Insights into Kinetics and Reaction Pathway of 2-Step conversion of $MAPb(I_xBr_{1-x})_3$ series via in-situ UV-vis measurements

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Metal halide perovskites are an interesting material for tandem solar cells according to their band gap tunability. Therefore, perovskite semiconductors with high band gaps up to 2.3 eV can be prepared by exchanging halides.[1] Burschka et al.[2] introduced the 2-step method also called sequential deposition as a preparation method for perovskite solar cells. Reaction parameters influence the formation of the perovskite thin film. Ummadisingu et al.[3] showed that illumination during the conversion step influences the transformation into perovskite by activating the nucleation. The mechanism might be an intercalation or dissolution-reconstruction process.[4] Understanding the formation process will help to form homogenous films with high band gaps.

$$PbI_2 + MABr \rightarrow MAPbBrI_2 \text{ (dicrect conversion product)}$$

$$PbI_2 + MABr \text{ (excess)} \rightarrow Pb^{2+} + MA^+ + 3\ Br^- \rightarrow MAPbBr_3 \text{ (dissolution/ reformation product)}$$

In this work, the second step of this sequential deposition is monitored by in-situ UV-vis measurements. The second step is the conversion from a lead iodide (PbI_2) film into a mixed halide perovskite film $MAPb(I_xBr_{1-x})_3$ by immersion of MABr. Using MABr we can distinguish different reaction products and hence reaction pathways and track the different conversion kinetics between a direct conversion and a dissolution-reformation process. The influence of following parameters is investigated: film thickness and morphology, reaction time and concentration of the MABr dipping solution. Additional UV-vis, SEM and XRD measurements after annealing are carried out to complete the study.

In-situ UV-vis measurements show a change of the evolution of the absorption onset of the direct conversion product, $MAPbBrI_2$, that disappears over time in favor ofa pure dissolution-reformation product of $MAPbBr_3$. Due to the two competing reaction pathways, the PbI_2 films are converted into a perovskite phase with varying halide composition in $MAPb(I_xBr_{1-x})_3$ depending on dipping time and film thickness. XRD shows residual PbI_2 not converted in the dipping step. Dependencies on reaction parameters are giving insights into the reaction pathway. Our experiments allow us to distinguish the two different reaction pathways and under which conditions one or the other product is favored. Understanding transformation is necessary to control degree of material conversion and morphology.

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