

**INVESTIGATION OF VOLTAMPERE CHARACTERISTICS OF DIODIC STRUCTURE
ON BASE OF THIN FILMS OF RHENIUM CHALCOGENIDES****E.A.Salakhova, D.B.Tagiyev, P.E.Kalantarova, N.N. Khankishiyeva**Laboratory of Electrochemistry of Rhenium Alloys and Electrocatalysis, Institute of Catalysis and
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ABSTRACT

Were investigated electro-physical properties of thin layers of rhenium chalcogenides' alloys, their dynamical and static volt-ampere characteristics. During the investigation of static and dynamical ampere-voltaic characteristics of rectifying contact of aluminium and rhenium chalcogenides' alloys the switching effects were found. The studying of the data got at present work shows the structure based on alloy of rhenium with chalcogenides AVC with S- and N sections of NR with straight and reverse current directions.

KEYWORDS: rhenium chalcogenides, semi-conducting materials, volt-ampere characteristics, electronic technics.

INTRODUCTION

Rhenium (Re) is a heat-resistant metal, which has won great acclaim as a high-tech material, which shows an exceptional combination of properties. This metal has some specific properties and finds its application in various fields of semi-conducting industry. In recent years a sphere of using these compounds was substantially widened space technique, electronics, IT sector and so on. There was also emerged a necessity to investigate their physical and chemical properties and to elaborate effective technology of getting alloys basing on these elements. Substantial mechanical strength, hardness, high electrical impedance and other properties of rhenium alloy rhenium and its alloys to be widely used in various fields of technique as well for production of special coating [1-5]. There are various methods for obtaining thin films of rhenium semi-conducting alloys. But the analysis of known methods of obtaining rhenium chalcogenides thin films showed that the most perspective and less expensive is electrochemical method which has those advantages, that it does not need sophisticated equipment, hightemperatures and alloys to produce an alloy of high purity. Using this method it is easy to control thickness, a composition of a coating, and, varying electrolysis regime, to get coatings with demanded composition. [6-10]

An investigation of electro-physical properties of semi-conducting materials pursues two aims. First these properties allow to become more deeply acquainted with physics-chemical nature of matter: kind of chemical bond, disorder in stiochiometric composition, impact of foreign matters and so on. Second, fields of technical application of semi-conductors mainly depend of their electro-physical and optical properties. So these properties of semi-conducting materials are to be considered in that minimal volume, that is necessary for right orientation of their practical use. As in all devices semi-conducting materials are using mainly in a form of thin films, it is very interesting to investigate a diode structure, composed from thin films on a base of rhenium chalcogenides. A use of alloys in a form of thin films in memory chips allows to increase substantially a speed of computers, as well as to minimize their size and reduce power consumption.

Recently they show a considerable interest to the materials in which under the effect of the electric field the resistance changes reversibly [11-12]. One of the numerous interesting phenomena from practical and scientific points of view, emerging in the strong electric field is an effect of switching over. Briefly "the effect of switching over" consists in the abrupt changes of electro resistance of the samples several times by value, at attaching to it quite strong electric field. The effect of switching over is the reversible process and consists in a sharp change of electro conductivity of a material depending on a value of a feeded tension. Nature of the process of changing electro conductivity several times in value, occurring with a high speed, has not been cleared yet at present. In modern technology of semiconductors both the flat and thin layers find a wide application. In the fast acting operative store they use the thin films, which at present are the most spreaded element of memory. In long term store of computer comparatively flat coatings several tens of microns in width are used. Recently an interest has increased to the phenomena in a solid connected with the negative resistance (NR). Most authors observed the negative

conductivity on thin oxide films, crystalline and glassy semiconductors. One of the important parameters of this class materials is the threshold tension of which semiconductor from a high ohmic state transfers into a low ohmic one. In connection with this, from the practical point of view the possible controlling a value of this parameter is of great importance.

Investigation on chalcogenide glasses display that a value of threshold tension depends on a width of a sample, temperature and nature of admixtures in semiconductors.

In some works by taking the dynamic and static volt-ampere characteristics it has been established that chalcogenides of rare metals in contact with aluminium electrode possess the effect of switching over with an electric store. Earlier we have obtained [13-19] thin films of rhenium chalcogenides in various electrolytes. The aim of the present work is a study of the peculiarities of VAC alloys of the system Re-X₂ (X-S, Se, Te) depending on width of coatings, composition and temperature of electrolyte. For this purpose there were taken the static and dynamic volt-ampere characteristics of thin coatings of rhenium chalcogenides, obtained by electrochemical way. The electric properties of comparatively scantily explored chalcogenide semiconductors and their contacts with different metals have been investigated. To study VAC. of rhenium chalcogenides alloys there were recommended thin coatings, received from the following electrolytes: 1. Thin coatings ReTe₂ (Re-42%, Te-58%), Electrolyte (mol/l): 0.05 NH₄ReO₄ + 0.05 TeO₂ + 1.5 H₂SO₄ + 0.01 (NH₄)₂SO₄; i_k=5mA/sm²; t=75°C; Electrode is copper. Width of coating=8µm. 2. Thin coatings ReSe₂ (diselenide of rhenium). Composition of the alloy (Re-54%, Se-46%). Electrolyte (mol/l): 0.03 NH₄ReO₄ + 0.03 SeO₂ + 2.0 H₂SO₄; i_k=4mA/sm²; t=75°C. Electrode-copper. Width of a coating=8µm. 3. Thin coatings ReS₂ (disulphide of rhenium). Composition of the alloy ReS₂ (Re-74.4%, S-25.6%). Electrolyte [mol/l]: 1.0 • 10⁻³ NH₄ReO₄ + 1.5 • 10⁻³ (NH₂)₂CS₂ + 1 • 2.3 • 10⁻³ H₂SO₄, i_k=35mA/sm²; t=60°C. Electrode - copper. Width of a coating=8µm.

MATERIALS AND METHODS

Polarization measurements were carried out in three-electrode glass cell with water-jacket. Polarization curves were measured by potentiostat P-5827 M and 2D register PDGM-002. Velocity of involution was 40 mV/s. As working electrodes were used platinum and tellurium ones with surface 0.15 sm², chlorine-silver electrode was used as electrode for comparison and platinum plate with surface 4 sm² was used as anode. Acidity of solution was defined by pH-meter 673 M with glass electrode and was 2.5-3.0. The temperature of electrolyte was controlled by thermostat IN. The electrolyses were carried out in interval of temperatures 298 - 353°K. Dynamical volt-ampere characteristics of rectifying contact of aluminium and alloys measured accordingly to scheme with use of oscillograph with special device powered from of generator of sinusoidal voltage G3-34 type with working frequencies range from 23 tp 2000 Hz. This scheme allows to see right and reverse sections of AVC separately.

RESULTS AND DISCUSSION

In Fig1. the typical volt-ampere characteristics of diodic structure of the alloys of a various composition, taken in a static regime, is presented. Static VAC, as is seen in Fig. 1. in an initial state at straight direction of current the diodic structure is in a high ohmic state. In the beginning at low values of the electric tension (U), current (I) at passing through an alloy increases linearly, depending on tension of the electric field, i.e. Ohm law is observed. Under tension U=U_{th} (for the given samples is equal to 4V respectively) from high ohmic stage to low ohmic stage is observed, with this low ohmic state is preserved even in case of lack of tension on a device. As is seen, all the alloys of rhenium chalcogenides possess switching over properties, i.e. resistance of the sample considerably decreases under effect of the electric field, exceeding a threshold value. VAC presented in Fig. 2., it is possible to distinguish three characteristic sections: horizontal, depicting high ohmic state (OS), vertical corresponding to a state with a low resistance (AB) and the third, connecting the edge points of a high-ohmic and a low ohmic states (OS). On case of this figure it is possible to look into the basic regularities of the phenomenon. On the first section corresponding to high ohmic state, dependence of current on tension has a linear character in an initial section this dependence is an ohmic one. At reaching a device increases, while the tension decreases. This process is depicted by section AB. An inclination of curve AB depends on a value of inner resistance of the source of feeding of the sample. With increase in resistance of a source steepness of the incline falls and is determined by own negative differential resistance of switching over element

A high-conducting state BC is characterized by non-ohmic dependence of current on tension. The resistance of contact will remain high ohmic at any change in reverse tension, right up to hole. To take contact from a high ohmic state it is possible only with one way-to run through it current of straight direction, after what at reverse direction of current, contact will turn out again in a low ohmic state. An interesting property of contact appeared to be "memorizing" its state within a long time, even at zero shift. Even more unusual turned to be that a value of

current of commutation depends on maximum value of direct current, running through contact. To make flow a current of definite value in straight direction through contact, it is possible to set beforehand value of commutation current.

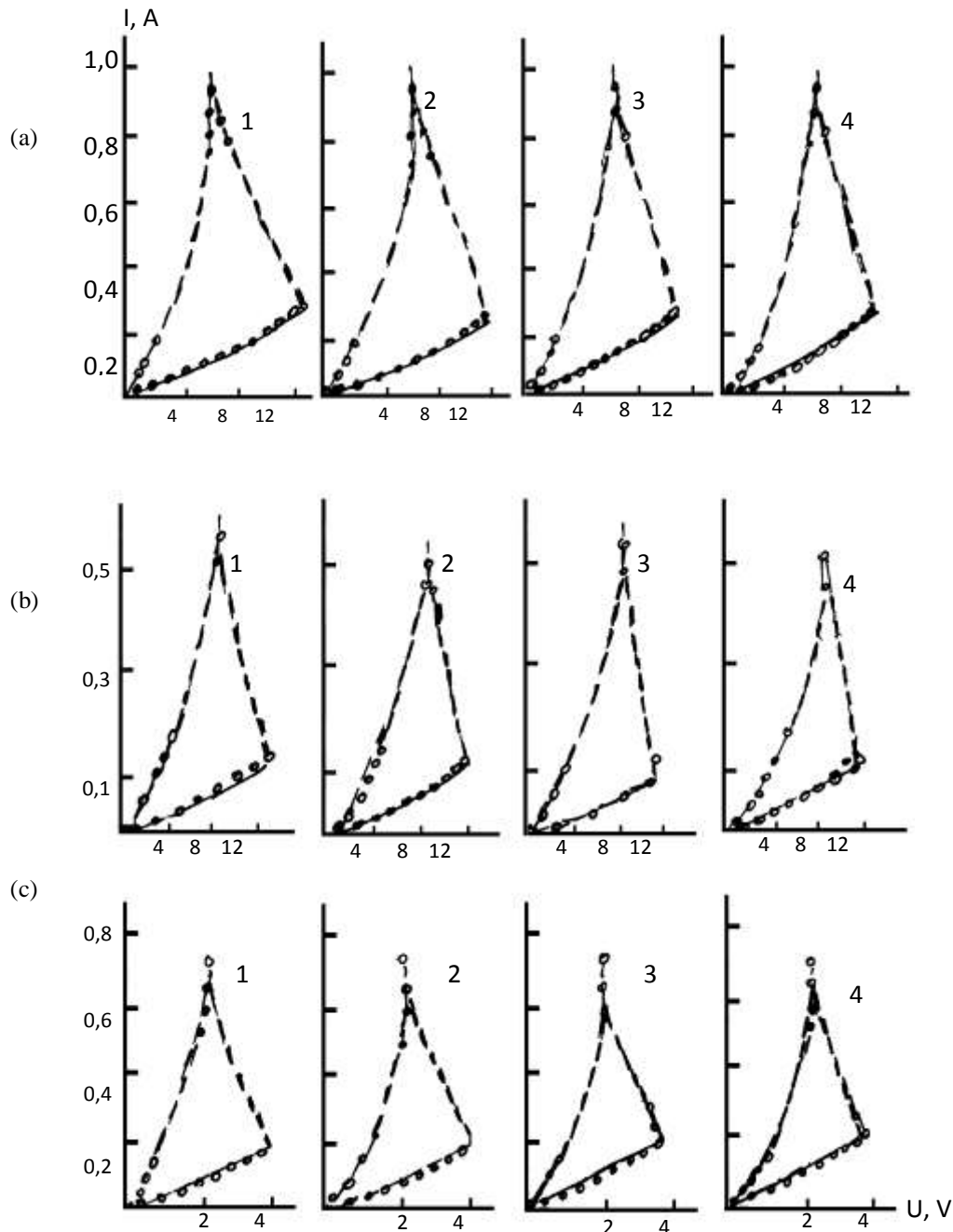


Fig.1. Volt-ampere characteristics of the alloys ReS_x (a), $ReSe_x$ (b), $ReTe_x$ (c) at $x=2(1)$; $1.96(3)$; $1.90(4)$

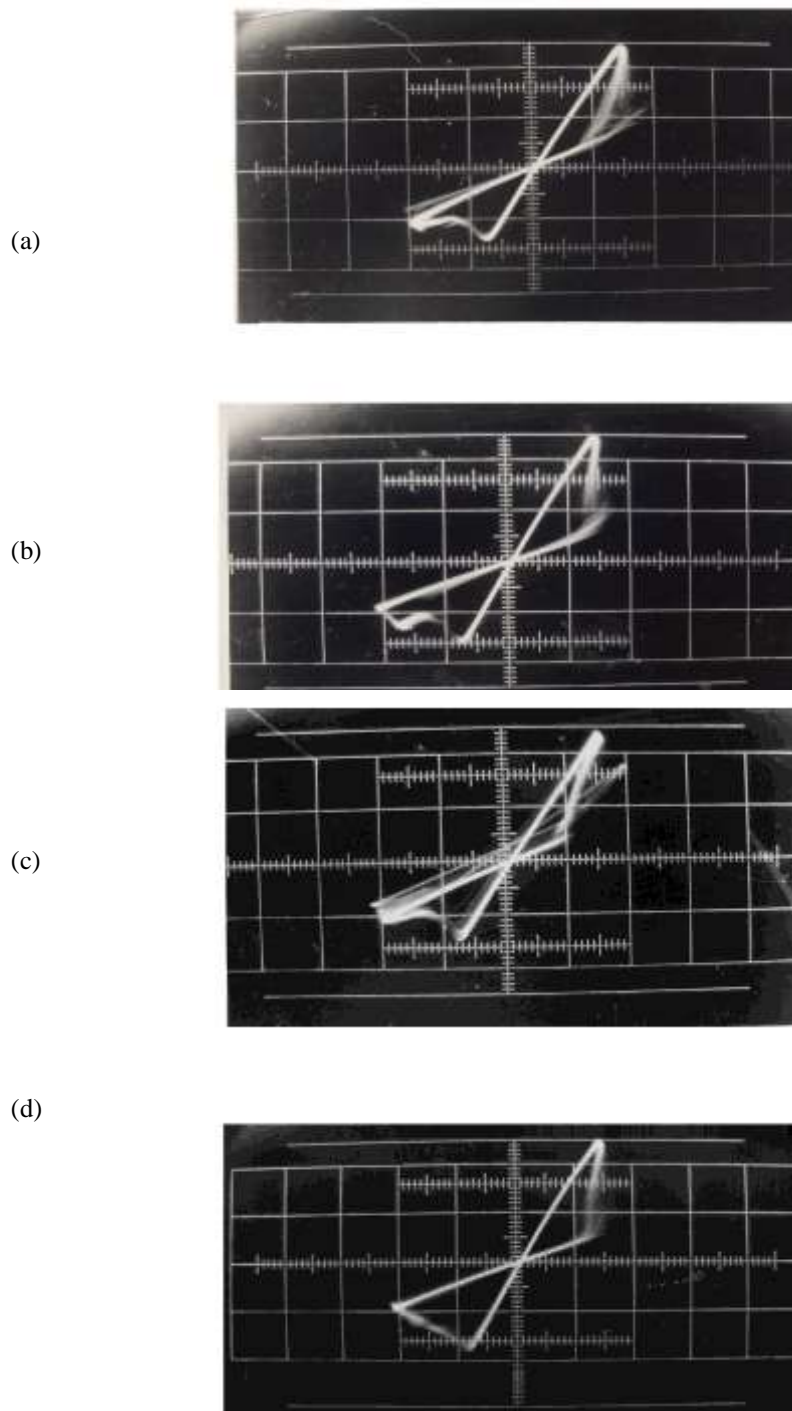


Fig.2. Dynamical volt-ampere characteristic of $Me-ReXe_2$ ($X = S, Se, Te$); a) alkaline electrolyte $Me-ReTe_2$, b) xloride-sulfate electrolyte $Me-ReTe_2$, c) sulfat electrolyte- $Me-ReSe_2$, d) thiourea electrolyte $Me-ReS_2$.

In contact of a metal with some chalcogenides there was observed the double-sided guided relay effect. At both directions of current, the contact is initially in high ohmic state at achieving critical tension U_{cr} . In a straight direction of current, contact resistance rapidly decreases and current increases by leap. With this, contact becomes low ohmic at both directions of current. In reversed direction when current reaches some critical value. Yes, contact resistance sharply increases, current decreases by leap and contact transfers again to high ohmic state. Besides the static VAC, there were also studied the dynamic characteristics of diodic structure $Me-ReX_2$ (Fig.2.) and (Fig.3.). As is known volt-ampere characteristics may be received either by measurement of current an tension by the points

through volt-ampere and amperimeter or using oscillograph. The second way of taking VAC-oscillographic one has a number of advantages, which afford possibility of visual supervision of VAC, as well as its change from time. Characteristic feature of VAC was also an existence on them the sections of negative resistance (NR) (Fig 2.) The section NR is that section where increase in current ΔI and tension ΔU are opposite by sign (i.e. negative increase in current ΔI corresponds to positive increase in tension and vice versa). The section AB and BD correspond to a field of negative (NR), whereas BD is a field of switched on state (device is open). (Fig3). At this time switching over takes place at the point A where $\frac{dU}{dI} = 0$. At the point D, where also $\frac{dU}{dI} = 0$, the device transforms into a close state. The section DO represents a reversed branch of VAC, when a structure transfers into high ohmic state. At this section $\frac{dU}{dI} > 0$ and by order of a value corresponds to the differential resistance. In Fig.4. the dependence a width of the samples $ReX_2(X-S, Se, Te)$ is cited. As is seen at $d \leq 10 \mu m$ for ReS_2 , $d \leq 15 \mu m$ for $ReSe_2$ and $d \leq 20 \mu m$ for $ReTe_2$ a value of U_{th} practically constant. It is associated with the notions of electronic mechanism U_{th} of switching over, which is conditioned mainly by the process of filling and subsequent devastation of trap centres in a prohibited zone of the studied phases. At $5 \leq d \leq 10 \mu m$ there is observed dependence of U_{th} a width of the samples which is of exponential character.

Exponential character of $U_{th}(d)$ testifies to that in the samples of the indicated width an electronic nature of switching over mechanism becomes evident. Like model explains an existence of a field of the negative resistance and time of delay before switching over and formation of the thread-like channels. An essential drawback of switching devices is non-stability of U_{th} . One of the ways of increasing stability of U_{th} is thermo stabilization.

We have made an attempt of increasing stability of U_{th} by periodical influence of tension at greater sequence of switching. At has been established that after 20-30 multiple switching over for $ReSe_2$ and 25-35 multiple switching over for $ReTe_2$, is being U_{th} stabilized. After this at long enduring a sample, U_{th} practically doesn't change (Fig.5.). According to $U_{th}(1/T)$ (Fig.6) in a range of 77-140k, at a rise in temperature the threshold tension decreases in dependence close to exponential one. In the range of 140-400 k, U_{th} practically doesn't depend on temperature and transforms into characteristic close to saturation. After this at long enduring the samples $ReSe_2$, U_{th} practically doesn't change. Note that

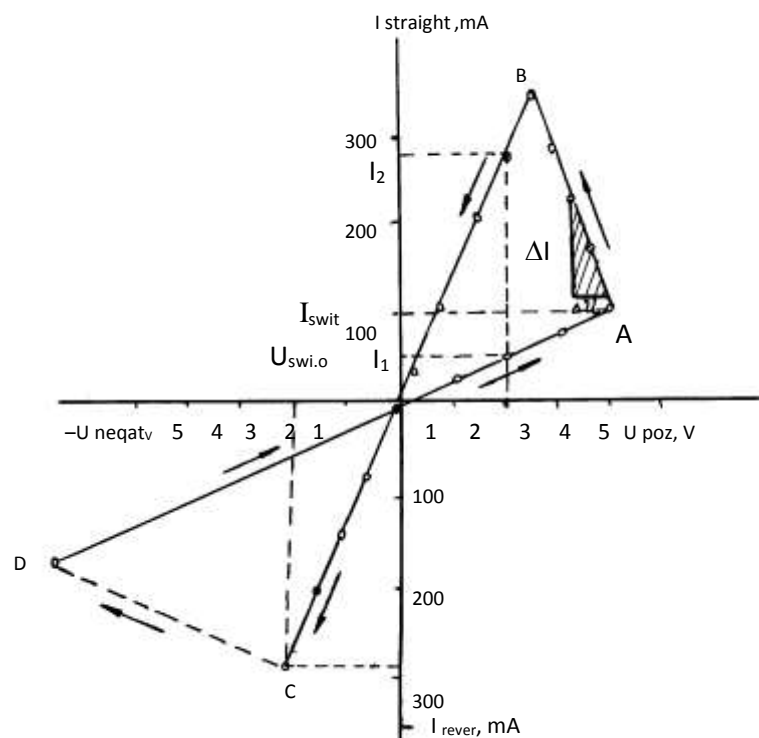


Fig.3 . Static VAC with a field of the negative resistance

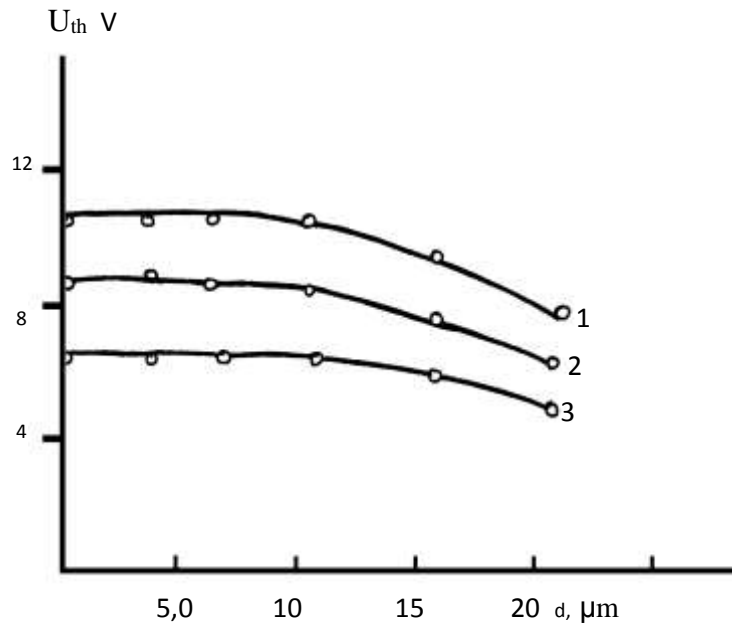


Fig.4. Dependence of tension of threshold switching over on a width of the samples ReS_2 (1), $ReSe_2$ (2), $ReTe_2$ (3)

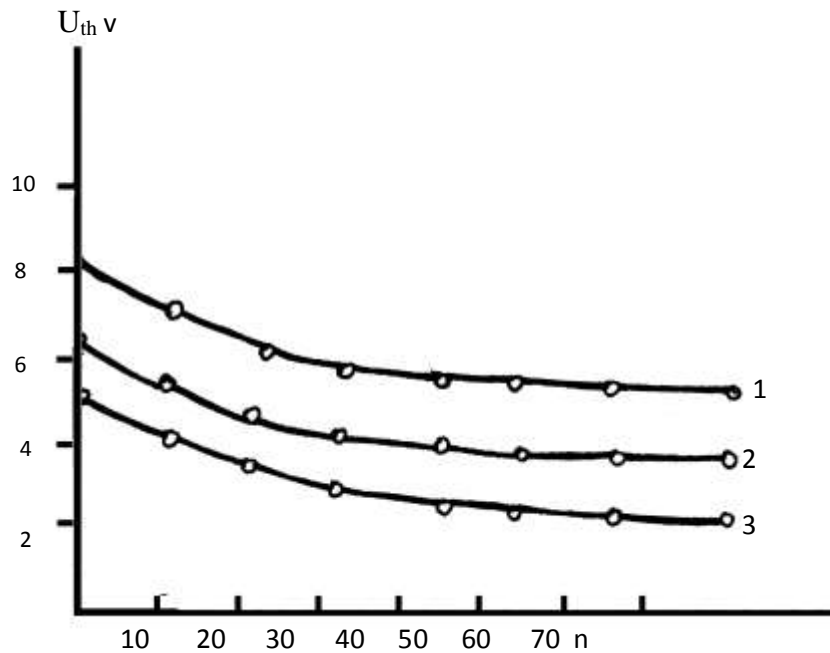


Fig.5. Dependence of tension of threshold switching on a number of switching for the samples ReS_2 (1), $ReSe_2$ (2), $ReTe_2$ (3)

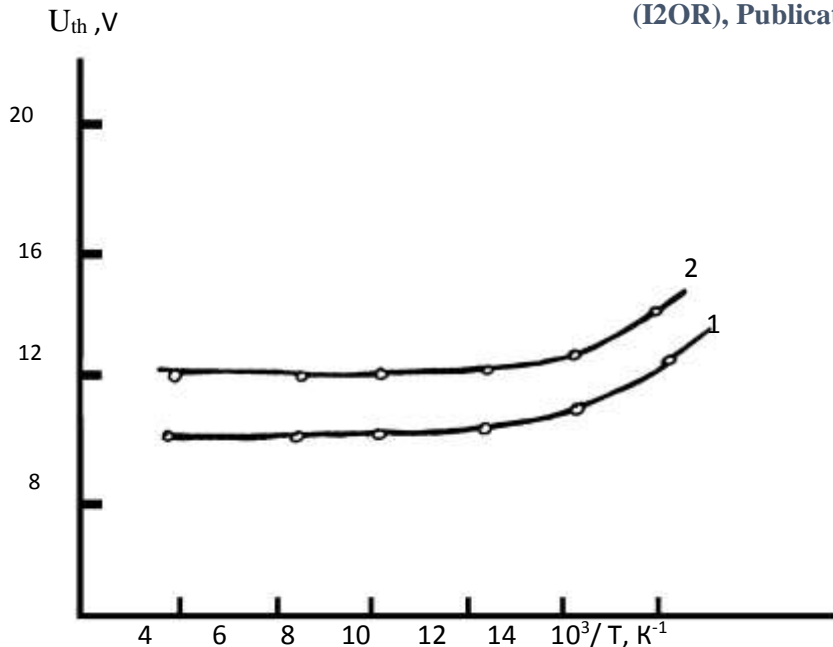


Fig.6. Temperature dependence of tension of threshold switching for $ReSe_2$ (2), $ReTe_2$ (1)

The obtained results on investigation of VAC of ReX_2 alloys permit to draw the following conclusions: at creation of the quick-working switching devices as the elements of microelectronics and computer technics, thin filmed samples are to be received which are less sensitive to temperature and do not practically have dependence of U_{th} on a width of the active field of switching element.

Consideration of the data obtained in the present work shows that a structure based on rhenium chalcogenide alloy has governable VAC with S and N, marked by the sections of NR in direct and reverse directions of current respectively and possess memorizing properties. Thus, in contrast to the other devices with the negative resistance (NR), the elements on a base of the indicated alloy of rhenium chalcogenide have a simple technology of making, capable of working in a wide range of temperatures, and these properties allow us to suppose that these devices based on these alloys may be widely adopted in the diverse mechanism of telemechanics, automated mechanisms and electronic technics.

CONCLUSION

1. Were Investigated electro-physical properties of thin layers of rhenium chalcogenides' alloys, their dynamical and static ampere-voltaic characteristics. During the investigation of static and dynamical ampere-voltaic characteristics of rectifying contact of aluminium and rhenium chalcogenides' alloys the switching effects were found.
2. The studying of the data got at present work shows the structure based on alloy of rhenium with chalcogenides AVC with S- and N sections of NR with straight and reverse current directions.
3. In contrast to other devices with NR, elements based at mentioned alloy have simple production technology and are able to work in wide range of temperatures. This property allows to suggest that devices based at alloy of rhenium chalcogenides may find wide use in various gadgets for tele-mechanics, automatics and computing technique.

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REFERENCES

1. E.F.Speranskaya.. In coll. Electrochemistry of Rhenium. Publishing House "Gylym", Alma-Ata, pp.253,1990
2. A.A. Pallant. Monograph Metallurgy of rhenium. Nauka, 2007, 298
3. A.Naor, N.Eliaz . Ammtiac quarterly. Properties and applications of rhenium and its alloys, (2010) 5(1) 11-15

4. M.Bouroushian. Electrochemistry of Metal Chalcogenides. 2010, XII, 358
5. R.Schrebler , M.Merino, P.Cury, et al. Electrodeposition of Cu-Re alloy thin films. Thin Solid Films. 2001, 388(1-2), 201-207
6. F.Contu , S.R.Taylor. Further insight into the mechanism of Re-Ni electrodeposition from concentrated aqueous citrate baths. Electrochimica Acta. 2012, 70, 34-41
7. M.C.Sagiv , N.Eliaz, et al. Incorporation of iridium into electrodeposited rhenium-nickel alloys. Electrochimica Acta, 2013, 88, 240-250
8. A.Naor , N.Eliaz, et al. Electrodeposition of rhenium-nickel alloys from aqueous solutions. Electrochimica Acta. Journal homepage: 2009, 6028-6035.
9. A. Naor , N.Eliaz, et al. Electrodeposition of Alloys of Rhenium with Iron-Group Metals from Aqueous Solutions. J.Electrochem.Soc.2010, 157(7), D422-D427.
10. A. Naor , N.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.
11. E.N. Zamanova , S.M. Bagirova , M.A. Jaffarov , Switching structures based on films CdS. 10.02.1987 №977-B87
12. S.A. Kutopin , "The switching effect in amorphous semi-conductors and fields of their use. Moscow, CNII,Electronika, 1973, vol.4 (110), p.24
13. E.A.Salakhova Electrochemical Production of Thin Films of System Rhenium-Selenium Alloys. The Journal "Inorganic Materials", (2003) 39, 142-146
14. E.A.Salakhova , V.A.Majidzada , Electrochemical preparation of Thin Rhenium-Tellurium Coatings Chloride-Borate Electrolyte. Russian Journal of Electrochemistry (2011) 47(8) 877-882
15. E.A.Salakhova, 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
16. E.A.Salakhova , 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
17. E.A. Salakhova . Receiving thin films Re-Te from chloride-sulfate electrolyte and the influence of the various factors on composition of alloys. //Chemical industry today, 2008, No.6, p.p.43-47
18. E.A .Salakhova, V.A.Majidzada. Semiconducting properties of thin covers of rhenium chalcogenides, J. Chemistry and Chemical Technology, 2009, 52(5), 117
19. E.A.Salakhova."The electrochemical production of thin films of rhenium chalcogenides" Monograph, LAP LAMBERT Academia, 2014,100p