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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Deposition of Thin Electroplated Cd–Se Layers

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Abstract—Cadmium–selenium alloys were electrodeposited from a sulfuric acid electrolyte. The effect of the H_2SeO_3, $CdSO_4$, and sulfuric acid concentrations, current density, and temperature on the composition and quality of cathode deposits was studied.

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Recently, the interest in electrochemical deposition of thin CdSe layers has considerably increased [1–5]. This method is distinguished by technological simplicity and enables control over the composition, quality, and properties of the layers obtained by varying the electrolysis mode and electrolyte composition. In addition, the interest in CdSe is due to the considerable prospects for use of thin films of this material in various fields of semiconductor industry, and primarily in fabrication of solid-state solar cells and photovoltaic and photoelectrochemical cells [6].

Previously, cyclic voltammetry has been used to study the fundamental aspects of joint electrodeposition of cadmium and selenium from a sulfuric acid electrolyte and to determine the potentials at which the layers of the Cd–Se alloy with a composition close to stoichiometric CdSe are formed on the cathode.

This communication reports the results of a study of the influence exerted by various factors (current density, concentration of main electrolyte components, and temperature) on the composition and quality of the deposits obtained.

EXPERIMENTAL

The electrodeposition was performed from sulfuric acid solutions containing H_2SeO_3 and $CdSO_4$. The electrolysis was carried out in a 100-ml glass vessel. A platinum plate with an area of 5 cm^2 served as the cathode, and a combined selenium + platinum electrode, as the anode. The electrolytic cell was thermostated with a U-10 ultrathermostat. The deposited alloy was analyzed by the procedure described in [8], with selenium precipitated with hydrazine hydrochloride and a saturated solution of sulfur dioxide gas. The content of cadmium was found from the difference of masses of the cathode deposit and selenium. The outward appearance of a coating was assessed visually. The conduction type of the layers was determined with a thermoprobe [9]. The film thickness was measured with an MII-4 Linnik interference microscope. The quantity of electricity passed through the electrolyte was $Q = 5\ 102$ C dm^{-2}.

Figure 1 shows the dependence of the selenium content of the deposit on the current density for electrolytes containing various concentrations of H_2SeO_3 and constant concentrations of $CdSO_4$ and H_2SO_4. It can be seen that the selenium content of the cathode deposits decreases with increasing current density. Deposits closely similar in composition to

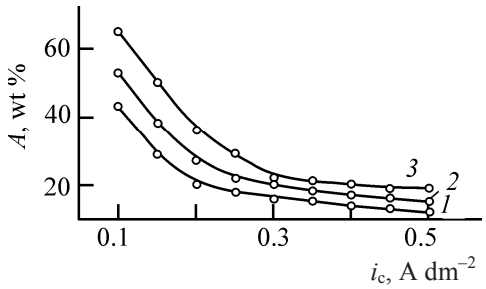

Fig. 1. Effect of the current density i_c on the selenium content A of a deposit at various H_2SeO_3 concentrations. Electrolyte composition (M): $CdSO_4$ 0.5, H_2SO_4 2; temperature 20°C; the same for Fig. 2. H_2SeO_3 concentration (M): (*1*) 0.005, (*2*) 0.0075, and (*3*) 0.01.

CdSe (41.6 wt % Se) are formed at current densities of about 0.2 A dm^{-2} from an electrolyte containing 0.005 M H_2SeO_3 (Fig. 1, curve *1*), and at current densities of 0.3–0.4 A dm^{-2} from an electrolyte with 0.01 M H_2SeO_3 (curve *3*).

At higher current densities, the cadmium content of cathode deposits sharply increases. This occurs because the potential at which pure cadmium is deposited is already reached at higher current densities and, as a result, the cathode deposits are enriched in cadmium. At low current densities, the cathode deposits are mostly composed of selenium. High-quality deposits of the required composition are obtained at current densities of 0.2–0.5 A dm^{-2}.

The composition of the cathode deposits is also noticeably affected by the H_2SeO_3 concentration in the electrolyte. It can be seen in Fig. 2 that, at any current density, raising the concentration of H_2SeO_3 in the electrolyte from 0.002 to 0.01 M leads to an increase in the selenium content of the deposits. Under certain electrolysis conditions, deposits that are close in composition to CdSe and have thicknesses of up to 5 μm can be obtained from all the electrolytes studied. For example, a deposit containing 42 wt % Se is obtained from an electrolyte containing 0.0075 M H_2SeO_3 at a current density of 0.2 A dm^{-2} (Fig. 2, curve *1*), and that with 41 wt % Se, from an electrolyte containing 0.0075 M H_2SeO_3 at a current density of 0.3 A dm^{-2} (Fig. 2, curve *2*).

Data on the effect of the $CdSO_4$ concentration and current density on the deposit composition are listed in Table 1. It can be seen that the Se content of the deposit decreases as the $CdSO_4$ concentration in the electrolyte and current density become higher.

As temperature is raised, the selenium content of the cathode deposits increases (Fig. 3). This effect, particularly noticeable at $T > 50$°C, results from a change in the properties of selenium deposited on the cathode. Up to 50°C, the initial stage of electrolysis yields deposits of red amorphous selenium having high electrical resistivity, whereas at higher temperatures, deposits of black color characteristic of CdSe are formed on the cathode. Presumably, as temperature is raised, the number of carriers on the deposit surface grows, which leads to an increase in its electrical conductivity, and this, in turn, facilitates reduction of selenium and makes higher its content in the deposit.

Table 1. Se content of deposits at various $CdSO_4$ and H_2SeO_3 concentrations and current densities H_2SO_4 concentration 2 M, temperature 20°C

$c(CdSO_4)$, M	Se content, wt %, at indicated i_c, A dm^{-2}			
	0.2	0.3	0.4	0.5
H_2SeO_3 concentration, 0.01 M				
0.25	65	57	50	48
0.50	56	50	40	39
0.75	55	40	38	38
1.00	50	39	37	36
H_2SeO_3 concentration, 0.005 M				
0.25	55	51	46	40
0.50	40	36	33.6	32
0.75	35	30	27	27
1.00	30	25	24	23

High-quality compact deposits were obtained at temperatures lower than 60°C. Above 60°C, black deposits falling-off from the cathode surface were obtained.

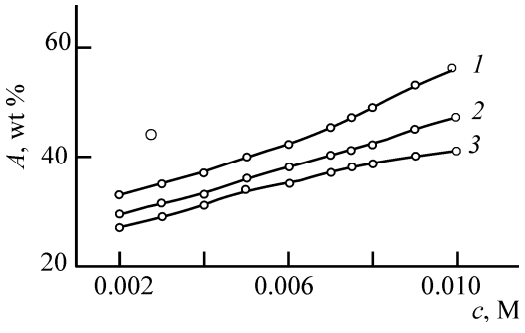

Fig. 2. Effect of the H_2SeO_3 concentration c on the selenium content A of a deposit. Current density (A dm^{-2}): (*1*) 0.2, (*2*) 0.3, and (*3*) 0.4.

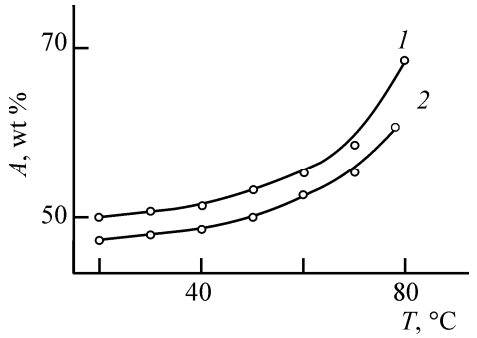

Fig. 3. Effect of temperature T on the selenium content A of a deposit. Electrolyte composition (M): H_2SeO_3 0.0075, $CdSO_4$ 0.5, H_2SO_4 2.0. Current density (A dm^{-2}): (*1*) 0.3 and (*2*) 0.4.

Table 2. Se content of deposits at various H_2SO_4 concentrations and current densities. Electrolyte composition (M): H_2SeO_3 0.01, $CdSO_4$ 0.5; temperature 20°C

$c(H_2SO_4)$, M	Se content, wt %, at indicated i_c, A dm^{-2}			
	0.2	0.3	0.4	0.5
0.50	63	68	56	50
0.75	62	56	50	48
1.00	59	54	44	44
1.50	57	46	42	41
2.00	56	42	40	39

Sulfuric acid affects the outward appearance of the cathode deposits. At an H_2SO_4 concentration in the electrolyte of 0.25 M, dark red deposits having poor adhesion to the electrode surface are formed on the cathode. The optimal H_2SO_4 concentration for obtaining high-quality deposits is 0.5–2.0 M. Changes in the H_2SO_4 concentration affect the composition of cathode deposits. As can be seen in Table 2, an increase in the H_2SO_4 concentration leads to a decrease in the selenium content of the cathode deposits.

Such an influence of H_2SO_4 on the composition of the deposits can be accounted for by the fact that the ionic composition of the electrolyte changes as the H_2SO_4 concentration grows: at low H_2SO_4 concentrations, hydrolysis yields water-insoluble basic salts of cadmium, but, as the acid concentration increases, hydrolysis gradually disappears and the solubility of the cadmium salt becomes higher. This, undoubtedly, creates conditions that favor a rise in the concentration of simple cadmium ions in solution. The presence of the simple ion leads, in contrast to that of basic compounds of cadmium, to a higher activity, with the kinetic hindrance to Cd^{2+} discharge diminished and the deposit enriched in cadmium.

The thermoprobe method was used to determine the conduction types of thin deposit layers of various compositions. The layers close in composition to stoichiometric CdSe and containing an excess amount of selenium were *p*-type, and those containing an excess of cadmium, *n*-type.

Thus, it was found that the composition and properties of the Cd–Se deposits obtained can be controlled by varying not only the concentrations of H_2SeO_3, $CdSO_4$, and H_2SO_4 in the electrolyte, but also the current density.

On the basis of the results obtained in this study, the following conditions for obtaining high-quality semiconducting layers of the Cd–Se alloy with varied amounts of the components can be recommended: electrolyte composition (M): H_2SeO_3 0.002–0.01, $CdSO_4$ 0.5–1.0, H_2SO_4 1–2.0; electrolysis mode: current density 0.2–0.5 A dm^{-2}, temperature 20–60°C.

The electrolyte composition should be adjusted as regards $CdSO_4$ and H_2SO_4 on the basis of chemical analysis data [10]. Because of the low concentration of H_2SeO_3, its constant concentration in the electrolyte is provided by using a combined anode composed of selenium and platinum, with the surface area ratio of these compounds, $S_{Se} : S_{Pt} = 1 : 2$.

CONCLUSIONS

(1) It was found that the selenium content of the deposits increases as the H_2SeO_3 concentration and temperature become higher. Raising the concentrations of $CdSO_4$ and H_2SO_4 or the current density leads to a decrease in the selenium content of the deposit.

(2) Sulfuric acid electrolytes for deposition of electroplated layers of a selenium–cadmium alloy of variable composition were developed.

(3) It was shown that the Cd–Se alloys obtained in the study have semiconducting properties. Deposits containing an excess amount of selenium are *p*-type semiconductors, and those rich in cadmium, *n*-type.

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