Growth of lead selenide thin films by the successive ionic layer adsorption and reaction (SILAR) technique

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This paper describes the growth of lead selenide (PbSe) thin films on glass and on ITO-covered glass substrates at room temperature under normal pressure utilising the successive ionic layer adsorption and reaction (SILAR) technique. Aqueous precursor solutions, lead acetate complexed with triethanolamine and sodium selenosulfate, were used for lead and selenide, respectively. The films were found to be metallic and adherent. The properties of the films were characterised by means of X-ray diffraction (XRD), Rutherford back-scattering spectrometry (RBS), nuclear reaction analysis (NRA) and scanning electron microscopy (SEM).

Lead selenide (PbSe) has numerous possible applications in the field of IR detection owing to its suitable bandgap.[1] Thin films of PbSe are easily prepared by chemical bath deposition (CBD).[1-7] Other methods for the fabrication of thin films of PbSe are molecular beam epitaxy (MBE)[8] and vacuum deposition;[9] and recently electrochemical deposition has also been used.[10] Gas phase growth has the disadvantage of a gaseous selenium precursor, which can be highly poisonous. The CBD method and electrochemical deposition, on the other hand, utilise aqueous precursor solutions, thus gaseous selenium compounds can be avoided. In the CBD method all the precursors together with the substrate are present in the reaction solution at the same time. Spontaneous precipitation is eliminated by selecting a fairly stable complex of the metal ion. The complexed precursor provides a controlled number of free ions. As a result, thin film deposition occurs by a controlled ion-by-ion reaction. In contrast to CBD, the successive ionic layer adsorption and reaction (SILAR) technique utilises sequential treatment of the substrate by the precursors, which is an advantage for process control. Like the CBD method, the SILAR method also has the benefit of aqueous conditions.

The SILAR technique has been applied mainly for the growth of II–VI compounds since its invention.[11,12] In addition, the growth of lead sulfide (PbS) thin films by SILAR utilising different lead and sulfide precursors has been studied.[13,14] Since the complexed lead precursor solution clearly affected the growth rate and the orientation of the PbS thin film, it was used in this work, too. The basic requirements for the selenium precursor are solubility in water and a suitable oxidation state. In CBD growth the precursors used for selenide (Se^{2-}) were selenourea [(NH$_2$)$_2$CSe][1] and sodium selenosulfate (Na$_2$SeSO$_3$).[2-7] Of these two molecules the latter was claimed to be more stable and simpler to prepare.[2,6,7] Accordingly, the selenium precursor used in this work was sodium selenosulfate, which was synthesised using a similar method as that described for CBD growth.[15]

Experimental

A SILAR apparatus as described in ref. 14 was used in the depositions. The lead precursor solution was 0.1 mol dm^{-3} lead acetate [Pb(CH$_3$COO)$_2 \cdot$3H$_2$O; Merck, p.a.) complexed with 0.2 mol dm^{-3} triethanolamine [tea, N(CH$_2$CH$_2$OH)$_3$; Riedel-deHaën, p.a.). The pH value of this solution was 7.8. This lead precursor was selected because it resulted in the highest growth rate, and because of its orientating effect on the growth of lead sulfide by SILAR.[14] A stock selenide (Se^{2-})

solution was synthesised by refluxing 2.0 g of elemental Se powder (B.H.D. Chemicals) with 6.3 g of sodium sulfite (Na$_2$SO$_3$; Merck, p.a.) in 40 ml water for 6–8 h. The resulting solution was cooled, kept overnight and filtered.[15] The actual precursor solution was diluted from this synthesised sodium selenosulfate (Na$_2$SeSO$_3$) solution, the Se^{2-} concentration being 0.02 mol dm^{-3}. Hydrazine hydrate (5 ml; N$_2$H$_4 \cdot$H$_2$O; Fluka, purum) was added to this reaction solution in order to avoid the formation of elemental selenium and to enhance the reduction of Se^{2+} in sodium selenosulfate to Se^{2-}. The pH of the anion precursor solution was adjusted to 12 with sodium hydroxide (NaOH; Eka Nobel).

The adsorption and reaction times for the lead and selenide precursor solutions were 20 and 40 s, respectively. The substrates were rinsed with pure water between each adsorption and reaction step and the rinsing time was adjusted to 100 s. The flow rate of the rinsing water was *ca.* 250 ml min^{-1}.

Soda lime glass microscopic slides and indium tin oxide (ITO, 150 nm) covered soda lime glass were used as substrates. The dimensions of the substrates were 26 × 76 × 1 mm^3. The substrates were cleaned ultrasonically in an acetone bath for 10 min and in an ethanol bath for 10 min. Finally the substrates were dried in a desiccator overnight.

The film thickness was determined by dissolving the film in concentrated nitric acid and measuring the amount of Pb^{2+} ion either using a Techron atomic absorption spectrophotometer, or in basic media with a Metrohm 626 Polarograph. The nominal film thickness was calculated by using the bulk density of PbSe (8.1 g cm^{-3}).

The film crystallinity was determined with a Philips MPD 1880 X-ray powder diffractometer using Cu-Kα radiation.

The surface morphology of the films was characterised with a Zeiss DSM 962 scanning electron microscope (SEM).

The chemical composition and the thickness of the films were also studied by Rutherford back-scattering spectrometry (RBS) of 2.0 MeV ^{4}He$^+$ ions from the 2.5 MV Van de Graaff accelerator of the Accelerator Laboratory, University of Helsinki.[16]

Hydrogen profiling was carried out by the nuclear reaction analysis (NRA) technique using a ^{15}N^{2+} beam from the 5 MV tandem accelerator EGP-10-II to `excite the 6.385 MeV resonance of the ^{1}H(^{15}N,α,γ)^{12}C reaction.[17]

Results and Discussion

According to the principles of SILAR, each deposition cycle begins with the immersion of the substrate into the cation precursor solution. Owing to the stability constant of log β =

8.03, the dominant lead species in the solution at pH 7.8 is $[Pb(tea)_2]^{2+}$.[18] During the immersion the positively charged metal ions in the solution adsorb onto the substrate. Consequently, an electrical double layer is formed. In the lead precursor solution this double layer contains the adsorbed lead ions on the inner side and their counter ions on the outer side.

In the alkaline anion precursor solution the sodium selenosulfate hydrolyses to give HSe^- ions[2] according to eqn. (1):

$$Na_2SeSO_3(aq) + OH^- \rightleftharpoons Na_2SO_4(aq) + HSe^- \qquad (1)$$
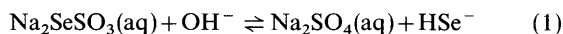
During the anionic immersion the hydrogen selenide (HSe^-) ions [or selenide (Se^{2-}) ions] come into contact with the adsorbed lead ions. Owing to the low solubility of lead selenide, a solid lead selenide is formed in the heterogeneous reaction. In CBD growth of the PbSe thin films the pH is usually *ca.* 10.[2,5,6] In fact, above pH 11.4 no reaction was observed.[2] On the other hand, a very high pH, $\geqslant 13$, was also found to be suitable for the CBD growth of PbSe thin films.[6] In this work, however, the SILAR growth required a pH of *ca.* 12 as well as an addition of $N_2H_4 \cdot H_2O$, otherwise no growth took place. $N_2H_4 \cdot H_2O$ was also needed to grow ZnSe thin films by CBD.[15] Hydrazine hydrate is known to be a powerful reducing agent.[19] The role of the hydrazine hydrate may, under the given conditions, be twofold: (i) to enhance the production of HSe^- (or Se^{2-}), *i.e.* the reduction of the sodium selenosulfate in the anion precursor solution, or (ii) to prevent the formation of elemental (and in this case chemically inert) selenium, either directly or by reducing the dissolved oxygen. In some of the growth experiments without the addition of the hydrazine hydrate, which did not produce any PbSe thin film, the lower part of the anion precursor solution vessel had a slight orange colour due to the formation of selenium. Consequently the latter explanation for the function of $N_2H_4 \cdot H_2O$ in the SILAR growth is probable.

Growth rate

The highest growth rate of lead selenide, *i.e.* the nominal thickness of the PbSe thin film divided by the number of cycles, on a glass substrate using solutions of 0.1 mol dm^{-3} lead acetate complexed with 0.2 mol dm^{-3} tea and 0.02 mol dm^{-3} sodium selenosulfate was *ca.* 0.18 nm cycle^{-1}. Because higher sodium selenosulfate concentrations contaminated the rinsing water very rapidly, they could not be used. After *ca.* 600 cycles the growth rate began to diminish gradually; at 1000 cycles the growth rate was *ca.* 0.12 nm cycle^{-1}. As the growth experiments were carried out continuously using 250 ml reaction vessels we conclude that the growth rate decrease is caused by the depletion of the concentrations in the precursor solutions.

XRD

According to the XRD pattern, as depicted in Fig. 1, the as-grown PbSe thin films were polycrystalline and cubic. Only reflections corresponding to those of a PbSe powder could be identified. The most intense reflection was always the (200) reflection, but the relative intensities of the other peaks varied by several tens of percents between the different samples, though the intensities were still close to those of the powder data. On ITO-coated glass the XRD pattern was similar to that on a pure glass substrate; however, the polycrystalline ITO masked some of the PbSe reflections. Annealing for 2 h at 120 °C in air reduced the FWHM of the peaks by at least 20% and increased the intensity of the [200] diffraction. Interestingly, in comparison to PbS, which also has a cubic structure with very similar dimensions (2.969 and 3.062 Å for PbS and PbSe, respectively) the non-orientation is striking despite the fact that the same tea-complexed lead precursor solution was found to enhance the orientation of the SILAR-
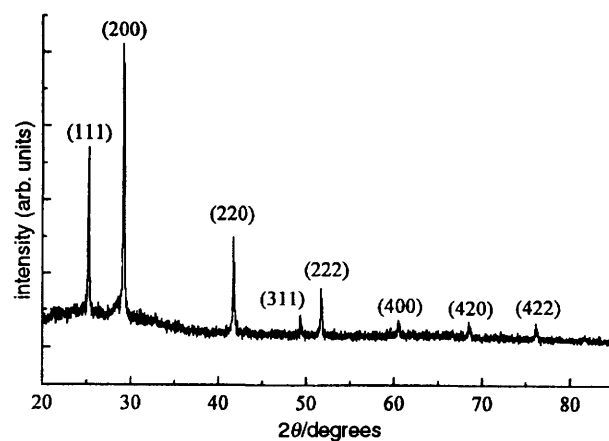

Fig. 1 X-Ray diffraction pattern of an as-grown 200 nm thick PbSe thin film deposited using the SILAR technique

grown PbS thin films remarkably.[13,14] On the other hand, it is known that lead selenide films are in general less well structured than lead sulfide films.[1,3]

RBS and NRA

The chemical composition and the stoichiometry were examined for both as-grown and annealed films (2 h at 120 °C in air), by RBS and NRA techniques. Owing to the roughness of the films the RBS analyses were not easy to perform and their accuracy was not very good, ($<5\%$). The as-grown and annealed films were found to consist of lead and selenium in a Pb:Se molar ratio of *ca.* 1:1. In addition, 5 atom% oxygen and *ca.* 8 atom% of other light-atom impurities, (N, C or H) evenly distributed in the films, were detected. According to the hydrogen analysis (NRA), the as-grown films contained 8 atom% hydrogen. Annealing reduced the amount of hydrogen to 5 atom%, indicating the removal of water entrapped into the film during the growth. Owing to the relatively high pH of the lead solution (7.8), the formation of lead hydroxide species cannot be ruled out completely, although the big difference in solubility constants $\{pK_s[Pb(OH)_2] \approx 15$ and $pK_s (PbSe) \approx 40\}$[20,21] strongly favours the formation of lead selenide. The NRA was carried out both inwards into the sample and outwards towards to the film surface. Both in as-grown and in annealed samples the amount of hydrogen was reduced when measured towards to the surface of the substrate. Evidently, highly volatile compounds, *e.g.* water, still left in the film are moved out of the film as the sample is heated during the measurement by the primary beam.

The aqueous conditions are possibly the origin of these impurities. Similar behaviour and about the same amount of impurities is common to other SILAR-grown thin films.[12,14] SILAR-grown PbSe thin films contain less oxygen than the CBD films grown from aqueous solution. By exploiting XPS several tens of percents of oxygen were found both in as-grown and in etched (15 nm) CBD-grown PbSe thin films.[6] However, oxygen plays an important role in PbSe IR detectors. Without oxygen sensitisation little or no photoconductivity was observed with the CBD PbSe thin films. After the final sensitisation the amount of oxygen was rather high (*ca.* 64%).[1]

Apart from the aqueous conditions, the oxygen-containing precursors such as the tea and SO_3 groups in the lead and selenide solutions, respectively, are possible sources for oxygen and other light-atom impurities in the films.

Besides the difference in oxygen content, the SILAR and CBD PbSe thin films differ in stoichiometry, since the CBD films were clearly Pb rich.[6]

The effect of storage on the PbSe thin films is an important factor which must also be considered. According to the literature, the following observations have been made: the as-grown
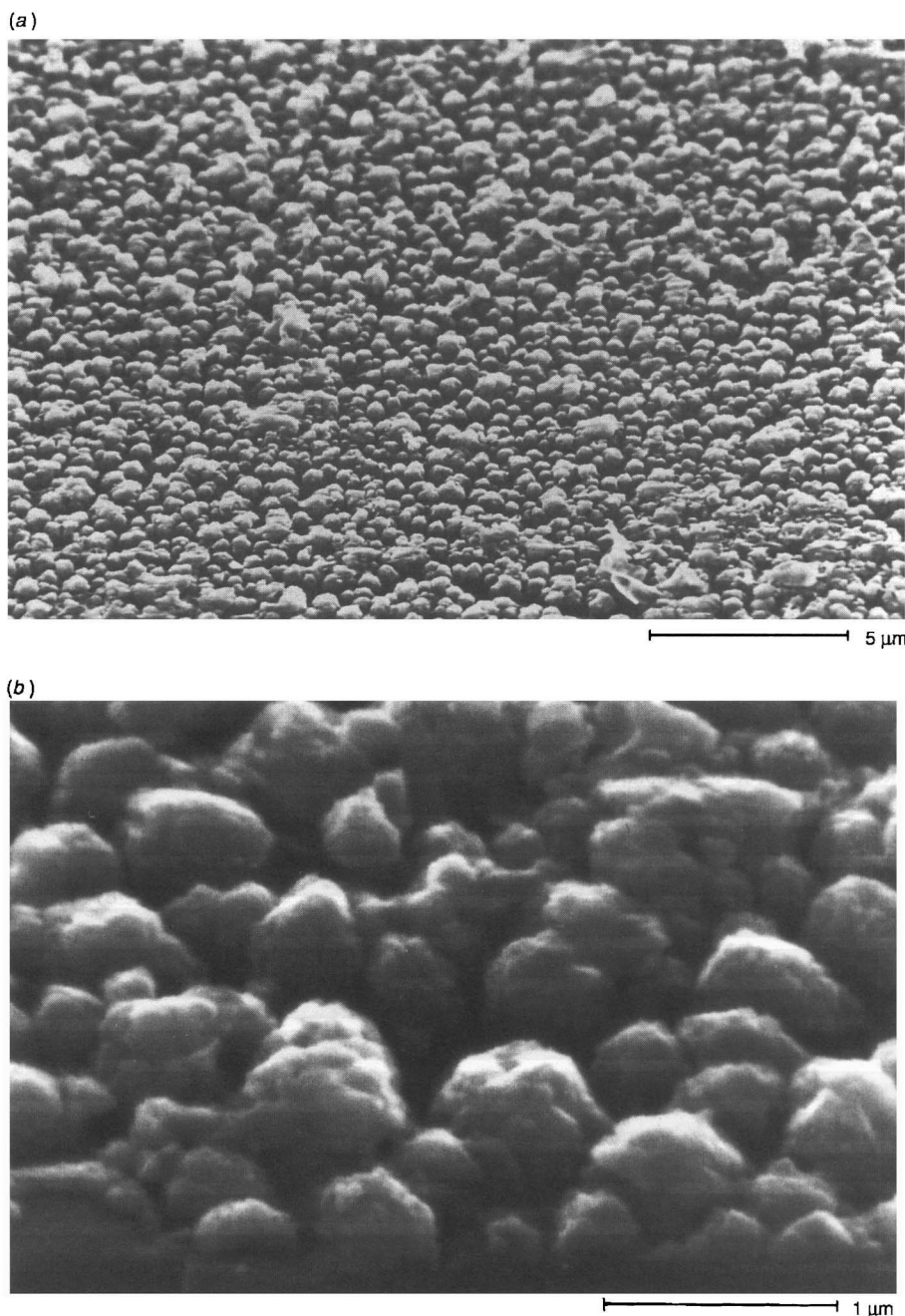
(a)

(b)

Fig. 2 SEM images of a PbSe thin film. The nominal thickness of the film was measured to be 130 nm. Magnification (a) 5000 × and (b) 30000 ×.

vacuum-evaporated PbSe thin films changed their resistance and conductance during exposure to air, whereas H_2 and N_2 gases had no effect.[22,23] According to ref. 22, the phenomenon was due to oxygen adsorption. Moreover, the electrical properties could not be re-established completely by annealing in an H_2 atmosphere, indicating a very strong bond formation between oxygen and lead selenide.[22] Consequently, as the samples were stored in air, it is very plausible that some of the impurities (in particular oxygen) are of atmospheric origin. The roughness of the films enables the gaseous species to enter deep into the film during storage, and not just adsorb on the surface.

SEM

The morphology of a PbSe thin film after 1100 cycles as revealed by Fig. 2(a) is rather rough. In fact, at this stage the film is not a continuous film but consists merely of separate and more or less round-shaped particles. The particles are rather identical in size and uniformly spread out over the substrate. At greater magnification these particles were found to be formed from small aggregates, possibly PbSe crystallites [Fig. 2(b)]. The nominal thickness of the depicted film was only 130 nm, whereas the vertical dimensions of the individual particles derived from Fig. 2(b) are 100–300 nm. The biggest of these particles have a value close to the theoretical growth rate (0.3062 nm cycle^{-1} × 1100 cycles = 337 nm) of the cubic PbSe. Apparently growth is very strongly preferred on already deposited PbSe instead of on glass. Nucleation centres initially formed during the first cycles presumably govern the growth causing the strong particle formation. In comparison to the SILAR-grown PbS thin films, the selenide films are very rough.[14]

Conclusions

Adherent and metallic lead selenide thin films were grown on soda lime glass and on ITO-covered soda lime glass by exploiting the successive ionic layer adsorption and reaction

(SILAR) technique. The precursors were diluted aqueous bis(triethanolamine)lead(II) acetate and sodium selenosulfate solutions. The highest growth rate per cycle was 0.18 nm cycle^{-1}. The as-grown films were stoichiometric PbSe films containing 5 atom% oxygen as well as 8 atom% of other light-atom (H, N and C) impurities, as revealed by RBS analysis. NRA showed the other impurities to be most probably hydrogen. The morphology of the films was rough and the films showed very strong particle formation. Furthermore, the particles were rather uniform in size and were evenly distributed over the substrate area. According to XRD analysis, the films were polycrystalline and cubic. Annealing at 120 °C for 2 h in air reduced the amount of impurities and enhanced the crystallinity of the films.

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