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A study of microstructural properties and quantum size effect in SILAR deposited nano-crystalline CdS thin films

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ABSTRACT

The paper reports deposition and characterization of CdS thin films by micro-controlled SILAR technique using $CdCl_2$ and Na_2S as precursors. The thickness of the films was found to increase with number of immersion cycles, and also with the concentration of precursor solutions. But this increase in thickness was observed only up to a certain limit beyond which films showed peeling effect. The films were found to be polycrystalline with cubic structure. The lattice constant, crystallite size and average strain on the films were found from detailed XRD analysis. Optical characterization revealed that the films exhibit quantum size effect due to their nano crystalline nature.

1. Introduction

Cadmium sulphide (CdS) is a II–VI group compound semiconductor with a direct bandgap of 2.4 eV [1,2]. Being a direct bandgap material, CdS has immense potential applications in optoelectronics: such as solar cells, photodetectors, LEDs etc. [1–16]. Unlike silicon, CdS can yield high quantum efficiency in optoelectronic devices due to its direct bandgap. Photodetectors based on CdS, CdTe/CdS based thin film solar cells are already in commercial use [10,11]. However, there are many more possible applications of CdS which are yet to be fully explored. The cost of production of device grade CdS material and the lack of technical knowledge regarding the correlation between the manufacturing process and the properties of the material produced have been the major reasons impeding the large scale commercial utilization of CdS.

Of late, one of the major challenges ahead of the renewable energy researchers has been that of making the solar cell technology economically viable. As a result of this, extensive efforts are being made to explore economical methods of producing semiconductors both in bulk and thin film form. Successive ion layer adsorption and reaction (SILAR) is one such simple and economical method which can yield semiconductor films of reasonably good quality [12]. Although; the films produced by SILAR may lack those excellent structural and electrical characteristics possessed by the films produced by high-end, expensive techniques; the low cost of manufacturing, ease of large scale production and low maintenance requirements have made SILAR very popular among researchers. SILAR is basically an improved version of chemical bath deposition (CBD) technique. In CBD, all the precursors required for the deposition of the film are taken in a single vessel which may eventually cause precipitation and wastage of the material. But in SILAR, the anionic and cationic precursors are taken in separate vessels so that there is very little possibility of precipitation [12]. The substrates are dipped alternatively in anionic and cationic solutions until a film of desired thickness is produced. Many of the commercially available CdS/CdTe solar cells use chemical bath deposition (CBD) to deposit CdS layer [10,11]. One major disadvantage of CBD technique is the unwanted precipitation of material which results in material wastage [12]. On the other hand; SILAR technique, being a refined version of chemical bath deposition, reduces precipitation problem to a great extent and thereby decreases harmful cadmium wastage during preparation of solar cells. Besides, as seen in the present research work, the quality of SILAR deposited CdS films are very similar to those obtained by CBD. Hence SILAR technique is a viable alternative to CBD technique in the fabrication of photovoltaic and optoelectronic devices.

Although reports are already available on SILAR deposited semiconductor thin film, including CdS, the reproducibility of the reported results has remained questionable as many of these researchers have employed manual (hand operated) SILAR deposition process. Since SILAR is a slow sequential deposition process, consistency of parameters over a long period of time is essential to obtain reproducible results. This can be achieved only if automated SILAR deposition units with high precision control mechanisms are employed. In the present work we have used a precision micro-controlled SILAR unit which can maintain the

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deposition parameters fixed at desired levels over a prolonged period of time.

The paper reports deposition and characterization of CdS films by micro-controlled SILAR deposition using $CdCl_2$-Na_2S precursors. The effects of number of immersion cycles and precursor concentration on the properties of the films have been discussed. The films were found to exhibit quantum size effect due to their nano-crystalline nature.

2. Experimental details

All films used in the present work were deposited on glass substrates. Prior to the deposition; the substrates were immersed in acetone for about 15 min, rinsed with distilled water and then dried. The depositions were carried out in a micro-controlled HOLMARC™ SILAR deposition unit (from HOLMARC™ opto-mechatronics, Kochi, India). The design and operation of the unit has been described in our previous publication [2]. The deposition of CdS from $CdCl_2$ and Na_2S is described below.

As usual in SILAR deposition, the anionic and cationic precursors were taken separately in two beakers. In the first step of deposition cycle, well cleaned glass substrates were immersed in cationic precursor solution of $CdCl_2$ so that the cadmium ions get adsorbed to the surface of the substrate. The substrates were then rinsed in distilled water to remove loosely adsorbed ions. The chemical reactions involved in this step are as follows:

$$CdCl_2 \text{ (Aqueous)} \rightarrow Cd^{2+} \text{ (Adsorbed)} + 2Cl^{-} \text{ (In solution)} \tag{1}$$

In the second step, the substrates were immersed in the anionic precursor solution of Na_2S. In this step, sulphur ions react with adsorbed cadmium ions on the substrate to form CdS. The substrates were again rinsed in distilled water to remove loosely bound ions. The chemical reactions in this step take place as follows:

$$\begin{aligned} &Na_2S \text{ (solid)} + H_2O \rightarrow 2Na^{+}\text{(In Solution)} + SH^{-}\text{(In Solution)} \\ &\quad + OH^{-}\text{(In solution) } SH^{-}\text{(In solution)} \\ &\quad + OH^{-}\text{(In solution)} \rightarrow S^{2-}\text{(In soultion)} + H_2O \; Cd^{2+}\text{(Adsorbded)} \\ &\quad + S^{2-}\text{(In solution)} \rightarrow CdS \text{ (Adsorbded)} \end{aligned} \tag{2}$$

The above two steps together constitute one complete cycle of deposition which is repeated several times to get CdS thin films of desired thickness. The thickness of the films was determined by gravimetric analysis and later reconfirmed by taking cross-sectional SEM images of the films (Fig. 6a).

The films deposited under different deposition conditions were characterized to understand the correlation between the properties of the films and the deposition conditions. The crystal structure of the films was studied by powder XRD (Rigaku Minflex X-ray diffractometer) analysis. The surface morphology of the films was studied by scanning electron microscope (Philips). Chemical composition of the films was determined by EDAX analysis and the optical parameters of the films were determined by spectrophotometer (Ocean Optics).

3. Results and discussion

The thickness of the films was found to increase with the number of immersion cycles (Fig. 1a). Ideally, in SILAR process, only a monolayer of film material gets deposited on the substrate in one cycle of deposition. As the deposition process continues, more and more layers of the film material get deposited and hence the overall thickness of the film increases. However, the thickness of the films obtained from $CdCl_2$-Na_2S saturated at around 100 cycles. Further continuation of the deposition, beyond 100 cycles, did not increase the thickness of the films. Instead, cracks developed on the surface of the films and the material of the films started to come off from the surface (Fig. 2b). This phenomenon has been given the name 'peeling effect' by some researchers [6]. The peeling of film material is common in chemical deposited films and is mainly due to the relatively poor adhesion. The adhesion in chemically deposited films is usually good enough only to hold the films intact up to a particular thickness. Beyond that, the film material peels off from the surface. In our case, the films deposited up to 100 cycles were intact and well adherent (Fig. 2a). Even after a long storage period of about a month, inside a desiccator, these films did not show any signs of cracks or peeling.

The rate of deposition was found to be marginally higher in $CdCl_2$-Na_2S case than in the CdS films obtained from cadmium acetate-thiourea precursors; reported in our previous publication [2]. A somewhat different result has been reported by G. Sivakumar et al. [9], who compared the rate of deposition of chemical bath deposited CdS films from $CdCl_2$ and cadmium acetate with thiourea as the anionic precursor. They have reported that the rate of deposition was faster in cadmium acetate than in $CdCl_2$. It can be noted that, they have employed chemical bath technique where both cationic and anionic precursors are taken in a single chemical bath. Besides, the anionic precursor used for $CdCl_2$ is different (thiourea) from what has been used in our work and hence the overall dynamics of the chemical reactions is different.

In addition to the number of immersion cycles, thickness of the films was also found to vary with the concentration of the precursor solutions (Fig. 1b). When the concentration of the precursor (both anionic and cationic) solutions was increased, keeping number of immersion cycles constant (at 100), the thickness of the films was found to increase. However, it was also observed that the thickness of the films saturates at higher concentrations (around 0.15 M) of $CdCl_2$ and Na_2S. Precursor concentration higher than 0.15 M resulted in material loss from the

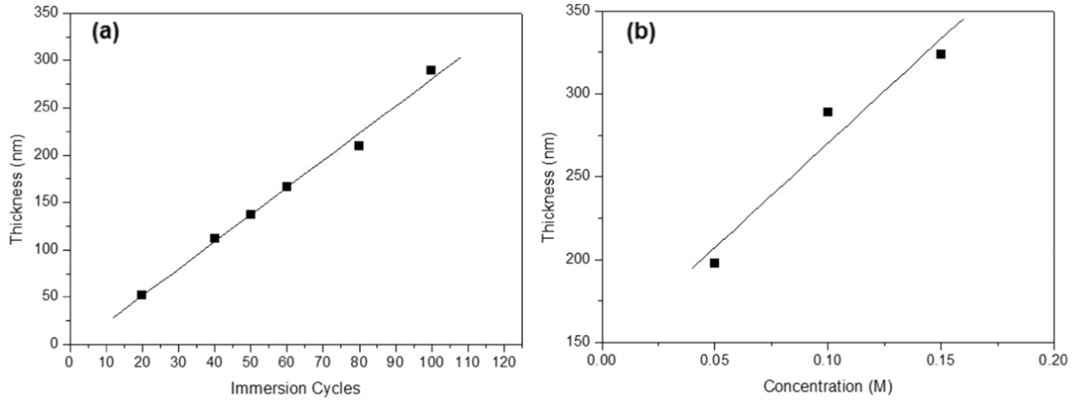

Fig. 1. The variation of thickness with (a) number of immersion cycles (for constant precursor concentration of 0.1 M) and (b) molar concentration (for 100 immersion cycles).