

Solution chemistry and reaction mechanism taking place during the chemical bath deposition of $\text{In}(\text{OH})_x\text{S}_y$

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The development of the chemical bath deposition (CBD) technique has gained lots of attention during the last years as a method for preparing thin films of chalcogenide compounds. The majority of the studies related to CBD are normally restricted to the characterisation of deposited films. Hence, the basic chemical aspects related to solution chemistry and reaction kinetics of that process are most of the times neglected. This leads to a limitation to the development of the CBD method on comprehensive grounds. On the basis of our experience in the field of the chemical bath deposition of $\text{In}(\text{OH})_x\text{S}_y$ thin films [1, 2, 3] we present here our studies concerning the composition of the bath before and after the $\text{In}(\text{OH})_x\text{S}_y$ deposition.

The solutions used in the chemical bath deposition of $\text{In}(\text{OH})_x\text{S}_y$ contain InCl_3 , acetic acid and thioacetamide. As it was stated in a previous work [4], the chemical species present in the solution and the rate of thioacetamide hydrolysis, depend on the solution pH. Therefore, the pH of solutions containing thioacetamide, acetic acid and InCl_3 was measured at room temperature. In all cases, the addition of thioacetamide did not change the solution pH. In the case where no InCl_3 was added, the theoretical values almost matched the experimental ones. In contrast, when InCl_3 was present, the solution pH was always lower than the calculated values. This deviation of the experimental pH can be in part due to the ionic strength of the solution and in part due to the formation of either indium-acetate complexes or other complexes containing hydroxide ions or even to the formation of hydroxide colloids [3, 5, 6].

From the pH values the molar percentage of the species present in the solution can be calculated using the equilibrium constants found in the literature [7]. In Figure 1 it can be seen that the predominant species in our system are the chloro complexes, the acetate complexes, and the chloro-hydroxo complexes and that this predominance depends on the acetic acid concentration and therefore on the solution pH.

The hydrolysis reaction of the sulphide precursor is another point that should be considered when a CBD process is studied. In the case of the thioacetamide, the most recent mechanism for the hydrolysis in an acidic medium has been proposed by O. M. Peeters and C. J. de Ranter [8]. From the kinetic equations deduced by these authors the molar percentage of the reaction products can be calculated as a function of the reaction time. An example of such calculations is represented in Figure 2. In order to compare the theoretical values with experimental results the organic products formed after the $\text{In}(\text{OH})_x\text{S}_y$ precipitation were investigated using gas-mass chromatography. The compounds identified were mainly acetonitrile and thioacetic acid, but surprisingly no acetamide was detected. The $\text{In}(\text{OH})_x\text{S}_y$ precipitation therefore seems to take place through a mechanism which is not the hydrolysis of the thioacetamide and which leads to different products depending on the solution pH. As a

result of these investigations a reaction mechanism for the formation of $\text{In}(\text{OH})_x\text{S}_y$ can be proposed.

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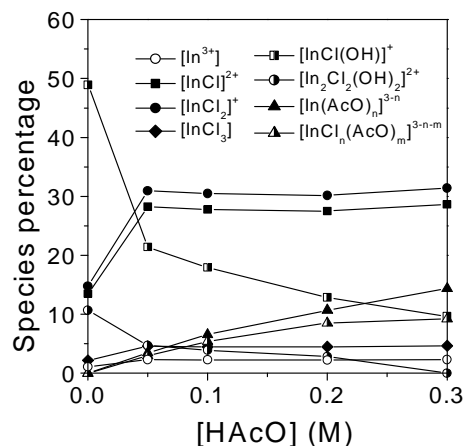


Figure 1. Calculated molar percentage of the species composing the $\text{In}(\text{OH})_x\text{S}_y$ deposition bath as a function of $[\text{HAcO}]$.

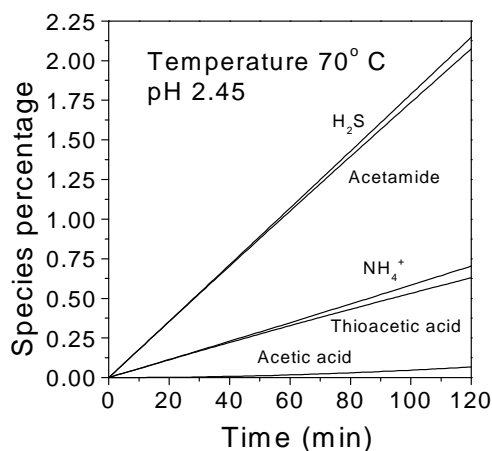


Figure 2. Calculated molar percentage of the products formed during the thioacetamide hydrolysis.

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