

Ultra-thin charge selective heterojunctions with hydroxy-sulphides

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Introduction: Semiconducting metal sulphides are characterized by large absorption coefficients and bear the potential for very low cost application in photovoltaics. A major issue is the charge selectivity of contacts concomitant with the passivation of defects in related layers. It is well known that defects can be passivated, for example, by hydrogen and hydrogen containing species as $-OH$. We propose to use hydroxy-sulphides for ultra-thin charge selective heterojunctions prepared at very low temperatures. From surface photovoltage (SPV) measurements it was found that ultrathin $In(OH)_xS_y$ and $Pb(O)S$ layers behave like n- and p-type semiconductors, respectively [1]. As a working photovoltaic system, $TiO_2 / In(OH)_xS_y / Pb(O)S / PEDOT:PSS$ was demonstrated [1].

Preparation of ultra-thin hydroxy-sulphide layers: Ultra-thin sulphide layers were deposited by the SILAR (successive ionic layer adsorption and reaction) technique which gives excellent conformal coverage. The SILAR preparation was performed in 4 steps for one coating cycle: (i) adsorption of metal ions in aqueous solutions of $InCl_3$ or $Pb(AcO)_2$, (ii) rinsing in distilled water, (iii) reaction with sulphur ions in aqueous solution of Na_2S and (iv) rinsing in distilled water. An optimum was reached for 35 and 15 coating cycles for $In(OH)_xS_y$ and $Pb(OH)_xS_y$ layers, respectively. After SILAR preparation, the layers were annealed in air at temperatures (T_{ann}) between 50 and 325 °C. The experiments were carried out on $In(OH)_xS_y$ and $Pb(OH)_xS_y$ layers which were separately annealed and on $In(OH)_xS_y/Pb(OH)_xS_y$ structures with joint annealing.

Stoichiometry analysis: Investigation with ERDA (elastic recoil detection analysis; highly energetic Au^{26+} ions were used) showed that about 10^{15} $In(Pb)$ atoms / cm^2 were deposited during one SILAR coating cycle which can be related to a layer thickness of the order of 1 nm for one cycle. Further, the as-deposited layers were close to the stoichiometry of In_2S_3 and PbS while the relatively large amount of hydrogen points to a disordered structure with terminating $-SH$ groups. The content of oxygen increased and the content of hydrogen decreased with increasing T_{ann} . At $T_{ann} = 250$ °C, hydrogen vanished practically completely. Important to note, simulated spectra of the In yield in a double layer structure agreed excellently with the measured spectra, i.e. no intermixing or alloying of In and Pb was observed.

Band gaps and electronic defects: The band gap (E_g) and defects below the band gap (E_t – energy parameter of the exponential defect distribution) were investigated by SPV spectroscopy. For $In(OH)_xS_y$, the value of E_g decreased from 2.7 to 2.0 eV with decreasing T_{ann} . This decrease of the band gap anti-correlates with the oxygen content and can be explained by increasing size of sulphide clusters in the layer. E_t increased from 0.18 to 0.2 eV with increasing T_{ann} up to 200°C for $In(OH)_xS_y$. For larger T_{ann} , E_t increased strongly to values above 0.25 eV, due to strong effusion of hydrogen. Surprisingly, the SPV spectra of the $Pb(OH)_xS_y$ layers were much less affected by T_{ann} and E_g was practically constant (about 0.8 eV).

Preparation of (very) small area solar cells: All investigated devices were prepared on glass substrates coated with conductive SnO₂:F as front contact. Compact and rough TiO₂ layers were prepared by the sol-gel technique and annealed in air at 500°C for 2 hours after sol-gel processing. As hole conductor, PEDOT:PSS was spin coated. The area of the solar cell structures was defined by the small diameter of the back contact (carbon ink dot). Structures with separate In(OH)_xS_y and Pb(OH)_xS_y layers showed only very bad solar cell performance while promising results were obtained only for solar cells containing In(OH)_xS_y / Pb(OH)_xS_y heterojunctions. Therefore, the In(OH)_xS_y / Pb(OH)_xS_y heterojunction is crucial for charge selectivity in the given system.

Separate annealing: The specific influence of the ultra-thin In(OH)_xS_y and Pb(OH)_xS_y layers was investigated by annealing the layers separately, i.e. the Pb(OH)_xS_y layer was deposited after the annealing of the In(OH)_xS_y layer. The characteristics of the solar cell structures correlated strongly with the preparation conditions of the In(OH)_xS_y layer (T_{ann}, layer thickness) whereas preparation conditions of the Pb(OH)_xS_y layer were not so pronounced. For example, the short circuit current (I_{SC}) correlated and the open circuit voltage anti-correlated with the band gap of the In(OH)_xS_y layer. Further, the open circuit voltage (V_{OC}) is limited to about 0.2 ... 0.3 V for appropriate short circuit currents.

Role of joint annealing process: A joint annealing process of the In(OH)_xS_y and Pb(OH)_xS_y layers lead to an increase of V_{OC} to up to 0.67 V while large values of I_{SC} (up to 14 mA/cm² for illumination with a halogen lamp with 100 mW/cm²) could be maintained. The TiO₂ or the PEDOT:PSS layers were replaced in some experiments while V_{OC} remained high and I_{SC} dropped by about one order of magnitude. Therefore, the charge selectivity is dominated by the In(OH)_xS_y / Pb(OH)_xS_y heterojunction and the TiO₂ or PEDOT:PSS layers act more a barrier layers for holes or electrons and suppress recombination at the front and back contacts.

Influence of traps: Light soaking is essential for the ultra-thin In(OH)_xS_y / Pb(OH)_xS_y heterostructure under illumination. The value of V_{OC} increases while I_{SC} decreases within several minutes and saturate under illumination. Further, quantum efficiency spectra did not show the pronounced feature of a band gap and depended on the modulation frequency of the light intensity. Therefore, the charge selectivity of the ultra-thin In(OH)_xS_y / Pb(OH)_xS_y heterostructure largely controlled by traps in both layers. However, more detailed experiments are needed for better understanding of the role of traps in the given system.

Conclusions: In a joint annealing process of the In(OH)_xS_y and Pb(OH)_xS_y layers, a heterocontact can be formed under additional linking by -Pb-S(O)-In= bonds and stress can be avoided due to a common local relaxation of hydroxy-sulphide clusters. These two properties, more intimate linking and better relaxation of local stress, are responsible for a high efficiency of charge selectivity. The passivation of defects with hydrogen and hydrogen containing species is crucial for high short circuit currents. It seems real that solar cells with relevant efficiencies can be prepared with ultra-thin heterostructures based on hydroxy-sulphides. This opens new opportunities for low-cost technologies and a lot of unanswered questions.

[1] R. Bayon, et al., Solar Energy Materials & Solar Cells **89**, 13 (2005).