

Nano-scale origins of High Visible-light Photoactivity in ZnS/GaP Multilayer Film using High-resolution Transmission Electron Microscopy (HRTEM)

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Photoelectrochemical (PEC) water splitting is one such clean energy technology, which uses sunlight to produce hydrogen, thus allowing solar energy to be stored and transported. However many commonly studied PEC materials are oxides, which often have wide bandgaps, meaning that they can only absorb UV light and hence have very poor solar-to-hydrogen conversion efficiencies. We have shown that ZnS thin films can demonstrate tremendous potential as visible-light PEC materials due to the presence of defect sites. Recently, theoretical studies by Hart and Allan showed that the band gap of ZnS could be tuned significantly by addition of GaP^[i], which was subsequently experimentally realized by Park *et al.* in nanowires^[ii].

In this work, we have used an interface engineering approach where we create multilayers of ZnS (Z)/GaP (G) stacked in an alternating fashion. We find an enhanced PEC activity under visible light in such synthetic thin film heterostructures. The focus of the work presented here is a systematic study of the atomic-scale resolved structure and local chemistry by Transmission Electron Microscopy (TEM) to understand the origins of this high visible-light activity. To investigate individual interfaces, we employed a double Cs-corrected scanning transmission electron microscopy (STEM). A series of ZG/ x (where x is the number of the interfaces) heterostructures with varying number of interfaces were grown on (100) silicon by Pulsed Laser Deposition (PLD). The TEM specimens were prepared by mechanical polishing followed by PIPS (i.e. cutting, grinding, dimpling, polishing and Ar-ion milling with a liquid nitrogen cooling stage). Scanning-TEM/TEM investigations were carried out in a Tecnai F30 and double aberration corrected Titan Cubed Themis G2 300 TEM operated at 300kV. The thicknesses of the observed regions were estimated to be less than 30nm by measuring the intensity ratio between the plasmon loss and the zero-loss peaks in Electron Energy Loss Spectroscopy (EELS).

Our TEM studies (including the atomically resolved STEM images following by EDS mapping) directly confirm the existence of a ~ 5 nm diffusion area at each interface although structurally the interfaces appear sharp (Fig1). The inter-mixing at each interface leads to a locally confined solid solution of ZnS and GaP, which has an electronic structure that is conducive to stronger visible-light activity than either ZnS or GaP on their own, as previously predicted for ZG mixturesⁱ. The film with the highest number of ZG interfaces achieves the highest photocurrent for visible-light PEC water splitting, confirming that this activity arises from the interfaces. Thus, we microscopically identify the origins of the observed enhanced visible-light photoactivity as (i) the interdiffused area at the Z/G interfaces where the local chemical composition is effectively a solid solution thereby possessing a reduced bandgap, and (ii) structural defects including 3D defects such as dislocations and plans of twinning, which possibly affect local stoichiometryⁱⁱⁱ.

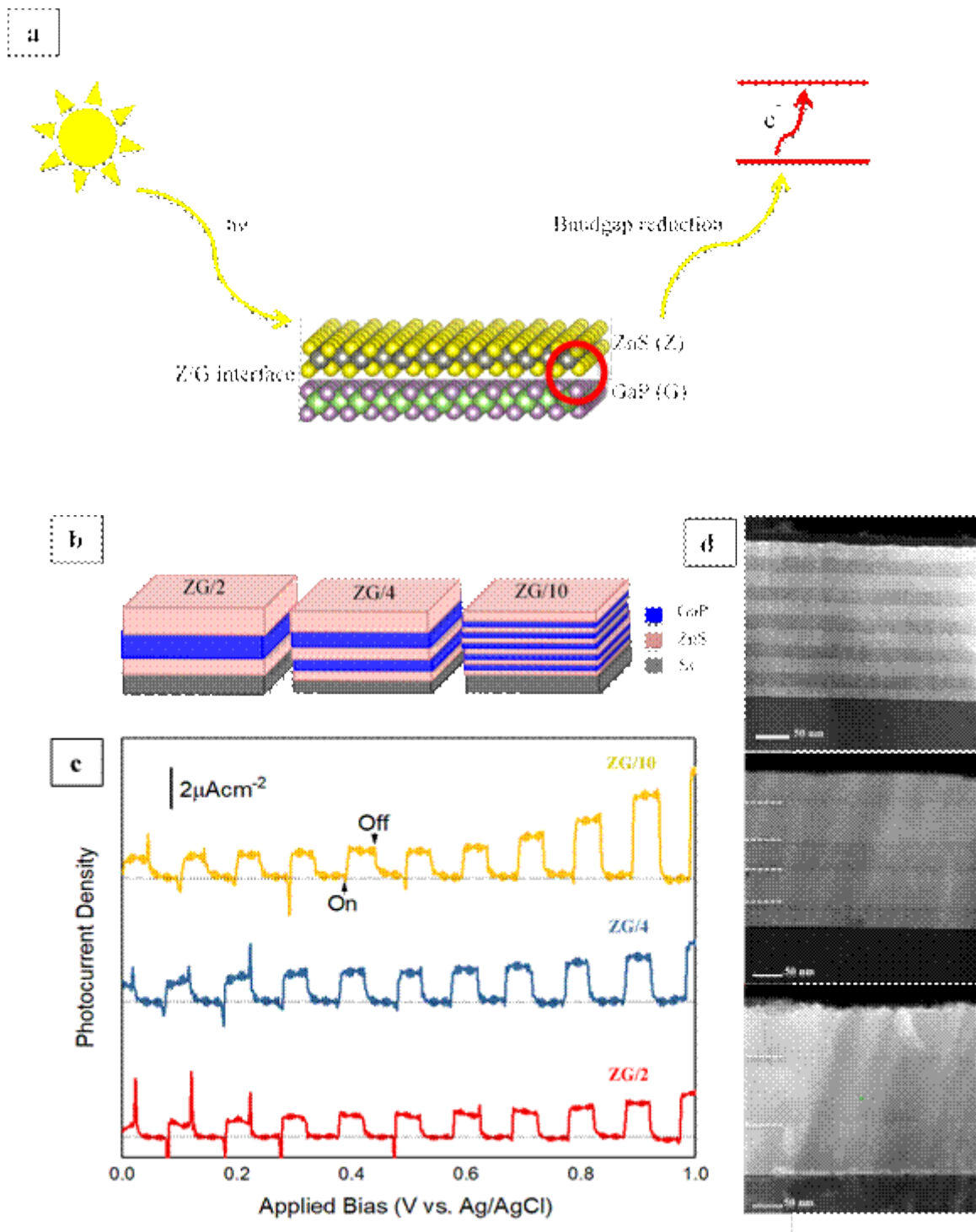


Figure 1. (a) Schematic illustration of the ZnS-GaP multilayer films with different numbers of interfaces on silicon substrates. (b) Result of cyclic voltammetry measurement of the multilayer films from -1 to 1 V. (c) High-angle annular dark-field (HAADF) cross-section images of the multilayer films for ZG/2, ZG/4 and ZG/10, which confirm that perfect interfaces are elongated coherently between layers. (ZG/ x , x is the number of interface)

Reference:

- ⁱ J. Hart and N. Allan, *Advanced Materials* **25** (2013), p. 2989-2993.
- ⁱⁱ K. Park, J.A. Lee, H.S. Im, C.S. Jung, H.S. Kim, J. Park, C.L. Lee, *ACS Nano Letters* **14** (2014), p. 5912-5919.
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