

Fast-Response Single-Nanowire Photodetector Based on ZnO-WS<sub>2</sub> Core-Shell Nanowire Heterostructures

Boris Polyakov, Edgars Butanovs, Sergei Piskunov, Alexei Kuzmin

ABSTRACT

The surface plays an exceptionally important role in nanoscale materials, exerting a strong influence on their properties. Consequently, even a very thin coating can greatly improve the optoelectronic properties of nanostructures by modifying the light absorption and spatial distribution of charge carriers. To use these advantages, ZnO-WS<sub>2</sub> core/shell nanowires with a few layers thick WS<sub>2</sub> shell were fabricated. These heterostructures were thoroughly characterized by scanning and transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. Then, a single-nanowire photoresistive device was assembled by mechanically positioning ZnO-WS<sub>2</sub> core-shell nanowires onto gold electrodes inside a scanning electron microscope. The results show that a few layers of WS<sub>2</sub> significantly enhance the photosensitivity in the short wavelength range and drastically (almost 2 orders of magnitude) improve the photoresponse time of pure ZnO nanowires. The fast response time of ZnO-WS<sub>2</sub> core-shell nanowire was explained by electrons and holes sinking from ZnO nanowire into WS<sub>2</sub> shell, which serves as a charge carrier channel in the ZnO-WS<sub>2</sub> heterostructure. First-principles calculations suggest that the interface layer iWS<sub>2</sub>, bridging ZnO nanowire surface and WS<sub>2</sub> shell, might play a role of energy barrier, preventing the backward diffusion of charge carriers into ZnO nanowire

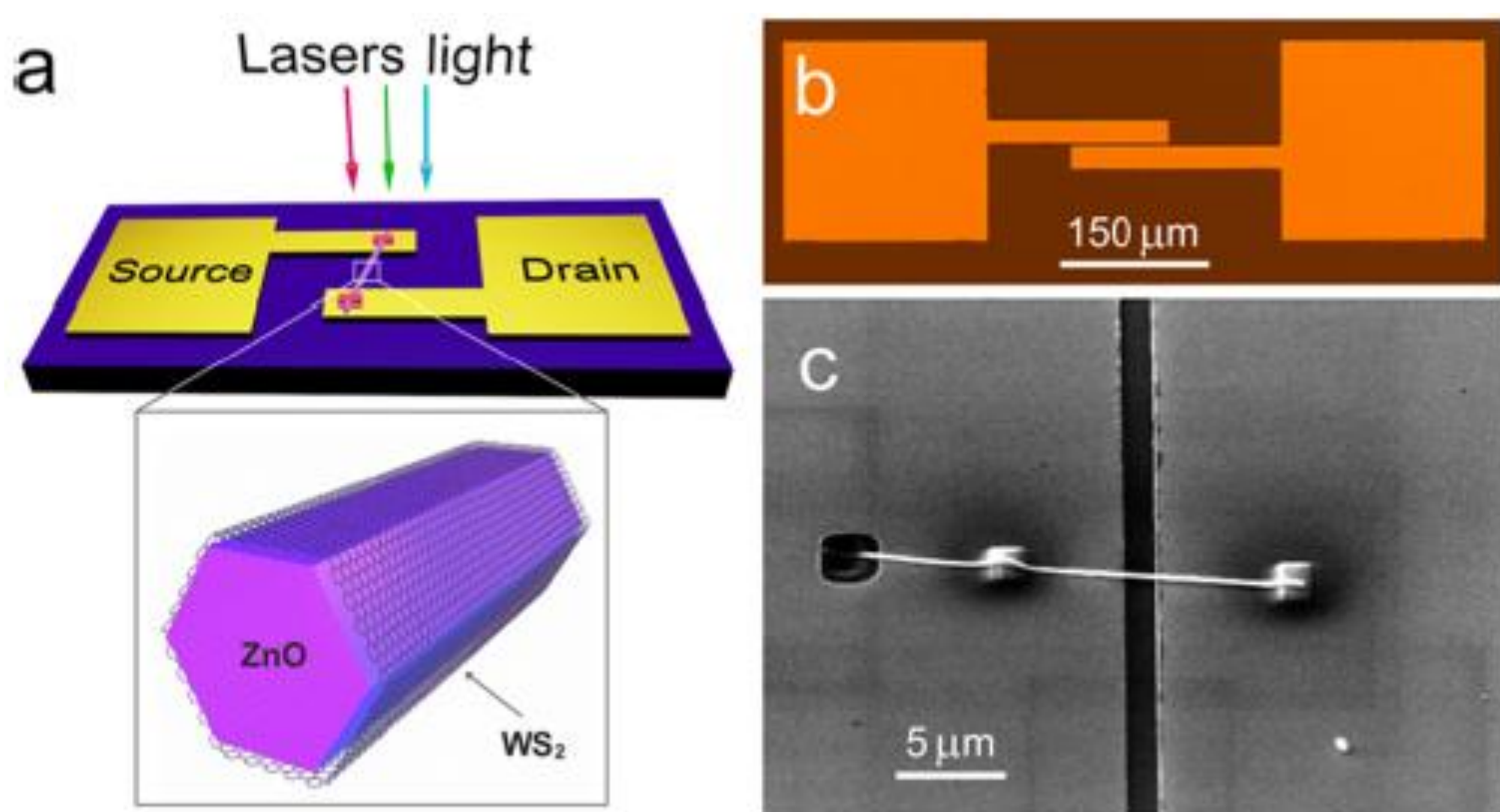


Figure 1. Schematics of ZnO/WS<sub>2</sub> core/shell nanowire-based photodetector (a). Optical microscope image of gold microelectrodes on the oxidized silicon substrate (b). SEM image of a typical nanowire photoresistor (c).

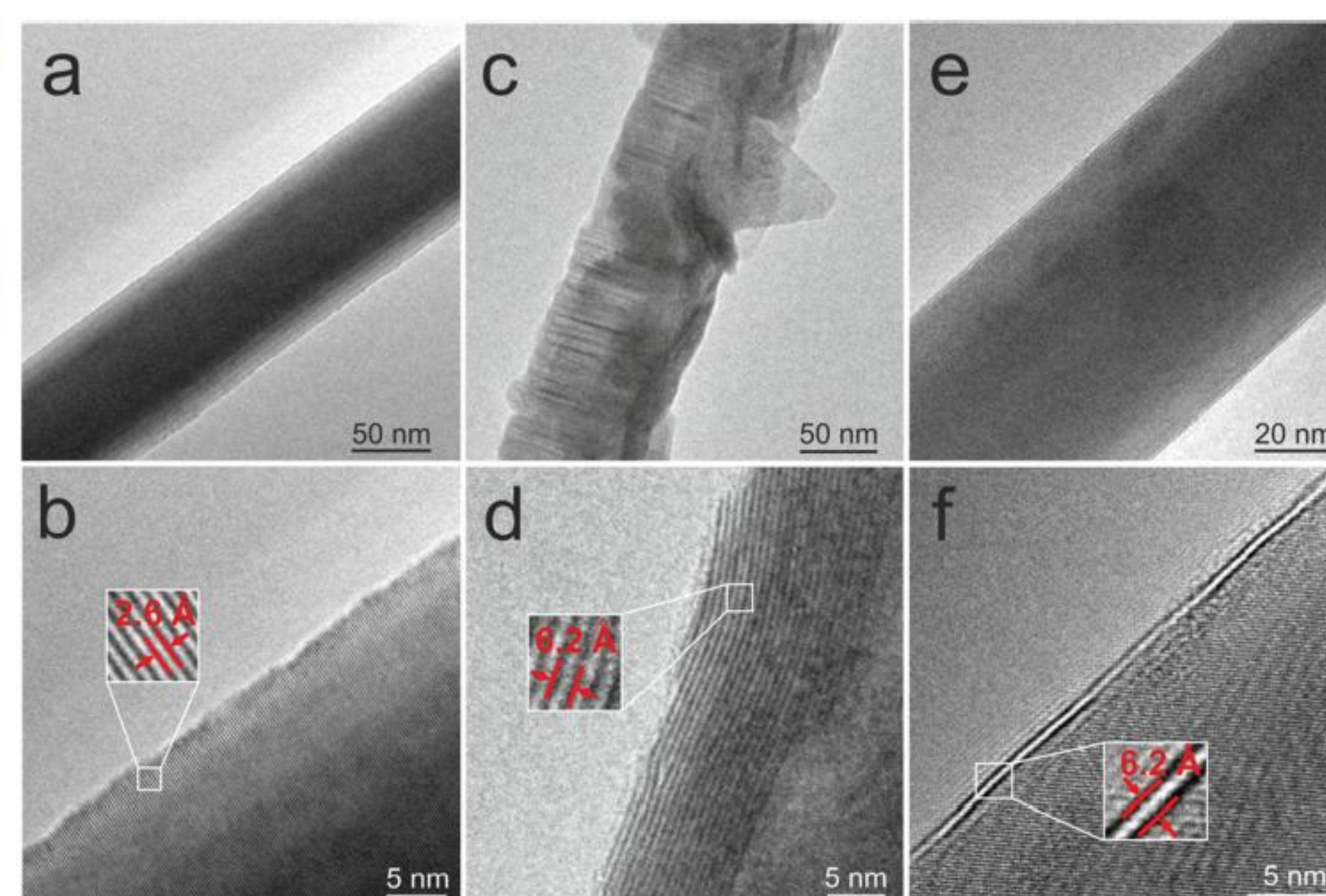


Figure 2. TEM images of pure ZnO nanowire (a, b), ZnO/WS<sub>2</sub> nanowire annealed in sulfur atmosphere (c, d), and ZnO/WS<sub>2</sub> nanowire additionally annealed in an inert atmosphere (e, f).

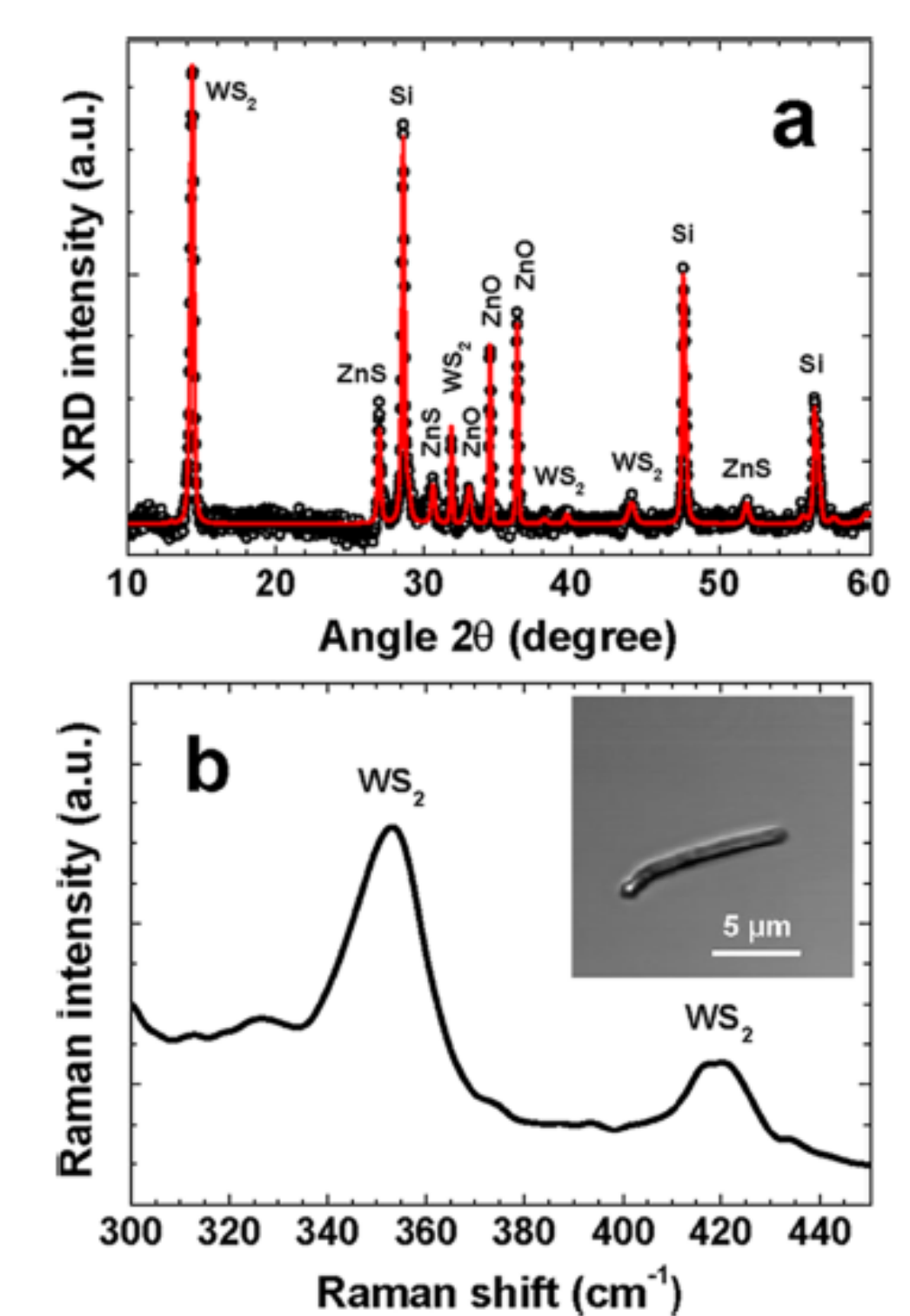


Figure 3. X-ray diffraction pattern of the ZnO/WS<sub>2</sub> sample (a). Raman spectrum of the ZnO/WS<sub>2</sub> NWs (b).

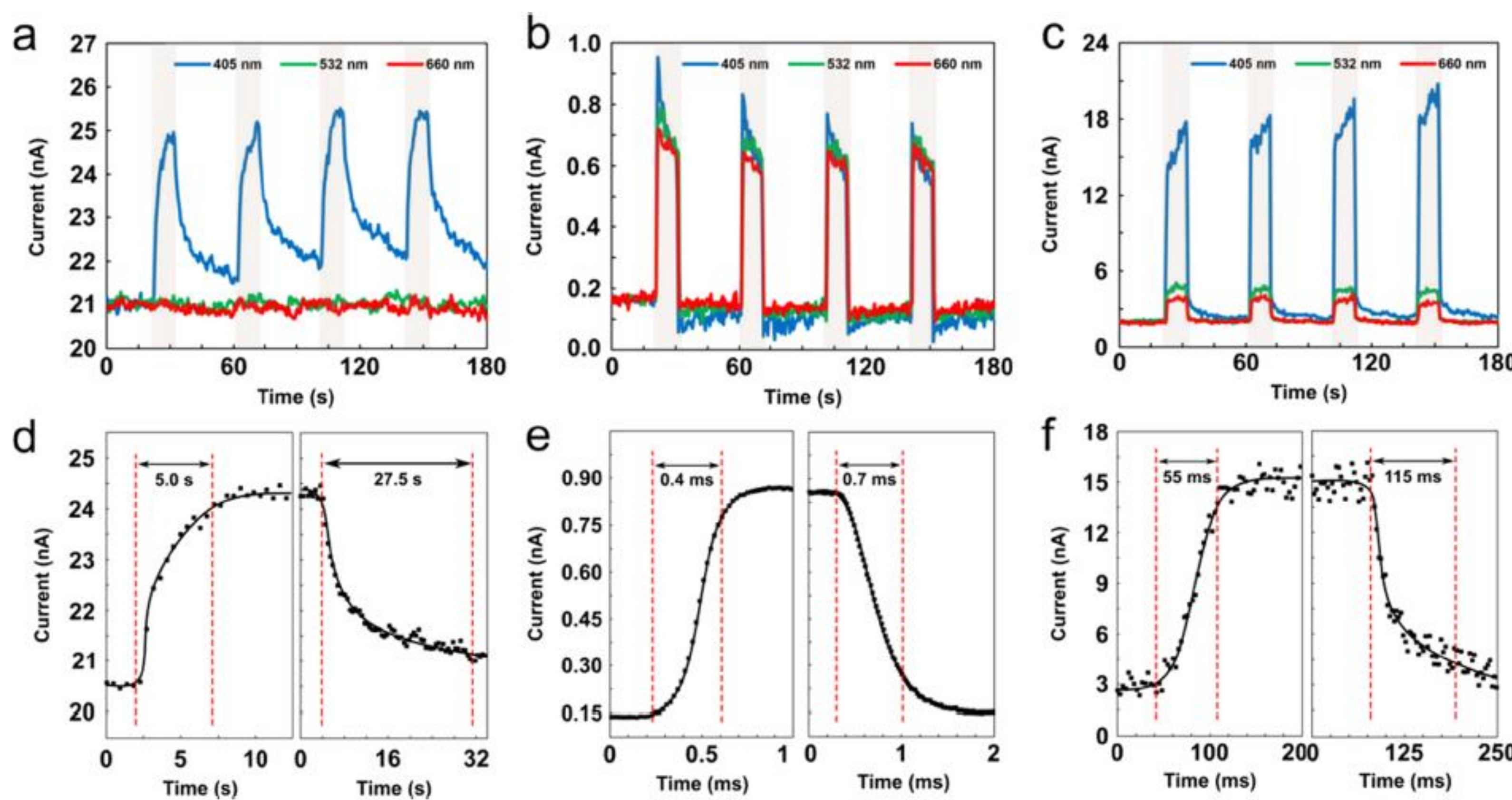


Figure 4. On-off photoresponse measurements of ZnO nanowire (a, d), WS<sub>2</sub> flakes (b, e), and ZnO/WS<sub>2</sub> nanowire (c, f) photoresistors at 1 V bias voltage and light illumination using 0.5 W/cm<sup>2</sup> light intensity of 405, 532, and 660 nm wavelengths.

Table 1. Characteristic Parameters of Photodetectors Fabricated from Pure ZnO and ZnO/WS<sub>2</sub> Core/Shell NWs as well as WS<sub>2</sub> Flakes

Table 1. Photoresponse (Rise and Decay) Time of Photodetectors Fabricated from Pure ZnO and ZnO/WS<sub>2</sub> Core/Shell NWs as well as WS<sub>2</sub> Flakes

wavelength (nm)	ZnO NWs		WS <sub>2</sub> flakes		ZnO/WS <sub>2</sub> NWs	
	rise (s)	decay (s)	rise (ms)	decay (ms)	rise (ms)	decay (ms)
405	5	27.5	0.4	0.7	55	115
532			0.3	0.65	21	95
660			0.53	1.35	22	50

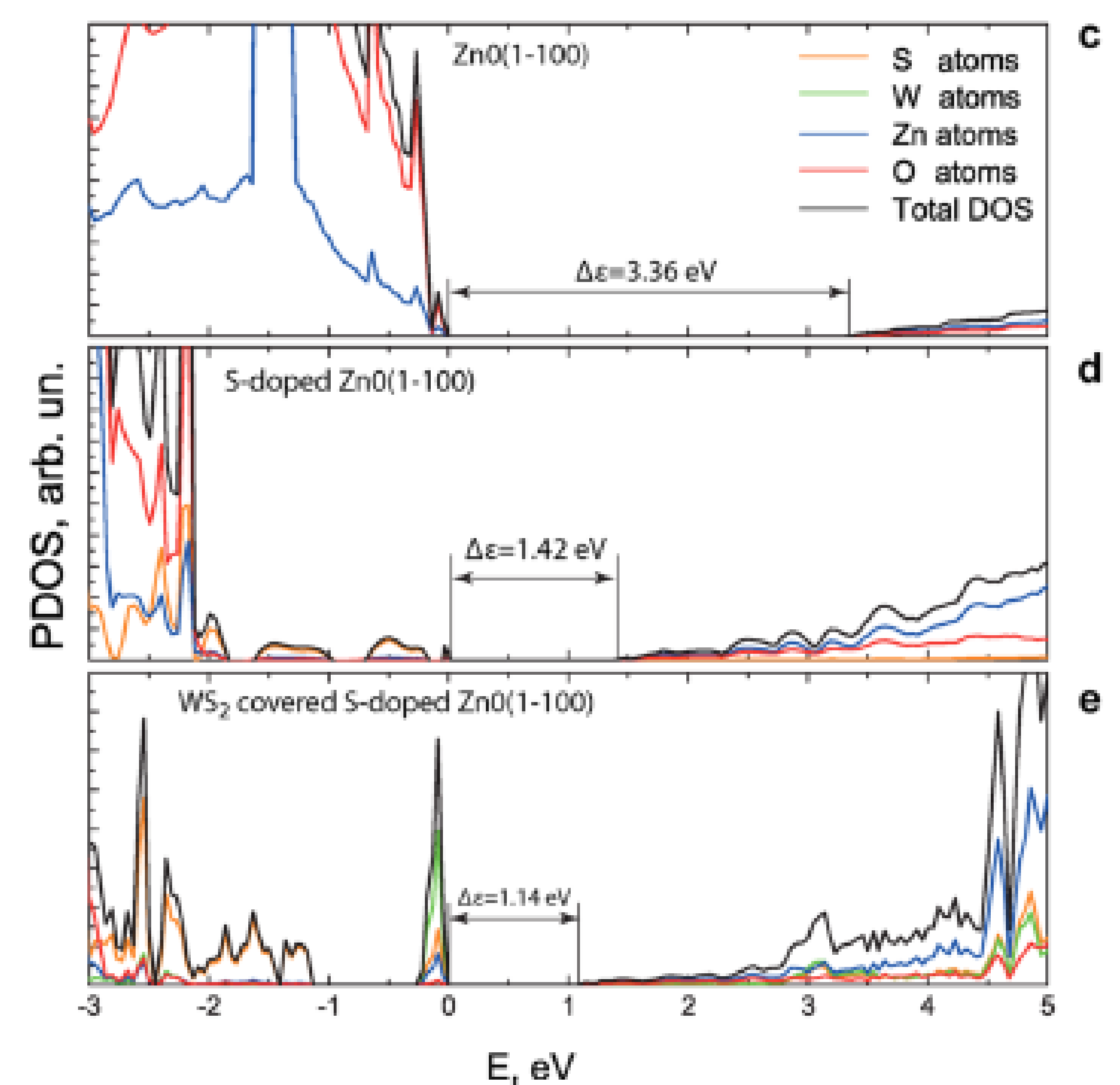


Figure 5. Simplified band diagram of the ZnO/WS<sub>2</sub> core-shell NW (a). Atomic structure of ZnO/WS<sub>2</sub> interface (b). Total and projected densities of states (DOSs) of (c) n-type ZnO (1100) substrate, (d) S-doped ZnO (1100) substrate, and (e) WS<sub>2</sub> covered S-doped ZnO (1100) substrate as calculated by means of density functional theory. Zero energy corresponds to the top of the valence band.

In summary, an effective photodetector based on ZnO/WS<sub>2</sub> core/shell nanowire (with a few layers of WS<sub>2</sub>) is demonstrated in this work. The photodetector responds to illumination at the wavelengths of 660 nm ( $R\lambda = 1.75$ ), 532 nm ( $R\lambda = 2.25$ ), and 405 nm ( $R\lambda = 7$ ). The ZnO/WS<sub>2</sub> core/shell nanowire-based device shows a clear advantage over pure ZnO nanowire-based photodetector in terms of both higher responsivity (4.6-fold) and faster operation (90-fold) for 405 nm illumination. The photodetector band diagram was supported by the first principles calculations, suggesting that the interface layer i-WS<sub>2</sub>, bridging ZnO nanowire surface, and WS<sub>2</sub> shell, might play an important role in preventing backward diffusion of charge carriers into the ZnO nanowire, whereas WS<sub>2</sub> shell serves as a charge carrier channel in the ZnO/WS<sub>2</sub> heterostructure. The obtained results clearly show the potential of combining layered 2D TMDs materials with semiconducting nanowires to create novel core/shell hetero-structures with advanced optoelectronic properties

CONTACT PERSON  
Boris Polyakov  
boris@cfi.lu.lv

REFERENCES

- [1] E. Butanovs, S. Vlassov, A. Kuzmin, S. Piskunov, J. Butikova, B. Polyakov. Fast-response single-nanowire photodetector based on ZnO/WS<sub>2</sub> core/shell heterostructures. ACS Appl. Mater. Interfaces. 10, 13869-13876 (2018)
- [2] B. Polyakov, K. Smits, A. Kuzmin, J. Zideluns, E. Butanovs, J. Butikova, S. Vlassov, S. Piskunov, Y. Zhukovskii. Unexpected epitaxial growth of a few WS<sub>2</sub> layers on {11-00} facets of ZnO nanowires. J. Phys. Chem. C. 120, 21451-21459 (2016)