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Electrodeposition of selenium from 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate

A. Abdel Aal^{a,b,c,*}, F. Voigts^a, D. Chakarov^b, F. Endres^{a,**}

^a Institute of Particle Technology, Clausthal University of Technology, 38678 Clausthal-Zellerfeld, Germany

^b Chalmers University of Technology, Department of Applied Physics, SE-412 96 Göteborg, Sweden

^c Central Metallurgical Research & Development Institute, CMRDI, P.O. 87 Helwan, Cairo, Egypt

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ABSTRACT

Electrodeposition of Se films from air and water stable 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ionic liquid was studied in open air conditions. The electrochemical behavior of H_2SeO_3 on gold and copper substrates was investigated in ionic liquid–water mixtures, and the influence of the deposition parameters such as time and bath temperature on the crystallinity of the film was examined. For the gold substrate, a reddish deposit containing amorphous, hexagonal and rhombohedral Se phases was identified at room temperature, while a grayish film of hexagonal and rhombohedral phases was formed at higher temperatures. The reddish Se film was found to exhibit a smoother surface with lower reflectivity in comparison to the grayish one. The band gap of the reddish film was close to that of pure amorphous red Se reported in literature, while the band gap of the grayish film was close to the pure hexagonal film. Photoelectron spectroscopy and energy dispersive X-ray spectroscopy show that both films consist of pure Se with only slight surface contaminations by remnants from the electrodeposition. In the case of a copper substrate, the electrodeposition of Se was accompanied by the formation of copper–selenide due to the reactivity of copper in H_2SeO_3 .

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1. Introduction

Due to their good semiconducting properties and light sensitivity, selenium thin films attract considerable attention. Similarly, compound semiconductors containing selenium (i.e. InSe. CdSe or CuInSe₂) are of interest for optoelectric applications, including advanced solar cells, IR detectors and solid-state lasers [1]. Selenium appears in different phases. The amorphous phase (red, brown and black) exhibits low electronic conductivity. The crystalline phases, include several solid allotropes, namely, the rhombohedral one, the α , β and γ monoclinic ones and the trigonal (hexagonal) one. Hexagonal Se is gray and it is the densest and the most stable of all phases [2]. Black Se consists of large polymeric rings having up to 1000 atoms per ring [3], the red amorphous Se has a deformed chain structure, and upon heat treatment it transforms to the stable hexagonal phase [4]. The monoclinic form is thermodynamically metastable and spontaneously converts to the trigonal one at higher temperature [5]. Selenium generally can adopt any of the allotropic modifications in its solid state and there is no clear distinction between amorphous and vitreous states [6,7]. Consequently, the formation of insulating allotropes can only be avoided by careful control of electrodeposition conditions (e.g., temperature and current density), furthermore, a careful selection of substrate materials is required [8].

In literature, a large variety of techniques is described for the preparation of Se thin films such as photodeposition, radiofrequency sputtering and vacuum deposition [9-11]. However, a low cost method, such as electrodeposition, would be beneficial for large-area thin film production. Usually, the electrodeposition of selenium from conventional aqueous solutions at low temperature leads to the formation of amorphous red selenium, which is an insulator. Graham et al. reported that amorphous Se layers with thicknesses up to 500 nm can be plated using acidic (pH 0.7–0.9) or slightly alkaline (pH 7.5-8.0) electrolytes in the temperature range of 20–40 °C [12]. However, they noticed that colloidal Se is formed near the cathode surface due to the plating process. The particles aggregate and increase in number and size with time causing defects in the deposited Se film in the form of particle inclusions. Uzoh and Aksu avoided such defects by addition of an anti-coagulation agent, like 1,4-bis(3-aminopropyl) piperazine, which inhibits the growth of Se particles and promotes the dispersal of such Se particles during the plating process of Cu-Se [13]. Hippel could successfully deposit gray Se using an acidic electrolyte composed of saturated selenium dioxide in 9 molar H₂SO₄ at a





^{*} Corresponding author. Tel.: +49 5323722494; fax: +49 5323722460. ** Corresponding author.

E-mail addresses: ibrahim.alsayed@tu-clausthal.de (A.A. Aal), frank.endres@tu-clausthal.de (F. Endres).

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temperature of 100 $^{\circ}$ C [14]. Such harsh operating conditions for the deposition of gray Se can hardly be applied to a mass production process.

Alternatively, our group suggested the utilization of ionic liquids for Se deposition due to their wide electrochemical window and extremely low vapour pressures, which allow deposition at temperatures above 100 °C. Our previous studies showed that gray Se can easily be deposited at temperatures of more than 100 °C, which is practically impossible in aqueous galvanic baths [15]. The only shortcoming is that the employed SeCl₄ and the whole bath have to be handled under dry box conditions, which would complicate a technical process. The most recent research by Steichen and Dale focused on the influence of precursor salt on the electrochemical behavior, as well as the phase, morphology and crystallinity of the Se deposits from 1-ethyl-3-methylimidazolium tetrafluoroborate/chloride at temperatures >100 °C [16]. They found that applying different precursors (SeCl₄ and SeO₂) leads to the deposition of amorphous and high aspect ratio single-crystalline trigonal Se nanorods films.

In the present paper, we demonstrate that the deposition of crystalline Se can be realized at higher temperatures $(70-110 \,^{\circ}\text{C})$ from the air and water stable 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate (Py_{1,4}[CF₃SO₃]). The electrodeposition of Se on gold and copper electrodes was studied in water containing ionic liquids in open air conditions. Water is essential for the deposition of Se from H₂SeO₃, furthermore it enhances the solubility of the Se precursor. Since Py_{1,4}[CF₃SO₃] does not react with water, electroplating baths based on air and water stable ionic liquids containing water might be a promising way for the deposition of Se in open air conditions. We would like to mention that there is an effect of cations on the Se deposits which will be reported elsewhere.

2. Experimental

 H_2SeO_3 powder (Sigma–Aldrich, 99.99%) was used as selenium source. The ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate (IOLITEC, commercial quality), employed as electrolyte, was slightly yellowish from a Li free synthesis with Cl⁻ <100 ppm and butylpyrrolidin <5000 ppm. Other chemicals used in this work were obtained in analytical grade and used without further purification. The dissolution of H_2SeO_3 in $Py_{1,4}[CF_3SO_3]$ electrolyte was examined in pure ionic liquid and its mixture with water (1–5 vol%). It was found that addition of 5 vol% water enables the dissolution of H_2SeO_3 .

The cyclic voltammetry and electrodeposition experiments were carried out in open air conditions, using a three-electrode cell setup. Platinum was used as counter electrode and a quasireference electrode, respectively. We have to mention that the Pt quasi-reference electrode is definitely not optimal, as during the massive electrolysis the reference electrode potential can shift by 100-200 mV. However, there is no other reference electrode which does definitely not react with the Se precursor under these conditions. Gold substrates from Arrandee (200-300 nm thick gold films deposited on chromium-covered borosilicate glass), and Cu sheets (99.99%) were used as working electrodes, respectively. Directly before use, the gold substrates were very carefully heated in a hydrogen flame to red glow while the copper sheet electrodes were polished, etched by 5% HNO₃ and sonicated in iso-propanol for 10 min. An electrochemical cell made of polytetrafluoroethylene (Teflon[©]) was clamped over a Teflon covered Viton[©] o-ring onto the substrate, thus yielding an exposed surface area of 0.6 cm². Prior to use, all parts in contact with the solution were thoroughly cleaned in a mixture of $50/50 \text{ vol}\% \text{ H}_2\text{SO}_4/\text{H}_2\text{O}_2$ followed by refluxing in bidistilled water. All electrochemical measurements were performed using a VersaStat 263A Potentiostat/Galvanostat (Princeton Applied Research) controlled by the PowerCV and PowerStep software. All experiments were performed under a hood in open air conditions. After deposition, the samples were rinsed with iso-propanol to ensure removal of the ionic liquid and subsequently dried under vacuum at room temperature for 2 h.

A high-resolution field emission scanning electron microscope (Carl Zeiss DSM 982 Gemini) was utilized to investigate the surface morphology of the electrolysis product. The X-ray diffractogram of the electrolysis product was acquired by a Siemens D-5000 diffractometer with CoK α radiation.

Reddish and grayish films deposited at a room temperature and a temperature of 110 °C were imaged by tapping-mode atomic force microscopy (Veeco/DI Dimension 3000, USA) in air using NSC15 cantilevers (MikroMasch). Images were plane-fit and analyzed using the Scanning Probe Image Processor (SPIP, version 3.0.0.9, Image Metrology Inc., Denmark). Because the surface roughness is a function of the thickness of the films, the same thickness of films (500 nm) were fabricated in order to compare the surface roughness.

The reflectivity of reddish and grayish films was measured using Cary 5000 Spectrophotometer with external reflectance accessories (DRA 2500 Integrating Sphere) at room temperature. The samples where mounted in the centermount position [17].

X-ray photoelectron spectroscopy (XPS) was performed in an ultrahigh vacuum (UHV) apparatus with a base pressure of 1×10^{-10} hPa using a hemispherical analyzer (Omicron EA 125) in combination with a non-monochromatic X-ray source (Omicron DAR 400). During XPS, X-ray photons hit the surface under an angle of 45° to the surface normal. For all measurements presented here, the Mg K α line with photon energy of 1253.6 eV was used. Electrons were recorded by the hemispherical analyser with a calculated analyser resolution of 0.83 eV for detail spectra and 2.07 eV for survey spectra. The analyser was mounted at an angle of 45° to the surface normal, analysing a spot of about 1.5 mm in diameter. All XPS spectra were displayed as a function of electron binding energy with respect to the Fermi level.

For quantitative XPS analysis, background substraction after Shirley was employed [18]. Photoelectron peak areas were calculated via mathematical fitting with Gauss-type profiles using OriginPro 7G including the PFM fitting module, which uses Levenberg-Marquardt algorithms to achieve the best agreement possible between experimental data and fit. Photoelectric crosssections calculated by Scofield [19] and inelastic mean free paths calculated by Seah and Dench [20] as well as the transmission function of our hemispherical analyzer are taken into account when calculating stoichiometry. The composition of the samples was given in relation to the deposited layer, i.e. contributions from the substrate are not included in the calculation.

For all XPS experiments, the sample was mounted on a molybdenum holder and introduced into the UHV by means of a sample transfer system. No additional pretreatment is performed except stated otherwise.

Where stated, the samples were cleaned by etching with argon ions from an Omicron ISE 5 ion source. For this process, Ar^+ ions with 2 keV kinetic energy were used, which results in target currents of 10 μ A. For a single sputter cleaning cycle, the Ar^+ bombardment was sustained for 300 s.

3. Results and discussion

3.1. Films on gold substrate

3.1.1. Electrodeposition at room temperature

The current–potential curves of gold in pure $Py_{1,4}[CF_3SO_3]$, its mixture with 5 vol% H₂O and $Py_{1,4}[CF_3SO_3]/5$ vol% H₂O with 0.16 M H₂SeO₃ are presented in Fig. 1. For the cyclic voltammogram of



Fig. 1. Cyclic voltammograms of (a) $Py_{1,4}[CF_3SO_3]$, (b) $Py_{1,4}[CF_3SO_3]$ /5 vol%H₂O and (c) $Py_{1,4}[CF_3SO_3]$ /5 vol%H₂O with 0.16 M H₂SeO₃ on gold at room temperature, scan rate: 10 mV/s, Pt as a quasi-reference electrode.

 H_2SeO_3 (0.16 M) in $Py_{1,4}[CF_3SO_3]/5 vol%H_2O$, two cathodic peaks (C1, C2) are obtained and at C1 the deposition of a reddish film, presumably red Se, is observed.

According to recent studies by Lai et al., for aqueous solutions, the first peak C1 might be associated to the electroreduction of H_2SeO_3 to Se^0 onto the gold substrate through a four-electron step as shown by Eq. (1) [21]. The second peak C2 might be related to the six-electron reduction of H_2SeO_3 to Se^{2-} species, according to Eq. (2). This is also supported by the area under the peak (charge) involved in peak C2 which is much higher than that involved in peak C1. The product Se^{2-} is subsequently subjected to a conproportionation reaction with H_2SeO_3 in solutions (Eq. (3)), leading to the chemical formation of Se^0 .

$$H_2 SeO_3 + 4H^+ + 4e^- = Se + 3H_2O$$
 (1)

 $H_2SeO_3 + 6H^+ + 6e^- = H_2Se + 3H_2O$ (2)

$$H_2SeO_3 + 2H_2Se = 3Se + 3H_2O$$
 (3)

The scan rate dependence of the peak currents in our experiments is not straightforward and we assume that kinetic phenomena lead to the peak shape in the CV. In [22], we discussed that solvation layers of ionic liquids might influence electrochemical reactions. Thus, it is also possible that the reduction of H_2SeO_3 to Se occurs differently to the mechanism reported for aqueous solutions.

The surface morphology of Se films deposited at C1 onto the Au substrate was investigated at different deposition times (10, 30, 120 min). SEM images showed that the surface coverage increases with increasing the deposition time from 10 to 30 min (Fig. 2).



Fig. 2. SEM of Se film deposited at -1.2 V on gold after (a) 10 min, (b) 30 min, and (c) 120 min at room temperature.

However, a film deposited in 120 min was loosely adhering and peeled off during rinsing.

The phase structure of the deposited Se films was characterized by X-Ray diffraction and is presented in Fig. 3. The XRD exhibits different sharp peaks confirming the crystalline nature of the as-deposited films. The XRD pattern also exhibits a peak at 2θ of 40.3° corresponding to the gold substrate. The comparison of the observed peaks at 2θ of 27.3, 31.7, 34.6 and 36.6° with the standard data proves that the reddish deposited Se is a mixture of textured rhombohedral (JCPDS 32-0992) and hexagonal (JCPDS 42-1425) crystal phases. The reddish color is related to the formation of amorphous red Se having no lattice (Bragg peaks), and cannot be visible in XRD pattern.



Fig. 3. XRD pattern of Se film deposited at -1.2 V for $120 \min$ on gold at room temperature.

3.1.2. Electrodeposition at higher temperatures

The effect of bath temperature on the Se film deposition and its morphology was also investigated. The electrochemical behavior of H_2SeO_3 in $Py_{1,4}[CF_3SO_3]/5$ vol% H_2O at temperatures of 70, 90 and 110 °C was studied. Fig. 4 shows the cyclic voltammogram of $Py_{1,4}[CF_3SO_3]/5$ vol% H_2O and H_2SeO_3 (0.16 M) at 70, 90 and 110 °C on gold. Similar to the CV at room temperature, two cathodic peaks (C1 and C2) are observed. However, this time a grayish deposit was



Fig. 4. Cyclic voltammogram of $Py_{1,4}[CF_3SO_3]/5 \text{ vol}\%H_2O$ mixture with 0.16 M H_2SeO_3 on gold at temperatures of (a)70 °C, (b) 90 °C and (c) 110 °C scan rate: 10 mV/s, Pt as a quasi-reference electrode.



Fig. 5. X-ray diffraction analysis of Se film deposited at -1.2 V for 60 min on gold from Py₁₄[CF₃SO₃]/5 vol%H₂O mixture with 0.16 M H₂SeO₃ at temperatures of (a) 70 °C, (b) 90 °C and (c) 110 °C.

obtained at C2. In the reverse scan, a small anodic peak (A1) was observed which seems to be due to the partial oxidation of the surface Se species deposited at C2. Crossing of the reverse anodic scan with the cathodic one is a hint for nuclei formation on the electrode surface [23]. The peak C3 is probably due to the reduction of Se⁰ to Se^{2–} species which are soluble in the electrodeposition bath. At temperatures of 90 and 110 °C, the CV measurements exhibited similar trends as in the case of lower temperatures (Fig. 4b and c). As higher temperatures are known to favor the reaction rate due to higher diffusion rate and less viscosity, an increase of the area under the peaks was observed.

The phase structure and the chemical composition of the grayish deposited films were characterized by XRD and EDX, respectively. The analysis of the obtained XRD pattern for the grayish film deposited at 70, 90 and 110 °C confirmed that the observed peaks at 2θ of 27.3, 31.7, 34.6 and 36.6° can be ascribed to the gray hexagonal phase of Se (JCPDS 42-1425) with lattice parameters *a* = 4.36 Å and *c* = 4.95 Å and the rhombohedral phase (JCPDS 32-0992) (Fig. 5a). The spectra also revealed that increasing of temperature from 90 to 110 °C leads to sharper XRD peaks confirming the formation of well-crystallized Se films (Fig. 5b and c). The EDX analysis indicated that the products were pure Se without any detectable impurities.

The SEM analysis of the grayish film deposited at 70 °C showed different, quite interesting structures. Fig. 6a-e presents images of Se deposited during 10 min. The deposit is composed of regular micrometer-sized spheres with smooth surfaces and a diameter of \sim 500 nm (Fig. 6a). Surprisingly, a careful observation revealed that on the surface of some microspheres an outer shell seemed to grow (Fig. 6b and c). In some areas, a hole on the sphere appeared, and thus the inner core became visible (Fig. 6d). On other areas, Se micro-rods were observed to grow from the spheres, either from one side or from both sides (Fig. 6e). With increasing the deposition time to 60 min, solely spheres with a diameter of \sim 250 nm were observed (Fig. 6f). We can currently not explain why such a different morphology is observed. It is possible that the shell consists of a different phases leading to a limited number of nucleation sites, maybe further influenced by the varying bath composition during deposition.

The morphology of the deposited films at temperatures of 90 and 110 °C is shown in Fig. 7. It is clear that both films show a similar surface structure at low and high magnification, where the deposit consists of crystalline particles. Such similarity in morphologies might indicate that at temperature \geq 90 °C, the nucleation and crystal-growth mechanism are apparently temperature independent. Further studies are required to achieve detailed information



Fig. 6. Different magnifications of SEM images of the Se microstructure deposited at -1.2 V and a temperature of 70 °C on gold for 10 min (a-e) and 60 min (f).

on the nucleation process as well as a better control of growth kinetics, orientation and morphology.

3.2. Characterization of Se deposits

3.2.1. Surface topography

Surface topography of Se films deposited at room and higher temperature (110 °C) was examined using atomic force microscopy. Fig. 8 presents the typical AFM image of a $5 \times 5 \,\mu m^2$ area of deposited reddish and grayish films at a vertical z-scale of 72 and 922 nm, respectively. As shown from images, the reddish Se film has smoother surface with root main square roughness of ~8 nm, peak-to-valley height of ~58 nm, whereas the grayish Se film showed rough surface with an average root main square roughness of ~85 nm and peak-to-valley height of ~560 nm. The coarse particles of grayish film are formed due to the increased deposition rate at higher temperature.

3.2.2. Optical properties

The purpose of these measurements is to investigate the optical properties of reddish Se thin film deposited at room temperature comparing with the grayish one obtained at $110 \,^\circ$ C. Since the films were opaque, the reflectance measurement was the proper test. Fig. 9 shows the diffuse reflectance (*R*,%) spectra in the visible and

near infrared regions. It is clear that the films have different absorption edges, where the reddish Se exhibited higher reflectance (less absorption and scattering) than that of the corresponding grayish one. The increased absorbance of the grayish film is thought to be due to a roughening effect and higher surface area (Fig. 8).

The reddish Se film has a reflectance minimum (absorption maximum) at 2.30 eV whereas the gravish film shows a broad peak in the range of 1.89 to 2.37 eV. Taking into account that the gravish film is composed of rhombohedral phase besides the main hexagonal one, the obtained results are close to that measured by Prosser and Henisch for pure red (amorphous) and gray (hexagonal) Se [24]. They reported two reflectance peaks for hexagonal Se: the long wavelength peak at 1.85 eV and the short wave length peak at 2.4 eV. Moreover, Stuke et al. has also reported two peaks for hexagonal Se at 1.95 and 2.25 eV [25]. Gates et al. reported that the lowest energy transition (i.e. grayish film in our results) from the bonding states could be attributed mostly to interchain interactions by calculating the electronic charge distributions, while, the higher energy transitions (i.e. reddish film) were determined to arise from covalent bonds within the selenium chain [26]. Spectroscopic absorption studies by Bogomolov et al. on isolated helical chains of Se atoms further confirmed that the strong absorption at ~2.2 eV came from the intermolecular transition between the spiraling chains of selenium [27].



Fig. 7. Different magnifications of SEM images of the Se microstructure deposited at -1.2 V on gold at temperatures of 90°C (a,b) and 110°C (c,d).

The diffuse reflectance spectra were translated into the absorption spectra by the Kubelka–Munk's equation that is described as follows [28,29]:

$$a = \frac{(1-R)^2}{2R} \tag{4}$$

In Eq. (4), α and *R* represent the absorption coefficient and reflectivity, respectively. This conversion is available to estimate the band gap from powder diffuse reflection spectra. [30]. The optical band gap energy, was calculated on the basis of recorded optical spectra using the well-known relation:

$$a\,h\nu = C(ah\nu - E_g)^n\tag{5}$$

where *C* is constant, hv the photon energy, while *n* depends on the nature of the transition. For direct transitions n = 1/2 or 3/2 while for indirect ones n = 2 or 3, depending whether they are allowed or forbidden, respectively. The best fit of $(\alpha hv)/n$ versus the photon energy, in the case of both reddish and grayish Se thin films, was obtained for n = 1/2 [31]. The values of the direct optical band gap

 E_g were determined by extrapolating the linear region of the plots to zero absorption ($\alpha hv = 0$). The optical band gap of the deposited reddish film from the inset Fig. 9 is ~2.04 eV which is closed to these results reported for amorphous Se (2.05 eV) by Zienab Mandouh [32] and 2.09 eV by Bindu et al. [33]. The value of band gap of the grayish film is found to be 1.71 eV in agreement with a previously reported one for the pure hexagonal gray Se of 1.85 eV by Yan et al. [34] and 1.8 eV by Daveln [35].

3.2.3. XPS analysis

Fig. 10 shows XPS results from the reddish Se film as introduced into the UHV. Emission from the deposited selenium layer and the gold substrate as well as from several remnants due to the production process can be detected on the surface. The contributions from oxygen (6 at% of the deposited layer) and fluorine (2 at%) can be removed completely by a short sputter process, (see the second scan). The carbon fraction in the layer decreases from 28 to 10 at% during the sputter cleaning process. The peak at 784 eV is attributed



Fig. 8. AFM images of Se films deposited at -1.2 V on gold (a) at room temperature and (b) at 110 °C.



Fig. 9. Reflectivity of reddish and grayish Se films deposited at -1.2 V on gold.

to not completely removed impurities of barium or cobalt (<1 at% in both cases).

The detection of carbon, oxygen and fluorine with XPS is not a contradiction to the EDX result, but is caused by the much higher surface sensitivity of XPS. The fact that a short sputter process can remove these remnants suggests that it is a very thin surface layer only. Fig. 11 shows results from grayish Se in the same manner as Fig. 10. Like on reddish Se, remnants from the production process can be detected. The fraction of oxygen (8 at% of the deposited layer), fluorine (3 at%) and sodium (<1 at%) can be sputtered away easily. The carbon contribution is reduced from 25 to 4 at% during sputtering.

Fig. 12 shows a chemical shift analysis performed on detail spectra from the Se 3d region for the reddish film and the grayish Se. For this analysis, results from the sputtered samples are used. The experimental data is shown as black dots while the Gaussians used for the fitting procedure are drawn as blue and green lines. The bold red line represents the sum of all Gaussians. The function used for Shirley background subtraction is shown as the solid black line at the bottom.

The main double peak is due to emission from the metallic Se $3d_{5/2}$ and Se $3d_{3/2}$ orbitals (blue Gaussians). In addition to these contributions additional intensity can be detected on the high



Fig. 10. XPS spectra of reddish Se film deposited at -1.2 V on gold as introduced into the UHV and sputtered.



Fig. 11. XPS spectra of grayish Se film deposited at -1.2 V on gold as introduced into the UHV and sputtered.

binding energy side (green Gaussians). This is due to emission from Se 3d orbitals in a different chemical environment (core level shift). The shift amounts to 2.3 eV for the reddish film and 2.5 eV for the grayish Se. That is too small to originate from a SeO₂, which exhibits a chemical shift of 4.4 eV [36]. It may be due to a surface layer of oxidized Se^{δ +} with 0< δ <4.

The comparison of the peak areas reveals that more than 93% of the reddish film in this sample is in the metallic state Se⁰, while only less than 7% is in the oxidized state Se^{δ +}. For the grayish film, the analysis reveals that the fraction of Se^{δ +} in that sample is about 4 at%.

3.3. Films on copper substrate

As Se is one component in the CuInSe₂ compound semiconductor, we also tested the deposition of Se on copper. Fig. 13 presents the CV of $Py_{1,4}[CF_3SO_3]/5 \text{ vol}\%H_2O$ and its mixture with H_2SeO_3 (0.16 M) at room temperature onto copper. In contrast to gold under comparable conditions, the voltammetric curve showed three cathodic peaks at -0.5, -1.2 and -1.9 V besides an anodic process. The peaks C2 and C3 might be attributed to the



Fig. 12. XPS detail spectra from the Se 3d region of the sputtered reddish Se film (left) and sputtered grayish Se film (right).



Fig. 13. Cyclic voltammogram of $Py_{1,4}[CF_3SO_3]/5 \text{ vol}\%H_2O$ (a), $Py_{1,4}[CF_3SO_3]/5 \text{ vol}\%H_2O$ with 0.16 M H_2SeO_3 on copper at a room temperature (b) and a temperature of 70 °C (c), scan rate: 10 mV/s, Pt as a quasi-reference electrode.

reduction of selenium ions as suggested in Eqs. (1)-(3). The peak C1 seems to be correlated to the formation of Cu–Se compounds. The voltammetric features of the Cu/Se system in aqueous solutions were studied by Mishra and Rajeshwar [37]. The data on the binary system were consistent with the facile formation of a Cu_{2-x}Se solid phase with *x* varying from 0 to 1. Additionally, Skyllas-Kazacos and Miller concluded from their hydrodynamic voltammetry data on Cu disk electrodes that a reaction between Cu and Se leads to the postulated formation of Cu₂Se [38]. Pottier and Maurin have confirmed the formation of Cu₂Se via X-ray diffractometry [39]. On the other hand, Ueno et al. found no evidence for Cu₂Se formation, but instead reported X-ray diffraction evidence for the Cu₃Se₂ phase [40].

The EDX analysis in our experiments indicated that the blackish film deposited at C2 consists of Se (24 at%) and Cu (6 at%), contaminated by adsorbed ionic liquid components as C, F, S and N. However, the phase structure of CuSe (JCPDS 20-1020) was identified as illustrated by XRD peaks at 2θ of 31.3 and 46.1° (Fig. 14a) in good agreement with Villalvilla and Velasco who found that CuSe is the most likely compound formed by reaction of Cu with H₂SeO₃ at room temperature [41]. From the thermodynamic point of view, CuSe is the most stable compound at room temperature on the phase diagram of the Cu–Se binary system [42].

For comparison, a typical CV was obtained for the copper substrate in $Py_{1,4}[CF_3SO_3]/5 \text{ vol}\% H_2O$ with H_2SeO_3 (0.16 M) at a temperature of 70 °C (Fig. 13c). In this case, the deposited film obtained at C2 was gray. Although the current peaks (C2, C3) well agree with those ascribed to the four-electron and six-electron reduction of Se(IV) on gold, XRD peaks at 2 θ of 31.3, 36.3, 48.1 and 52.1°, in Fig. 14b, clearly indicated the presence of cubic Cu_{1.8}Se phase with the berzelianite structure (JCPDS 71-0044) besides the rhombohedral Se phase (JCPDS 32-0992). The EDX spectrum confirms that the deposited film is composed of Cu (62.8 at%) and Se (36.1 at%) with an atomic ratio of 1.74 that is close to the



Fig. 14. XRD of Se film deposited at -1.2V for 30 min on copper (a) at room temperature and (b) at a temperature of 70 °C.



Fig. 15. EDX analysis and SEM image of Se film deposited at $-1.2\,V$ for 30 min on copper at temperature of 70 $^\circ$ C.

stoichometry of $Cu_{1.8}$ Se (Fig. 15). Consequently, selenium is deposited at low electrode potentials and the copper electrode is subject to a compound formation with Se. It is known that Hg, Ag and Cu electrodes can react with Se [43–45]:

$$H_2SeO_3 + M + 4e^- + 4H^+ = M_nSe + 3H_2O$$
(6)

where *M* is Cu, Ag or Hg, and *n* is 1 for Hg and 2 for both of Cu and Ag. Our results reveal that the cathodic peak at C1 is attributed to the formation of copper–selenides film (Cu_{1.8}Se).

Fig. 15 shows the SEM images of the film deposited onto Cu substrate at 70 °C. The deposited $Cu_{1.8}$ Se film shows some dendrites. We also found cubes with edge lengths ranging from 100 to 500 nm. These different morphologies are a hint for different mechanisms in the deposition process.

4. Conclusions

In this study, the electrodeposition of Se films from the air and water stable 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ionic liquid with 5 vol% water in open air conditions was presented. The results showed that reddish Se (amorphous, hexagonal and rhombohedral) film is deposited at room temperature, while a gravish one (hexagonal and rhombohedral) is deposited at a temperature of \geq 70 °C on gold substrates. The smooth reddish Se film showed lower absorption comparing with the rough gravish one. In addition, the nucleation and growth mechanism are dependent on the operating temperature up to \sim 90 °C, while at higher temperature, the deposited films show similar morphology. Using ionic liquid enables the crystalline Se deposition to be applied in open air conditions even at higher temperatures (>100 °C) which is impossible to be applicable in aqueous solutions. The analysis with photoelectron spectroscopy and energy dispersive X-ray spectroscopy shows that the deposited films consist of Se with only small impurities from the electrochemical process at the surface. The Se films are shown to be mostly metallic Se⁰. The possibility of the Se deposition on copper substrates was also investigated, and copper-selenides (CuSe and Cu_{1.8}Se) are formed at lower and higher temperatures. Our results show that the process of Se deposition is highly complicated where the morphology, the phase structure and the surface properties of deposited films depend on different variables as deposition time, applied temperature and substrate type.

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