Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Pressure and electric field-induced metallization in the phase-engineered ZrX_2 (X=S,Se,Te) bilayers

Ashok Kumar[1*], Haiying He[2], Ravindra Pandey[3*],P. K. Ahluwalia[4] and K. Tankeshwar[1*]

[1]*Department of Physics, Panjab University, Chandigarh 160014, India*
[2]*Department of Physics and Astronomy,Valparaiso University, Valparaiso, Indiana 46383, USA*
[3]*Department of Physics, Michigan Technological University, Houghton, Michigan 49931, USA*
[4]*Department of Physics, Himachal Pradesh University, Shimla 171005, India*

(Jun 15, 2015)

*Email:

Ashok Kumar (ashok.1777@yahoo.com)

Ravindra Pandey (pandey@mtu.edu)

K. Tankeshwar (tankesh@pu.ac.in)

Table S1: Bulk ZrX_2– trigonal phase: The structural parameters and band gap calculated at DFT level of theory. The number of bands crossing the Fermi level that gives the ballistic quantum conductance (in the unit of G_0) is also given for $ZrSe_2$ and $ZrTe_2$.

Material	level	a (Å)	c (Å)	E_g (eV)
ZrS_2	PBE	3.70	5.54	0.63
	PBE+vdW	3.65	5.46	0.47
	PBE+vdW+U	3.72	5.56	0.95
	EXP.	3.661[a]	5.815[a]	1.68[a]
$ZrSe_2$	PBE	3.82	5.81	Metal ($1G_0$)
	PBE+vdW	3.77	5.74	Metal ($3G_0$)
	PBE+vdW+U	3.87	5.93	0.5
	EXP.	3.773[a]	6.13[a]	1.20[c]
$ZrTe_2$	PBE	4.04	6.18	Metal ($5\ G_0$)
	PBE+vdW	3.98	6.16	Metal ($5G_0$)
	PBE+vdW+U	4.10	6.39	Metal ($3G_0$)
	EXP.	3.949[b]	6.629[b]	---

[a]Ref. [R1], [b]Ref. [R2], [c]Ref. [R3]

Table S2: Interlayer separation (R_0) of ZrX_2 bilayer at different level of theory.

Material	Phase	R_0 (Å)		
		PBE	PBE+vdW	PBE+vdW+U
ZrS_2	Trigonal	3.78	2.98	3.05
	Hexagonal	3.37	3.08	3.11
$ZrSe_2$	Trigonal	3.62	3.02	3.08
	Hexagonal	3.27	3.13	3.15
$ZrTe_2$	Trigonal	3.53	3.20	3.21
	Hexagonal	3.82	3.29	3.33

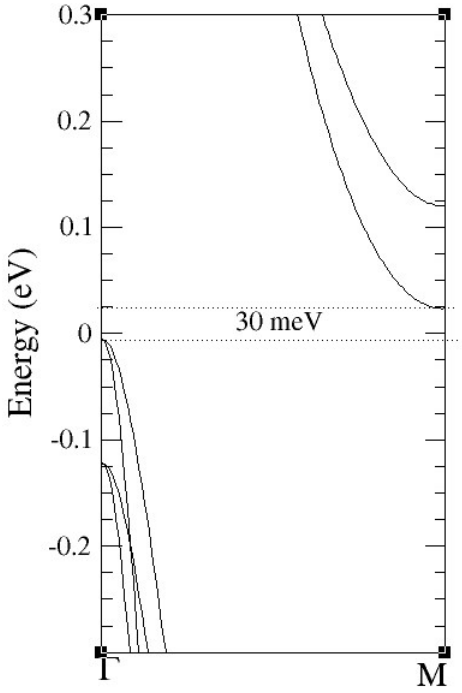

Figure S1: The electronic band structure of T-$ZrTe_2$ showing an indirect band gap (Γ→M) of ~ 30 meV.

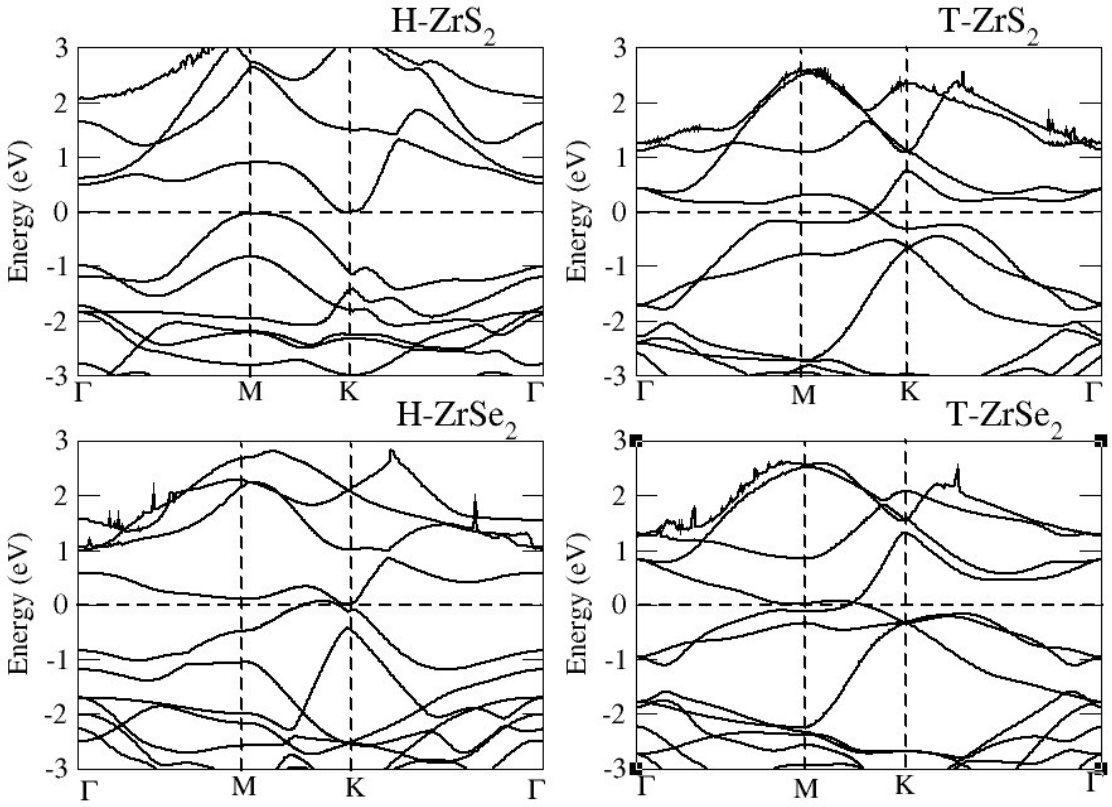

Figure S2: Electronic band structure of ZrS_2 and $ZrSe_2$ bilayers at the strain $\varepsilon = 0.7$.

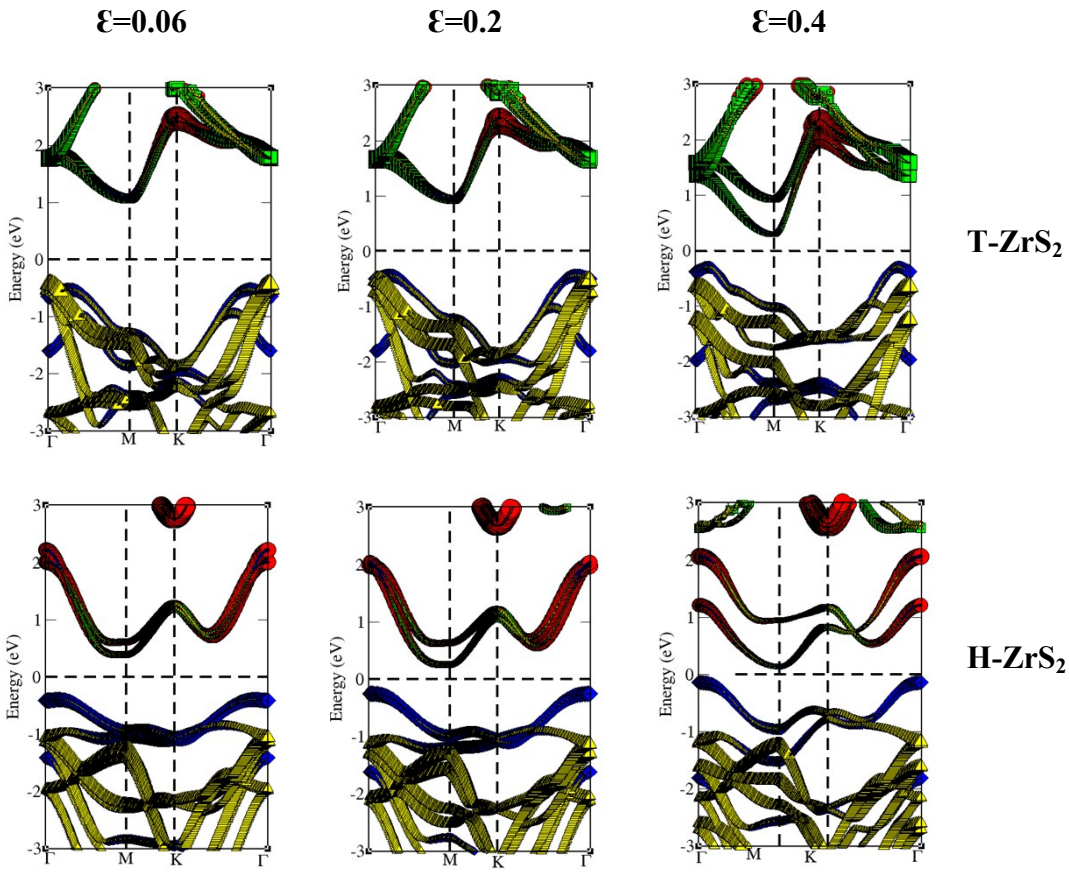

Figure S3: Electronic band structure at different values of strain Ɛ forZrS_2 bilayer (for T-phase in upper panel and for H-phase in lower panel). The red and green color represents $e_g(dx^2\text{-}y^2$ and $dz^2)$ and t2g (d_{xy}, d_{yz}, d_{xz}) orbitals of Zr atoms, respectively. The blue and yellow bands indicate the p_z and (p_x, $p_{y)}$ orbitals of S atoms, respectively. Fermi level is at zero.

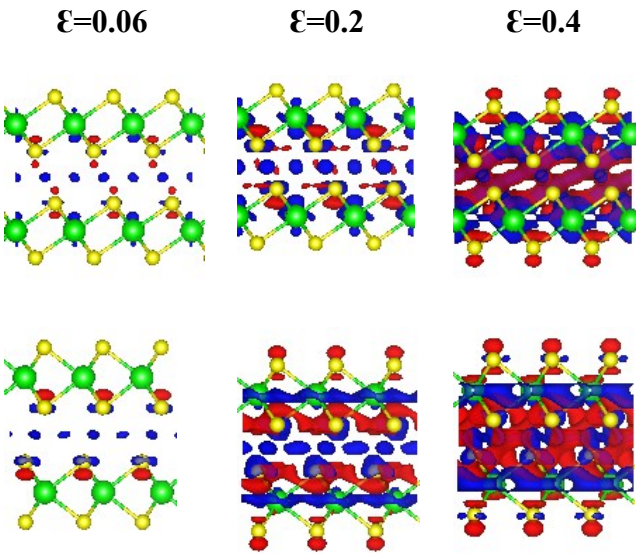

Figure S4: A side view of charge density difference profile of bilayer ZrS_2(upper panel for T-phase and lower panel for H-phase) at different strain values. The blue (red) region corresponds to accumulation (depletion) of charge. The isosurface is 2 x 10^{-4} e/Å^3.

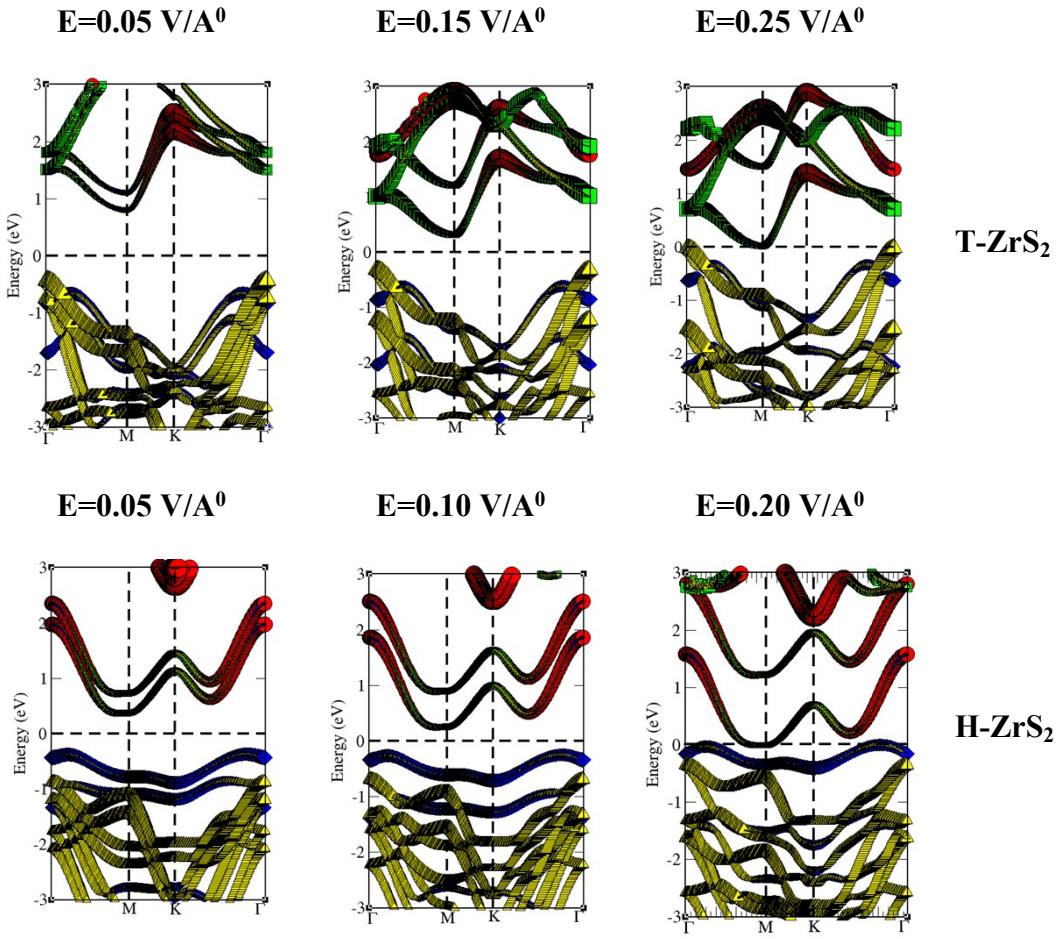

Figure S5: Electronic band structure at several values of E for ZrS_2 bilayer (for T-phase in upper panel and for H-phase in lower panel). The red and green color represents $e_g(dx^2\text{-}y^2$ and $dz^2)$ and t2g (d_{xy}, d_{yz}, d_{xz}) orbitals of Zr atoms, respectively. The blue and yellow bands indicate the p_z and (p_x, $p_{y)}$ orbitals of S atoms respectively. Fermi level is at zero.

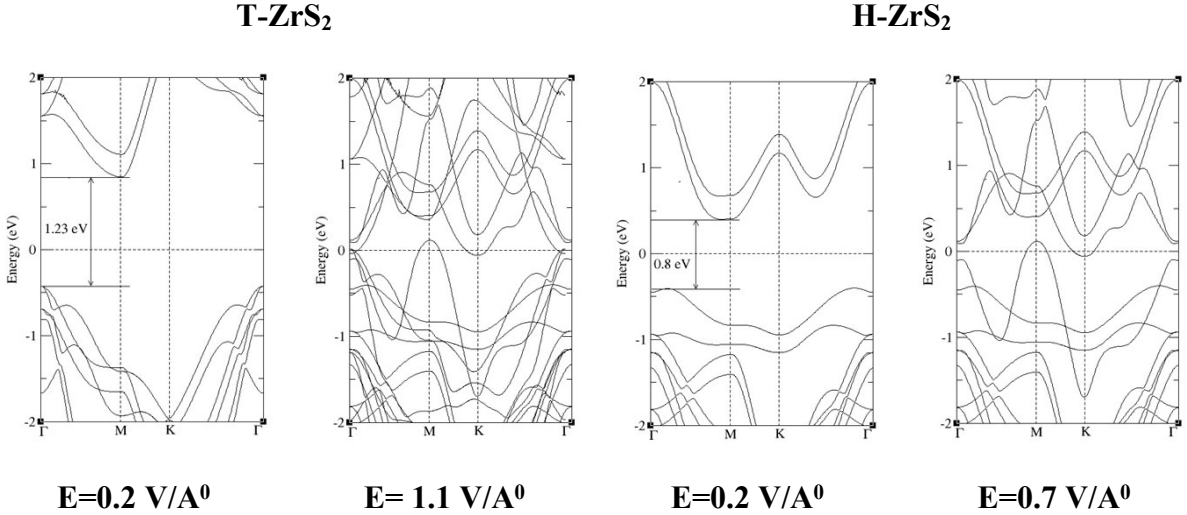

Figure S6: Electronic band structure as a function of electric field (E) (**without imposing symmetry constraints**) for ZrS_2 bilayer. Fermi level is at zero.

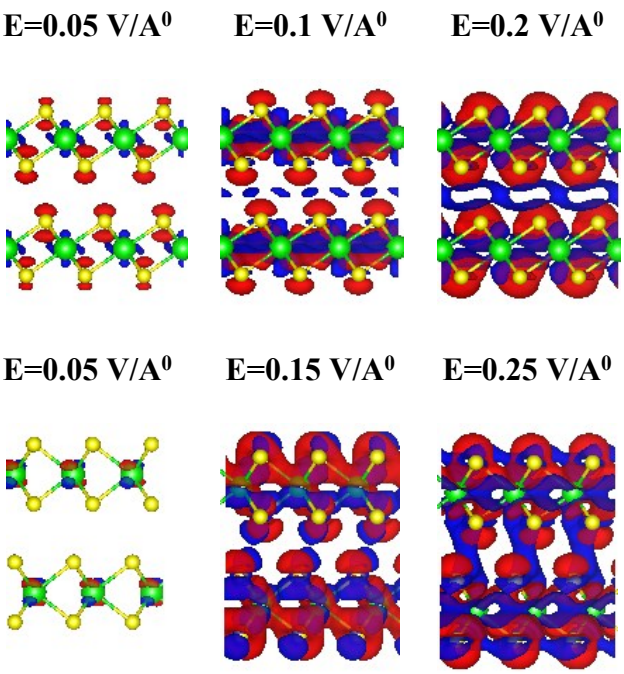

Figure S7:A side view of charge density difference profile of bilayer ZrS_2(upper panel for T-phase and lower panel for H-phase) at various electric field values. The blue (red) region corresponds to accumulation (depletion) of charge. The isosurface is 1 x 10^{-5} e/Å^3.

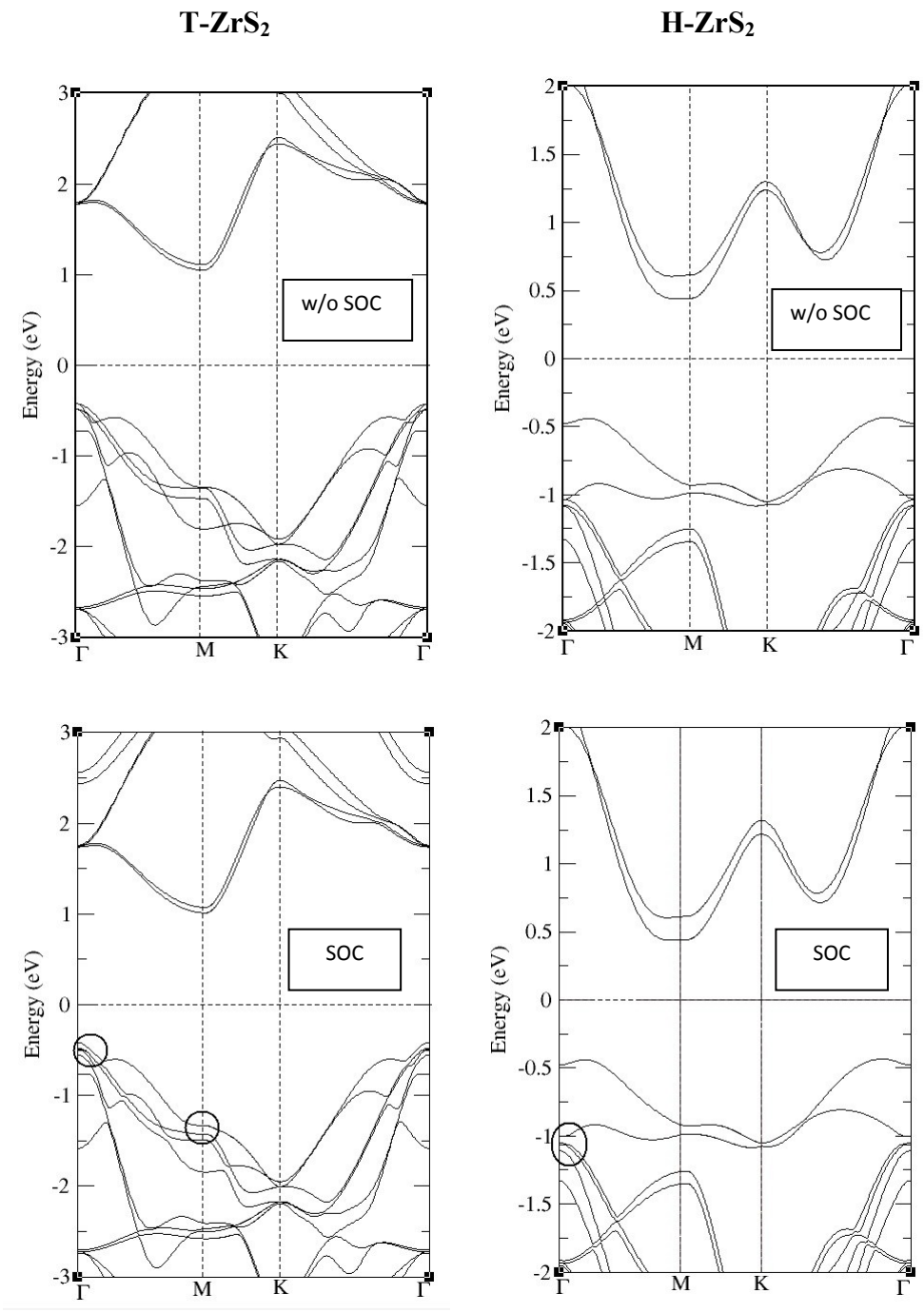

Figure S8: Electronic band structure with and without spin orbit coupling (SOC) effect for ZrS_2 bilayer. Fermi level is at zero. The splitting of bands are shown within the drawn circles.

References:

R1. D. L. Grenwayand R. Nitsche, *Prepration and optical properties of group IV-VI_2chalcogenides having the CdI_2 structure,*J. Phys. Chem. Solids. **26,** 1445 (1965).

R2. W. G. Wyckoff, *Crystal structures*, **Vol. 1** 2nd ed. pp 269 (1965).

R3. P. A. Lee, G. Said, R. Davis and T. H.Lim, *On the optical properties of some layer compounds,*J. Phys. Chem. Solids. **30,** 2719 (1969).