Evolution of CBD-In(OH)$_x$S$_y$ thin film band structure with its optical band gap

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The substitution of Chemical Bath Deposited (CBD)-CdS buffer layer in chalcogenide based solar cells by a Cd-free material is nowadays an active research topic. So far one of the alternative buffer layer materials, which leads to the best photovoltaic conversion efficiencies, is the CBD-grown indium hydroxide sulfide (In(OH)$_x$S$_y$) [1]. Some of the intrinsic properties of the CBD-In(OH)$_x$S$_y$ thin films have been already reported [2, 3, 4]. From the point of view of the optical properties of such thin films the band gap can be tailored between 2.4 eV and 3.6 eV by varying the composition of the chemical bath. In principle both, the presence of hydroxyl groups substituting the sulfur or the occurrence of a quantum size effect due to a small crystal size, have been suggested as the origin of the band gap variation. However, no proof of such effects has yet been given. Hence, the aim of the presented work is to determine which effect leads to the optical band gap increase. For that, both the composition of the films and the optical properties have been analyzed in detail using XPS and NIR/VIS/UV spectroscopy respectively.

In figure 1 the value of the optical band gap of the In(OH)$_x$S$_y$ thin films has been plotted as a function of their sulfur content, i. e. the atomic ratio S/In. It can be observed that the optical band gap linearly increases when the atomic ratio S/In decreases, i. e. when the hydroxide amount of the films increases. This suggests that the presence of hydroxide in the film composition strongly affects the energy gap of the film.

Using the XPS semi-direct technique, the valence band discontinuity at the interface n$^+$-SnO$_2$/n-In(OH)$_x$S$_y$ has been also determined [5]. Through this technique the evolution of both the conduction and the valence band of the In(OH)$_x$S$_y$ has been deduced as the optical band gap increases. In figure 2.a the absolute value of the valence band discontinuity at the interface n$^+$-SnO$_2$/n-In(OH)$_x$S$_y$ has been plotted for different values of the optical band gap. As it can be seen, when the optical band gap of In(OH)$_x$S$_y$ increases, its valence band maximum moves towards lower energies. In contrast, the conduction band is shifted towards higher energies (see figure 2.b). Quantitatively, the influence of the band gap increase on the valence band maximum position is at least four times higher than on the conduction band position.

In the case of a quantum size effect occurs, the shift of both conduction and valence band is usually the same [6]. On the other hand Robles & al. [7] have shown that the occupied part (i. e. valence band) of the density of state (DOS) of In$_2$S$_3$ is formed mainly by sulfur p-states, whereas these states slightly contribute to the unoccupied part of the DOS (i.e. conduction band). The contribution of p-orbitals should be affected by the substitution of sulfur atoms in the In$_2$S$_3$ crystalline matrix by other atoms or groups such as OH. From the observations detailed in the present work, we can assign the increase of the optical band gap of the CBD-In(OH)$_x$S$_y$ to be mostly due to the decrease of the sulfur content of the thin films, i.e. an increase of the hydroxide content. However, as the minimum of the conduction band shifts as well, the occurrence of a quantum size effect cannot be disregarded completely.

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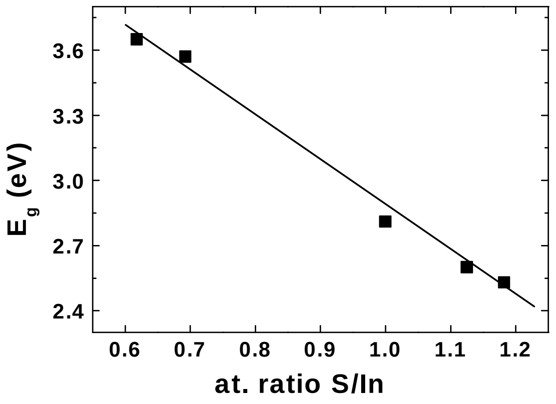

Figure 1: Evolution of the optical band gap E$_g$ of In(OH)$_x$S$_y$ thin films as a function of their sulfur content.

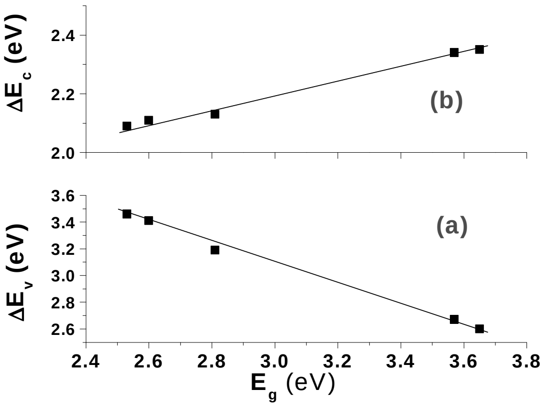

Figure 2: Absolute value of the valence band (a) and conduction band (b) discontinuity at the interface n$^+$-SnO$_2$/n-In(OH)$_x$S$_y$ as a function of the optical band gap of the In(OH)$_x$S$_y$ thin films.