

## THE DOPING OF $\text{Cu}_{2-x}\text{S}$ MAGNETOSENSITIVE AND COMPONENT (Sm) FILMS IN ELECTROSYNTHESIS PROCESS

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The technology of electrosynthesis and doping in electrosynthesis process of  $\text{Cu}_{2-x}\text{S}$  magnetosensitive and component (Sm) films has been developed. It is established, that the electrolytic sediments and films, precipitated on nickel, platinum planes have monocline syngony, correspond to  $\text{CuSmS}_2$  composition, p-type conductivity and are the magnetosensitive material, can be applied in the magneto optic devices.

The wide use of the semiconductor films with big square in earth sun energy has made the problem of the obtaining of the semiconductor layers on simple and chip technology, actual at the saving of optical, electric and photoelectric properties of the films on high enough level. In this respect, the method of the chemical precipitation from the solution (OR) presents interest, i.e. the films with big range of electric and optical properties [1-4] can be obtained by this method, regulating the ion composition of solution and precipitation mode.

The doping technology of  $\text{Cu}_{2-x}\text{S}$  of magnetosensitive and component (Sm) films during electrosynthesis has been developed by us.

The electrodeposition was carried out from the electrolyte solution by the composition:

Cuprum sulfate – 0,4÷0,5 mol/l,  
Sulfuric acid – 0,15÷0,20 mol/l,  
Sodium thiosulfate – 0,15÷0,20 mol.l,  
Samarium oxide – 0,015÷0,02 mol/l.

The electrolysis was carried out at the current density 10÷60  $\text{mA}/\text{cm}^2$ , temperature 20÷22°C and precipitation time 5-10 min. In the capacity of the cathode the polished planes from nickel, platinum and stainless steel were used and in the capacity of anode the plane from the platinum was used in all cases.

The concrete samples of the electrolytic obtaining of  $\text{CuSmS}_2$  compound at the different electrolyte compositions, current densities and electrolysis time, and results of chemical analysis are given in the table 1.

Table 1

The samples of the obtaining of Cu-Sm-S alloy, electrolysis modes and results of chemical analysis

	The composition of main components of electrolyte, mol/l	Current density, $\text{mA}/\text{cm}^2$	Temperature °C	Alloy composition, weight, %			Alloy composition	Electrolysis duration, min	Thickness of covering, $\mu\text{m}$
				Sm	Cu	S			
1	$\text{CuSO}_4 - 0,40$ $\text{Na}_2\text{S}_2\text{O}_3 - 0,15$ $\text{H}_2\text{SO}_4 - 0,50$ $\text{SmO} - 0,015$	10	20	23,8	27,5	46,6	$\text{CuSmS}_2$	5	3,2
2	$\text{CuSO}_4 - 0,40$ $\text{Na}_2\text{S}_2\text{O}_3 - 0,18$ $\text{H}_2\text{SO}_4 - 0,53$ $\text{SmO} - 0,016$	20	20	26	20,8	53	$\text{CuSmS}_2$	5	3,4
3	$\text{CuSO}_4 - 0,48$ $\text{Na}_2\text{S}_2\text{O}_3 - 0,18$ $\text{H}_2\text{SO}_4 - 0,57$ $\text{SmO} - 0,018$	40	22	26,1	24,3	49,48	$\text{CuSmS}_2$	10	3,6
4	$\text{CuSO}_4 - 0,50$ $\text{Na}_2\text{S}_2\text{O}_3 - 0,20$ $\text{H}_2\text{SO}_4 - 0,80$ $\text{SmO} - 0,019$	50	22	26	24	49,8	$\text{CuSmS}_2$	8	3,8
5	$\text{CuSO}_4 - 0,50$ $\text{Na}_2\text{S}_2\text{O}_3 - 0,20$ $\text{H}_2\text{SO}_4 - 1,0$ $\text{SmO} - 0,020$	60	22	27,7	23,7	48,5	$\text{CuSmS}_2$	8	3,8

The films  $\text{CuSmS}_2$  were subjected to the spectral analysis for the establishment of the film purity (table 2). As it is seen from the table 2, the obtained film  $\text{CuSmS}_2$  has the purity 99,99%. The samples, obtained at the current density

40  $\text{mA}/\text{cm}^2$ , electrolysis duration 10 minutes are subjected to the roentgen-phase analysis on the substrate from nickel. The crystallographic constants have been defined and they are compared with the analogical parameters of monocystal, the

composition of which corresponds to  $\text{CuSmS}_2$ . The given data in the table 3 allow to suppose, that electrolytic sediments have monoclinic syngony and are correspond to  $\text{CuSmS}_2$  composition.

Table 2  
The results of spectral analysis of Cu-Sm-S films, obtained by the electrochemical method at the different current densities

Electrolyte, mol/l	Current density, mA/sm <sup>2</sup>	Impurities, %			
		Fe	Si	Mg	CuSmS <sub>2</sub>
CuSO <sub>4</sub> – 0,50	10	0,0001	0,01	0,001	99,99
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> – 0,20	20	0,0001	0,01	0,001	99,99
H <sub>2</sub> SO <sub>4</sub> – 1,0	40	0,0001	0,01	0,001	99,99
SmO – 0,020	50	0,0001	0,01	0,001	99,99
	60	0,0001	0,01	0,001	99,99

Table 3  
The results of roentgen-phase analysis of electrochemically precipitated film  $\text{CuSmS}_2$   
Mode: 40kV, 6mA,  $\text{CuK}_\alpha$  ( $\lambda=1,5418\text{\AA}$ ), eks 15 hour. Ni is filter

NN	Interplanar spaces from the single crystal [1,3]		Experimental data from electrochemically precipitated film $\text{CuSmS}_2$	
	D	I	d	I
1	4,109	7	4,166	6
2	3,691	7	3,721	1
3	3,233	1	3,265	1
4	2,924	6	2,942	5
5	2,834	6	2,820	1
6	2,560	7	2,566	4
7	2,337	7	2,327	9
8	2,127	6	2,117	10
9	2,036	1	2,012	1
10	1,954	1	1,977	1
11	1,897	3	1,893	9
12	1,730	2	1,707	6
13	1,545	2	1,580	1

The results of roentgen-phase analysis are given in table 3. The calculated of interplanar spacings of the monoclinic lattice are turned out identical with data, obtained from monocrystal of the analogical composition [1,3] with parameters of lattice:  $a=6,496$ ;  $b=7,13$ ;  $c=6,799\text{\AA}$ ,  $\beta=98^\circ 21'$ ,  $P2/C'$ ,  $Z=4$ .

The influence of the samarium ions on the process of the combined precipitation sulfur and cuprum have been studied

by us. For the precipitation the platinum plane was used in the capacity of the cathode, and the polished nickel electrodes were used in the capacity of the anode. The polarized measures were carried out in the dependence of the samarium concentration in electrolyte and medium temperature. As it is seen from the table 4 the potential shifts to the negative side with the increase of the temperature and decrease of the samarium concentration in electrolyte.

Table 4  
The shifting of the potential from electrolyte temperature and samarium concentration in the electrolyte

Temperature, °C	The potential shifting, volt			
	$C_{\text{Sm}}=0,02$ mol/l	$C_{\text{Sm}}=0,04$ mol/l	$C_{\text{Sm}}=0,06$ mol/l	$C_{\text{Sm}}=0,08$ mol/l
25	+0,05	+0,15	+0,15	0
50	-0,05	0	0	0
70	0	0	0	-
90	0	-0,13	-0,3	-

It is known, that reconstruction potential is defined by that energy, which is needed to spend on the destruction of the crystalline lattice. The perfect the crystalline structure is the more energy is needed to spend on its destruction. It is consequent that reconstruction potential will shift to the negative side in the case of the samples with the perfect structure.

The velocity of the electrochemical reaction increases with the temperature increase that is seen from the increase of values of the limiting current and decrease of the region of its existence.

Thus, at the high temperatures the most favourable conditions for the combined precipitation of the components are created, i.e. the rapprochement of their potential separation because of the energy of mixing carries out. However, the best adhesion of the precipitating alloy with base is achieved at the temperature 25°C. The part of the precipitated alloy crumbles from electrode surface with the increase of the temperature and increase of the crystallization velocity, the covering is obtained irregular by the thickness. That's why; from the practical point of view the most interest are samples, obtained at the temperature 25°C. The microscopic photos of the transversal sections, fixed on microscope MIM-7 show, that samples are one-phase.

The use of the proposed technology for the coating of the triple alloy  $CuSmS_2$  supplies the following advantages in the

comparison with the known ones:

a) the possibility of the coating of the semiconductor high-resistance covering with the magnetosensitive component electrolyte composition in practically allowed variation intervals, current density and synthesis temperature

$CuSO_4 - 0,4-0,5$  mol/l,

$Na_2S_2O_3 - 0,15-0,20$  mol/l,

$H_2SO_4 - 0,5-1,0$  mol/l.

$SmO - 0,015-0,02$  mol/l.

$I_k = 10 \div 60$  mA/cm<sup>2</sup>;  $t = 20 \div 22$  °C, precipitation time  $\tau = 5 \div 10$  min,

b) quick decrease of the power inputs,

c) the simplicity and cheapness of the synthesis technology, the absence of the necessity of pressings, heat treatments and cooling.

Thus, this method allows to obtain the films of the triple alloy, consisting from the cuprum, samarium and sulfur-rare-earth semiconductor (RES) of p-type with  $\rho = 2 \cdot 10^3 \div 10^{10}$  Ohm-cm at the room temperature, which are the paramagnetic material; in the temperature interval (77-373)K and can be applied at the recording and transformation of the optical information in the magneto-optical devices by the method of the electrochemical precipitation as the analysis results show [4].

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**ELEKTROSİNTEZ PROSESİNDƏ  $Cu_{2-x}S$  TƏBƏQƏLƏRİNİN MAQNİTOHƏSSAS KOMPONENT İLƏ (Sm) AŞQARLANMASI**

$Cu_{2-x}S$  təbəqələrinin elektrosintez yolu ilə alınması və maqnitohəssas komponent ilə (Sm) aşqarlanması texnologiyası işlənib. Təyin edilib ki, elektrolitik çöküntü və təbəqələr nikel, platin altlıqlar üzərində monoklin sinqoniyaya,  $CuSmS_2$  –tərkibə, p-tip keçiriciliyə malik olan, maqnitohəssas materiallardır.

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**ЛЕГИРОВАНИЕ ПЛЕНОК  $Cu_{2-x}S$  МАГНИТОЧУВСТВИТЕЛЬНОЙ КОМПОНЕНТОЙ (Sm) В ПРОЦЕССЕ ЭЛЕКТРОСИНТЕЗА**

Разработана технология электросинтеза и легирования в процессе электросинтеза пленок  $Cu_{2-x}S$  магниточувствительной компонентой (Sm). Установлено, что электролитические осадки и пленки, осажденные на никелевые и платиновые пластинки, имеют моноклинную сингонию, соответствуют составу  $CuSmS_2$ , р-типу проводимости, являются магниточувствительным материалом, могут найти применение в магнитооптических приборах.

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