# Growth Kinetics of Thin Film Cadmium Sulfide by Ammonia-Thiourea based Chemical Bath Deposition

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We have successfully fabricated Thin Film Transistors using CBD deposited CdS semiconductor layers. These devices clearly demonstrated transistor actions. More importantly, the device characterization data indicated that an effective mobility around 2 $cm^2/Vs$ was achieved in this device. This performance is comparable to most amorphous Si (0.1 to 1 $cm^2/V$ s) and much better than a typical organic thin film transistor ($10^{-2}$ $cm^2/Vs$). The electron mobility of single crystal CdS is around 200 $cm^2/Vs$. There are still plenty of room to improve the deposition process for better device performance. One major problem in CBD process is the particle formation. We have performed a detail investigation of CBD CdS process with a focus on the role of particle formation.

Historically, the first application of CBD was the fabrication of lead sulfide photoconductive detectors in 1884 by J. E. Reynolds [1]. CBD is an aqueous analogue of Chemical Vapor Deposition (CVD). It is known that CBD is capable of producing an epitaxial layer (e.g., CdS) on single crystal surface [2]. The earlier studies [3] suggested a colloidal-by-colloidal growth model. However, a thorough investigation by Ortega-Borges *et al.* [4], based on initial rate studies using a Quartz Crystal Microbalance, suggested differently. They identified three growth regimes: an induction period with no growth observed, a linear growth period, and a colloidal growth period. They proposed a molecular level heterogeneous reaction mechanism. Their model has provided a foundation for our understanding of CBD process at the molecular level.

In this work, CBD CdS deposition process was monitored using a Quartz Crystal Microbalance (QCM) as a function of time, temperature, reactant concentration (ex-situ atomic absorption measurement), and pH level. It was found that the reaction could be limited by mass transport at certain concentration ranges. A series of CdS film thickness versus time curves under different stirring rate are given in Figure 1. These growth curves have several interesting features. First, it has clearly shown that the film growth rate was strongly depending on the stirring rate. This was demonstrated by taking the slope of linear portion of the curves in Figure 1. The second feature of Figure 1 is the strong dependence of the terminal film thickness on the stirring rate. This result can be explained through the competition between the homogeneous particle formation and the heterogeneous film growth. It is likely that the increasing stirring rate reduced the boundary layer thickness and thus increased the deposition rate through mass transported limited reaction. On the other hand, the homogeneous reaction for the particle nucleation and growth is not. The heterogeneous and homogeneous reactions were competing for reactants before they got depleted. In other words, the reactants would be depleted mostly by homogeneous reaction if the heterogeneous reaction were relatively slow.

It has been well established in the literature that the reactions at higher concentration are not mass transfer limited. A typical growth curve in these conditions clearly shown four distinct growth regimes identified by previous researchers. We have performed measurements of total cadmium concentration in the solution, the moles of CdS particles, and the mole of CdS in the film. The most striking feature from these measurements is that even though the total Cd concentration in the solution changes dramatically in the linear growth regime, the deposition rate remains constant. This peculiar behavior requires a re-thinking of our current understanding of the CBD CdS heterogeneous reaction mechanisms. Since all the models suggest a near first order dependence on cadmium total concentration.

There are several possible hypotheses that could explain this discrepancy. For example, for a linear growth curve region to occur with such a large concentration change suggests the reaction is not operating in a surface reaction limited regime, but in a desorption-limited regime. However, this possibility could be ruled out based on previous studies, which show a clear dependence of growth rate on initial reactant concentration [4]. The conditions of the present work are well within the experimental conditions of the previous studies, which suggest other hypotheses. One possible explanation is that the linear growth regime proposed is actually a combination of molecular-by-molecular and cluster-by-cluster growth. It is likely that CdS nano-clusters were formed and adhered on the growth surface similar to an ionized cluster beam deposition [5]. Similar mechanism has been proposed for CdS CBD process [6]. To test this hypothesis, we have performed a real time laser light scattering measurement to monitor the CBD CdS reaction. We clearly observed an increasing scattering signal right after the reactants mixed. The reagents were filtered with 0.02 µm filter prior to reaction. Since dust and pollen and typical airborne particles are on the order of 0.1 µm in size, this evidence suggests that particles were not caused by the heterogeneous reaction occurring on foreign seed particles. This observation indicated that small particles were forming and growing even at the beginning of the process, which provided evidence for this hypothesis.

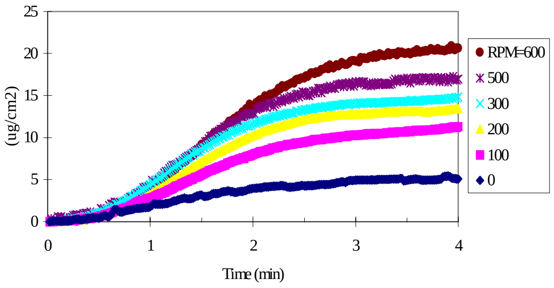

Figure 1. Influence of stirring rate on film growth curves. $[CdCl_2]=3.7\times10^{-4}$,$[SC(NH_2)_2]=3.6\times10^{-3}$,$[NH_3]=1.86\times10^{-3}$,$[NH_4Cl]=1.1\times10^{-3}$, T=75° C.

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