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Procedure for solution growth of ZnS, CdS and $Zn_{1-x}Cd_xS$ thin films by successive ionic-layer adsorptions and reactions

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1. Introduction

A new process of chemical solution deposition of thin films of ionocovalent compounds by successive ionic-layer adsorptions and reactions (SILAR), has been invented by one of the authors [1, 2]. The process involves alternate immersions of a substrate in a solution of a soluble salt of the cation of the compound to be grown and in a solution of a soluble salt of the anion of the compound to be grown. The substrate supporting the growing film is rinsed in high-purity deionized water after each immersion. Polycrystalline or epitaxial thin films of ZnS and of CdS have been grown following this process on different substrates at room temperature [2].

A growth mechanism of ZnS or CdS thin films by SILAR has been proposed based on growth rate and on electrokinetic potential measurements as a function of concentration and solution pH [3, 4]. During alternate immersions in solutions containing zinc (or cadmium) cations and sulphur anions, the growing solid–solution interface is alternately positively and negatively charged by specific adsorption of $ZnOH^+$, $ZnCl^+$ (or $CdOH^+$, $CdCl^+$) cations and HS^- anions respectively. The growth alternately proceeds at the interface by two chemical reactions: one between specifically adsorbed zinc (or cadmium) cations with sulphur anions diffusing towards the interface, another between specifically adsorbed sulphur anions and zinc (or cadmium) cations diffusing towards the interface, involving charge annulment.

We describe here an improved deposition machine and in order to determine the optimum values of the parameters giving a maximum growth rate, we discuss the influence of the technological parameters on the growth rate of polycrystalline films.

2. Equipment

The equipment consists of a specially designed deposition machine supplied with high purity water by a deionized water station and programmed by a computer. The assembly drawing of the deposition machine is shown in Fig. 1. The details of the circulation of fluids and the detailed construction of the immersion and rinsing vessels are shown in Fig. 2.

Eight substrates (1), of maximum 12 cm in length and 7 cm width, are attached vertically by means of PVC tweezers (2) on a moving PVC crown (3) supported on a stainless steel spindle. The spindle turns and glides in a tight bearing driven by two stepping motors; its translation speed is adjustable between 1 and 2 cm s^{-1}. The substrates are alternately immersed in eight quartz immersion beakers (4) containing the solutions and in eight PVC rinsing beakers (5) lying on the circulary PVC tray (6) in the machine.

The solutions are recirculated between the immersion beakers and the five litre polyethylene bottles (7) by means of all PTFE pumps (8) through 0.2 μm PFTE filters (9), at a flow rate of 0.25–1 l min^{-1}. The solutions are stirred inside the immersion beakers by means of magnetic stirrers (11) turning at 400–500 rpm. Conductivity cells, glass (12), ion selective, or reference electrodes or counterelectrodes may be introduced in the immersion beakers. The substrates may be polarized. PTFE tubing and SVL fittings are used.

The rinsing vessels (13) contain the rinsing beakers. The rinsing beakers have a rectangular section of 2 × 8 cm^2. High purity water passes through eight rotameters (14) and flows upwards inside the rinsing beakers and pours into the rinsing vessels. In order to homogenize the water flow, the rinsing beakers are equipped with polyethylene sieves of 75 μm mesh (15). Rinsing (ebb and flow) pulses are operated by means of an intermittently opening electrogate (16). The electrogate is kept closed for the time necessary to drain off the rinsing beakers by means of siphons. Usually, an efficient ebb and flow rinsing is carried out 14 times, consisting of 4 s flow at 1.66 l min^{-1} and 3 s ebb at 0.5 l min^{-1}. The rinsing water collected by the draining pipe (17) is evacuated through the electrogate (18) so long as its resistivity monitored by the conductivity cell (19) is lower than 1 MΩ cm; but is reused as soon as its resistivity exceeds 1 MΩ cm.

The whole, that is, spindle, crown, substrates, tray, immersion and rinsing vessels, are enclosed in a glove-box 1 m^2 in area. The glove-box is nitrogen flushed at a flow rate of 10 l min^{-1}. The nitrogen passing through a rotameter (20) is introduced into the glove-box through the immersion beakers containing the zinc (or cadmium) salt solution just over the solution level. It is evacuated through the immersion beakers containing the Na_2S solution also just over the solution level. This nitrogen path is necessary in order to impede the precipitation of ZnS (or CdS) at the zinc (or cadmium)

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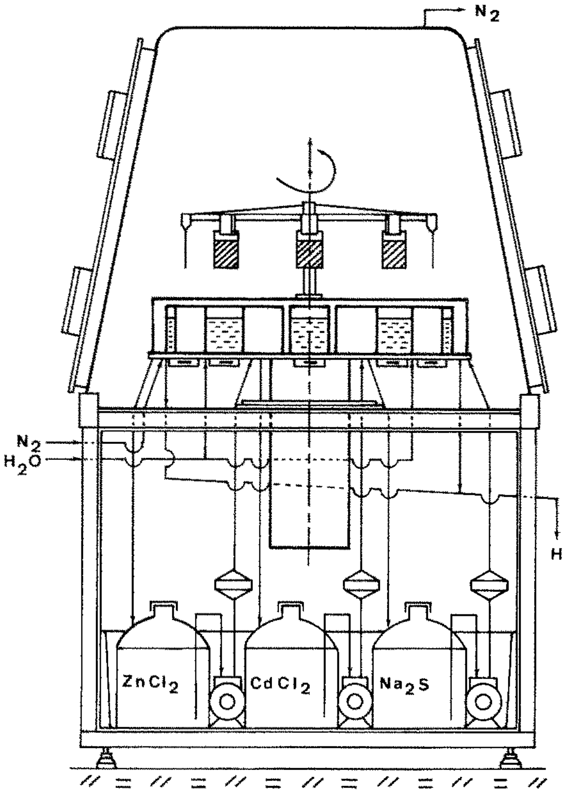

Fig. 1. Assembly drawing of the deposition machine.

salt solution–nitrogen interface, by traces of H_2S released by the Na_2S solution. In order to impose this path the successive zinc (or cadmium) and sulphur compartments (22) and (23), respectively, are separated by walls. Each compartment contains an immersion beaker and a rinsing beaker.

Another glove-box (not drawn in Fig. 1) is joined to the glove-box containing the deposition machine by means of a common lock chamber. This serves for cleaning and etching the substrates under dust and oxygen free atmosphere just before deposition.

The deionized water ($\rho = 18\,\text{M}\Omega\,\text{cm}$ at 20° C) is kept free of oxygen by nitrogen bubbling up to an oxygen mean concentration of 1 ppm, free of micro-organisms, as obtained by inverse osmosis, and filtered ($0.2\,\mu$m).

Special software has been designed enabling the computer to drive the deposition machine by means of an appropriate interface. The menu asks for the immersion times, the number of rinsing pulses, the time of flow, the time of ebb and the number of cycles. In order to grow $Zn_{1-x}Cd_xS$ films doped with indium (or manganese) we can use either a solution of a mixture of salts or separate zinc, cadmium, indium (or manganese) salt solutions. In this later case the menu asks also for the number and the order of successive Zn–S, Cd–S and In (or Mn)–S cycles.

3. Growth rate

The most important technological parameters determining the growth rate are: (i) the nature and the concentration of the solutions, (ii) their pH, (iii) the immersion times, (iv) the rinsing times (numbers of pulsations) related to the water flow rates and (v) the hydrodynamics of rinsing. The substrate nature, orientation if single crystalline, and its surface state play an important role only on the nucleation of the films.

3.1. *The nature, concentration and pH of solutions*

As was formerly stated [3], the growth rate per immersion (GR) increases with solution concentration. The range of practical interest is from 0.5 to 2.5 M. Within this concentration range small pH modifi-

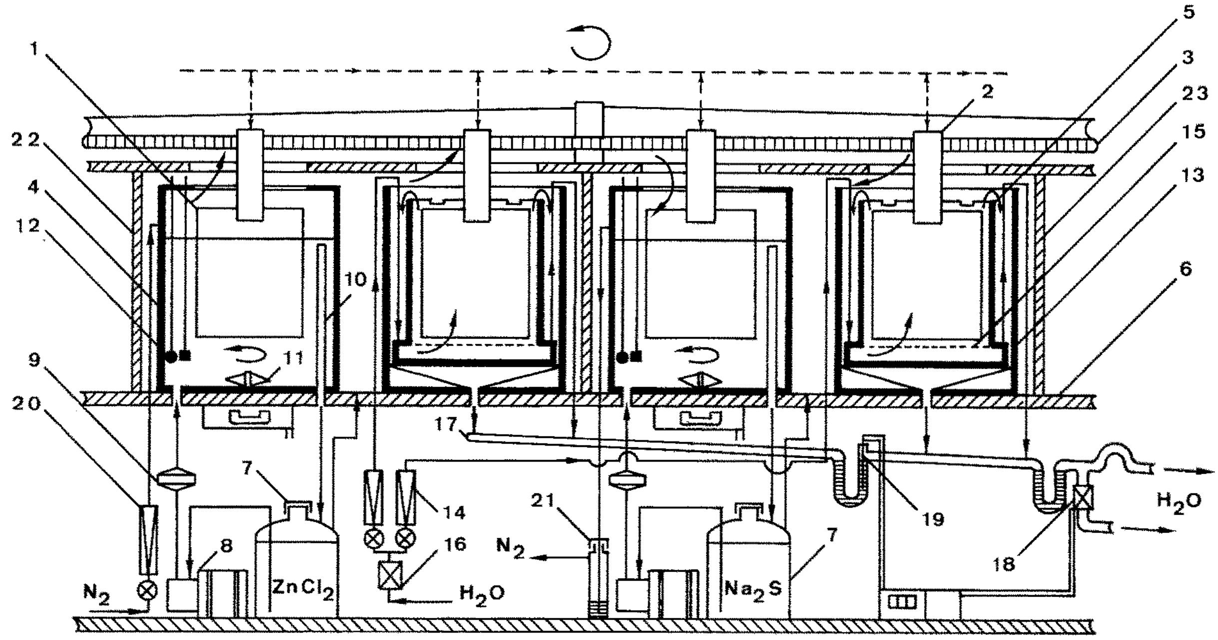

Fig. 2. Detailed drawing of the circulation of fluids and of the immersion and rinsing vessels: (1) substrates, (2) tweezers, (3) moving crown, (4) immersion beakers, (5) rinsing beakers, (6) circulatory tray, (7) bottles, (8) pumps, (9) filters, (10) overflows, (11) magnetic stirrers, (12) electrodes, (13) rinsing vessels, (14) rotameters, (15) sieves, (16) electrogate, (17) draining pipe, (18) electrogate, (19) conductivity cell, (20) rotameter, (21) bubbler, (22) zinc (or cadmium) compartments, (23) Sulphur compartments.

cations of the pH of the zinc or cadmium salt solutions do not produce significant variations in the GR. However, in order to reach a maximum adsorption of ions, the pH of the zinc or cadmium salt solutions is adjusted up to 0.2 pH units less than the precipitation pH of zinc or cadmium hydroxides respectively. The GR decreases with decrease of pH of the zinc or cadmium salt solution below pH ~ 3 and at a pH ~ 2 the ZnS and the CdS films do not grow further, though they do not dissolve. The GR of ZnS and of CdS films should increase slightly by decreasing the pH of the diluted Na_2S solution, below 0.01 M, from 12 to 9 [4]. But it is of no practical interest to decrease the pH of the concentrated Na_2S solution owing to the troublesome increases of the release of H_2S inside the glove-box. Increasing the pH of the Na_2S solution by NaOH additions decreases the GR.

No CdS GR differences are observed when $CdCl_2$ solutions are used instead of $CdSO_4$ solutions of equal concentration and pH. In contrast, ZnS GRs obtained using $ZnCl_2$ solutions are regularly higher than those obtained using $ZnSO_4$ solutions of equal concentrations and pH whatever the Na_2S concentration. Using solutions of equal concentrations ZnS GRs are always higher than CdS GRs. All these experimental results have been explained taking into account: (i) the hydrolysis and the dissociation equilibria of the aqueous salt solutions (ii) the adsorption strength of the different ions, (iii) the structure of the electrical double layer at the sulphide–solution interface and (iv) the structural transformations of the electrical double layer during the successive immersions.

The maximum ZnS and CdS GRs per immersion, i.e. 0.30–0.31 nm and 0.13–0.14 nm respectively, are obtained using quite saturated solutions, viz. 5 M $ZnCl_2$ and $CdCl_2$ solutions and a 2.8 M Na_2S solution. GRs of 0.22, 0.14 and 0.6 nm are obtained using a 1 M Na_2S solution and respectively 1 M solutions of $ZnCl_2$, $ZnSO_4$ and $CdCl_2$. Economically, the best concentrations are 2.5 M $ZnCl_2$ or $CdCl_2$ and 2 M Na_2S.

3.2. *The immersion and rinsing times*

The growth of a monomolecular ZnS (or CdS) layer can be decomposed into four successive stages, namely: the diffusion of ions from the solution towards the sulphide-solution interface across the water diffusion layer, the specific adsorption, the chemical reaction and the crystallization. The rate determining stage being the specific adsorption, the immersion must last the time necessary for the specifically adsorbed ions i.e.: $ZnOH^+$, $ZnCl^+$ ($CdOH^+$, $CdCl^+$) and HS^- to approach the adsorption equilibria at the ZnS (CdS)-solution interfaces, respectively.

To the best of our knowledge there are only a few experimental studies dealing with the adsorption kinetics of ions from solutions. Thus, the adsorption time of sulphur ions from a 50 mM Na_2S solution necessary in order to saturate a CdS electrode was 300 s [5]; the adsorption time of I^- anions in order to saturate a gold electrode from a 1 mM NaI solution was not longer than 30 s [6] and the adsorption half-time of $Cu(NH_3)^{2+}$ cations on silica from a 0.1 mM $Cu(NH_3)_4(Cl_3CCOO)_2$ solution was 14 s [7]. All these measurements were undertaken on initially dry solid surfaces without stirring the solutions.

In order to decrease the time necessary to approach the adsorption equilibria the solutions were stirred. For lack of an appropriate kinetic study we have experimentally determined the GRs of polycrystalline ZnS and CdS, from 0.5 M $ZnSO_4$, 0.5 M $CdSO_4$ and 0.5 M Na_2S solutions, respectively, for different immersion times. The GRs increase rapidly with the immersion times up to about 20 s. But increasing the immersion times beyond 20 s did not produce appreciably higher GRs and consequently we kept all the immersion times constant at 20 s.

In order to avoid the parasitic homogeneous precipitation of colloidal ZnS (CdS) particles in the diffusion layer, the ebb and flow rinsing times, the number of pulses, the water flow rates, the cross section and the volume of the rinsing beakers should be experimentally determined. Accordingly, for instance in the case of ZnS, the residual activity of $HS^-_{aq,r}$ anions in the diffusion layer after rinsing $[HS^-_{aq.r}]$ (after immersion in the Na_2S solution) is $[HS^-_{aq.r}] < K_{so} K_1 [H^+_{aq}]/[Zn^{2+}_{aq}]$ and the mean residual activity of the $Zn^{2+}_{aq,r}$ cations in the diffusion layer after rinsing $[Zn^{2+}_{aq,r}]$ (after immersion in a zinc salt solution) is $[Zn^{2+}_{aq,r}] < K_{so} K_1 [H^+_{aq}]/[HS^-_{aq}]$.

Here $K_{so} \approx 10^{-25}$ is the ZnS solubility product. $K_1 \approx 10^{15}$ is the protonation constant of S^{2-}. $[H^+_{aq}]$ and $[Zn^{2+}_{aq}]$ are the H^+_{aq} and Zn^{2+}_{aq} activities in the $ZnSO_4$ solution respectively. $[HS^-_{aq}]$ and $[H^+_{aq}]$ are the HS^-_{aq} and the H^+_{aq} activities in the Na_2S solution respectively. Actually, since the nucleation of the parasitic homogeneous precipitation needs a large supersaturation, the limited concentrations of the residual ions can be surpassed by several orders of magnitude before precipitation occurs. Consequently, the rinsing should last the time necessary for the diffusion of HS^- anions (after immersion in the Na_2S solution) and respectively of Zn^{2+} (or Cd^{2+}) cations (after immersion in the zinc (or cadmium) salt solution) from the diffusion layer of solution in the rinsing water. If the diffusion layer is thick and the ionic concentration very high the necessary rinsing time may be undesirably long.

Our experimental rinsing conditions gave an ionic layer-by-layer growth, avoiding the parasitic homogeneous precipitation of colloidal ZnS particles in the diffusion layer even when 2.5 M solutions were used. We adopted the pulsatory ebb and flow rinsing system after trying many other systems. The necessary number of rinsing pulses can be approximately determined by recording the resistivity of the used rinsing water. As seen in Fig. 3 the resistivity of the used rinsing water flow returns to its initial value after 14 rinsing pulses. TEM examination of the CdS thin films grown using 14 rinsing pulses on $(\bar{1}\,\bar{1}\,\bar{1})$ InP, (0 0 1) GaAs and (1 1 0) Ge shows epitaxial growth [8], possible only by a heterogeneous ionic layer by ionic

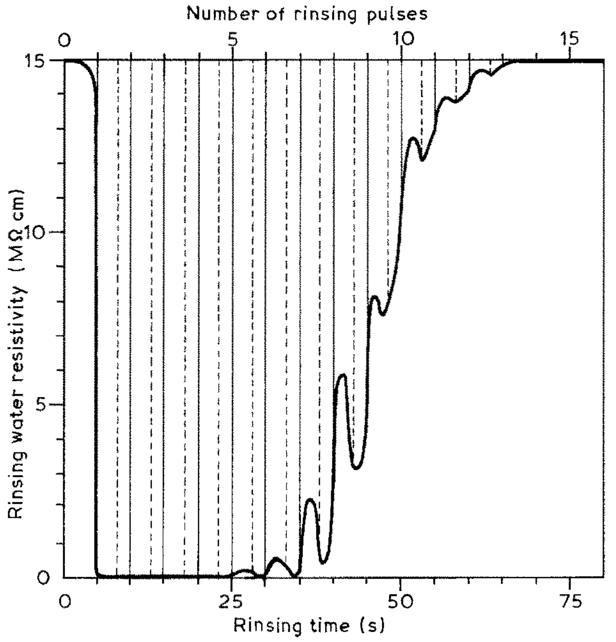

Fig. 3. Time dependence of the used rinsing water resistivity. The vertical lines work the change from ebb to flow state, the slashed lines mark the opposite change.

layer growth mechanism. This means that $[HS^-_{aq,r}]$ and $[Cd^{2+}_{aq,r}]$ fulfilled the above mentioned conditions, i.e. the number of the rinsing pulses exceeded a necessary number.

The desorption of the specifically adsorbed ions proceeds very slowly. Thus increasing the number of rinsing pulses considerably beyond 14, and thus the total rinsing time, does not produce lower GRs. Some ZnS GR decrease is, however, observed only when concentrated zinc salt solutions, in the range from 1 M to 5 M, are used. Some zinc desorption occurs because the surface coverage by zinc adsorption from concentrated solutions is quite large and the zinc electrosorption valence is known to be smaller than that of sulphur [9].

The thickness of the films is very uniform, (within 1–3%) over the whole surface, since it is determined only by the adsorption of the different ions and independent of fluid convection. Only ZnS films, obtained using concentrated zinc salt solutions, are thinned at the substrate edges owing to some convection enhanced desorption of absorbed zinc cations at the substrate edges during rinsing.

Taking into account the immersion, rinsing and transfer times allowed by the present state of the art, the growth of polycrystalline ZnS and CdS films ranges between 100–200 nm per day and 40–80 nm per day respectively, depending on the solution concentration. As compared with the growth rate of ZnS films obtained by atomic layer epitaxy, the growth rate of ZnS films obtained by SILAR is an order of magnitude lower. However by increasing the number of substrates and their dimensions it is possible to reach a productivity of the same order of magnitude as with other thin film deposition processes.

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