ADVANCED ENERGY MATERIALS

Supporting Information

for *Adv. Energy Mater.,* DOI: 10.1002/aenm.201900940

Boosting the Performance of WO_3/n-Si Heterostructures for Photoelectrochemical Water Splitting: from the Role of Si to Interface Engineering

*Yihui Zhao, Geert Brocks, Han Genuit, Reinoud Lavrijsen, Marcel A. Verheijen, and Anja Bieberle-Hütter**

Supporting Information

Boosting the Performance of WO_3/n-Si for Photo-electrochemical Water Splitting: the Role of Si to Interface Engineering

*Yihui Zhao, Geert Brocks, Han Genuit, Reinoud Lavrijsen, Marcel A Verheijen, Anja Bieberle-Hütter**

Films deposition

Table 1

Sputtering process parameters for WO_3 deposition.

Parameter	Value
Target power	100 W
Base pressure	$<10^{-8}$ mbar
Deposition pressure	10^{-2} mbar
Substrate temperature	Room temperature
O_2 flow rate	10 sccm
Ar flow rate	40 sccm

Figure S1 shows the flow diagram of the thin film depositions.

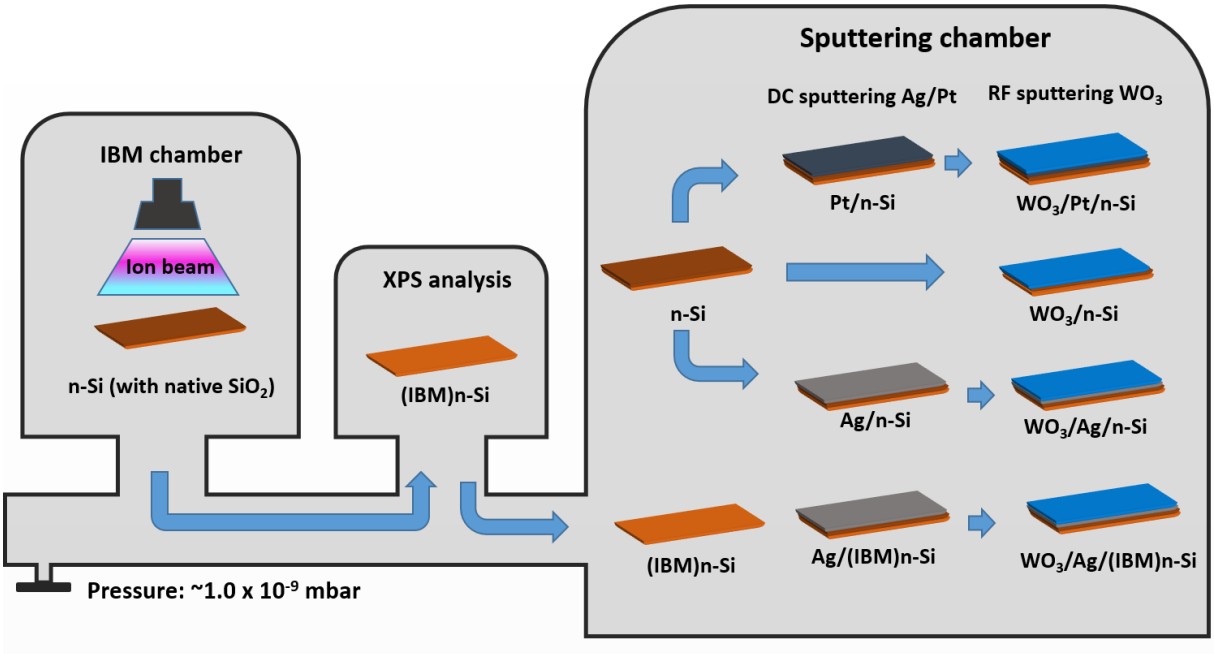

Figure S1: Flow diagram of WO_3/n-Si, WO_3/Ag/n-Si, WO_3/Ag/(IBM)n-Si (ion beam milling treated n-Si) and WO_3/Pt/n-Si deposition. The entire process is carried out without breaking the vacuum.

Atomic Force Microscope (AFM) of WO_3/n-Si and WO_3/FTO

Figure S2 shows the surface roughnesses of WO_3/n-Si and WO_3/FTO, which were measured by AFM. The surface roughnesses of WO_3/n-Si and WO_3/FTO are R_a = 2.2 nm and R_a = 7.1 nm, respectively.

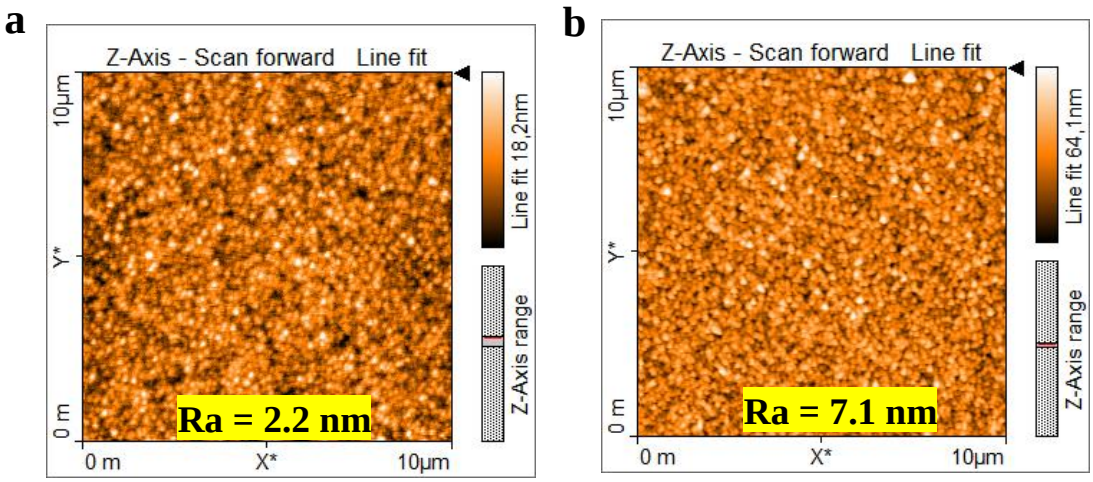

Figure S2: Atomic Force Microscope (AFM) of (a) WO_3/n-Si and (b) WO_3/FTO after annealing in the Ar.

Cross-section HAADF-STEM of WO_3/n-Si and WO_3/FTO

Cross-section HAADF-STEM images confirm that an intimate contact is obtained for both WO_3/n-Si and WO_3/FTO interfaces, as shown in Figure S3.

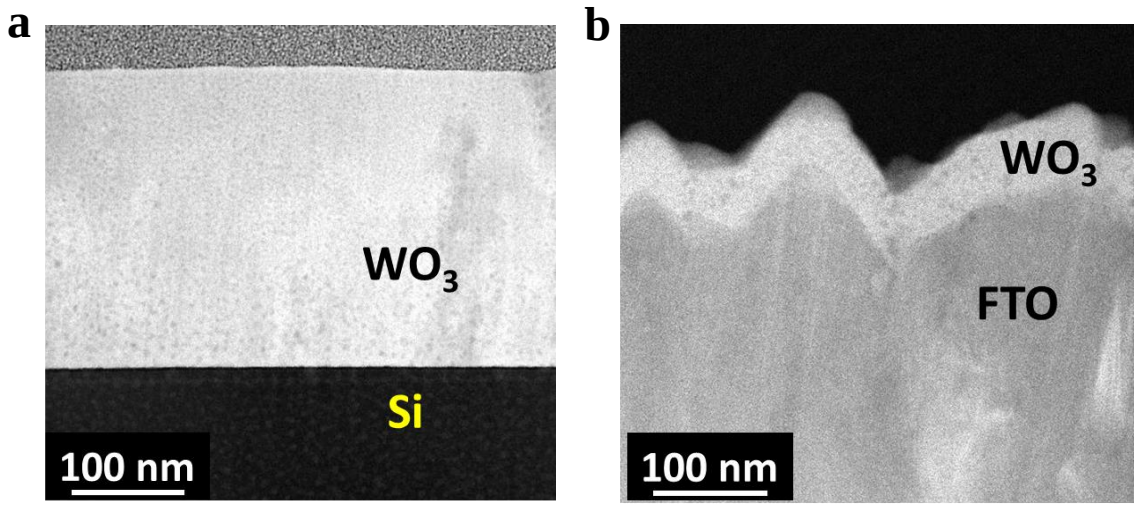

Figure S3: Cross-section HAADF-STEM images of (a) WO_3/n-Si and (b) WO_3/FTO.

GIXRD of WO_3/n-Si and WO_3/FTO

The GIXRD spectra of the WO_3/n-Si and WO_3/FTO after annealing in Ar at 450℃ for 1 h are shown in Figure S4. The diffraction peaks agree well with monoclinic WO_3 corresponding to JCPDS No. 83-0950 indicating that monoclinic WO_3 was obtained for both electrodes after annealing.

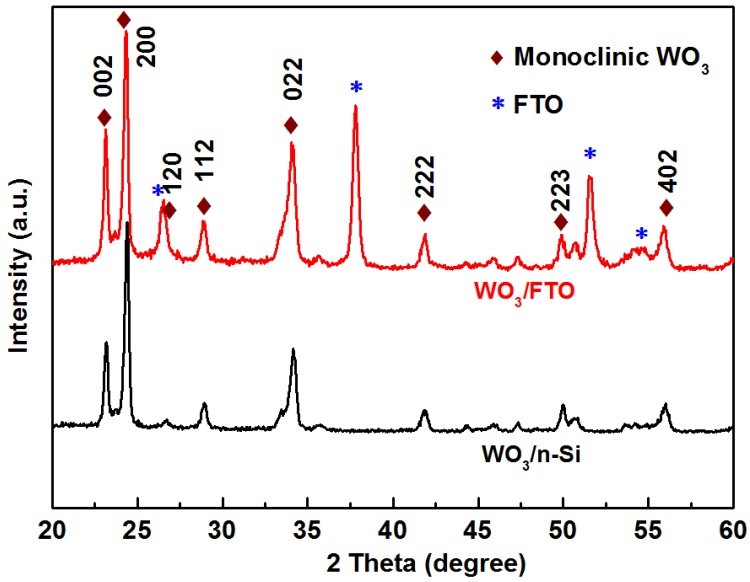

Figure S4: GIXRD spectra of WO_3/n-Si (black) and WO_3/FTO (red) after annealing in Ar. The brown diamonds and the blue dots are monoclinic WO_3 (JCPDS No. 83-0950) and FTO (JCPDS No. 83-0950), respectively.

Relative energy band levels

Figure S5 shows the energy band diagrams of n-Si, WO_3, Ag, Pt and H_2O. The band gap of n-Si is ~1.1 eV[1] and the Fermi level is about -4.25 ± 0.1 eV vs vacuum level[1–3]. The band gap of WO_3 is about 2.8 - 3.0 eV and the Fermi level is about -5.25 ± 0.1 eV[4–7]. The work functions of Ag and Pt are 4.5 ± 0.15 eV and 5.7 ± 0.1 eV vs vacuum level[8].

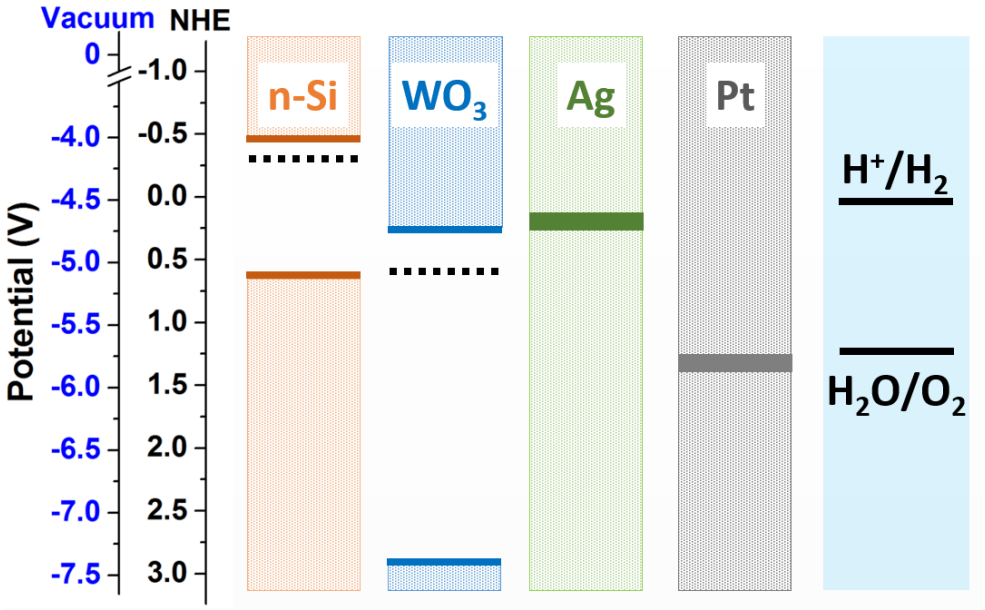

Figure S5: Diagram of relative energy band levels of n-Si, WO_3, Ag, Pt, and H_2O. The diagram is constructed from literature data[1–8].

Reference

[1] S. Y. Reece, J. a. Hamel, K. Sung, T. D. Jarvi, a. J. Esswein, J. J. H. Pijpers, D. G. Nocera, *Science* **2011**, *334*, 645.

[2] M. T. Mayer, C. Du, D. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 12406.

[3] Y. J. Hwang, A. Boukai, P. Yang, *Nano Lett.* **2009**, *9*, 410.

[4] Y. Zhao, S. Balasubramanyam, R. Sinha, R. Lavrijsen, M. A. Verheijen, A. A. Bol, A. Bieberle-Hütter, *ACS Appl. Energy Mater.* **2018**, *1*, 5887.

[5] P. Dias, T. Lopes, L. Meda, L. Andrade, A. Mendes, *Phys. Chem. Chem. Phys.* **2016**, 5232.

[6] H. Li, H. Yu, X. Quan, S. Chen, Y. Zhang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 2111.

[7] J. Y. Zheng, A. U. Pawar, C. W. Kim, Y. J. Kim, Y. S. Kang, *Appl. Catal. B Environ.* **2018**, *233*, 88.

[8] J. Hölzl, F. K. Schulte, H. Wagner, *Solid Surface Physics*; Springer-Verlag Berlin, 1979.