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FABRICATION OF NANOCRYSTALLINE {111} TEXTURED Ag_2Se THIN FILMS BY A CHEMICAL SOLUTION METHOD

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Abstract: A novel, inexpensive chemical bath technique for nanocrystalline Ag_2Se thin films deposition on transparent polyester sheets is developed. The deposition process is essentially based on a hydrolytic decomposition of selenosulfate. The deposited films were characterized by X-ray analysis, and also optical and electrical investigations were performed. X-ray analysis of the films confirmed that the deposited material is {111} textured silver selenide, with an average crystal size of 9.2 nm. The sheet resistance of the annealed films is about 10 Ω/cm^2 while for the as-deposited ones it is about 20 times higher. The optical investigations show that the films exhibit gradually increasing transparency in the 320 – 820 nm region. Using the optical absorption data, the optical band gap for the deposited thin films was determined to be 1.7 eV. Such somewhat higher value than the previously reported ones is attributed to size quantization effects.

Key words: Ag_2Se films, chemical bath deposition, semiconductors, textured thin films, nanocrystalline thin films, size quantization effects.

1. Introduction

An increased interest in semiconductive films on non-conductive organic polymers is noticeable in recent years [1-10]. This is due to the possibility for application of such materials 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]. Like other semiconductive metal chalcogenides, Ag_2Se is a rather interesting material. It has been used in IR detectors, photoconductors, photovoltaic cells, electrochemical storage cells, electrochemical potential memory devices, semiconductive optical devices for the visible region, etc [14-19]. Considerable attention has been devoted by various authors to the preparation of silver selenide thin films and study of their electrical and optical properties [20-28]. However, all of these methods require special techniques and deposition conditions. This paper presents a novel method for chemical bath deposition of nanocrystalline, textured Ag_2Se thin films on transparent polyester non-conductive substrates. The proposed method is very simple, non-hazardous, and allows a relatively fast deposition of films from one chemical bath, under moderate conditions.

2. Experimental procedure

Thin solid films of silver selenide were deposited on polyester uncoated substrates such as the transparent films commonly used for overhead projectors (Zweck Form, Catalogue No. 3555). Substrate sizes were the same as those of a standard microscope glass. In order to achieve a good adhesion of the coating material onto the substrate surface, special attention was paid to the preparation of substrates. These were first washed with a liquid detergent, rinsed with deionized water and then soaked into fresh 0.03% aqueous solution of tin chloride, $SnCl_2$, for a few minutes. Then they were washed with deionized water and dried in air before use. The treatment with $SnCl_2$ solution provides a uniform wetting of the substrate surface and improves film adhesion. It is possible that an ultra-thin layer of Sn(OH)Cl is created on substrate surface, which also initiates good adherence.

The proposed methodology is similar to those previously used by us for deposition of other metal selenide thin films [29, 30]. The silver selenide films growth is based on a chemical deposition in alkaline media. The deposition mixture used contained $AgNO_3$, NH_3 and Na_2SeSO_3. It was prepared in the following manner. First, 10 cm^3 0.1 mol/dm^3 $AgNO_3$ were placed into a 100 cm^3 laboratory beaker and diluted (1:1) ammonia solution was introduced with constant stirring. The obtained system had dark-brown color as a result of Ag_2O formation. Afterwards, about 80-90 cm^3 of distilled water were added and the system was cooled to 0 °C. Finally, 5 cm^3 of previously cooled 1 mol/dm^3 Na_2SeSO_3 solution were introduced into the beaker. The total volume of the chemical bath was about 100 cm^3. The pH of the bath was approximately 10-11. Previously cleaned and activated substrates were then vertically supported against the walls of a laboratory beaker. The temperature was kept constant at 0 °C during deposition. The Na_2SeSO_3 solution was prepared in the following manner. First, 1 mol/dm^3 aqueous solution of sodium sulfite was prepared and a stoichiometric amount of powdered selenium was added. Subjected to constant stirring, the mixture was heated and kept at 90 °C for about an hour. After cooling to room temperature, unreacted selenium was filtered off and the selenosulfate solution was placed and stored in a dark bottle. It is recommended to make small volumes of selenosulfate stock solution and to use it within one day. After the deposition, the coated polyester substrates were taken out, washed with deionized water and dried in air before examining their physical properties.

3. Results and Discussion

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

$$2\,Ag^{+} + SeSO_4^{2-} + 2OH^{-} \rightarrow Ag_2Se + SO_4^{2-} + H_2O$$

First, a brown precipitate is formed as a result of the reaction between silver nitrate and ammonium hydroxide:

$$AgNO_3 + NH_4OH \rightarrow AgOH + NH_4NO_3; \quad 2AgOH \rightarrow Ag_2O + H_2O$$

In excess of NH_4OH, the formed Ag_2O is dissolved:

$$Ag_2O + 4NH_4OH \rightarrow 2[Ag(NH_3)_2]OH + 3H_2O$$

The ammonia complex assures presence of the silver ions at low concentrations in the bath. The sodium selenosulfate, on the other hand, upon hydrolytic decomposition in alkaline media, gradually releases selenide ions as follows:

$$SeSO_3^{2-} + OH^{-} \rightarrow HSe^{-} + SO_4^{2-}; \quad HSe^{-} + OH^{-} \rightarrow H_2O + Se^{2-}$$

Of course, the possibility for formation of silver selenosulfate complexes (in excess of selenosulfate) and silver sulfite complexes (with the excess of sodium sulfite which did not react with selenium) can not be excluded. Formation of mixed complexes as $[Ag(NH_3)_x(SeSO_3)_y(SO_3)_z]^{1-2y-2z}$, is also possible. Since a bulk precipitation is observed during the film deposition process, most probably it occurs via the cluster mechanism (instead of ion-by-ion one). The concentration of free silver 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.

The deposited material as well as the bulk precipitate were identified by X–ray diffractometry, using nickel filtered Cu K_α radiation, on a D/MAX-IIB model diffractometer. Optical spectra were taken on a (Hewlett Packard) HP 8452A spectrophotometer in the UV-VIS spectral region. The sheet resistance of the coatings was measured between two silver pasted electrodes 1 cm in length and 1 cm apart, using a Radio Shack Digital Multimetar model 22-168. The thickness of the films was determined by gravimetric method.

X-ray difractograms were recorded for as-deposited as well as for the annealed films (7h at 120°C), and also for the bath precipitate. There is no significant change in crystallinity of the films upon annealing. The comparison of the observed diffraction peaks with the standard (JCPDS powder diffraction data set # 24-1041 from the 1-46 database) confirmed that most of the bath deposited material is the orthorhombic modification of silver selenide known as neumannite. As can be seen from the X-ray diffractograms, the thin solid films of silver selenide are {111} textured (all {111} crystal planes point upwards in the same direction). The average crystal size calculated from the Debye-Scherrer formula is 9.2 nm.

The electrical resistance of the as-deposited films is about 200 Ω/cm^2 (depending on the film thickness), while upon annealing it reduces approximately twenty times. The dependence of the electrical resistance on the temperature was measured at atmospheric pressure. From the plot of $\ln(10^3\ \Omega/R)$ vs. $1/T$ for the obtained silver selenide films, two distinct regions of conductivity are seen, that exhibit typical Arrhenius behavior [31]. The corresponding activation energies are 0.24 and 0.02 eV. Such findings are in line with the fact that more than one conduction mechanisms are involved [31, 32]. The lower-temperature part (straight line with a lower gradient) is attributed to the hopping conduction, which is expected at such temperature range, while the higher temperature region corresponds to the intrinsic conduction mechanism. The appearance of the intermediate part suggests that the concentration of impurities/defects is rather low.

As can be seen from the optical spectra of the films, they show gradually increasing transparency in the 320 – 820 nm region. On the basis of the optical absorption data, the optical band gap was determined from a plot of $(\alpha h\nu)^2$ vs. E. It is well known that for direct transitions, $(\alpha h\nu)^{1/n}$ 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 Ag_2Se films, the best fit of $(\alpha h\nu)^{1/n}$ vs. the photon energy was obtained for n =1/2. The extrapolation of the linear part gave a band gap energy of 1.7 eV, which is somewhat higher than the value of 1.33 eV reported previously [24]. Such a higher value of the band gap energy is due the size quantization effects, which lead to a series of discrete states in the conduction and valence bands resulting in the increase of the effective band gap [33, 34].

Апстракт: Развиена е нова, евтина техника за депозиција на тенки филмови од сребро селенид на транспарентни полиестерски фолии. Предложениот метод е базиран на хемиска депозиција во

алкална средина. Процесот на депозиција е во основа базиран на хидролиза на селеносулф Рендгенската анализа покажа дека добиениот материјал е {111} текстуриран сребро селенид просечна големина на кристалите од 9,2 nm. Степенот на кристалност не се зголемува значител при термички третман. Отпорот на греаните филмови изнесува околу 10 Ω/cm^2 а на негреанит околу 20 пати поголем. Оптичките испитувања покажаа дека транспарентноста на филмови постепено се зголемува во областа од 320 – 820 nm. Оптичката ширина на забранетата зо определена од зависноста на $(\alpha h\nu)^2$ од фотонската енергија, изнесува 1.7 eV. Ваква неш повисока вредност од досега соопштените е припишана на квантни ефекти заради големина зрната.

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