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MAGNETIC FIELD EFFECT ON THE ELECTRODEPOSITION OF ZnSe

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The effect of magnetic field on the process of ZnSe electrodeposition was studied. The applied magnetic field generates additional convection, which affects mostly the rate of the deposition of zinc selenide. The obtained coatings were characterized by X-ray diffraction, wavelength X-ray fluorescence and, additionally, the morphology of the deposits was analyzed by scanning electron microscopy.

Introduction. Zinc selenide, ZnSe, is a wide gap II-IV semiconductor ($Eg = 2.7\,\text{eV}$). With this band gap, it can find some applications in either electroluminescent devices or photovoltaic cells. It can act in LEDs as well as in n-type window layers in solar cells [1], [2]. Zinc selenide itself can be produced by several methods, e.g., vacuum deposition, chemical vapor deposition, metal-organic chemical vapor deposition, closed-spaced vapor transport or sputtering [2]. The properties of the obtained material depend on the chosen method since the production conditions influence the number of defects, structure, and impurities in the crystal. Since in electronic devices thin films are usually applied, the methods mentioned above are cumbersome because usually they are applied at high temperature. This fact is especially inconvenient if the structure of one material is supposed to match the surface structure of the other. Therefore, an electrochemical method seems to be very attractive for the deposition of semiconductor thin films, mainly due to its possibility to work at low temperature [1], [3], [4], [5]. Moreover, it has some other potential advantages, such as simplicity, low energy consumption and accurate control of film thickness, composition and morphology of deposited coatings. For the above reasons, the electrochemical method is applied for the deposition of thin films of many kinds of materials [6]. Among many parameters which affect the process of electrodeposition, the magnetic field has attracted more interest recently as an additional parameter applicable for the process of electrolysis [7], [8], [9], [10]. Referring to the literature, uniform magnetic fields applied parallel to the electrode surface can significantly influence the deposition process as well as the morphology, texture and composition of the coatings. The origin of these effects is in Lorentz-force-driven convection, which is responsible for magnetohydrodynamic (MHD) effect. MHD introduces additional convection in the electrolyte and, therefore, reduces the diffusion layer and increases the concentration gradient of electroactive species close to the electrode. Additionally, it has been shown that magnetic gradient fields are able to influence the electrochemical reaction rates significantly due to a field gradient force acting on paramagnetic species. Mostly the magnetic field is applied at the deposition of metal alloys [11], [12]. There is a limited number of papers about magnetic field application at the electrodeposition of semiconductor compounds [13].

The present work describes the effect of applied magnetic field on the process of synthesis of semiconductor compounds by the electrochemical method. Particular attention was paid to the rate of co-deposition of zinc and selenium, as well as to the composition, structure and morphology of the obtained coatings.

1. Experiment details. A conventional three electrode system was employed with a platinum foil as a counter electrode ($6\,\mathrm{cm}^2$) and a saturated calomel electrode (SCE) as the reference electrode. The substrate for electrodeposition was a copper sheet ($2.8\,\mathrm{cm}^2$). The copper sheets were chemically etched in a $HNO_3 : CH_3COOH : H_3PO_3$ 1 : 1 : 1 mixture for 60 s at the temperature 60°C prior to the process of deposition. All chemicals used in this work were of analytical grade. The concentrations of solutions were 0.001 M H_2SeO_3 and 0.2 M $ZnSO_4$. The pH was adjusted to 2.0 by a sulfuric acid addition. The EDAQ EA163 Potentiostat was used for the deposition process in the potentiostatic mode. The electrodeposition was conducted subject to an applied external magnetic field with parallel orientation of the magnetic induction vector about the surface of the working electrode. The film was being grown for 60 min. XRD diagrams were obtained by the Rigaku Miniflex II diffractometer with CuK_a radiation. The morphology of the product was studied by scanning electron microscopy (SEM) on an SU 70 instrument (Hitachi). The chemical composition of electrodeposits was characterized by the wavelength dispersive X-ray fluorescence method (WDXRF) by Rigaku PriMini.

2. Results and discussion. According to our previous measurements, the process of ZnSe synthesis can be realized when a large excess of zinc ions is present in the solution [14], [15]. It is a result of the more positive equilibrium potential of H_2SeO_3/Se compare to Zn^+/Zn [16]. Proper adjustment of the bath composition should lead to the formation of a stoichiometric compound and may exclude the presence of selenium excess while the solid phase is being formed [14], [17]. Consequently, the electrolysis was carried out in a solution containing 0.001 M H_2SeO_3 and 0.2 M $ZnSO_4$.

According to the previous measurements, the reduction of selenium acid is under diffusion control and the zinc concentration is high enough to follow the selenium deposition and an almost stoichiometric compound is obtained [15], [18], [19]. The process of ZnSe electrodeposition starts with the initial formation of a Se layer followed by Zn deposition according to the reactions:

$$H_2SeO_3 + 4H^+ + 4e^- = Se + 3H_2O, \tag{1}$$

$$Se + Zn^{2+} + 2e^- = ZnSe \tag{2}$$

Zinc is deposited on selenium below its equilibrium potential and it starts at –0.6 V vs. SCE. The underpotential deposition of zinc is due to the interaction with the firstly deposited selenium. Applying more positive potentials results in a higher excess of selenium in the deposit. In turn, applying a more negative potential decreases the efficiency of the Zn-Se codeposition due to hydrogen evolution and, additionally, the deposited selenium is reduced to H_2Se according to the reaction:

$$Se^0 + 2H^+ + 2e^- = H_2Se. \tag{3}$$

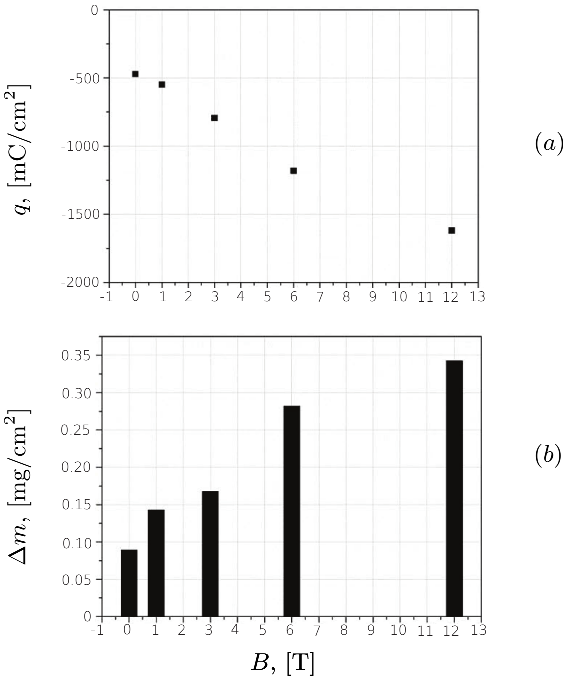

Fig. 1. (*a*) The total charge, and (*b*) the mass increase of the electrodes registered after deposition of coatings from the electrolyte 0.001 M H_2SeO_3 and 0.2 M $ZnSO_4$, pH = 2 at potential –0.6 V vs. SCE.

Moreover, with a more negative potential, selenious acid can be also reduced by the six electron reaction to:

$$H_2SeO_3 + 6H^+ + 6e^- = H_2Se + 3H_2O. \tag{4}$$

Consequently, the potential –0.6 V vs. SCE was applied during the process of deposition. The magnetic field was oriented parallel to the surface of the electrode and its intensity was changed up to 12 T. According to the obtained I-t transients during the electrodeposition, the charge was calculated (Fig. 1*a*). The applied magnetic field effectively increased the charge passing during the electrolysis and unambiguously indicated the increase of the rate of the electrode reactions. Moreover, the increase of the mass of the electrode was higher when the magnetic field of higher intensity was applied (Fig. 1*b*). The results confirm that the applied magnetic field increases the rate of deposition according to the MHD theory. As the depositions were performed in a mass-controlled regime of selenous acid reduction, this observation indicates an enhanced mass-transport of H_2SeO_3 species to the electrode, leading to the increased deposition rate. Respectively, the rate of zinc ions reduction increases, too, and confirms the proposed mechanism of underpotential deposition of zinc on selenium. The efficiency of the codeposition of zinc and selenium was very high and reached about 100 % (Fig. 2*a*). This is a very important issue and it indicates that the magnetic field does not promote the competitive electrode reactions and, hence, does not decrease the Faradaic efficiency of electrolysis. It is very essential that the magnetic field does not promote the hydrogen evolution reaction, which is very common in aqueous solutions when acid pH is applied [20]. The hydrogen evolution reaction affects the morphology of the selenide coatings and characteristic cauliflower structures appeared for deposits [15].

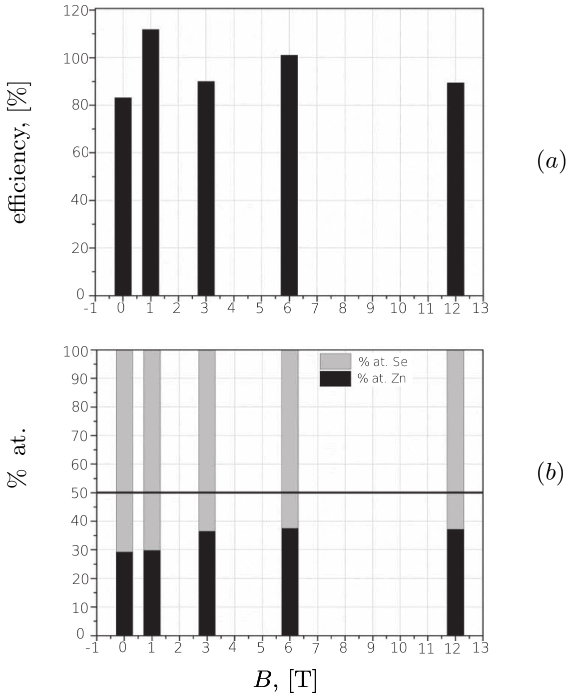

Fig. 2. (*a*) The Faradaic efficiency, and (*b*) the composition of the deposited coatings from the electrolyte 0.001 M H_2SeO_3, 0.2 M $ZnSO_4$, pH = 2 at potential –0.6 V vs. SCE.

The composition of the coatings changed when the magnetic field was applied (Fig. 2*b*). The content of zinc increased from 30 to almost 40 at.%, when the higher intensity magnetic field was applied. This positive effect of the increased zinc content in the deposits allowed us to approach to the stoichiometry of the ZnSe compound. Additional convection of the electrolyte close to the surface of the electrode activated by the MHD effect caused a gentle stirring and promoted the underpotential deposition of zinc on the previously deposited selenium. The phase analysis of the coatings was hindered. The diffractograms mostly exhibit peaks related to the copper substrate and only one, very small peak was associated with the ZnSe phase. This is due to the amorphous structure of the deposits and to the very thin layer of the coatings [14], [15]. This effect is characteristic for coatings obtained in a limiting current regime [6], [15].

The morphology of the Zn-Se coatings mostly depend on the applied potential and is related to the coating composition [15]. The obtained layers were electrodeposited at the same potential and the composition of the films varied in the range of 10 at.%. We can assume that the observed variations in morphology are mostly associated with the applied magnetic field. The surface was characterized by scanning electron microscopy, and the results are depicted in Fig. 3. When the intensity of the magnetic field increased, the morphology of the deposits changed significantly. All the coatings had a quite compact layer structure with a small porosity randomly distributed over the surface. Higher magnification revealed the bigger size of grains for samples obtained in the magnetic field of higher intensity. It is in good agreement with Koza results indicating that the growth of the nuclei is enhanced, but the nucleation processes are unaffected by the magnetic field [21]. Unfortunately, the estimation of the grain size by the Scherrer's method was impossible due to the low intensity of the peak related to the ZnSe phase (Fig. 4).

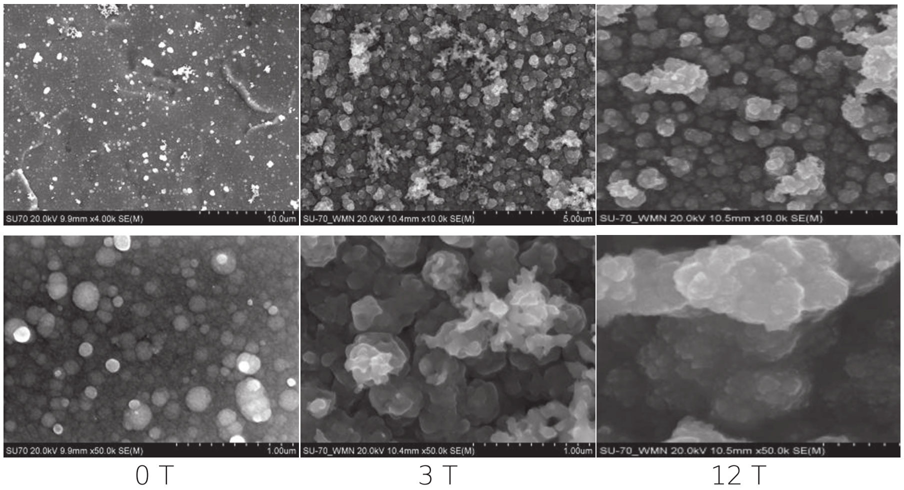

Fig. 3. Surface morphology of deposited layers obtained using a Cu substrate. Bath composition: 0.001 M H_2SeO_3, 0.2 M $ZnSO_4$, pH = 2, at potential –0.6 V vs. SCE.

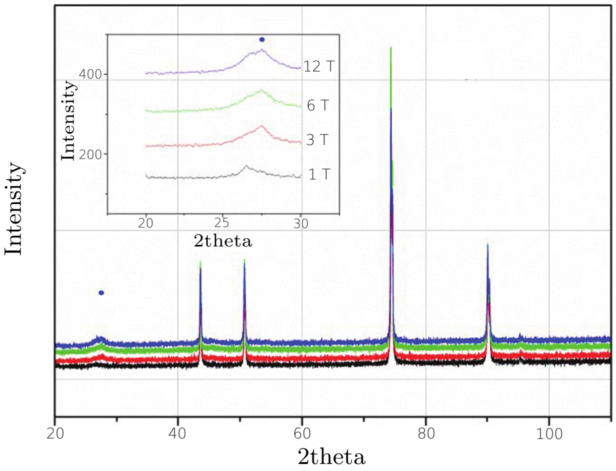

Fig. 4. XRD patterns of the Zn-Se coatings deposited from the electrolyte 0.001 M H_2SeO_3, 0.2 M $ZnSO_4$, pH = 2 at potential –0.6 V vs. SCE.

3. Conclusions. A thin film of zinc selenide was deposited by the electrochemical method under the influence of the magnetic field. The analysis of the results has revealed that the magnetic field applied parallel to the electrode increases the rate of codeposition of zinc and selenium during the electrolysis. The presence of the magnetic field does not decrease the efficiency of the deposition process, hence, it does not promote other competitive reactions, e.g., hydrogen evolution. The composition of the films varies when the intensity of the magnetic field increases. The zinc concentration increases slightly and the composition of the film is closer to the stoichiometry of the zinc selenide compound. It facilitates the zinc ions transport towards the already deposited selenium and the ZnSe synthesis. The morphology of the coatings is modified by the applied magnetic field. The SEM observation suggests the bigger size of the nucleus when the higher intensity magnetic field is applied.

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