

Synthesis and processing of CdS/ZnS multilayer films for solar cell application

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Abstract

We demonstrate that homogeneous $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films can be synthesized from chemical bath deposited CdS/ZnS multilayers through low-temperature chemical and thermal-activated diffusion. The secondary ion mass spectrometry depth profiles indicate that Cd diffuses into ZnS film more readily than Zn diffuses into CdS film. We also demonstrated how this approach could be used in improving the spectral response of CdTe-based solar cells.

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1. Introduction

The zinc-based binary and ternary II–VI compounds (ZnS, $\text{Cd}_{1-x}\text{Zn}_x\text{S}$, ZnSe, and $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$) are of great importance in the optoelectronic application [1,2]. Because of their bandgaps, any of these materials, could be an excellent window layer in CdTe thin film solar cells. Since chemical bath deposition (CBD) is known to produce solar cell grade films over a large area at a low cost and low temperature, efforts have been made by many researchers [3–10] over the years to grow these materials by this method. However, because of difficulties in growing the films of these chalcogenides of zinc by CBD in the basic aqueous medium there seem to be some controversies in the reported results.

For example, Chu [3] used NH_3 as the complexing agent in the synthesis of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films with no success. Whereas Sharma and Garg [4], with the same NH_3 as a ligand grew $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ (with $0 \leq x \leq 1$) films. Padam and Malhotra [5] with triethanolamine (TEA) and NH_3 as ligands reported the growth of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ throughout the

composition range ($0 \leq x \leq 1$). However, Pramanik and Biswas [6], also using TEA and NH_3 as complexing agents for the growth of ZnSe films, reported that film or precipitate formation is impossible without hydrazine (N_2H_4) presence in the reaction bath. Dona and Herrero [7], with NH_3 as the major and N_2H_4 as the complementary complexing agents, reported the growth of ZnS films. The latter went further to say that the presence of N_2H_4 is not essential, but its absence causes a very low grow rate (about $5 \text{ \AA}/\text{min}$); and its presence improves the homogeneity and specularity of the film. Estrada et al. [8], on the other hand, used NH_3 and citrate ions as complexing agents in the growth of ZnSe and recorded a success. Yamaguchi et al. [9] also reported a CBD of (Cd, Zn)S films with NH_3 and I^- as complexing agent, when the reagents are mixed together in certain order. Recently, Oladeji and Chow [10] performed a battery of experiments using NH_3 and N_2H_4 as complexing agents separately and together in the growth of ZnS thin films. When these agents are used separately they reported that negligible film growth takes place. However, they succeeded in growing films when both agents are used together.

We first note that the hydrolysis of thiourea and selenourea, the precursors of S and Se, respectively, are similar in a basic aqueous bath. Thus, the ability to grow the

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Zn-based materials of these chalcogens by CBD depends on Zn or any other constituent metal. Now, from the revelation above, it is apparent that for the growth of ZnS or ZnSe films by CBD in a basic aqueous bath, if NH_3 is used as a complexing agent, there is a need for either N_2H_4 or citrate ion or iodine ion as the secondary complexing agent. In our previous work [10] based on the analytical and experimental studies of the CBD growth mechanisms of ZnS thin film in a hydrazine–ammonia medium, we rationalize our observation by the following arguments:

- (1) In the NH_3 only medium, the Zn–amine complex is mostly in the form $[\text{Zn}(\text{NH}_3)_4]^{2+}$ with $10^{8.9}$ [7] as the stability constant (k). This high k value in our opinion prevents the complex ion from being easily adsorbed by the substrate, or if absorbed the zinc–ligand bonds of the complex do not relax for the heterogeneous reaction with S precursor to take place; and no film grows.
- (2) On the other hand, in the bath containing N_2H_4 as the only complexing agent, the Zn complex is predominantly in the form $[\text{Zn}(\text{N}_2\text{H}_4)_3]^{2+}$ with $k=10^{5.5}$ [7,11]. This low k value encourages Zn ion presence in a concentration which, together with S ion, allows a homogeneous reaction instead of a heterogeneous reaction necessary for the film growth to take place; and no film grows either.
- (3) From our experience, CdS and CdSe thin films are easily grown by CBD with NH_3 as the complexing agent. Thus, $[\text{Cd}(\text{NH}_3)_4]^{2+}$ being the major precursor in the heterogeneous growth of CdS and CdSe thin films [12] with $k=10^{6.9}$, it is logical to infer that a metallic complex that can partake in CBD must have a stability constant that is about this value. That we are able to grow ZnS film when NH_3 and N_2H_4 are present together in the same bath indicates that Zn complex that satisfies the latter condition is present. This is found to be true if N_2H_4 concentration is about twice [6] that of NH_3 . Since the Zn– NH_3 complex has a higher k than the Zn– N_2H_4 complex, we can infer that the common ion effect, or some other effects not known to us, forced most of the Zn– NH_3 complex to acquire the form $[\text{Zn}(\text{NH}_3)_3]^{2+}$. The stability constant of the latter [11] is $10^{6.6}$. This value is moderate and a lot closer to the magical $10^{6.9}$ number quoted above, and makes this complex conform to CBD growth mechanism, in other words, it makes $[\text{Zn}(\text{NH}_3)_3]^{2+}$ a major Zn precursor in the ZnS film growth. Similar arguments can equally be applied for NH_3 –citrate ion bath and NH_3 – I^- ion bath. O'Brien et al. [13] and Bayer et al. [14] in their recent articles have supported this view and the argument advanced here.

Now, for the growth of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ or $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$, the reaction bath must contain N_2H_4 (our preferred choice) for the Zn element to be incorporated in the film. Unfortunately,

the chemical effect of N_2H_4 on the Zn–amine complex is similar to that of the Cd–amine complex. This means more Cd–amine complex will exist in the form $[\text{Cd}(\text{NH}_3)_3]^{2+}$. Since the unsaturated Cd–amine complex, $[\text{Cd}(\text{NH}_3)_3]^{2+}$ with [11] $k=10^{6.2}$ is less stable than that of Zn, the concentration of Cd^{2+} present in the bath is high and together with S^{2-} or Se^{2-} concentration they easily exceed the solubility product constant of CdS or CdSe. Homogeneous reaction resulting into CdS or CdSe colloid formation therefore dominates the reaction. These colloids eventually induce $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ or $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ precipitation. Extensive work on the growth of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films during the course of this study in the hydrazine–ammonia medium always leads to negligible film growth and mostly the precipitation of ternary compounds, confirming the argument above. An alternative way of synthesizing the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films by CBD for solar cell application was therefore sought.

This study focuses on (1) improving the quality of CBD grown ZnS thin films, (2) synthesizing ZnS/CdS multilayer films and finding how chemical and thermal activated interdiffusion between these layers can be used to convert this multilayer to $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films for optoelectronic applications.

2. Experimental details

From our previous work [10], it is observed that the growth of ZnS thin film at room temperature in $\text{NH}_3/\text{N}_2\text{H}_4$ medium leads to less adherent thicker film. Although the growth at temperatures higher than the room temperature improves somewhat the adherence, the excessive homogeneous reaction that comes with this approach minimizes the heterogeneous reaction, hence the resulting minimum film thickness. As a result, for the growth of adherent thicker ZnS thin films at about 55°C , potassium nitrilotriacetate (KNTA) was introduced as an additional complexing agent.

The experimental procedure for growing ZnS thin films is the same as described previously [10], with the exception that KNTA was added to the reaction bath after NH_4OH and prior to adding $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The growth of CdS layers, on the other hand, followed the same procedure as described in Ref. [15]. With the CBD growth of ZnS and CdS already well established, we dipped the substrate into ZnS and CdS growth bath one after the other to grow ZnS/CdS multilayer structures. The substrates used in this experiment are either quartz glass or transparent conducting oxide coated soda lime glass (TCO/glass).

The grown films were annealed in argon ambient at 400°C . The CdS, ZnS, and CdS/ZnS multilayer films were annealed for 60 min. Ultraviolet–visible (UV–VIS) spectrophotometer, secondary ion mass spectrometry (SIMS), Rutherford backscattering (RBS), and X-ray diffraction (XRD) were used to characterize both annealed as well as unannealed films. Film thickness was measured by an Alpha-step profilometer.

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