Electronic Structure of Self-Assembled Monolayers on ZnO Surfaces

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\section*{INTRODUCTION}

Controlling the electronic properties at the interface between organic and inorganic materials is an issue of high interest since it is known to strongly affect the charge injection and the overall efficiency of opto-electronic devices.\textsuperscript{[1]} Self-assembled monolayers (SAMs) can be used to shift the bands of the underlying inorganic material and optimize the charge injection occurring at the interface.\textsuperscript{[2]} This work aims to theoretically investigate the shift in the conduction band at the surface when SAMs are deposited on ZnO and compare these data with experimental observation.


To a first approximation, ZnO nano-particles are considered to only be covered by (0001) polar and (10-10) non-polar surfaces. While this approximation is not expected to be representative of reality, our aim is to observe how much the shift in the conduction band is dependant on the surface orientation.

\textbf{Computational details:} Program SiESTA 3.0 with PBE (functional), D2P (basis set), 2x2x1 k-point mesh

\section*{Polar surface}

Modeling bare (0001) ZnO surface results in an artificial stabilization process via an electron transfer from O in the bottom layers towards the surface Zn. It results in the formation of a 2D metallic band on both surfaces. One solution is to partially cover the surface –OH groups to avoid this metallization problem. This is a realistic representation of the ZnO surface since water dissociates on its room temperature.

On both polar and non-polar surfaces the shift induced by PY is in the same direction with a similar magnitude. The system seems not to be dependent on the surface orientation nor on the presence of –OH groups at the surface. On the non-polar surface, an inversion in the shift is observed between BA and PY. For BA, the type of binding mode is observed to also affect the shift of CB. This effect is more pronounced when BA is partially connected through an H-bond (BM1).

\section*{Experiment}

Keeping the concentration of conduction band electrons (n\textsubscript{CB}) fixed in spectro-electrochemical measurements we can extract the conduction band shift and also extract the SAM molecule influence on charge recombination.

\textit{i)} Band edge tuning with charge species or surface dipole

\textit{E}\textsubscript{CB} = \textit{E}\textsubscript{CB} + \textit{E}\textsubscript{CB} \text{SAM} + \textit{k}_B T \ln \frac{n\textsubscript{SAM}}{n\textsubscript{CB}}

\textit{ii)} Minimize losses due to energy carrier for charge recombination/charge redistribution.

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Reference of the experimental methodology:
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