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ELECTRODEPOSITION OF Ag-Se COATINGS

ELEKTROOSADZANIE CIENKICH WARSTW Ag-Se

Silver–selenide coatings with different content of Se have been electrodeposited galvanostatically onto copper substrate from aqueous acid solutions, containing silver iodide complex. By cyclic voltammetry it was established that electrodeposition of the Ag-Se system was characterized by two cathodic maxima onto Pt substrate; pure silver is deposited during the first cathodic reaction and the next phase of Ag-Se system are formed at more negative potentials than the potential of silver deposition. By X- Ray analysis was confirmed, that in deposit Ag_2Se phase is presented with excess of Ag. SEM shows that nearly stoichiometric Ag_2Se deposit has dendritic morphology.

Keywords: Cyclic voltammetry, electrodeposition, iodide electrolyte, silver selenide, semiconductor

Stosując metodę galwanostatyczną osadzono na miedzi warstwy selenku srebra o zmiennej zawartości selenu. Proces elektrolizy prowadzono stosując wodne roztwory zawierające kompleksy jodku srebra. Badania przeprowadzone metodą cyklicznej woltamperometrii pokazały istnienie dwóch pików: w pierwszej kolejności obserwujemy redukcję srebra, a następnie tworzenie się fazy Ag_2Se. Ta druga reakcja zachodzi przy potencjale bardziej ujemnym niż potencjał osadzania Ag. Analiza rentgenowska wykazała, że powłoka otrzymana metodą galwanostatyczną zawiera nadmiar srebra. Dokładna analiza z wykorzystaniem SEM sugeruje, że faza o składzie zbliżonym do stechiometrycznego związku Ag_2Se ma formę dendrytów.

1. Introduction

According to the Ag-Se phase diagram [1] there is a phase Ag_2Se which is stable up to almost 1170 K. Ag_2Se is an intermetallic phase which is semiconducting. It has

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been used in IR detectors, optical devices, photovoltaic cells, multipurpose selective electrode [2- 6]. Recently it was reported [7, 8] that Ag_2Se shows large positive magnetoresistance. It is a promising material for the application in the magnetic field sensing devices. Many procedures exist for the production of silver selenide: an elemental

TABLE 1

Short review for electrodeposition conditions of silver selenide from aqueous solution

Ref.	Composition of electrolyte, concentration	Parameters of electrolysis			Cyclic voltammetry investigations	Other methods for the characterization of coatings	Conclusions
		WE(working electrode/ CE (counter electrode)	T°, C	i, A dm⁻²/(GS) U,mV /(PS)			
[14]	H_2SeO_3, pH=2	WE - Selenium CE -Se, Ag	85-95	galvanostatic	No available	X-Ray	Silver selenide formed onto the cathode
[15]	$AgNO_3 - 2,5 . 10^{-3}M$ $H_2SeO_3 - 20-30.10^{-3}M$ $HNO_3 - 15-60.10^{-3}M$ pH=1	WE -Pt,Ag CE -Ag, Pt	20-60	2- 4 mA cm⁻²	No available	I=f(E); semiconductivity, X – Ray,	Compact coatings onto Ag, rough onto Pt. Composition of the deposit-function of composition of theelectrolyte, T °,C, and substrates
[16]	$Ag^+ - 0.2.10^{-3}M$, $SeO_2 -0.2.10^{-3} M$ CTAB =$2.10^{-4}M$ / or $NaNO_3$/ pH=2	WE -Pt CE -Pt	room	potentiostatic	Onto Pt	X-Ray	Under different operating conditions (silver/selenium ratio), deposition potential, electrode rotation rate, the composition of the deposit changed a lot.
[5,17-18]	$AgNO_3 - 2 .10^{-3}M$ $Na_2SeO_3 -0.1M$ $H_2SO_4 - 0.5-0.6 M$ pH=1	WE-Pt CE-Ag		potentiostatic -70 mVvs. SCE	Onto Pt	I=f(E), Ray Flruorescence, X –Ray, EQCM to provide in situ information about the phase composition.	Very compact, bright Ag_2Se onto Pt if the molar ratio for $Ag:Se$ in the electrolyte varies from 1:25 to 1:60 and H_2SO_4 =1M
[19]	$AgNO_3 - 5.0. 10^{-3} M$ $SeO_2 -2.0 -3.0 .10^{-3}M$ $KNO_3 -0.05 M$ $KSCN - 0.5M$ $HNO_3 -$ to the pH=2.6	WE-ITO CE-Pt	20	potentiostatic -0.55 -0.75 V vs SCE,	Onto ITO	X-Ray	SCN was introduced as a complex ligand to lower the reduction activity of Ag^+. Annealing of deposit improved crystallinity of Ag_2Se film.

combination at elevated temperature [1], decomposition of organometallic precursor [3], chemical bath deposition [9], template–based synthesis [10], solid synthesis [11] and electrodeposition from non- aqueous solutions [12]. One of the inexpensive and well-controlled process is the electrodeposition from aqueous solutions [13].

In 1963 V o n G o b r e c h t et al. [14], have announced the first attempt of simultaneous electrodeposition of silver and selenium from aqueous solution. It was found that obtained deposit exhibited semiconducting properties. Difficulties in electrodeposition of Ag- Se coatings are connected with the very positive potential of reduction of Ag^+/Ag. Some previously known electrolytes for deposition of this compound are presented in Table 1 [7, 14-19].

It can be seen, from Table 1, that there exists a gap concerning the effects of current densities on the composition of Ag-Se coatings in the recent investigations.

Attempts have been made in order to establish the galvanostatic conditions for obtaining the compact Ag-Se coatings onto copper substrate for the future investigations of Ag-Se coating properties with different Se content in deposit.
For this purpose we had to:
1. Find the most suitable electrolyte for obtaining compact coatings in a wide range of current densities.
2. Investigate the behavior of the electrolyte, containing Ag and Se species by cyclic voltammetry.

2. Experimental

Cyclic voltammetry experiments were performed in a 100 cm^3 volume glass cell. A platinum sheet sized $1 \times 0.5 \times 0.03$ cm was used as a cathode. Platinum anode with an area of 4 cm^2 was placed. A reference electrode was SCE. The electrode was placed in a separate cell filled with saturated KCl solution. It was connected to the cell by a Haber-Luggin capillary through an electrolyte bridge containing saturated KCl solution. The investigations were carried out by cyclic voltammetry using a computerized potentiostat/galvanostat ATLAS 98 EII at room temperature, using Pol-99 software with a sweep rate of 20 mV s^{-1}. Prior to each experiment, the platinum working electrode was etched in 20% solution of HNO$_3$.

The Ag-Se coatings were deposited onto copper plates with an area of 2×1 cm in the cell for cyclic voltammetric experiments under galvanostatic conditions, with deposition time one hour. The preliminary preparation of the copper cathodes includes a standard procedure of chemical decreasing followed by pickling in a 20% solution of sulphuric acid. In order to avoid the cementation of silver, the cathode was immersed into electrolyte under current. The surface morphology was studied by means of scanning electron microscopy (SEM) Philips XL30 and the composition of the coatings was determined by energy dispersive spectroscopy analysis. Phase analysis was performed at room temperature by means of a TYP G2M diffractometer at Θ angles from 5° to 55° using Co-Kα irradiation. UV–Vis spectra were taken from Shimadzu

spectrophotometer (UV-2501 PC, Japan) working in the range from 190 to 900 nm at room temperature.

The composition of the electrolyte used in this study is presented in Table 2.

TABLE 2

Electrolyte composition

Compound	Concentration, mol dm^{-3}
Ag as AgNO$_3$ /POCh S.A/	$0.5 \cdot 10^{-3} - 1 \cdot 10^{-1}$
Ag as Ag$_2$SO$_4$ /POCh S.A/	$1 \cdot 10^3 - 1 \cdot 10^{-1}$
SeO$_2$ /Aldrich/	$1 \cdot 10^{-3} - 5 \cdot 10^{-2}$
KSCN /POCh S.A./	0.1-1
KJ /POCh S.A./	0.1-0.5
H$_2$SO$_4$; HNO$_3$	For the adjusting of pH up to 2.2-2.5

The electrolytes were prepared using chemicals of *pro analisi* purity and bidistilled water.

3. Results

Using already known electrolytes [Table 1] we tried to deposit Ag-Se coatings galvanostatically. In most cases the compact coatings onto copper were impossible to obtain. If the copper cathode was covered by thin layer of silver, the coatings of Ag-Se were compact in the wider range of working current densities, but still not enough, to assure continuous measurement of chemical composition of the deposit. According to the literature data, selenium has been coelectrodeposited from strongly acidic electrolytes. The theoretical background of the process of electrodeposition of Se from acidic aqueous solution has been described recently in details by K o w a l i k et al. [20]. The theoretical prediction of the process of codeposition of Ag and Se has been given by N e s h k o v a et al. [5].

In our case, we established empirically (by adjusting the bath composition) the possibility of obtaining the compact Ag-Se coatings from two complex electrolytes in quite wide range of current densities. First of them, thiocyanate electrolyte, was suggested as a possible choice to obtain *Ag$_2$Se* by C h e n et al.[19], but these authors worked with working electrode an indium-doped tin oxide (ITO) covered glass with a sheet resistance of 20 Ω cm under potentiostatic conditions.

The second, iodide electrolyte, to our knowledge has not been yet reported for codeposition of selenium–consisting coatings. This electrolyte was chosen for the following reasons:

1) precipitation of Ag was not observed after adjusting pH up to the acidic region. Usually in acid region silver ions precipitate, but in iodide electrolyte shifting of the pH of solution in acid region doesn't lead to the precipitation of Ag.

2) the electrochemical processes during the deposition of Ag from complex iodide electrolytes are well known [21, 22].

TABLE 3

The appearance and content of Se in the deposit, obtained under galvanostatic conditions onto copper substrate

Complex agent	Thiocyanate		Iodide	
I, A dm^{-2}	Apperance	Se in deposit, wt. %	Apperance	Se in deposit, wt. %
0.1	Grey	<2	Silver-like	<0.5
0.2	Pale, light grey	8	Silver-like, darker	2-3
0.4	Gray-black	8-10	Light grey, visible heterogeneous	5-7
0.6	Dark gray	15	Greyish	10
0.8	Brown – grey	18	gray	10-12
1.0	Incompact, some shiny spots	—	Grey, mirror – like	>26

The appearance and content of Se in the deposit, obtained under galvanostatic conditions onto copper substrate, are shown in Table 3.

Concentrations of Ag —1mM and SeO$_2$ – 3 mM in both electrolytes are equal. It is obvious from Table 3, that Se content in the deposit doesn't increase uniformly with current density. The appearances of higher content of weight percent of Se in deposit are changing abruptly; but coatings are compact.

Next, these two electrolytes were chosen for successive investigation by cyclic voltammetry regardless of better results from iodide electrolytes (it can be seen, that higher content of Se in deposit has been reached from iodide electrolyte). Though the whole process seems to be very complicated, experiments with cyclic voltammetry may explain basic reactions responsible for the electrodeposition of Ag_2Se phase onto Pt substrate.

Figure 1 shows the CV curves of an electrolyte containing both Ag and Se, and using the SCN- as complex ligand with the different content of Se in the solutions. The first cathodic maximum at about –255 mV (curve 1) corresponds to the deposition of silver. It is obvious, because after increasing the concentration of Se in solution (curve 2) this peak does not change its position. The second cathodic maximum, not very sharp in the vicinity of about – 830 mV, corresponds to pure Se deposition. It can be seen during the electrolysis, that red, amorphous selenium deposit appears at the surface. During the anodic period a sharp peak near –50 mV is observed in the area of silver dissolution and a second one observed at more positive potentials. The appearance of these two peaks in the anodic cycle is probably due to the dissolution of different phases of Ag-Se coating. When the concentration of Se is higher, with other conditions of experiments fixed (curve 2), the same position of pure silver deposition peak (a) can be observed. The next peak (b) at about –750 mV can be associated with
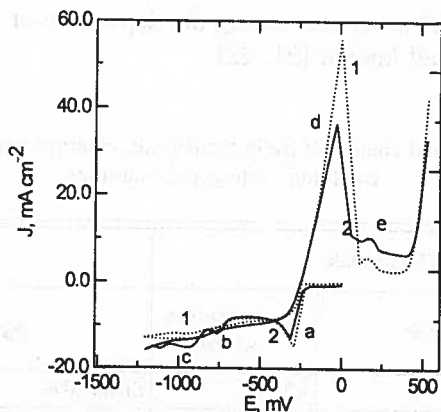
Fig. 1. CV curves of an electrolytes, containing Ag and Se together, registered at v = 20 nmV s^{-1}, pH = 2.3-2.5 ($C_{Ag\ as\ AgN3}$ = 1 mM, C_{KSCN} = 0.5 M): curve 1 (........)C_{SeO2} = 1mM; curve 2 (——) C_{SeO2} = 3mM

the formation of Ag_2Se phase, due to the appearance of the mirror-like grey deposit onto platinum cathode. At more negative potential, the red, amorphous selenium appeared. The increase of the SeO_2 concentration in the electrolyte at constant Ag concentration leads to the decrease of first anodic maximum (d). Probably the effect of the passivation of the phase with higher Se content is registered in the anodic cycle. An increase of the second anodic peak (e) in comparison with the smaller concentration of SeO_2 can be connected with the formation of Ag_2Se phase, which is clearly visible on curve 2.

Both, cathodic and anodic behavior of the thiocyanate electrolyte onto platinum substrate (curve 2) are similar to those, presented by C h e n et al [19], regardless to the different substrate and concentrations.

The deposition of silver strongly depends on the complex formation. The first cathodic maximum at about –550 mV in the iodide electrolyte (Figure 2, curve 1) corresponds to the electrodeposition of pure silver. This shift in the negative direction can be explained by the stronger complexion influence of the iodide ligand under these specific conditions of electrolysis.

According to V i a c h e s l a v o v et al., [21] the process of electrodeposition of silver from iodide electrolyte should pass through complex salts K$_2$AgJ$_3$, formation:

$$Ag_2SO_4 + 6KJ \leftrightarrow 2K_2AgJ_3 + K_2SO_4. \tag{1}$$
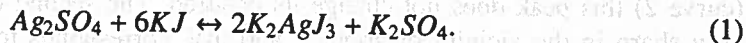
The second peak, at –800 mV (curve 1) can be connected with the formation of Ag_2Se phase, because it there appears bright, shiny deposit. The evolution of H$_2$ appears at more negative potentials, then –1200 mV. The coating deposited during the cathodic cycle dissolves during the anodic cycle with the sharp peak at — 380 mV. The increase in the concentration of SeO$_2$ (Figure 2, curve 2) leads to the changes mostly visible in the second cathodic peak. This peak, which is associated with the formation of nearly stoichiometric Ag_2Se phase is not so sharp and can be observed in
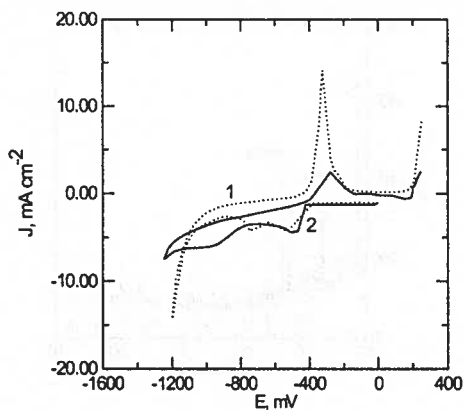
Fig. 2. CV curves of an electrolytes, containing Ag and Se together, registered at v = 20 nmV s^{-1}, pH = 2.3-2.5 ($C_{Ag \ as \ Ag2SO4}$ = 1 mM, C_{KJ} = 0.3 M): curve 1 (........)C_{SeO2} = 1mM; curve 2 (——) C_{SeO2} = 3mM

the range from –820 to –950 mV. Probably, the effect of the passivation of the phase with higher selenium content is registered in the anodic period. The solution changed its color from yellow to dark yellow -during the electrolysis (CVA measurement or galvanostatically deposition) a brown gas evolved from the anode.
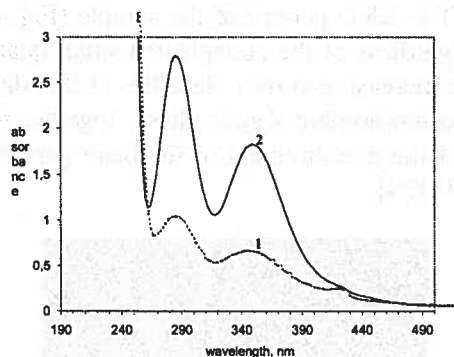

Fig. 3. $C_{AgasAg2SO4}$ = 1 mM, C_{SeO2} = 3 mM, C_{KJ}=0.3 M;
Spectra 1 (·······) — after first measurement, solutions is yellow;
Spectra 2 (——) — after fifty measurements, solution is dark brown

Spectrophotometric investigations of these different colored solutions (Figure 3) show two peaks, characteristic for J_2 (288 nm and 350 nm — [23]). Spectrum 1, in Figure 3 corresponds to the solution, in which one CV measurement in fresh electrolyte was done (solution was yellow). Spectrum 2 (Figure 3) corresponds to the solution, in which fifty CV measurements were done (solution was dark brown). The increase in absorbance of the spectra denotes the increase of the concentration of J_2, probably according to the reaction:
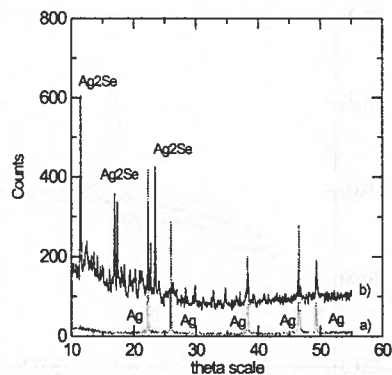
Fig. 4. XRD pattern of the samples, deposited at different current densities
$C_{Ag\ as\ Ag2SO4} = 1$ mM, $C_{SeO2} = 3$ mM $C_{KJ} = 0.3$ M; (a) 0.2 dm^{-2}; (b) 1.0 A dm^{-2}

$$2J{-}2e \rightarrow J_2. \qquad (2)$$

However, the detailed description of the CV experiments onto different substrate, including ITO glass, requires additional experiments [24].

X-Ray diffraction (XRD) pattern of the samples (Figure 4), deposited under galvanostatic conditions changes with the applied current densities (see Table 3, column with iodide electrolyte). The XRD pattern of the sample (Fig. 4a) shows the presence of a pure silver phase, regardless of the codeposited small quantities of selenium (2-3 wt.% selenium). With the increasing current densities (1.0 A dm^{-2}), XRD pattern (Fig. 4b) shows the peaks of orthorhombic Ag_2Se phase, together with the excess of pure Ag. Preliminary results of the measurement of the band gap of this deposit show that it is approximately 1.3 eV [24].
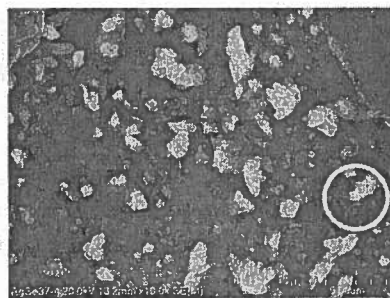

Fig. 5. SEM image of the surface, which indicates appearance of Ag_2Se, sample from XRD figure (4b). $C_{Ag\ as\ Ag2SO4} = 1$ mM, $C_{SeO2} = 3$ mM $C_{KJ} = 0.3$ M, J, A dm^{-2} = 1.0

The surface morphology of the coating, of such a sample, (Figure 4, curve b) is shown in Figure 5 and Figure 6. The deposit is heterogeneous, and onto relatively smooth background dendritic formations can be seen. The content of Se is more than

Fig. 6. SEM image with different magnification from the place, noted by ◯ in Figure 5. The EDAX analysis shows more than 33 wt. % Se in dendritic formation

33 wt.% (Figure 6). Dendrites of silver chalcogenide (compounds of silver with S, Te and Se), as a kind a fractal structure, received recently a lot of interest, because they can provide a natural framework for the study of disordered system [10].

4. Conclusions

1. It was established empirically, that iodide complex electrolyte is a suitable electrolyte for simultaneous deposition of Ag and Se. The compact heterogeneous Ag-Se deposits are obtained with high content of Se wt.%.

2. The CV experiments show the formation of silver and rich–Se phase in the cathodic cycle. [3.] Phases rich in Se dissolve at more positive potentials than pure silver. [4.] The increase in current density under galvanostatic conditions leads to an increase in Se content in the coating, which leads to the formation of Ag_2Se phase (which is mirror like and grey), together with pure Ag. [5.] Since Ag_2Se phase can be deposited electrochemically, now it can be possible to investigate its physical properties like reflectivity, band gap, magnetoresistance, etc.

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