Electronic Supplementary Material (ESI) for Nanoscale.

Structure and Properties of Intrinsic and Extrinsic Defects in Black Phosphorus

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1 Supplementary Information

1.1 IPR

The inverse participation ratio (IPR) is given by:

$$IPR(\psi_n) = \frac{\sum_{i=1}^{N} a_{ni}^4}{\left(\sum_{i=1}^{N} a_{ni}^2\right)^2} \ , \tag{1}$$

where

$$\psi_n = \sum_{i=1}^{N} a_{ni}\phi_i \tag{2}$$

is the n-th Kohn-Sham eigenvector, N is the number of atomic orbitals and ϕ_i is the i-th atomic orbital. Thus the more atomic orbitals contribute to a Kohn-Sham state, the lower its IPR value will be and conversely a peak in the spectrum signals a localised state. This technique is particularly useful to identify defect induced localised states.

1.2 Monovacancies

Fig. 1(a) shows a DFE plot for a MV in monolayer BP. It can be seen that the neutral MV is most stable at low Fermi level positions and a charge transition level from neutral to negatively charged MV is located at 0.55 eV. The positively charged MV is always higher in energy than the neutral MV and thus is not thermodynamically stable. Fig. 1(b) and (c) illustrate the DOS and IPR spectrum for a neutral and negatively charged MV, respectively. For the neutral vacancy a hole state is created in the bandgap, which is localised on the undercoordinated P atom of the MV. The band edges of a negatively charged MV show more localised character with defect induces states appearing at the VBM. These states are bonding orbitals of the MV as well as states, which were induced by the trapped charged (see discussion in main article).

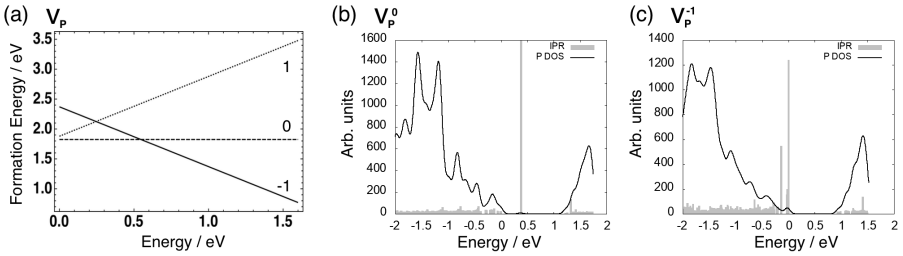

Figure 1: a) Defect formation energy diagram of a MV in monolayer BP. b) The total DOS (black) and IPR spectrum (grey) of neutral MV in monolayer BP. The peak at 0.4 eV corresponds to the unoccupied vacancy state (see also Fig. 3 in main article). c) The total DOS (black) and IPR spectrum (grey) of negatively charged MV in monolayer BP.

In order to obtain accurate DFEs charge corrections were performed. Standard techniques such as Makov-Payne (MP) or Lany-Zunger (LZ) are widely used techniques for charge corrections in bulk systems, but they are not applicable to 2D sheets in a large vacuum. Thus an extrapolation to infinite supercell sizes was performed based on the MP correction. The MP correction is given by:

$$E_{\mathrm{IIC}}^{MP} = \frac{q^2 \alpha_M}{2\epsilon L} \ , \tag{3}$$

where ϵ is the dielectric of the material, L is the separation between the defects and α_M is the Madelung constant. By inspection it becomes clear that the DFE scales with 1/L, where L is the supercell size. Thus, by calculating the DFE for various cell sizes, one can fit a linear regression to the data in order to deduce the infinite size limit, as shown in Fig. 2. We note that, since calculations were performed with 2D periodic boundary conditions, this removes any dependence on the out-of-plane dimension. The intercept of the linear fit with the y axis at x=0 gives the best estimate for DFEs of charged defects.

1.3 SW defects

The calculated barrier for SW1 formation is illustrated in Fig. 3: The forward barrier to form a SW1 defect is 3.08 eV while the backward barrier is 1.27 eV. To form a SW1 defect, two surface P-P bonds need to be broken and an in-plane P-P bond is rotated around the surface normal. The structure at the transition point is shown in the inset. Additionally, the creation of this SW defect leads to strain in the monolayer, as long range atom displacement can be observed, making the formation of this defect less favourable.

The barrier for a SW2 defect is shown in Fig. 4. Again two surface P-P bonds need to be broken to facilitate the creation of this defect. The transition point structure is illustrated in the inset. In order to create a SW2 defect a P-P bond between an upper and lower zigzag is rotated around the in-plane [100]

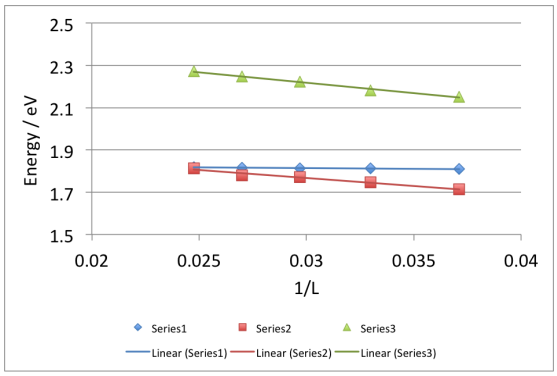

Figure 2: Extrapolation of DFE to infinite supercell limit for neutral, negatively and positively charged MV.

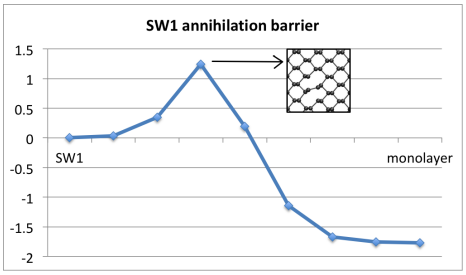

Figure 3: Barrier of SW1 formation/ annihilation in monolayer BP in eV.

direction. This rotation is energetically more favourable compared to the SW1 defect, reducing the barrier to 2.17 eV.

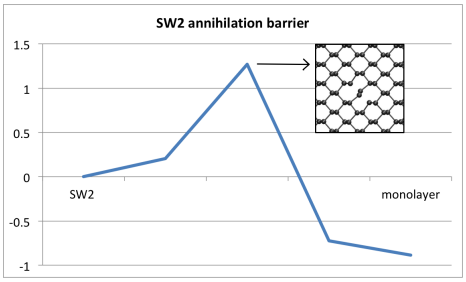

Figure 4: Barrier of SW2 formation/ annihilation in monolayer BP in eV.

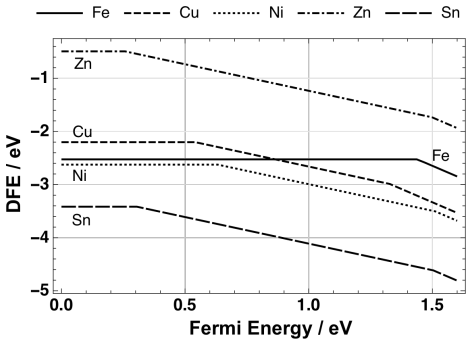

Figure 5: Defect formation energy diagram for metal substitution in monolayer BP.