Close Space Chemical Bath Deposition (CSCBD): An avenue for improving both fundamental understanding and manufacturabity. Case example of cadmium sulfide.

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Chemical bath deposition is becoming an important deposition technique for thin films of compound materials like chalcogenides [1], oxides and halides. A major success can be found in the recent period with the deposition of semiconducting cadmium sulfide or zinc sulfide buffer or window layers in efficient copper indium diselenide or cadmium telluraide thin film solar cells. It takes advantage of the use of a reaction from a solution were different precursors can be dissolved easily either in the ionic or molecular form and react chemically on the substrates leading to film formation. The key advantages are low cost, large area and low temperature atmospheric processing. One of the major drawback is that in the classical beaker configuration, the material yield for film formation is very low, about a few per cent, leading to an uneccessary waste production and increased treatment costs. The reason is that the volume to surface ratio is very high and that only a small part of the solution is contributing to the film formation, the remaining one leading to the formation of colloids in the bulk of the solutions.

To avoid this problem the idea is to carry out the reaction between two plates with a small spacing filled with the solution, the plates being directly the substrates which have to be covered [1,2]. The interest of this configuration is that it is like a 2D configuration with no limit on the area. It can be considered as a close space configuration by analogy with existing techniques in vacuum like close space chemical vapour transport (CSVT) or close space sublimation (CSS).

Experiments have been carried out on the well known case of cadmium sulfide by CBD [3]. Chemical bath deposition of CdS used the chemical reaction between complexed cadmium ions and thiourea in a basic environment

$Cd(NH_3)_4^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow CdS + 4 NH_3 + CN_2H_2 + 2 H_2O$

The reaction proceeds via a surface controlled reaction [4]. In parallel the formation of colloids takes place in the solution as a result of the the homogeneous process.

A systematic study has been carried out by varying the distance between the plates from less than 1 mm to 5 mm, the composition of the solution and the temperature. The growth of the films was characterized ex situ by profilometry and optical transmission and also in situ by introducing a quartz crystal microbalance within one plate. It is shown that the yield of film formation increased remarquably from a few percent to high values up to more than 90% when decreasing the distance between the plates. The yield also increases at a given distance when agitation of the solution is possible, highest values for small distances were obtained using ultrasonic stirring.

The modelization of this system has been undertaken by using computer methods with simplified assumptions, considering in particular the competition between the homogeneous precipitation process and the heterogeneous deposition reaction together with the transport properties of the reacting species in the solution. They allow to explain the results and to address fundamental aspects of the chemical bath deposition mechanisms, in terms of reaction kinetics. This approach could be useful both for the case of the inon by ion mechanism, as exemplified with CdS, but also for cluster by cluster growth as for ZnS [4,5].

References :

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