

ABSTRACT

This paper summarizes the publications in the last years. It analyzes more than 40 scientific papers on the production of rhenium chalcogenides by electrochemical method. A review using various electrochemical methods revealed the scientific basis of joint electrodeposition of rhenium with chalcogens patterns of different electrolytes and synthesized new semiconductor coating of rhenium chalcogenides. The electrolyte used sulfate, thiosulfate, chloride, borate, chloride and sulphate-alkaline solutions containing various concentrations of rhenium and chalcogen (S, Se, Te). Analysis of the results of measurements of cathode and anodic polarization curves for the joint electrodeposition of rhenium with the chalcogen (S, Se, Te) has shown that the co-deposition process is accompanied by depolarization, which proves the formation of a chemical compound or a solid solution based on these compounds and determines potential range in which to cathode stoichiometric compound are formed. It has been established that all of rhenium chalcogenides are semiconductor materials.

KEYWORDS: Chalcogenides of rhenium, thin films, electrochemical methods.

INTRODUCTION

Comprehensive interest to rhenium has increased in the last years in connection with the development of new technology. Increase in production of rhenium is due to complex of its unique properties. Rhenium alloys with platinum group metals can be used to make electrical contacts with improved performance properties. Rhenium characteristic feature is its resistance to spark erosion, preventing the burning of contacts [1-5].

Subsequently, opens a new field of application of rhenium - refining industry, where it is combined with platinum used as a catalyst and in reforming processes - production of high octane gasoline. The using of platinum-rhenium catalysts led to an increase in catalyst lifetime in the 5 times and increase process efficiency by more than 60%. Rhenium alloys with a number of metals are used in the electronics, electric, nuclear technology, as well as in the production of coatings of a special importance [6 - 21].

Rhenium alloys with sulfur are used as the photosensitive material in the form of thin coatings in semiconductor technology. In addition to sulfur-rhenium alloys are used as catalysts in the process of dehydrogenation of alcohols. In modern technology semiconductor materials have a special place. Relevant issue is the creation and study of new materials, including semiconductor ones, having valuable properties and the possibility of a wide practical application [22-26].

Due to the fact that the alloys of chalcogenides semiconductor materials are widely used in modern technology, their use to one or the other art due to the physico-chemical and physical properties. Therefore, when deciding on the use of semiconductor materials, first of all, you need to pay attention to their physical and electrical properties. The study of electrical properties of semiconductor materials has two purposes. First, these properties allow a deeper understanding of physical and chemical nature of the matter: the type of chemical bond, the violation of the stoichiometric composition, the effect of their impurities, etc. Second, the technical application of semiconductors mainly determined by their electrical and optical properties. Therefore, the properties of semiconductor materials are considered in the minimum extent necessary for the proper orientation of their practical application.

Due to intensive research and growing practical application of semiconductor compounds is the extremely urgent task of developing a scientific method of synthesis of new semiconductor coatings with predetermined properties. Still more opportunities in the preparation of semiconductor materials with opens "programmed properties" the physico-chemical analysis of semiconductor systems. With this electrical, optical, and other properties were studied. Physical and mechanical properties of electrolytic deposition are an essential feature of the quality of coatings and determine their applicability in a particular area of technology. Properties of electrolytic deposition are conditioned by the presence of inclusions in these of various foreign particles, and the degree of irreversibility of the reduction process of the electrode metal ions. The latter circumstance is due to the fact that the recovering ions passing through the electric double layer having higher tensity of electric field acquire greater velocity, immediately entering the crystal lattice, this leads to the formation of non-equilibrium lattice with changed parameters.

Of particular note are some interesting opening possibilities at a joint discharge of metal ions such obtaining coatings with properties that cannot be created in other ways. Thus, at it electrodeposition is possible to obtain alloys which cannot be obtained by crystallization from the molten state.

Alloys produced electrolytically, are nonequilibrium and differ greatly in their structure from the alloys obtained by thermal means. Therefore, the equilibrium phase diagram can be not mechanically endure the alloy obtained by electrolysis, as depending on the method of producing alloys differ both in structure and in properties. The deposition obtained electrolytically contain both metallic inclusions and a large number of nonmetallic inclusions, such as: hydroxide, oxide, hydrogen, halides, surfactants, and others. What that linked by their specific physico-mechanical properties, are linked with.

The availability of obtaining electrolytic coverings with different properties led to extension of their using in the industry.

The various methods are used to produce thin films of semiconducting rhenium alloys. However, analysis of the known methods for producing thin layers of rhenium chalcogenides found that the most promising and cost-effective is the electrochemical method.

Features of electrochemical method of producing films of rhenium chalcogenides dictate the conditions of their development process method, thereby determining the relevance of scientific research in this direction.

In this connection, the search and development of new methods for producing thin films of chalcogenide semiconductor rhenium on various substrates, including also metal ones and is relevant not only from a practical but theoretical standpoint, as well.

This work is devoted to the development of scientific bases of electrochemical deposition of thin semiconductor material of rhenium chalcogenides used in various fields of modern technology.

METHOD OF EXPERIMENT

Carrying out this work we used the following reagents: TeO₂ (chemically pure, c.p.); SeO₂ (reagent grade); NH₄ReO₄ (c.p.); KReO₄ (c.p.); HCl (c.p.); H₃BO₃ (c.p.); H₂SO₄ (c.p.); NaOH (pure for analyses, p.f.a.); (NH₄)₂SO₄ (p.f.a.); HNO₃ (c.p.); NH₂CSNH₂ (c.p.); SnCl₂ · 2H₂O (p.f.a.); H₃PO₃ (p.f.a.); CrO₃ (p.f.a.); Na₂SO₄ · 7H₂O (p.f.a.).

Above-mentioned reagents underwent purifying before use. Chlorine (c.p.) and sulphuric (c.p.) acids underwent double distillation. Aiming define chemical phase composition, microstructure, micro-hardness, inner stress of obtained alloys to platinum and copper electrodes with surface 4 cm² were used.

Polarisation measurements were carried out using platinum cathode having surface 0.15 cm², soldered in glass pipe. Before a plunging into solution the electrode was mechanically polished, degreased, boiled in 30 % nitric acid, then washed in appropriate electrolyte. The copper electrode every time before use was mechanically polished, degreased by Vienna lime, polished using electrochemical method, then twice washed by distilled water. Carrying out polarization measurements there was also used platinum electrode (S = 0.15 cm²), coated by layer of electrolytic tellurium, rhenium and selenium, obtained from appropriate solutions. For polarization

measurements a chlorine-silver electrode was used as a reference electrode. Auxiliary electrode was platinum wire of surface which several times surpassed the surface of exploring electrode.

For investigation of kinetics of cathode-anode processes of co-electrodeposition of rhenium and chalcogenes the methods of potentiostatic and cyclic voltametry were used. Measurements in potentiostatic conditions were made using potentiostat P-582 and potentiometer KSP-4, cyclic voltametric curves were measured using potentiostat P-5827M and register PDP4-002. Potentials were controlled by built-in high-impedance voltmeter working in scheme with potentiostat. Polarization curves were measured in glass cell provided with glass coating with volume 50 mm. When carrying out the measurements the surface of the platinum cathode was coated by appropriate metals and static potential was measured. In some cases there were used tellurium, rhenium, and selenium and platinum electrodes. Every experiment was carried out twice to prove results reproducibility. Temperature in electrolyser was sustained constant within 0.1 °C by potentiostat of U-10 mark. A composition of cathodic deposits of rhenium chalcogenides Re-X (X = S, Se, Te) was defined by the following method. A cathodic deposit, obtained by electrochemical method, was diluted in 10 ml of concentrated nitric acid at heating. After repeated evaporation in water bath there was added 5 n H₃PO₄ to solution. By the extraction, using isoamyl alcohol, rhenium was separated (from tellurium, selenium, sulphur) and then rhenium and tellurium were determined by photometry of tellurium thiocarbamide complex and rhenium thiocyanate at FEK-56. A selenium content was determined by thiocarbamide method. Then, photometry was carried out at the device SF-4 with respect to the zero solution at 390 nm in a cuvette with l = 1 cm.

The rhenium content was determined from a calibration curve made using standard solutions of rhenium. The amount of sulphur was determined gravimetrically.

To estimate the internal stresses of alloys a method of deformation of flexible cathode was used. As the cathode they used rather thin metallic plate with several centimeters length. Plate firmly is secured at its upper part, while its lower end is free to move. As an anode was used platinum plate, which was mounted parallel to the cathode. The cathode on the opposite side of the anode was covered with a thin layer of insulating material (varnish) to obtain the metal's deposition only on one side. As the metal is depositing, under the action of internal stresses occurring in the deposit the cathode plate is bending. To determine accurately the value of bending measurements were carried out using a horizontal microscope with a micrometer scale, model MIR-2. The measurements of micro-hardness of rhenium chalcogenides' alloys were carried out at device PMT-3 by pushing square diamond pyramid with load of 0.005-0.5 kgf.

Diamond tip in the form of a regular quadrangular pyramid pushed in the testing area of sample under load P is applied at a certain time. After removal of the load there was measured diagonally one square imprint remained on the sample surface.

Hardness number N (kgf/mm²) was determined by dividing the load F (kgf) on a notional side surface of remained imprint obtained.

RESULTS AND THEIR DISCUSSION

For the first time using a variety of electrochemical and physical-chemical methods we have revealed the scientific basis of the electrodeposition of rhenium chalcogenides out sulfate, chloride, sulphate and alkaline electrolyte [27-38]. By the temperature-kinetic method and removing the polarization and partial curves nature of polarization at different rates of potential development was determined at a separate deposition of rhenium and chalcogenes and at their joint deposition.

It was established that the electrodeposition of rhenium and chalcogen into the alloy is accompanied by depolarization and it shows the chemical interaction.

Based on the research process of electrodeposition rhenium with chalcogenes conditions were developed for producing semiconductor chalcogenide alloys rhenium Re-X (X = S, Se, Te) of sulphate, chloride and alkali sulphate electrolytes over a wide range of components ratios. The optimum compositions of the electrolyte and electrolysis mode providing obtaining high-quality semiconductor-based alloys of rhenium were determined and some of their electrical properties studied. To investigate the kinetics and mechanism of the joint electrodeposition of rhenium with selenium potentiostatic polarization curves were recorded by an electrochemical method, and cyclic voltammetry.

It is known that in the electrolysis of solutions containing two different ions (metal and chalcogen) able to recover, the alloy's formation occurs, which is a chemical compound, a solid solution or a mixture of the pure components. The chemical and phase composition produced at the cathode precipitation depends on many factors, the main ones being equal potentials of recovery of the alloy components, the value of the electronegativity of the deposited ions, the electrolyte composition, current density, and others.

A number of methods for convergence of the separation potentials of metal ions are known, the most effective of which is the binding of electropositive complexed components ions. If we take into account the fact that formation ability of complex components of many metals more than that of the chalcogen, as well as the fact that the recovery of metal ions, the potentials have a value more negative than the potentials of the ion recovery of chalcogen, it becomes clear that complexed components agent additive in the electrolyte at a joint electrodeposition of metal and chalcogen will be ineffective.

With the aim of approximation potential reduction of metal and a chalcogen ions, when the standard potentials of the deposited metal and the chalcogen very differed and they cathode do not interact with each other to expect the formation of pure components, although such a phenomenon often occurs during the electrolysis ions solutions of two different metals, it is rare at the joint electrodeposition of metal and chalcogen. In this case, there are basically alloys of solid solutions type or chemical compounds. This is facilitated by the very chemical nature of the chalcogen. Chalcogen has high reactivity, easily react with metals affinity for various metals increases with increasing the degree of electronegativity chalcogen, which varies from 2.5 to 2.1 for sulfur and to 2.1 for tellurium.

The high affinity of the chalcogen to metals significantly contributes to joint electrodeposition of metal and chalcogen, deffered sharply by recovery potentials.

At co-deposition of metal chalcogen and reduction potentials of the two components are displaced, and isolation of metal chalcogen on cathode either is facilitated or impeded. The data available in the literature testify to that the electrolysis process is a strong mutual effect of the metal and the chalcogen. Solated chalcogen during electrolysis probably acts on the metal ions in solution, as an additional reducing "agent", reduces the free energy of the metal, in a positive direction and thus, emergence of the alloy process in a field of the facilitates recovery of the metal and a chalcogen. Thus, the alloy flows in appearance potentials significantly more positive than the potential of the separate separation of metal on the cathode.

In order to clarify the nature of the relationship between the composition of the electrolytic rhenium chalcogenide alloy and some factors affecting the electrolysis, studied the influence of various factors (the total concentration of the components, the concentration of acid, complexing, current density, temperature) on the composition and properties of the sediments.

As electrolyte they used the sulfate, thiosulfate, chloride, sulfate and alkaline solutions containing various concentrations of rhenium and chalcogen (S, Se, Te). For the first time, by the potentiostatic temperature-kinetic, ampere-voltaic methods the kinetics and mechanism for the joint and separate electrodeposition of rhenium with chalcogenides from sulfate, thiosulfate, chloride, sulphate and alkaline electrolyte have been studied.

At various speeds the potential sweep determined nature of polarization during deposition of rhenium and chalcogen from different electrolytes and found that the recovery of rhenium in all studied electrolytes occurs primarily through the formation of intermediate compounds or the formation of rhenium oxide (Re_2O_5 , ReO_3). Installed regularity gives a base to conclude that the electrodeposition of rhenium chloride-sulphate electrolyte in the initial portions of rhenium recovery is limited by electrochemical polarization, and then the process is controlled by a mixed kinetics, gradually passing into the concentration. A bit of tellurium at the cathode in the chloride-sulphate electrolyte flows through the emergence of interfaces particles resulting from the previous chemical reaction of dissociation of the complex tellurium. And at more negative potentials process is limited by the mixed kinetics.

Analysis of the results of measurements of cathodic and anodic polarization curves for the joint electrodeposition of rhenium with the chalcogen (S, Se, Te) shows that the co-deposition process is accompanied by depolarization, which proves the formation of a chemical compound or a solid solution based on these compounds and identified the potential range in which to cathode formed compounds of stoichiometric composition.

It is established that co-electrodeposition mechanism of the rhenium with selenium from sulfate and an alkali electrolyte depends on the concentration of divalent selenium formed on the cathode, which optimizes recovery of rhenium ReSe_2 to form chemical compounds [28,31]. But the main role in the chemical co-deposition of tellurium with rhenium tellurium activity associated with its penchant for deep recovery and depolarization during the deposition of tellurium with rhenium from chloride-sulphate electrolyte is what associated with a change in the nature of tellurium electrode. With the formation on the surface of the cathode of divalent of tellurium ions (Te_2^-) occurs co-deposition of tellurium with rhenium (i.e. Te_2^- ions stimulate the deposition of the elements at more positive potentials with high depolarization [29-30]). For the first time there was carried out physico-chemical study of alloy in Re-S system under the joint electrodeposition of rhenium and sulfur from thiourea and thiosulfate electrolyte and on the basis of experimental data suggested interpretation of the cathode processes occurring in the various values of the cathode potential. It has been established that the joint electrodeposition of rhenium with sulfur of these electrolytes is dependent on the adsorption on the cathode colloidal sulfur and as rhenium, and sulfur is released into the alloy depolarization, indicating the formation of chemical compounds ReS_2 [32].

To study the regularities patterns and development of conditions for the production of thin semiconductor alloys of rhenium chalcogenides and clarify the technological features of the processes, ensuring the preparation of thin coatings of these alloys has been investigated the influence of various factors: temperature, current density, the total concentration of components, component ratio, acidity, agitation, and surfactants.

An optimal research composition of the electrolyte and electrolysis mode to produce high-quality semiconductor thin coverings of rhenium chalcogenides from sulfate, chloride, sulphate and alkaline electrolyte has been worked out. The systems studied first studied some physical and chemical properties of thin coatings of alloys of rhenium chalcogenides as the microstructure, phase composition, conductivity, micro-hardness, internal stress, electrical conductivity, the current-voltage characteristics and photoconductivity have been studied first.

It is known that rhenium chalcogenides and solid solutions on their basis are semiconductor materials. The method of thermal probe found that all the alloys of rhenium chalcogenides the p – type conductivity.

It is found that all the resulting coatings have semiconducting properties. The most characteristic physico-chemical properties of alloys by which it is possible to judge the phase structure are resistivity and hardness. Calculated for some typical semiconductor constants, activation energy, sensitivity coefficient, the temperature coefficient of electrical resistance. Thus, the dependence of the resistivity were made of thin films of rhenium chalcogenides on the temperature [34-35].

As has been established that with an increase in the resistivity of the of rhenium chalcogenides films temperature decreases, i.e., there is a "semiconductor" conductivity move. The temperature dependence of the resistivity obeys the normal conductor, exponential sign the entire temperature range investigated. The curves of the temperature depends of the logarithm of the conductivity has two linear sections, which correspond to different values of the activation energy of the carriers. The low - temperature area of conductivity varies slightly with increasing temperature, which corresponds to the impurity region of conductivity. With increasing temperature the transition from impurity conductivity to own takes place.

When comparing our data with published data it was revealed that electrolytic chalcogenides rhenium alloys have a lower electrical conductivity than those obtained by thermal means. The observed difference between the electrical conductivity can be explained by a different crystal size arising from the specific method of preparation. During electrodeposition alloys obtained crystals dimensions much smaller than their crystallization from the molten state.

However, reducing the electrical conductivity of electrolytic deposits it may also be caused by a severe impairment of the crystal lattice or inclusion of impurities into the electrolysis process. In the process of electrodeposition on the electrode alloys the emergence of all the existing types of violations of the crystal lattice can be expected. These disorders are caused mainly by the fact that the deposition precipitation often occurs at higher overvoltage cathode in the presence of competing agents.

The sensitivity factor (B) was calculated on the basis of experimental data characterizing the physical properties of the substance and for ReS₂ samples ReSe₂ and ReTe₂ band gap in the field of intrinsic and extrinsic conductivity was calculated.

From these data it follows that the electrolytic coating of rhenium chalcogenide alloys have very low values of temperature coefficient and electrical resistivity, allowing practical application of these films in the electronic art

Learning the internal stress and microhardness of alloys showed that the mechanical properties of electrolytic deposited alloys are largely different from those of alloys produced by other methods. Also, physical properties of electrolytic alloys can vary considerably depending on the conditions and electrolysis mode. It should be noted that the hardness of the electrolytic alloy is slightly larger than that of the respective metallurgical alloys. Electrolytic deposition hardening due to the inclusion of hydrogen in them, and various impurities, such as surfactants that cause distortion of the crystal lattice. Hardness is a function of the grain; smaller crystal of deposition than pellet, the greater its hardness.

The electrochemical method can obtain a coverage with rather varied and predetermined properties. We have studied the dependence of the microhardness cathode deposits of rhenium chalcogenide alloys of rhenium content in the alloy, and found that, depending on the electrolyte composition and the content of rhenium in the alloy microhardness may be different [36]. The curve changes microhardness of alloys of rhenium chalcogenides passes through a maximum. The maximum in the curve of microhardness of the alloy, which corresponds to X-ray analysis ReS₂ compound ReSe₂ and ReTe₂. It can be assumed that a high value of microhardness of alloys of this composition is due to the presence of chemical compounds at this site.

These data confirm once again that during the electrodeposition of rhenium with chalcogens on the cathode thin chemical coating of rhenium chalcogenides is obtained.

As well it was studied, that internal stresses are the result of all changes in the sediment, and the result of the change and the number of foreign substances included.

Internal stresses in the electrolytic deposition, characterizing their compressed or stretched state, exist in almost all cases. As a result, cracking occurs in deposition, leading to an increase in the number of pores, which reduces the quality of the corrosion-protective coating. The appearance of internal stresses often weakens the sludge adhesion to the substrate.

Internal stress may be formed as a result of interaction of the metal with the included impurities, the formation of chemical compounds, the volume of which is greater than or less than the volume of the original components. As a result, volume variation may occur in the internal voltage deposition.

Thus, in the actual conditions it is possible as a metal deposition empty action of one of these factors, and operated simultaneously for several reasons.

Therefore, in the elucidation of the causes of the internal stresses in each case the selection conditions may contribute to the electrodeposition of metals with predetermined values of the internal stresses.

Calculation of the internal stress of electrochemical deposition was determined by bending the cathode]. Internal stresses in the deposition causes voltage of opposite sign in the lining, which lead to its distortion and dimensional changes.

There has been studied the microstructure of anodic films chalcogenides rhenium Re - X (X = S, Se, Te), obtained electrochemically from various electrolytes [36]. The influence of electrolysis conditions and the concentration of the electrolyte components on the microstructure of the resulting films of rhenium chalcogenides has been studied. The appearance and structure of electrolytic deposits of rhenium chalcogenides was obtained by an electrochemical method, depending on the electrolysis conditions. In the process of studying the conditions of the electrolysis revealed that to obtain high-quality rainfall Re-Se the most suitable temperature 75-80°C. Microscopic study of the surface of the cathode deposits Re-Se showed that the cathode obtained dense, fine-grained black coating. Particularly strong influence on the quality of the sediment has a current density. More qualities deposits are obtained at low current densities. Increasing the current density leads to a gradual deterioration in the structure

of cathode deposits. On the micrograph ReSe₂ deposits derived from an alkaline electrolyte at low current densities (1 - 5 mA/cm²) at the cathode produced gleaming, fine-grained sediments in 5 microns of thick. At current densities higher than 10 mA/cm² on the cathode forms a fairly loose black deposition that easily lays on the metal base.

In order to elucidate the crystal structure, phase composition, and to confirm the results of the studying of the microstructure of rhenium chalcogenides thin coatings there was carried out X-ray study produced alloys DRON - 3, C - radiation[30-34].

At a cathode current density of 4 mA/cm², using an electrolyte of composition 0.05 M NH₄ReO₄ + 0.05 M SeO₂ + 1M NaOH, we obtained lustrous ReSe₂ (54 wt % Re) coatings. The formation of ReSe₂ was confirmed by XRD. This compound crystallizes in the triclinic system with lattice parameters a=6.7275 Å, b=6.6065 Å, and c=6.7196 Å. With the aim of clearing out the crystalloid structure of the obtained thin coverings ReS₂, their X-ray graphical investigation was carried out. According to RPA it was established, the ReS₂ complexes are crystallized in a triclinic syngony with the parameters of elementary cell: a=6.455Å, b= 6.363 Å, c =6.401 Å .

Thus, on the base of carried out experimental data there was elaborated an optimum regime and a composition of electrolyte for obtaining qualified semiconductive coverings of rhenium-sulphur alloy with 73-76% of rhenium content (according to rhenium mass) and 24-27% of sulphur, which are very close to ReS₂ complex. By thermo probe method it has been established, that all alloys of rhenium sulfide have p-type conductivity.

According to X-ray phase analysis data, ReTe₂ crystallized as an orthorhombic compound with unit cell parameters a = 1.301 nm, b = 1.307 nm, and c = 1.428 nm.

There has recently been considerable interest in the materials where an electric field reversibly changes resistance [39-40]. One of the many interesting, practical and scientific points of view, phenomena arising in strong electric fields, is a switching effect.

Briefly, the "switching effect" is dramatic, reaches several orders of magnitude of the electrical patterns change when subjected to a sufficiently strong electric field. Shift effect - a reversible process and is a sharp change in the electrical conductivity of the material, depending on the input voltage. The nature, happening of the high speed of the electrical changes in the process by several orders of magnitude, is not currently understood[39-40].

In modern semiconductor technology are widely used as the thick so thin layers. In the high-speed RAM used thin films, which are currently the most widely used memory element. In the long-term memory the computer uses relatively thick coatings - thickness of the order of several tens of microns.

We investigated features of the VAX system alloys Re-X₂ (X - S, Se, Te), depending on the thickness of the coating, the composition and temperature of the electrolyte. For this purpose, filmed static and dynamic current-voltage characteristics of thin coatings rhenium chalcogenides produced electrochemically [33-38].

The test material was used as the diode structure of thin coatings of rhenium chalcogenide alloys produced electrochemically.

To study the current-voltage characteristics of rhenium chalcogenides alloy thin coatings are recommended, obtained from the following electrolytes:

1. Thin coatings ReTe₂ (Re - 42%, Te - 58%). Electrolyte (mole / l):
0,05 NH₄ReO₄ + 0,05TeO₂+1,5HCl + 1,5 H₂SO₄ + 0,01 (NH₄)₂SO₄; i_k = 5 mA/cm²; t = 75°C. The electrode - copper. Coating thickness = 8 μm.

2. Thin coating ReSe₂ (rhenium disulphide). Alloy composition (Re - 54%, Se - 46%). Electrolyte (mole/l):
0,03 NH₄ReO₄ + 0,03 SeO₂ + 2,0 H₂SO₄; i_k = 4 mA/cm²; t = 75°C. The electrode - copper. Coating thickness = 8 μm.

3. Thin coating ReS₂ (rhenium disulphide). Alloy composition ReS₂ (Re-74,4%, S-25,6%). Electrolyte (mole/l):
1.0·10⁻³ NH₄ReO₄ + 1,5·10⁻³(NH₂)₂CS + 1.23· 10⁻³H₂SO₄;
i_k = 35 mA /cm²; t = 60°C. The electrode - copper. Coating thickness = 8 μm.

Consideration of the data obtained in this study shows that, based on an alloy of rhenium chalcogenide structure is controlled by VAX with S and N, designated portions of the operating system in forward and reverse current directions, respectively, and has a mass storage properties [38].

Therefore, unlike other devices with negative resistance (NR), the elements on the basis of said alloy chalcogenide rhenium have a simple manufacturing techniques capable of operating over a wide range of temperatures, and these properties suggest that based on these alloys devices can be widely used in a variety of remote control devices, automation and computer technology.

Solution to a majority of the problems in chemistry and chemical technology is bound up with carrying out the complicated and expensive experiments. Hence clear is the significance of the methods of optimum planning of the experiment permitting to reduce essentially the expenditures of time and material means on carrying out the research work in a number of cases.

The methods of optimum planning of experiment allow one to use the mathematical apparatus not only of stage at treatment of measurement results, but also at making ready and carrying out the test.

There has been carried out the mathematic model and process optimization for joint deposition rhenium with chalcogenides by Box and Wilson method. Equations have been completed for regression process of deposition of rhenium chalcogenides thin films binding composition of cathodic deposits with parameters of electrolysis. In the present work for receiving the mathematical model linking conditions of deposition of rhenium chalcogenides alloy ReX_2 ($X = S, Se, Te$) with a composition of cathodic sediment, as independent variables has been investigated. [41].

It is estimated that all the data obtaining concern equation regression exactly describe of the research process and allowed to determinate the composition of cathodic deposits for asked electrolysis modes.

CONCLUSIONS

For the first time using a variety of electrochemical methods, revealed the scientific basis of joint electrodeposition of rhenium with chalcogens patterns of different electrolytes and synthesized new semiconductor coating of rhenium chalcogenides. The electrolyte used sulfate, tiosulphate chloride-sulphate and alkaline solutions containing various concentrations of rhenium and chalcogen (S, Se, Te) were applied. Potentiostatic for the first time, the temperature-kinetic, volt-amperometric methods to study the kinetics and mechanism under the joint and separate electrodeposition of rhenium with chalcogenides of sulfate, thiosulfate, chloride, sulphate and alkaline electrolyte.

REFERENCES

- [1] Speranskaya Y.F.. In coll. Electrochemistry of Rhenium. Publishing House "Gylym", Alma-Ata, 1990, 253.
- [2] Pallant A.A. Monograph Metallurgy of rhenium. Nauka, 2007, 298
- [3] Naor, Eliaz N. Ammtiac quarterly. Properties and applications of rhenium and its alloys, (2010) 5(1) 11-15
- [4] Bouroushian M.. Electrochemistrty of Metal Chalcogenides. 2010, XII, 358
- [5] Schrebler R., M. Merino, P. Cury, et al., Electrodeposition of Cu-Re alloy thin films, Thin Solid FFilms 388 (1-2) (2001) 201-207.
- [6] Contu F., S.R.Taylor. Further insight into the mechanism of Re-Ni electrodeposition from concentrated aqueous citrate baths, Electrochemica. Acta. 70 (2012) 34-41.
- [7] Hahn B.P., K.J.Stevenson. Electrochemical synthesis and characterization of mixed molybdenium-rhenium oxides, Electrochimica. Acta. 55 (220 (2010) 6917-6925.
- [8] Pashova V., L.Mirkova, et al., Electrocatalytic materials of NiCoRe electrodeposited alloy for alkaline water electrolysis, ECS Transactions 25 (35) (2010) 395-401.
- [9] Zabinski P., A.Franzczak, et al., Electrodeposition of functional ni-re alloys for hydrogen evolution, Ecs Transactions 41 (33) (2012) 39-48.
- [10] Takada A., K.Okada, Electrodeposited Co-Ni-Re-W-P thick array of high vertical magnetic anisotropy, Magnetism, IEEE Transactions 41 (10) (2005) 41.
- [11] Lingling W., T.Liming, H.Greifang, Preparation of amorphous rare-earth films of Ni-Re-P (Re-Ce, Nd) by electrode position from an aqueous bath, Surface and coal. Technol. 192 (2-3) (2005) 209-212.

- [12] Povetkin V., S.Skifsky, E.Koreshkov, Electrolyte for deposition of Alloy copper-rhenium Patent 224560, MPK 25L3/38, Tyumen, Russia, 2004. (in Russian).
- [13] Agapova L., et al., Electrolytical deposition Re-contained alloys from aquatique liquids, Renum. Scientific Investigations, Technological Development, Industrial Application, 2013, p.90. (in Russian)
- [14] Guro V., Reducing waste of Re- contained alloys with obtaining pure ammonium perrenhate, in: Conference of Renum. Scientific Investigations, Technological Development, Indestrial Application, 2013, p.82. (in Russian)
- [15] Berk O., N. Eliaz and E. Gileadi " The Initial Stages of electrodeposition of Re-Ni Alloys". Journal of the electrochemical society, 161 (5) D219-D226 (2014)
- [16] Thomas G.Gray, Christina M.Rudzinski, Emily E.Meyer and Daniel G.Nocera. Excited-State Distortion of Rhenium (III) Sulfide and Selenide Clusters. J.Phys.Chem.A,2004, 108 (16), pp3238-3243
- [17] Contu F., S.R.Taylor. Further insight into the mechanism of Re-Ni electrodeposition from concentrated aqueous citrate baths. Electrochimica Acta. 2012, 70, 34-41
- [18] Sagiv M.C., Noam Eliaz, et al. Incorporation of iridium into electrodeposited rhenium-nickel alloys. Electrochimica Acta, 2013, 88, 240-250
- [19] Naor A., N.Eliaz, et al. Electrodeposition of rhenium-nickel alloys from aqueous solutions. Electrochimica Acta. Journal homepage: 2009, 6028-6035.
- [20] Naor Adi, Noam Eliaz, et al. Direct Experimental Support for the Catalytic Effect of Iron-Group Metals on Electrodeposition of Rhenium. Electrochemical and Solid-State Letters. Elec. Sol.-State Lett. 2010, 13(12), D91-D93.
- [21] Naor A., N.Eliaz, et al. electrodeposition of Alloys of Rhenium with Iron-Group Metals from Aqueous Solutions. J. electrochem. Soc. 2010, 157(7), D422-D427.
- [22] Enyashin A, Iqor Popov. Stality and electronic properties of rhenium sulfide nanotubes. Phys. State Solidi B, 246, № 1, 114-118 (2009)
- [23] Nemudry A., R.Scholhorn, Re₆S₁₂, a new binary rhenium cluster chalcogenide, J.Chem. Soc. Chem Comm. (1994) 2617-2618.
- [24] Fischer C., et al., Structure and photoelectrochemical properties of semiconducting rhenium cluster chalcogenides: Re₆X₈Br₂ (X=S, Se), J.of Alloys and Compounds 178 (1-2) (1992) 305-314.
- [25] Schubert B., H.Tributsch, Electrochemically formed transient ReS₂/Re₂O₇ heterojunction with high energy conversion efficiency, Journal applied Electro Chemistry 20 (1990) 786-792.
- [26] Bob L., K.Wheeler, PHotoelectrochemistry of p-ReS₂ and p-ReSe₂ in aqueous solutions, J.Electrochem. Soc. 133 (2) (1986) 358-361.
- [27] Salakhova E.A.. The Electrochemical Deposition of Rhenium Chalcogenides from Different Electrolytes. Journal of Chemical Engineering and Chemistry Research. Vol.1, num.3, 2014, pp.185-198
- [28] Salakhova E.A., Electrochemical Production of Thin Films of System Rhenium –Selenium Alloys. Thev Journal "Inorganic Materials", (2003) 39, 142-146.
- [29] Salakhova E.A., Receiving thin films Re-Te from chloride-sulfate electrolyte and the influence of the various factors on composition of alloSalakhova E.A., V.A.Majidzada, Electrochemical preparation of Thin Rhenium-Tellurium Coatings Chloride-Borate Electrolyte. Russian Journal of Electrochemistry (2011) 47(8) 877-882
- [30] Salakhova E.A., A.M.Aliyev, Obtaining the thin semiconductive covering Re-Se from sulphate electrolyte, Journal of Advanced in Materials and Physics Chemistry (2012) 2(4) 253-255
- [31] Salakhova E.A., A.M.Aliyev, K.F.Ibragimova, The obtaining of thin films Re-S from tiocarbamid electrolytes and influence of various factor s on the alloys composition, American Chemical Science Journal, 2014, 4(3), pp338-348
- [32] Salakhova E.A., V.A.Medjidzada, et al. the Electro-physical properties of rhenium chalcogenides thin films Journal of Chemistry and Chemical Engineering, 2013, 7(5), 518-521.
- [33] Salakhova E.A.. "The electrochemical production of thin films of rhenium chalcogenides". Monograph, LAP LAMBERT Academic Publishing, 2014, 108p.
- [34] Salakhova E.A., D.B.Tagiyev. Semiconducting properties of thin coatings of rhenium chalcogenides. Materials and Technologies for Energy Efficiency, 2015. p.58-63
- [35] Salakhova E.A., D.B.Tagiyev, K.F.Ibrahimova, P.E.Kalantarova. The investigation of microstructure and the X-ray phase analysis of Re-X alloys(X=S,Se,Te). Journal of Materials Science and Chemical Engineering, 2015, p.1-8, vol3, 10.
- [36] Salakhova E.A., D.B.Tagiyev, P.E.Kalantarova, K.F.Ibrahimova. Physico-chemical properties of thin rhenium chalcogenides coatings. Journal MSCE, 2015, 3, p.82-87

-
- [37] Salakhova E.A., D.B.Tagiyev, P.E.Kalantarova, N.N.Khankishiyeva. Investigation of volt-ampere characteristics of diodic structure on base of thin films of rhenium chalcogenides. *International Journal of Engineering Sciences & Research Technology*. 5.(3), March 2016.
- [38] Zamanova E.N., S.M.Bagirova, M.A.Jaffarov. Switching structures based on films CdS. 10.02.1987 №977-B87
- [39] Kutopin S.A., "The switching effect in amorphous semi-conductors and fields of their use. Moscow, CNI,Electronika, 1973, vol.4 (110), p.24
- [40] Salakhova E.A., D.B.Tagiyev, N.N.Xankisiyeva, A.F.Heybatova. Mathematical Modelling and Optimization of the Process for Chalcogenides Rhenium Alloys Obtaining. *IJECCE, Journal, Volum-6*, Issue-3, may 2015, p.370-374