CHEMICAL BATH DEPOSITION OF {111} TEXTURED MERCURY(II) SELENIDE THIN FLMS ON TRANSPARENT POLYESTER SHEETS

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Abstract: A novel method for mercury(II) selenide thin films deposition on transparent polyester sheets is developed. The proposed method is based on chemical bath deposition in alkaline media. A chemical reaction of hydrolytic decomposition of selenosulfate is involved in the deposition process. X-ray analysis confirmed that the deposited material is {111} textured mercury(II) selenide. Upon annealing, the film crystallinity increases, resulting in a red shift of the optical spectra due to quantum size effects. The sheet resistances of the annealed films are about 1.32 kΩ/cm^2 and for as deposited ones are about 10 times higher. Using the optical absorption data, optical bandgap for the deposited thin films was determined from a plot of $(\alpha h v)^2$ vs. the photon energy. The extrapolation of the linear part gave a bandgap energy of 2.5 eV. These thin films are potentially applicable in fabrication of display devices, opto-electronic devices, as well as active electrode materials in energy storage.

Key words: Mercury(II) selenide films, chemical bath deposition, semiconductors, thin films, textured films.

1. Introduction

There has been an increased interest in depositing electroconductive films on non-conductive organic polymers in the last several years [1-10]. This is due to the possibility for their applications in various fields of opto-electronic technology, such as fabrication of display devices [11], opto-electronic devices [12], as well as active electrode materials in energy storage [13]. Several techniques for preparation of HgSe thin solid films on various substrates have been reported so far. Becker *et al.* reported a molecular beam epitaxial growth method for preparation of HgSe thin films on GaAs substrates [14]. The same technique has been applied by Einfeldt *et al.* These authors have used ZnSe substrates, and investigated the electrical properties of the HgSe-ZnSe heterojunctions [15]. The latest system may be used for blue/green laser diodes and light emitting diodes fabrication, which have been investigated thoroughly by Yu *et al* [16]. Pramanic *et al.* have reported an aqueous reactive solution growth technique [17] for HgSe thin films deposition on glass substrates, starting from mercury(II) formamide and sodium selenosulfate as a selenide-releasing agent. The films obtained by their method are amorphous and p-type semiconductors.

2. Experimental

This paper presents a novel method for chemical bath deposition of HgSe thin films on polyester non-conductive substrates. The proposed method is very simple, non-hazardous and allows a relatively fast deposition of HgSe films, from one chemical bath, under moderate experimental conditions.

Thin solid films of mercury(II) selenide were prepared on polyester transparent uncoated substrates, such as transparent films commonly used for overhead projectors (ZweckForm, Catalogue No. 3555). Substrate sizes were the same as those of a standard microscope glass. Before deposition, substrates were cleaned in a warm detergent solution for 15 min. Then they were rinsed with deionized water and immersed in a fresh 0.03 %

aqueous solution of tin(II) chloride for 15 min. The treatment with tin(II) chloride solution provides a uniform wetting of the substrate surface and improves the film adhesion.

The technique for chemical bath deposition of HgSe was similar to the one we used earlier to deposit thin Cu_2Se films [18]. Previously prepared substrates were vertically supported against the walls of a 100 cm^3 laboratory beaker which contained the solution for chemical deposition. This solution was prepared by mixing 10 cm^3 c = 0.15 mol / dm^3 aqueous solution of $Hg(NO_3)_2$ with 4 cm^3 25 % NH_3(aq), cooling this system to 10 °C and adding 20 cm^3 of previously cooled Na_2SeSO_3. Na_2SeSO_3 solution was prepared in a following manner: 8 g selenium were mixed with a small portion of 1 mol / dm^3 aqueous solution of sodium sulfite and when a dense suspension was obtained then the rest of 100 cm^3 of the sodium sulfite solution was added. The obtained system was then heated at 90 °C for about one hour. After cooling to room temperature, the suspension was filtered off and deionized water was added to the filtrate, to make a total volume of the solution of 100 cm^3. The temperature was kept constant at 10 °C during deposition.

3. Results and Discussion

The overall chemical reaction of the deposition process may be represented with the following equation:

$$Hg^{2+} + SeSO_3^{2-} + 2OH^- = HgSe + SO_4^{2-} + H_2O$$
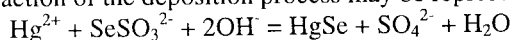
First, a white precipitate is formed as a result of the reaction between mercury(II) nitrate and the ammonia:

$$Hg^{2+} + NO_3^- + 2NH_3 = [HgNH_2]NO_3 + NH_4^+$$
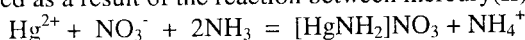
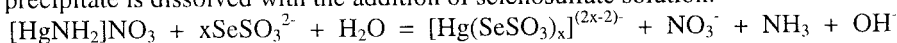The excess of ammonia reacts partly with the precipitate, forming a variety of complexes (with 1, 2, 3 and 4 ligand molecules):

$$[HgNH_2]NO_3 + (x-1)NH_3 + H_2O = [Hg(NH_3)_x]^{2+} + NO_3^- + OH^-$$
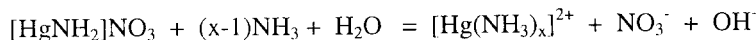
where $x \in \{1, 2, 3, 4\}$.

The rest of the precipitate is dissolved with the addition of selenosulfate solution:

$$[HgNH_2]NO_3 + xSeSO_3^{2-} + H_2O = [Hg(SeSO_3)_x]^{(2x-2)-} + NO_3^- + NH_3 + OH^-$$

With the excess of sodium sulphite which did not react with selenium, formation of other complexes is possible, also causing a dissolving of the precipitate:

$$[HgNH_2]NO_3 + xSO_3^{2-} + H_2O = [Hg(SO_3)_x]^{(2x-2)-} + NO_3^- + NH_3 + OH^-$$
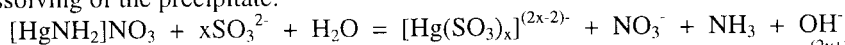
Of course, a possibility for formation of mixed complexes as $[Hg(NH_3)_x(SeSO_3)_y(SO_3)_z]^{(2y+2z-2)-}$, (where x + y + z ≤ 4) can not be excluded, too. The complexity of this system is thus, obvious. However, the free mercury(2+) ions (although present in rather small concentrations) react with the selenide ions released by the following reaction:

$$SeSO_3^{2-} + H_2O = Se^{2-} + SO_4^{2-} + 2H^+$$
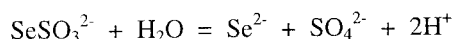
finally forming HgSe films:

$$Hg^{2+} + Se^{2-} \rightarrow HgSe$$
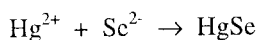
The concentration of free mercury(2+) ions may be considered as practically constant during the deposition, since it is controlled by the dynamical equilibrium between the precipitation and the dissociation of the complexes.

During the largest part of the deposition process, bulk precipitation is observable, accompanied with scattering of the coherent laser light. At the end of the deposition, the bulk precipitation reduces, and so the scattering. Thus, it can be concluded that the predominant deposition mechanism is the cluster one (not excluding the ion-by-ion at least at the end of the deposition process), where the clusters are probably colloids of Hg ammine species.

The sheet resistance of the films was measured between two silver-pasted electrodes, 1 cm in length and 1 cm apart, using a Radio Shack Digital Multimeter model 22-168. The thickness of the films was determined by the gravimetric method. The deposited films as well as the bulk precipitates were studied by X-ray diffraction, using a Rigaku model D/MAX-IIB diffractometer and a nickel filtered Cu K_α radiation. The optical spectra were recorded on a Cary 5 spectrophotometer in the VIS-NIR spectral region.

As can be seen from the x-ray diffractograms of as deposited and annealed (120 °C for 5 h) HgSe thin films, one highly intensive peak appears at 12.677 theta value, indicating a strong {111} texturing of the films. The comparison of the observed diffraction peaks of the bulk precipitate with the standards (JCPDS powder diffraction data set # 15-456 from the 1-46 database) confirmed that most of the deposited material is the cubic form of mercury(II) selenide (known as Tiemannite). On the basis of the full width at half maximum of the XRD

peaks, using the Debye-Scherrer expression [19,20] we have calculated the average crystal sizes of the unannealed and annealed films. The corresponding values are 7.7 and 7.9 nm. The slight increase in crystal size upon annealing is reflected in the appearance of the optical spectra of the films (exhibiting the slight red shift).

Optical absorption spectra in the UV/VIS/NIR region were recorded for the obtained mercury(II) selenide thin films. Using the optical absorption data, the optical bandgap of the HgSe films was determined from a plot of $(\alpha h v)^2$ vs. E. It is well known that for direct transitions, $(\alpha h v)^{1/n}$ depends linearly on the photon energy, where $n = 1/2$ or $3/2$, depending on whether the transitions are allowed or forbidden. In the case of HgSe films, the best fit of $(\alpha h v)^{1/n}$ vs. the photon energy was obtained for $n = 1/2$. The extrapolation of the linear part gave a bandgap energy of 2.50 eV for the unannealed films, while for the annealed ones it reduces to 2.44 eV. A value of 1.42 eV has been previously reported for amorphous HgSe films [17]. It is known that (bulk) HgSe has an inverted band structure (this means a negative value for the band gap energy [21]). In fact, the rather large positive values for the band gap measured both in Ref. 17 and in our case may be attributed to size quantization effects [19,22,23]. Strong quantum size effects for colloidal HgSe have been thoroughly studied by Nedeljkovic *et al.* [24]. In their paper, the value of 3.15 eV for the band gap is reported for colloidal particles with average size between 2 and 3 nm. Since the average size of the HgSe colloidal particles is smaller than the average crystal size in the case of our films, a higher band gap energy is expected. The size quantization in the case of our films is reflected in the appearance of the optical spectra as well. As can be seen from the optical spectra (taken against the substrate reference) of the unannealed and annealed films, a red shift is clearly observable upon annealing, indicating an increase in the crystal size. The observed red shift is in line with the decrease of the band gap energy, due to size quantization effects.

The measured electric resistance values for the as deposited films are about 13 kΩ/cm². Upon annealing (in air), due to the crystallization process, the electrical resistance decreases about ten times. From a semilogarithmic plot of the sheet resistance (measured between two silver pasted electrodes 1 cm apart and 1 cm long) vs. temperature, two distinct regions of conductivity are seen. The lower gradient part may be attributed to the hoping conduction mechanism, while the one with a larger gradient is due to the beginning of the crystallization process (accompanied with intrinsic conduction mechanism).

Апстракт: Развиен е нов метод за депозиција на тенки филмови од жива(II) селенид на транспарентни полиестерски фолии. Предложениот метод е базиран на депозиција во алкална средина. Основа на процесот е хидролитичкото разложување на селеносулфатот. Рендгенската анализа покажа дека добиениот материјал е <111> текстуриран жива(II) селенид. Со загревање, степенот на кристалност на филмовите се зголемува, што резултира во црвено поместување кај оптичките спектри, како резултат на квантни ефекти заради големина на зрната. Отпорот на греаните филмови изнесува 1.32 kΩ/cm² додека на негреаните тој е 10 пати поголем. Од зависноста на $(\alpha h v)^2$ од фотонската енергија, определена е оптичката ширина на забранетата зона на добиените тенки филмови, која изнесува 2.5 eV. Овие тенки филмови се потенцијално применливи за добивање на опто-електронски уреди, како и електродни материјали за конзервација на енергијата.

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