), 0.1 M Ga_2 $(SO^4)_3$, 0.1 M $NaHSeO_3$ and 1 M $GaCl_3$ were used. The concentration of gallium ions in these electrolytes was changed from $6\cdot10^{-3}$ to $1.2\cdot10^{-1}$ M and the concentration of selenium ions was maintained constant ($2\cdot10^{-3}$M).

The deposition of gallium selenide was carried out at a constant potential maintained by GillAC potentiostat with Version 5 ACM Instruments software, and at a temperature of 70° C that was maintained by using the LOIP thermostat. The electrolyte mixing was carried out using MM3M magnetic stirrer.

After deposition, the films were washed with distilled water and dried in the open air. Elemental analysis of the contents of components and micrographs of the surface of gallium selenide films were made using the JEOL (Japan "JSM6610 LV") electronic scanning microscope with the capabilities of microanalysis. The phase composition of the films was determined using the DRONE-4/07 instrument with a Co-tube.

Results and Discussion

Voltammetric measurements on a disk glassy carbon electrode. To determine the effect of the concentration of components in the electrolyte on the electrochemical process to reduce the ions, the cyclic voltamperometric dependencies (CVA) of a glassy carbon electrode in a sulfate electrolyte and citrate buffer solution were recorded. The scanning speed of potential was 20 mV/s in the 0 to -1.0 V range and in -1.0 to + 1.2 V range in case of inverse scanning. Eectrolytes with varying concentrations of gallium ions ($6\cdot10^{-3}$ M, $1.2\cdot10^{-2}$ M, $6\cdot10^{-2}$ M, $8\cdot10^{-2}$M, $1\cdot10^{-1}$ M and $1.2\cdot10^{-1}$M) at a constant concentration of selenium ions ($2\cdot10^{-3}$M) were investigated.

Figure 1 shows the CVA of a glassy carbon electrode for the reduction of Se(IV) и Ga(III) ions recorded in the sulfate electrolyte. Apparently, the cathode current increases already at 0 V potential indicating the reduction of Se (IV), which starts at more positive potentials. The figure 1 sidebar shows the CVA of Se(IV) ($2\cdot10^{-3}$ M) reduction against the background of sulfate electrolyte taken at a cathode potential scan of + 0.3 to -1.0 V. The reduction of Se (IV) is accompanied by the emergence of two peaks at potentials around zero V and at -0.5 V potential. The reduction processes and standard potentials of reactions are described by the equations:

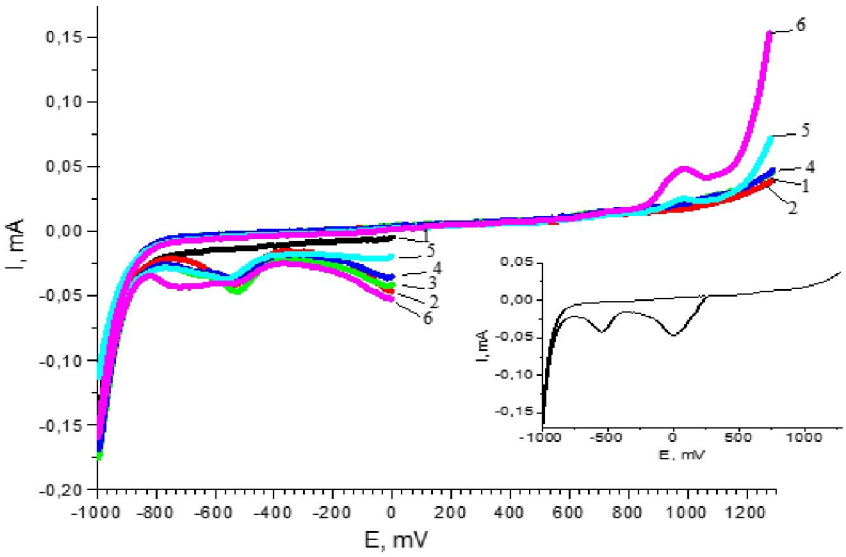

Figure 1 – The CVA of glassy carbon electrode in a sulfate electrolyte at various concentrations of selenium and gallium ions. 1 – support electrolyte; 2–6 – Se(IV) – $2\cdot10^{-3}$ M; Ga(III): 3 –$6\cdot10^{-3}$; 4 – $1.2\cdot10^{-2}$; 5 – $8\cdot10^{-2}$; 6 – $1\cdot10^{-1}$M. Side bar: Se(IV) – $2\cdot10^{-3}$ M