

## Electronic Supplementary Information

### Origin of p-type Conductivity in WSe<sub>2</sub> monolayer

Yuzhou Zhang,<sup>‡a,b</sup> Guo-jun Zhu<sup>‡a,b</sup> and Ji-Hui Yang<sup>\*a,b</sup>

<sup>a</sup> Department of Physics, Key Laboratory for Computational Science (MOE), State Key Laboratory of Surface Physics, Fudan University, Shanghai 200432, China

<sup>b</sup> Shanghai Qizhi Institution, Shanghai 200232, China

<sup>‡</sup> Authors contributed equivalently.

## Chemical potentials

To avoid formations of unintentional phases, the elemental chemical potentials are limited by this form:

$$\alpha\mu_A + \beta\mu_B < \Delta H(A_\alpha B_\beta)$$

where  $\Delta H(A_\alpha B_\beta)$  is the formation enthalpy of the unintentional phase referenced to their elemental phases  $A$  and  $B$ .

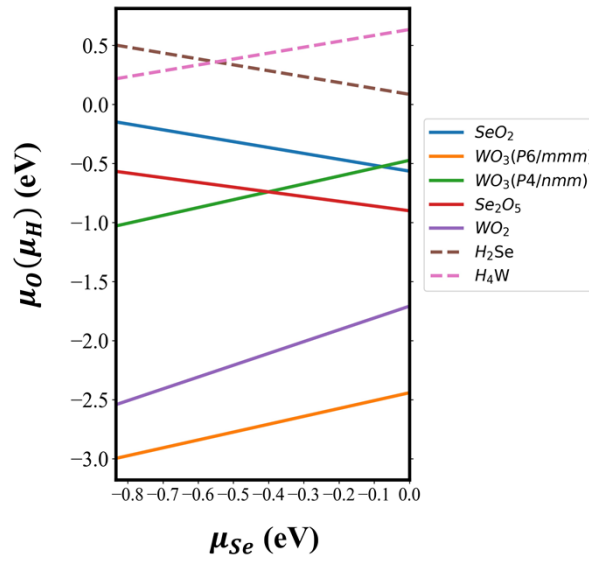


Fig. S1. The chemical potentials  $\mu_O$  (full lines) and  $\mu_H$  (dash lines) as functions of  $\mu_{Se}$ . Each phase is restrained below its function value.

## Optimized defect structures

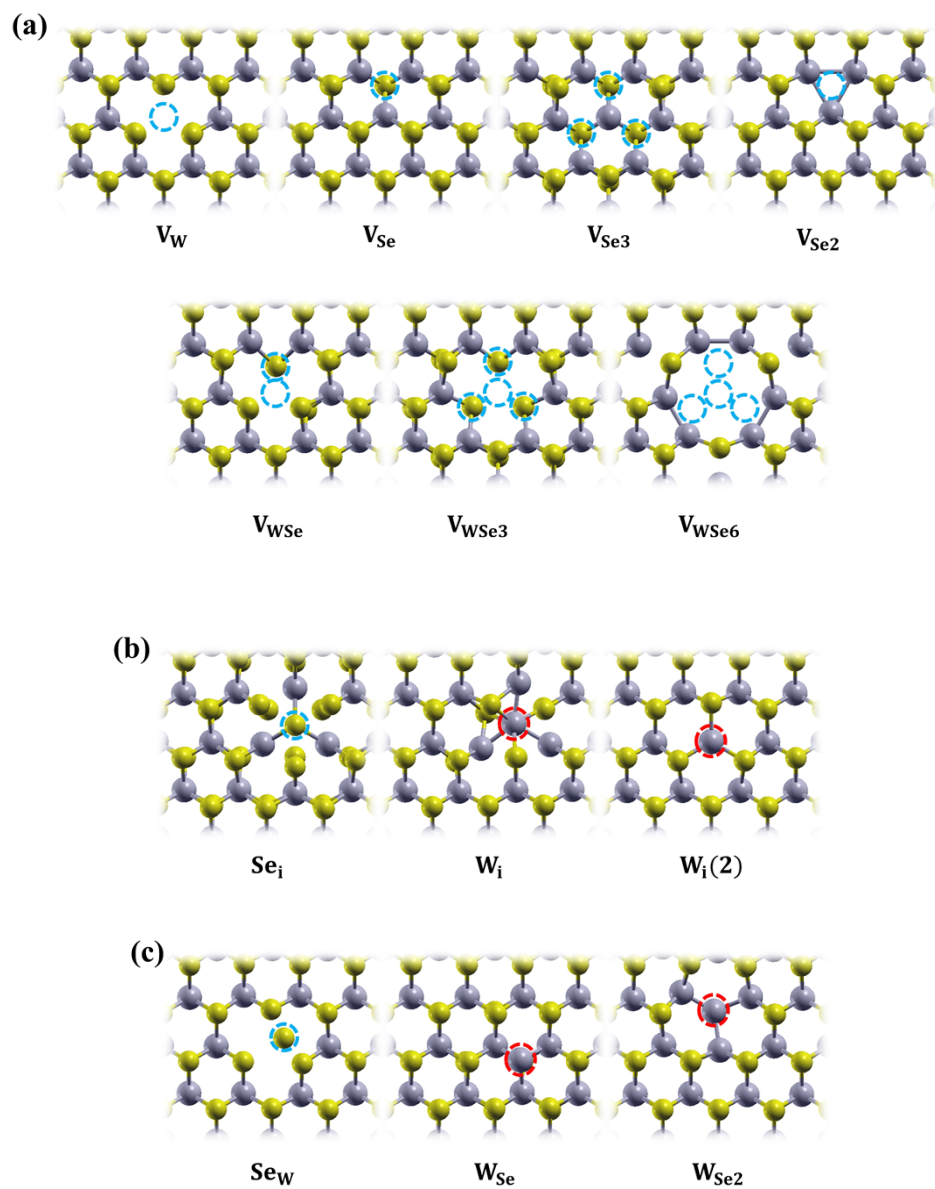


Fig. S2. Top view of the optimized structures of intrinsic (a) vacancy, (b) interstitial and (c) antisite point defects.

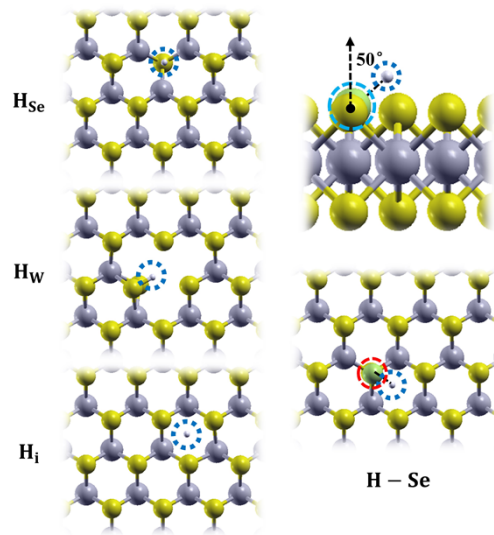


Fig. S3. Optimized structures of H-related point defects, containing the top and sideview of H adatom H-Se.

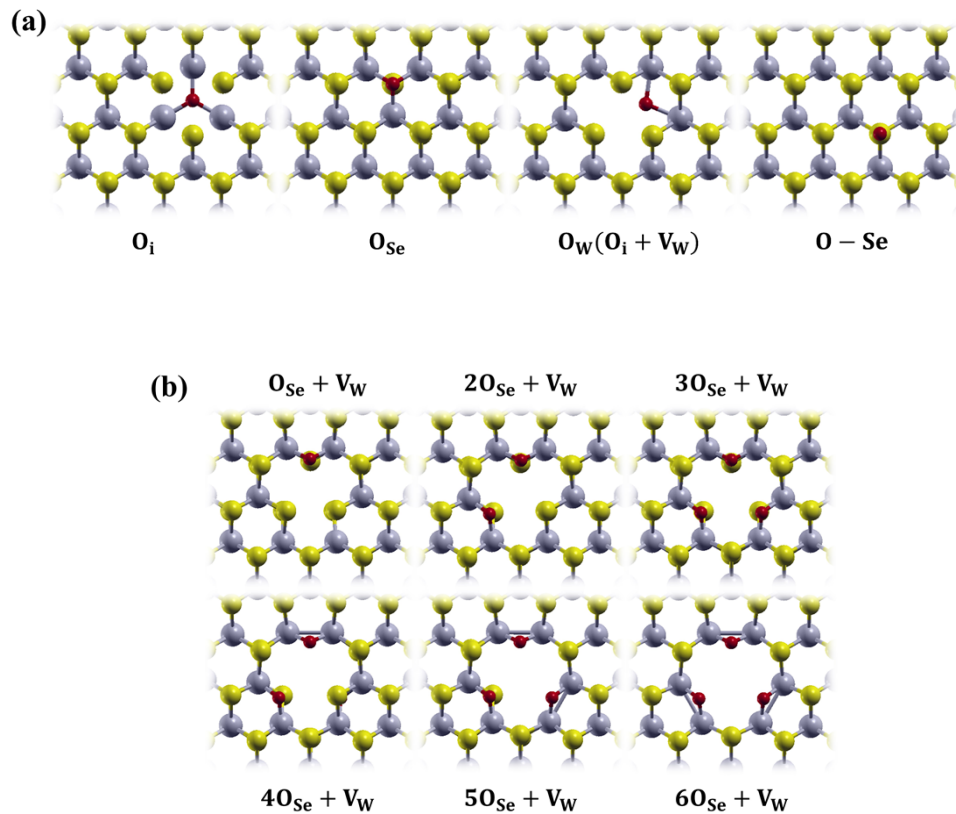


Fig. S4. Optimized structures of O-related point defects, as well as the (b) defect complexes  $nO_{Se}+V_W$ .

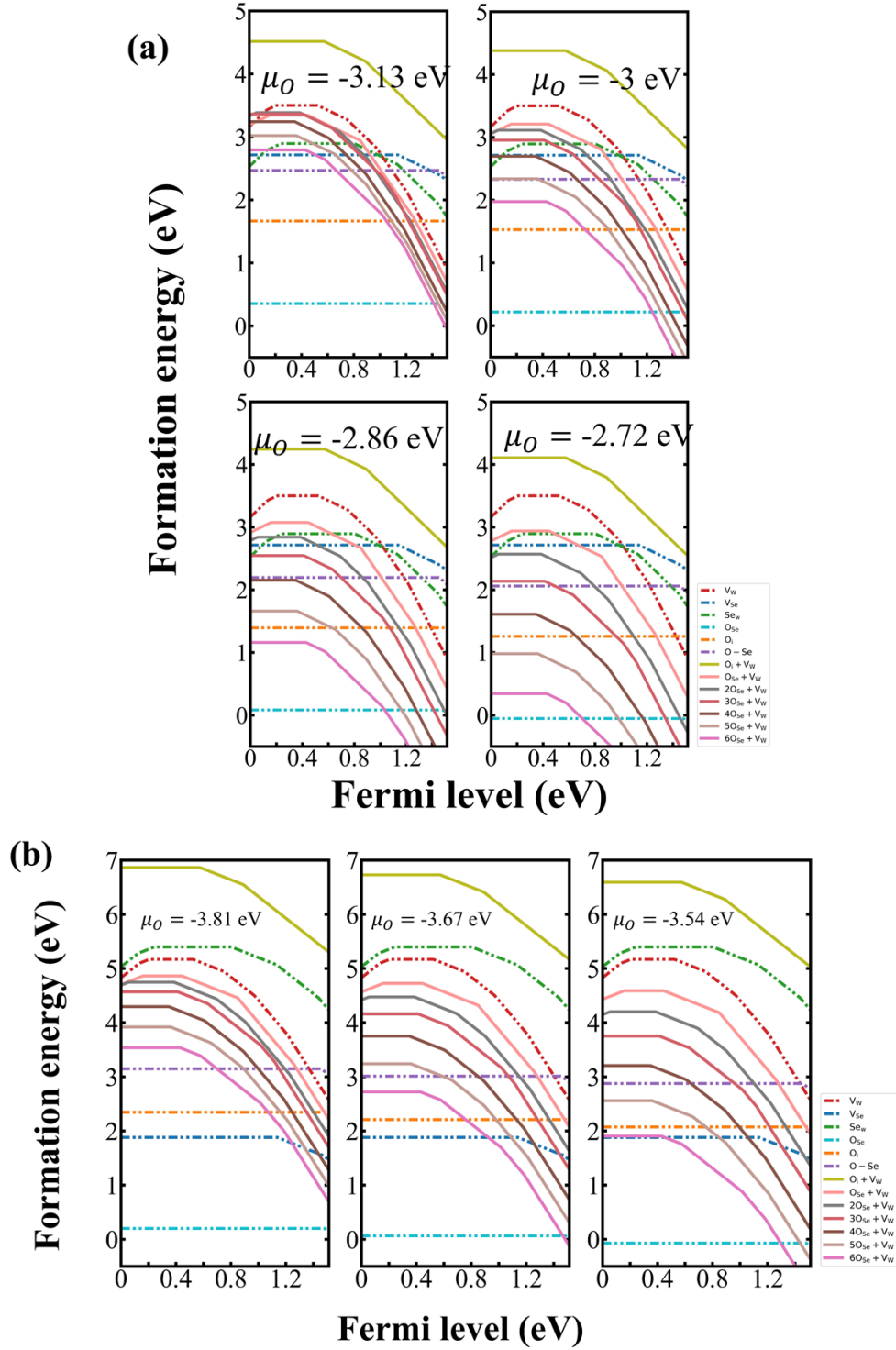


Fig. S5. The trend under (a) Se-rich and (b) W-rich conditions that O-related formation energies change with the chemical potential of O. Each  $\mu_O$  value is adopted avoiding the formation of second phases. Obviously, the formation energy of O-related defects decreases significantly with the increase of O's chemical potential, and the introduction of a large amount of  $O_{Se}$  can

effectively reduce  $V_W$ 's formation energy and ionization energy.

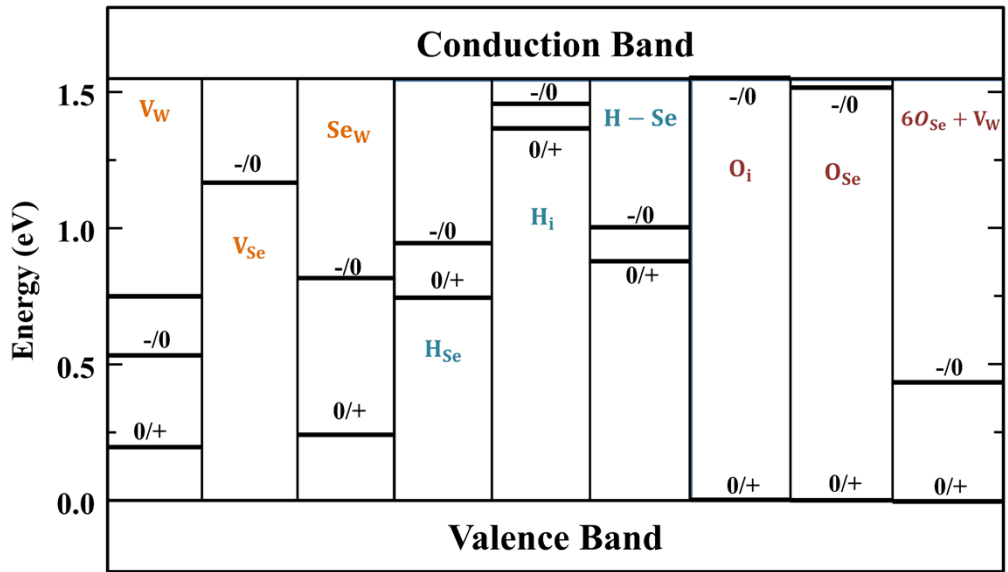


Fig. S6. Transition energy levels diagram for defects which possess the lowest formation energies. As shown, common intrinsic defects in WSe<sub>2</sub> except  $6O_{Se} + V_W$  cannot ionize effective carriers. The experimentally observed W vacancies and p-type WSe<sub>2</sub> are most likely due to the introduction of O.

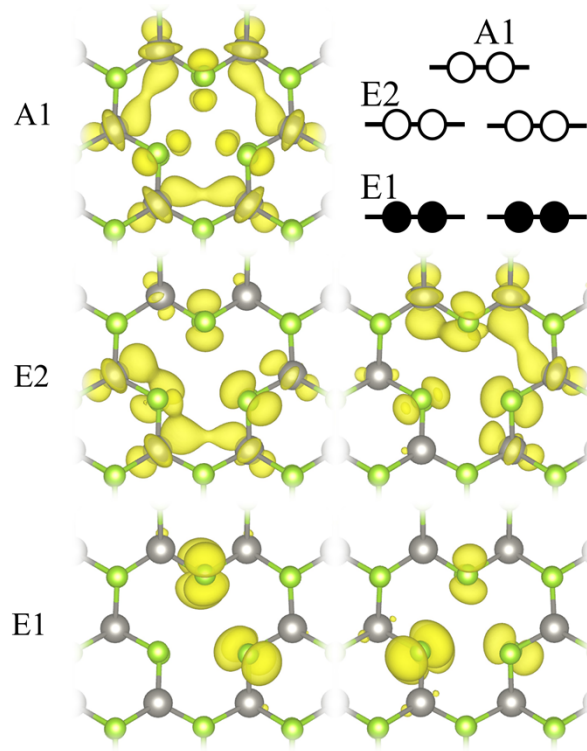


Fig. S7. The partial charge densities of neutral defect states in the gap of VW, denoted by the representations E1 (nonbonding), E2 (bonding), and A1 (antibonding). These bonding types are identified by the charge bonding patterns: E1 has no atomic charge bonding; E2 has p-d bonding between two nearest W and Se; A1 has antibonding between two nearest W and Se (W-W bonding).

## Relaxation energies

The total relaxation energy is defined by the form:

$$E_R = E^q - (E^0 - q\varepsilon_{de}^0)$$

where  $E^q$  is the total energy for the charge state  $q$ , and  $\varepsilon_{de}^0$  is the neutral energy level awaiting one electron's ( $q = 1$ ) or one hole's ( $q = 1-$ ) filling.

n	Total relaxation (eV)	
	+	-
0	-0.043	-0.022
1	-0.046	-0.008
2	-0.026	-0.001
3	-0.011	0.001
4	-0.016	-0.007
5	-0.016	-0.007
6	-0.018	0.005

Table. S1. Total relaxation energies of the defect complexes  $nO_{Se}+V_W$  with  $n = 0$  to 6, between neutral to charge states +1 or -1. These values have almost no impact on the transition energy levels.