# Active controls in the chemical bath deposition of metal sulfide thin films

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Chemical bath deposition (CBD) of compound semiconductor thin films currently receives a great deal of attention not only for its effectiveness in the reduction of cost and environmental stress associated with the materials production, but also for the high quality of the materials one can achieve by such a technique. The best performances of the CdTe and Cu(In, Ga)$Se_2$ based thin film photovoltaics are obtained in combination with CBD-processed window layers of metal sulfides such as CdS, $In_2S_3$ and ZnS.

CBD can be regarded as an analogue of chemical vapor deposition (CVD), which enables relatively facile control of materials composition and structure, and thus is widely used in the preparation of thin film materials for optoelectronic devices. In order for the CBD process to be further sophisticated to be comparable with the CVD process with respect to the controllability of the film growth and the materials quality, one should consider methods for the active control which are usually missing in the ordinary CBD processes.

The strategy for the active control varies depending on the mechanism of the film growth. In other words, one should reach the state of complete understanding of the mechanism for the proper controls. For example, the CBD of CdS from alkaline mixed solution of a Cd salt and S-sources such as thiourea (TU) and thioacetamide (TAA) proceeds in a typical atomic layer-by-layer mechanism, namely, the film growth is achieved by the crystal growth via surface chemical decomposition of the intermediate complex. Such a character has made epitaxial CBD of CdS thin films possible, when appropriate substrates are chosen.[1] However, the film growth in an ordered structure was often limited up to a thickness of typically ca. 100 nm, as the CdS particles formed in the bulk of the solution begin to stick to the growing surface of the CdS thin films. The presence of the Cd-hydroxide-like surface complex is crucial for the atom-by-atom growth of CdS. However, not only the film but also the precipitates are hydroxylated, so that their attachment to the film surface cannot be avoided in the conventional alkaline CBD processes.

In un-buffered acidic chemical bath such as the mixture of $CdCl_2$ and TAA, the atom-by-atom growth CdS is completely hindered, although the chemical precipitation of CdS powders does occur in the bulk of the solution. The primary reaction in this medium is acid-catalyzed hydrolysis of TAA to release $H_2S$, which is consumed by the precipitation of CdS. The precipitate formed in this way has a clear polycrystalline nature. However, a distinctively different reaction can be triggered by applying electrochemical reduction of protons at small current densities at the conductive substrate.[2] A long range homoepitaxial growth of CdS was made possible for a thickness exceeding 1 μm. The occlusion of CdS particles formed in the bath was not observed. One can consider hydroxylation of negatively polarized substrate surface to locally promote the atom-by-atom growth of CdS. It can also be (in fact, better) understood as the pH buffering effect by electrochemical reduction of protons co-produced during the surface chemical decomposition of Cd-TAA complex expressed in an overall reaction as,

$$Cd(II)(CH_3CSNH_2) + 2e^- \dashrightarrow CdS + H_2 + CH_3CN$$

The process should not be regarded as a version of electrodeposition but an electrochemically induced chemical deposition (EICD), because the faradaic process is not directly related to the formation of CdS but is only used to activate the surface chemical formation of CdS. In the alkaline CBD, the co-produced protons are spontaneously neutralized by the hydroxyl ions released from the surface Cd species. The similar effect has been indeed achieved by the addition of acetate and $In^{3+}$ ions to the bath which would effectively scavenge protons in the acidic solutions. One should remember the fact that active controls such as light illumination and local heating are used to activate the chemical decomposition of precursors in the CVD process. The electrochemical reactions can be effective means to achieve active controls in the CBD processes to let it get closer to the CVD.

The EICD of CdS in the acidic chemical bath containing $CdCl_2$ and TU was successful to prepare many thin films from a single bath, because TU is stable in the acidic bath but decomposes at the cathodized substrate.[3] The atom-by-atom growth of CdS can purposely be disturbed by adding strong surface adsorbates such as mercaptoethanol which hinders the crystal growth to produce nanoparticulate CdS thin films which exhibit a remarkable quantum size effect.[4]

By contrast to CdS, the CBD of ZnS thin films proceeds in a typical cluster-by-cluster mechanism, in which the film growth occurs simply by accumulation of ZnS nanocrystallites formed in the bath onto the substrate surface. There is almost no crystal growth during the film growth. We have made a complete kinetic analysis of the film growth in comparison with the homogeneous precipitation and found that the rate of the film growth is simply proportional to that of the precipitation.[5] The concentration of the two precursors, Zn acetate and TAA had a symmetrical effect to the rate of the ZnS precipitation, indicating that chemical decomposition of 1:1 complex is the rate determining step. However, one variable factor affected the rate of the film growth. The rate of the agglomeration of ZnS nanocrystallites was clearly enhanced when [Zn(II)] was in excess of [TAA] due to neutralization of surface charge of ZnS, which is usually negative in the slight acidic medium. The decreased repulsive force resulted in the more efficient agglomeration and thus the faster film growth.

The last example is the CBD of $In_2S_3$ thin films which shows both of the characters expected for the atom-by-atom and the cluster-by-cluster growth.[6] While the film growth follows the cluster-by-cluster mechanism at the beginning of the reaction, crystal growth as a consequence of surface chemical reaction is detected in the latter stage. This system still has to be tackled for the comprehensive understanding of the mechanism for the establishment of the active controls.

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