Advances in the fabrication and characterization of two-dimensional (2D) dichalcogenide semiconductors have reshaped the concept of thin transistor gate.\cite{1, 2} Unlike thin fully-depleted silicon channels, physically limited by the oxide interface, single layer metal dichalcogenides are intrinsically 2D and, therefore, have no surface dangling bonds. The monolayer thickness is constant, and the scale of the variations of the electrostatic potential profile perpendicular to the plane is only limited by the extent of the electronic wavefunctions. Hence, TMD can in principle be considered immune to channel thickness modulation close to the drain.

Building on these fundamental advantages, numerous field-effect transistor (FET) designs employing MoS$_2$ or WS$_2$ channels have been proposed. These range from 2D adaptations of the traditional FET structure, where the 2D semiconductor is separated by a dielectric layer from a top gate electrode, to dual-gate heterolayer devices where the transition metal dichalcogenide is straddled between two graphene sheets\cite{2}. Such FETs can be integrated into logic inversion circuits, providing the building blocks for all logical operations\cite{2}.

However, at present the success of TMD in electronics is limited by the difficulty in achieving high carrier concentrations and, by consequence, high electronic mobilities (current values range around 100 cm$^2$/V.s)\cite{3, 4}. In the absence of a chemical doping technology, the control of the carrier concentration relies solely on the application of a gate voltage perpendicular to the layer, which shifts the Fermi level position rendering the material $n$- or $p$-type\cite{3}. But in practice the gate voltage drop across the insulator cannot exceed its electric breakdown limit (about 1 V/nm for SiO$_2$, or lower for high-$\kappa$ dielectrics\cite{5}). A work-around demonstrated in graphene consists on gating with ferroelectric polymers\cite{2}, although at the expense of the thermal stability and switching time.

In this article we use first-principles calculations to show that MoS$_2$ and WS$_2$ can be doped both $n$- and $p$-type using substitutional impurities. This grants transition metal dichalcogenides an advantage over other semiconductor families where doping asymmetries are notorious: ZnS can be doped $n$-type but not $p$-type, while chalcopyrite CuInTe$_2$ and CuGaSe$_2$ can be $p$-type doped but not $n$-type doped\cite{6}, and SnTe has not yet been doped $n$-type\cite{7}. In transition metal dichalcogenides, even though chemical doping is mostly unexplored, there have already been some experimental reports of successful chemical doping\cite{10, 11} as well as some electronic structure calculations for impurities\cite{12, 13}.

Further, we find both $n$- and $p$-type dopants substituting in the $S$ lattice site or adsorbed on top of the $S$ layer. Leaving the transition metal layer nearly undisturbed, these substitutions promise less scattering to charge carriers at the Mo-derived states at the bottom of the conduction band (CBM) or at the top of the valence band (VBM).

Having established that doping is possible, it follows that 2D doped semiconductors stand out as superior to 3D semiconductors for high temperature applications because of fact that the electronic density of states, $N(E)$, close to the edge of the valence and conduction bands is, unlike the 3D case, energy independent. It is well-known that the intrinsic carrier concentration of a semiconductor is given by:

$$n_i(T) = \sqrt{N_c(T)N_v(T) \exp(-E_g/(2kT))}, \quad (1)$$

where $E_g$ is the gap energy, and $N_c(v)$ depend on $N(E)$ (and hence the dimensionality) of the semiconductor. In 2D we have:

$$N_c(v) = \frac{M_{c(v)}m_{c(h)}\ln 2}{\pi\hbar^2}kT, \quad (2)$$

$M_{c(v)}$ is the degeneracy of the conduction (valence) band, $m_{c(h)}$ is the effective mass of the conduction (valence) band electrons, and $T$ the temperature ($k$ and $\hbar$ are the Boltzmann and Planck’s constants, respectively). Hence, in 2D we have $n_i(2D) \propto T^{3/2}$ which should be contrasted the 3D counterpart where $n_i(3D) \propto T^{3/2}$. Figure 1 illustrates the relevance of the temperature dependence of the density of conduction electrons $n(T)$, by comparing the carrier density for $n$-type monolayer MoS$_2$ and Si.
doped with the same dopant concentration and dopant activation energy, as a function of temperature. While Si leaves the extrinsic regime (that is, the region of temperatures where \( n_i(T) \) becomes temperature independent) above 800 K, in MoS\(_2\) the \( n_i(T) \) curve is flat beyond 1000 K. The temperature stability of \( n_i \) ultimately reflects on transistor characteristics, in particular the gate voltage threshold.

We studied donor and acceptor impurities using first-principles calculations. These were based on density functional theory (DFT), as implemented in the QUANTUM ESPRESSO code[14]. Geometry optimizations and total energy calculations are non-relativistic. A fully relativistic formalism was used for the bandstructure calculations (see Supplementary Information). The exchange correlation energy was described by the generalized gradient approximation (GGA), in the scheme proposed by Perdew-Burke-Ernzerhof[15] (PBE). The Kohn-Sham bandgaps obtained in the non-relativistic calculations are respectively 1.65 and 1.77 eV for MoS\(_2\) and WS\(_2\). With spin orbit coupling, these values become 1.55 and 1.51 eV, respectively. We thus find that the GGA is a good approach for bandstructure calculations of these materials, and further exchange and correlation effects are likely to produce, in first approximation, only a rigid shift of the conduction band[16]. The energy cutoff used was 50 Ry. Further details of the calculation method can be found in Ref. 17.

The supercell consisted of \( 4 \times 4 \) unit cells of the single layer material, separated by a vacuum spacing with the thickness of two times the supercell lattice parameter. For charged supercells, the electrostatic correction of Komsa and Pasquarello was implemented.[18, 19] The Brillouin-zone (BZ) was sampled using a \( 4 \times 4 \times 1 \) Monkhorst-Pack grid.[20]

We have considered five dopants: Si, P, Li, Br and Cl. Any of these can occupy substitutional positions or be adsorbed on the S layer. The point symmetry of the S site is \( C_{3v} \). When replaced by P or Si, the resulting defect keeps the trigonal symmetry and there is little associated lattice distortion. In the case of neutral Cl\(_S\) and Br\(_S\), however, the lowest energy configuration is a \( C_s \) geometry where the neutral Cl\(_S\) and Br\(_S\) defects are displaced in the vertical plane, loosening one of the Cl/Br-Mo/W bonds (Fig. 2a). This unusual configuration results from the fact that the halogen partially donates the unpaired electron to the Mo/W \( d \) orbitals, whereas in most molecules Cl and Br receive an electron instead.

Li is most stable at the S3 position[13], shown in Fig. 2b, outside the S layer but on the top of a Mo atom. As for the adsorbed atoms, P, Si, Cl and Br take the S4 configuration as described in Ref. 13 on top of an S atom.

A requirement for successful doping is that the impurity must be stable at the lattice position where it is active, and comparatively unstable or electrically neutral at the competing positions. The equilibrium concentra-
atom is isoenthalpic for Br and Cl. Furthermore, for
where $V_{\text{S}}$ is the sulfur vacancy and $X_{\text{ad}}$ is the adsorbed atom is isoenthalpic for Br and Cl. Furthermore, for Cl the formation energy of the vacancy (1.3 and 1.7 eV in sulfur-poor MoS$_2$ and WS$_2$, respectively).

We have so far considered the stability of the neutral defects. Now the most important requirement for a dopant is that its ionisation energy $E_D^0$ is not greater than a few $kT$. The thermodynamic transition level $E_D(q/q + 1)$ can be defined as the value of the Fermi level for which charge states $q$ and $q + 1$ of the defect $D$ have the same formation energy. The position of the $E_D(q/q + 1)$ level relative to the valence band top $E_v$ can be found from the formation energies (see Eq. (3) [24])

$$E_D(q/q + 1) = E_f[X^q] − E_f[X^{q+1}] − E_v.$$  
(7)

Thus for acceptors $E_D(0/+) ≡ E_D^0$ and for donors $E_D(-/0) ≡ E_g − E_D^0$.

For comparison, we have also calculated the same defect levels using the marker method (MM). In this method, the ionisation energies/electron affinities of defective supercells are compared with those of the pristine supercell [22] and the spurious electrostatic interactions are partially canceled. There is good agreement between the levels calculated using the two methods, in most cases within about 0.1 eV. Another indication of the quality of the method is the agreement between the gap obtained from total energy difference $E_g = E_S^g(+) + E_S^g(−) − 2E_S^g(0) − 2gF$, where $E_S^g$ is the energy of the pristine supercell in charge state $g$ and $δF$ is the electrostatic correction of Ref [18] and the Kohn-Sham gap. These are respectively $E_g^0=1.64$ and 1.87 eV for MoS$_2$ and WS$_2$, and $E_g=1.65$ and 1.77 eV for MoS$_2$ and WS$_2$.

Adsorbed Li is a shallow donor with a small ionisation energy <0.1 eV both in MoS$_2$ and WS$_2$. This is mainly due to two effects. First, the relaxation of Li in the positive charge state, which is of the order of 30 meV and is a physical effect; second, a spurious band filling effect [26,27] which are larger in WS$_2$ due to the greatest dispersion of the lowest conduction band. The bandstructure shows unequivocally that Li$_{\text{ad}}$ is a shallow donor. In effect, it merely gives out an electron to the conduction band, changing little the lattice bandstructure in the vicinity of the gap (Supplementary Figure 1).

Substitutional Br and Cl are shallow donors only above room temperature. They contribute with an additional electron to populate a perturbed conduction band state. The shallowest of them is Br$_{\text{ad}}$ which is of the order of 30 meV and is a physical effect; second, a spurious band filling effect which are larger in WS$_2$ due to the greatest dispersion of the lowest conduction band. The bandstructure shows unequivocally that Li$_{\text{ad}}$ is a shallow donor. In effect, it merely gives out an electron to the conduction band, changing little the lattice bandstructure in the vicinity of the gap (Supplementary Figure 1).

Substitutional P is found to be a very shallow acceptor, with activation energy ~0.1 eV in MoS$_2$, and <0.1 eV in WS$_2$, comparable to the uncertainty of the calculation. Si is also an acceptor, though deeper.

It is noticeable that ionisation energies in WS$_2$ are usually smaller, despite its larger calculated bandgap, suggesting that this material is easier to dope.
In summary, we have shown that it is possible to dope MoS$_2$ and WS$_2$ with electrons or holes by chemical substitution at the S site or adsorption on the top of the layer. Amongst the shallow donors, Li$_{S}$ has the lowest ionisation energy. The donated electron is predominantly localized on the transition metal atom d states. However, Li diffuses extremely fast in most materials and therefore is not a good choice for high temperature applications. Besides, Br$_{S}$ and Cl$_{S}$ are also donors, but have a higher ionisation energy. The higher temperature required to excite the carriers is a trade-off for the higher temperature stability of the defects.

Phosphorus is a shallow acceptor with a very low ionisation energy, comparable to the uncertainty of the calculation. The wavefunction of the unpaired hole state is a valence-band like state, predominantly localized on the transition metal layer. Amongst the shallow donors, Li is not a good choice for high temperature applications.

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FIG. 3. Isosurfaces of the unpaired electron state of Li\textsubscript{ad} (a) and of the unpaired hole state of P\textsubscript{S} (b), in MoS\textsubscript{2}, as generated by fully relativistic calculations. The former is a donor, whereas the latter is an acceptor. The square of the wavefunction is represented. W and S are represented by cyan and yellow spheres, respectively.

| Defect | $E_{F}^{S^{-}\text{poor}}(D_{S})$ | $E_{F}(D_{ad})$ | $E_{F}^{S^{-}\text{poor}}(D_{S})$ | $E_{F}(D_{ad})$ |
|--------|-------------------------------|----------------|-------------------------------|----------------|
| Br\textsubscript{S} | -1.0 | -0.7 | -0.3 | -0.7 |
| Cl\textsubscript{S} | -1.5 | -0.9 | -0.9 | -0.9 |
| Li\textsubscript{S} | -0.7 | -2.0 | -0.9 | -1.5 |
| P\textsubscript{S} | -2.9 | -0.7 | -2.7 | -0.6 |
| Si\textsubscript{S} | -2.6 | -1.6 | -2.0 | -0.9 |

TABLE II. Defect-related levels in MoS\textsubscript{2} and WS\textsubscript{2}. $E(-/0)$ is given relative to $E_{c}$ and $E(0/+)$ is given relative to $E_{v}$. FEM and MM stand for Formation Energy Method and Marker Method, respectively (see text). All values are in eV.

| Method | MoS\textsubscript{2} | WS\textsubscript{2} |
|--------|------------------|-----------------|
|        | $(-/0)$ | $(0/0)$ | $(0/+)$ | $(0/+)$ |
|        | FEM | MM | FEM | MM |
| Br\textsubscript{S} | - | - | 0.15 | 0.22 |
| Cl\textsubscript{S} | - | - | 0.18 | 0.27 |
| Li\textsubscript{ad} | - | - | -0.02 | 0.12 |
| P\textsubscript{S} | 0.11 | 0.06 | - | - |
| Si\textsubscript{S} | 0.39 | 0.34 | - | - |

| Method | WS\textsubscript{2} |
|--------|-----------------|
|        | $(-/0)$ | $(0/0)$ | $(0/+)$ | $(0/+)$ |
|        | FEM | MM | FEM | MM |
| Br\textsubscript{S} | - | - | 0.14 | 0.14 |
| Cl\textsubscript{S} | - | - | 0.18 | 0.22 |
| Li\textsubscript{ad} | - | - | -0.36 | -0.16 |
| P\textsubscript{S} | 0.02 | -0.09 | - | - |
| Si\textsubscript{S} | 0.23 | 0.12 | - | - |
Supplementary Information on: Donor and Acceptor Levels in Semiconducting Transition Metal Dichalcogenides

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\[\text{FIG. 1.} \text{ Fully relativistic Kohn-Sham bandstructures of defects in monolayer WS}_2. \text{ The bandstructure of the pristine monolayer is represented shaded, in the same energy scale as the respective defect bandstructure. The calculations were performed in a supercell consisting of 4 × 4 primitive cells.}\]