Scalable Substitutional Re-doping and its Impact on Optical and Electronic Properties of Tungsten Diselenide

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Abstract

Reliable, controlled doping of 2D transition metal dichalcogenides (TMDCs) will enable the realization of next-generation electronic, logic-memory, and magnetic devices based on these materials. However, to date, accurate control over dopant concentration and scalability of the process remains a challenge. Here, we report a systematic study of scalable in-situ doping of fully coalesced 2D WSe₂ films with Re atoms via metal-organic chemical vapor deposition (MOCVD). Dopant concentrations are uniformly distributed over the substrate surface, with precisely controlled concentrations down to <0.001% Re achieved by tuning the precursor partial pressure. Moreover, the impact of doping on morphological, chemical, optical, and electronic properties of WSe₂ is elucidated with detailed experimental and theoretical examinations, confirming the substitutional doping of Re at the W site leads to n-type behavior of WSe₂. Transport characteristics of fabricated back-gated field-effect transistors (BGFTs) are directly correlated to the dopant concentration, with degrading device performances for doping concentrations exceeding 1% of Re. Our study demonstrates a viable approach to introducing true dopant-level impurities with high precision, which can be scaled up to batch production for applications beyond digital electronics.

Introduction

Doping is the cornerstone of semiconductor technology, enabling the success of modern digital electronics. Two-dimensional (2D) transition metal dichalcogenides (TMDCs) are promising material platforms for future electronics applications where its wafer-scale synthesis and controllable doping will be a required prerequisite to drive the next technological revolution.^[1–6] Successful realization of wafer-scale, electronic grade, intrinsic 2D TMDCs via common deposition methods is rapidly progressing, however, advances in scalable doping still remain in the “proof-of-concept” stage, delaying the large scale fabrication of logic circuits based on extrinsic 2D semiconductors.^[7–12] Moreover, integration of 2D TMDCs with Si complementary metal-oxide-semiconductor (CMOS) at the back-end-of-line (BEOL) is being actively explored for diffusion barriers, liners, and thin-film-transistors (TFTs) to improve the overall integrated circuit performance.^[13–16] However, BEOL production lines are usually limited to temperatures $< 500\text{ }^{\circ}\text{C}$ whereas current state-of-the-art synthesis (and doping) of TMDCs is carried out at front-end-of-line (FEOL) temperatures ($> 700\text{ }^{\circ}\text{C}$).^[17,18] In addition, realization of scalable intrinsic and extrinsic 2D TMDCs can find its application beyond digital electronics such as chemical sensors,^[19,20] electrodes in Li ion batteries,^[21] and room temperature 2D magnets,^[22] to name a few. Hence, large scale, highly controlled doping strategies of 2D-TMDCs must be developed at FEOL *and* BEOL compatible temperatures to fully impact next generation technologies.

Over the course of the last decade, numerous doping strategies were developed utilizing a range of approaches, such as physisorption of aromatic molecules,^[23] electrostatic doping,^[24] substitutional doping,^[25] the introduction of various adatoms,^[26,27] plasma doping,^[28,29] laser-assisted doping,^[30] to name a few.^[31] Among all, substitutional doping is the most desirable and stable technique, where intentionally introduced impurity atoms substitutionally replace metal or chalcogen atoms and incorporate into the host lattice via covalent bonding. Pioneering studies utilized bulk crystals of Nb, Re, V doped MoS_2 and WSe_2 grown via chemical vapor transport (CVT), followed by mechanical exfoliation of mono/few-layer flakes.^[32–35] More recently, in-situ substitutional doping of monolayer TMDCs via powder vaporization and gas-source chemical vapor deposition was achieved. The superior tunability of optical and transport properties as a function of doping concentration and environmental stability are demonstrated in such monolayer films.^[36–40] However, tight control over the doping concentration and fundamental understanding behind homogenous dopant distribution over large areas still remains a challenge.

In this study, we report scalable doping of 2D WSe_2 with Re via gas-source metal-organic chemical vapor deposition (MOCVD) at FEOL and BEOL compatible temperatures using $\text{W}(\text{CO})_6$, H_2Se and $\text{Re}(\text{CO})_{10}$ as metal, chalcogen and dopant precursors, respectively. Epitaxial, monolayer FEOL films are obtained on crystalline *c*-plane sapphire whereas BEOL counterparts are synthesized on amorphous SiO_2/Si substrates. By precisely controlling the $\text{Re}(\text{CO})_{10}$ flow rate, doping concentrations as low as $< 0.001\%$ can be readily achieved verified by high-resolution X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass-spectroscopy (ToF-SIMS). Moreover, optical properties probed by room-temperature Raman and photoluminescence (PL) spectroscopy reveal an increase in defect activated modes as well as quenching and redshift of the PL spectra with increasing dopant concentration. First-principles density functional theory (DFT) calculations combined with scanning transmission electron microscopy (STEM), scanning tunneling microscopy and spectroscopy (STM/STS) further demonstrate that Re dopants substitutionally replace W atoms and introduce donor levels that lie close to the conduction band (CB) edge. However, we also demonstrate that Re dopants remain electrically inactive and do not contribute an extra electron to the conduction band due to the high ionization energy of the donor level - a critical factor in choosing dopants for controlled carrier concentration.

Results and Discussions

Tungsten diselenide and Re-WSe₂ are synthesized on *c*-plane sapphire substrates via a multi-step growth process in a gas source CVD reactor (Figure S1) using W(CO)₆, Re₂(CO)₁₀, and H₂Se precursors at 800 °C in a H₂ gas environment (FEOL-compatible conditions).^[7,12] All films are fully coalesced monolayers with some bilayer regions (Figure 1 a-c) where the introduction of Re₂(CO)₁₀ at this temperature leads to a modification of WSe₂ surface morphology, with the film losing continuity, and sharp edges of the triangular-shaped domains becoming less prominent. Furthermore, the overall growth rate of WSe₂ does not change as a function Re₂(CO)₁₀ partial pressure, but the density of bilayer regions increases in which Re atoms serve as nucleation sites for secondary layers (Figure 1 b-c). As a result, the average domain size in doped WSe₂ are significantly smaller (450-500 nm) compare to intrinsic films (800-900 nm). Conversely, growth of Re-doped WSe₂ at 450 °C on amorphous SiO₂/Si substrates (BEOL conditions) yields fully coalesced multilayer films (3-4 layers) with 150 nm domains (Figure S2 a-c).¹⁸ Compositional analyses of the films via high-resolution XPS and ToF-SIMS indicate that the Re₂(CO)₁₀ precursor decomposes^[41] and is readily incorporated into the WSe₂ at all investigated temperatures. Each film exhibits the characteristic W 4f_{7/2}, W 4f_{5/2} and W 5p_{3/2} and Se 3d_{5/2}, Se 3d_{3/2} XPS peaks at 32.7 eV, 34.8 eV, 38.1 eV and 54.9 eV, 55.7 eV, (Figure 1d) respectively - similar to the values reported for exfoliated WSe₂.^[42] Moreover, as the Re concentration is increased to 0.5 % and 1.1%, Re 4f_{7/2} and Re 4f_{5/2} XPS signatures are readily detectable at 42 eV and 44.4 eV (Figure S3), respectively corresponding to Re-Se bonding, indicating substitutional Re doping at the W site.^[43,44] The XPS detection limit is ~0.5% Re-WSe₂, thus ToF-SIMS is employed to evaluate the Re concentration below the XPS detection limit (Figure S4). Detailed statistical analyses indicate that the Re concentration is correlated with the Re₂(CO)₁₀ flow rate (Figure S5), where dopant concentrations as low as <0.0001% could be achieved (Table S1). For the case of BEOL compatible growth and doping, it was found that lower flow rates of the Re precursor (see methods) yields similar doping levels and trends (Figure S6 a-b) as FEOL grown WSe₂, as identified by the XPS Re 4f_{7/2} and Re 4f_{5/2} peaks at 42 eV and 44.3 eV, respectively.

Figure 1. Structural, compositional, and optical characterization of FEOL WSe₂ and Re-WSe₂ as a function of Re concentration. SEM images of (a) pristine, (b) 0.5% and (c) 1.1% Re-doped WSe₂ where the surface morphology of the films is significantly affected after the introduction of Re atoms (2 μm scale bar). (d) XPS analyses further verifies the presence of Re in the WSe₂ lattice at higher Re concentrations (1.1 % and 0.5%) where Re 4f_{7/2} and Re 4f_{5/2} peaks are found at 42 eV and 44.4 eV (zoom in green box is shown in Figure S3), respectively. (e) and (f) Corresponding Raman and PL data present increased density of defect activated modes, redshift and quenching of the PL spectra as a function of Re concentration, respectively.

Raman spectroscopy verifies the presence of dopants (defects) in the host lattice.^[36,39,45] Pristine and Re-doped FEOL WSe₂ display peaks at 249 cm⁻¹ and 261 cm⁻¹ corresponding to A+E and 2 LA(M) characteristic in-plane and out-of-plane Raman active modes (Figure 1e) where the absence of A_{1g}² mode further confirms the monolayer nature of the films.^[46,47] As the doping concentration increases, the intensity of ZA(M) and LA(M) modes at 109 cm⁻¹ and 128 cm⁻¹ become prominent (Figure 1e) corresponding to the defect-activated bands of WSe₂.^[48-50] As Re atoms are introduced, they break translational symmetry in the WSe₂ and increase structural disorder leading to these defect activated modes.^[36,39,48,50] BEOL films exhibit similar Raman spectral trends as a function of Re concentration (Figure S6 c, S7 c), with the addition of the A_{1g}² mode at 309 cm⁻¹ indicating multilayer growth that is validated by AFM (Figure S2 a-c). Room temperature PL spectra exhibit similar dopant concentration dependence where pristine FEOL WSe₂ displays an optical band gap of 1.65 eV while Re-WSe₂ is redshifted by 40 meV and is quenched by a factor of two (Figure 1f). Similarly, BEOL Re-WSe₂ is redshifted by 10 meV and quenched by 30% (Figure S6 d) with respect to the pristine WSe₂ (WSe₂ = 1.63 eV). The reduced PL intensity and redshift of Re-WSe₂ are most likely due to an increased density of trions induced by electron doping.^[23,40,51] Unlike neutral excitons, trions are charged and strongly attract to the Re impurities by Coulombic forces. As a result non-radiative trion recombination quenches the PL for a Re concentration exceeding 1.1%.^[52] The difference in PL spectra for FEOL and BEOL films is due to differences in crystal quality, domain size, and thickness. Furthermore, in-plane x-ray diffraction XRD (Figure S8 a-b) shows epitaxial growth of FEOL films with an epitaxial relation of [11 $\bar{2}$ 0] WSe₂ || [11 $\bar{2}$ 0] α -Al₂O₃. Re doped FEOL films show a similar epitaxial relationship to the sapphire; however, in-plane XRD provides evidence that the increased Re doping leads to a slight rotational misorientation – noted as broadening of in the in-plane XRD ϕ (ϕ) scans (Figure S8 b).^[53] The in-plane XRD measurements are not possible on BEOL counterparts due to the amorphous SiO₂/Si substrate and polycrystalline nature of the films.

First principles density-functional theory (DFT) calculations provide insight on the Re atomic positions and the electronic properties of the doped films (See *Materials and Methods* for details of calculations). Comparison of the formation energies of neutral Re dopants at seven different sites (Figure 2 a-c) - including substitutional (Re_W, Re_{Se}), interstitial (Re_{int-split}, Re_{int-hex}), and three adatom sites (Re_{ad-W}, Re_{ad-hex}, Re_{ad-Se}) - reveal that substitutional Re on a W site is energetically most favorable (Table S2). Moreover, the formation energy of the Re dopant at the next most stable site (substitutional Re on Se site) is ~ 3 eV higher (Table S2), which suggest it is highly unlikely. The strong preference for Re to substitute at a W site is in good agreement with our experimental observations where Re-Se bonding is confirmed via high-resolution XPS. Hence, only the substitutional Re dopant on W site is considered in subsequent DFT calculations of the electronic structure of Re-doped WSe₂.

DFT calculations of electronic structure including spin-orbit coupling indicate that Re dopants introduce electronic states within the band gap (Figure 2d). These defect states lie close to the conduction band minimum (CBM), further implying n-type doping characteristics nature of Re in WSe₂, which is expected since Re atoms have one more valence electron than W. In the neutral charge state, the defect states are partially occupied by the additional electron. However, this electron can be excited into the conduction band, leaving behind a positively charged dopant which has the electronic structure depicted in Figure 2d. Spin-orbit coupling is responsible for the approximately 0.2-0.3 eV splitting between the defect bands, which lie about 0.1-0.4 eV below the CBM based on our calculations. The in-gap defect states are composed primarily of Re 5d_{z²} and 5d_{x²-y²}/d_{xy} orbitals. The binding energy of the Re donor state is considerably larger,^[54] compared to common shallow dopants in bulk semiconductors such as phosphorous (E_b=45 meV) and boron (E_b=45 meV) in silicon requiring higher activation energies to ionize the dopant. Significantly deeper doping levels and higher ionization energies are generally expected due to strong quantum confinement and reduced screening in 2D semiconductors.^[54]}

Atomic resolution electron microscopy imaging of Re atoms in the WSe₂ lattice based on the contrast difference is challenging due to comparable mass of W and Re. To locate Re within the WSe₂ layer, we directly measure the lattice spacing of the hexagonal honeycomb structure of doped and undoped WSe₂ lattice. High-resolution transmission electron microscopy (HRTEM) image of 1.1% FEOL Re-WSe₂ (Figure 2 e-g, Figure S9) shows that the substitutional Re atoms exhibit a noticeable shift off center from the lattice site, breaking the threefold symmetry of the hexagonal honeycomb WSe₂ lattice (Figure 2f) as predicted by the DFT simulation of the neutral (un-ionized) Re dopant (Figure 2h). Furthermore, selective area electron diffraction (SAED) (Figure S10) shows slightly enlarged or distorted spots due to the additional spacing values at the Re_W regions which are very close to the undoped WSe₂ regions. These spacings also match simulations (Figure S11) after applying rotational averaging on the enlarged spots (Figure S10).

Figure 2. First-principles density functional theory (DFT) computations of position, band structure, and projected density of states of a Re dopant in the WSe₂ lattice and their corresponding atomic resolution images obtained via HRTEM. (a)-(c) Schematics showing seven possible sites for a Re dopant in the WSe₂ lattice including (a) substitutional sites (Re_W, Re_{Se}), (b) interstitial sites (Re_{int-split}, Re_{int-hex}), and (c) adatom sites (Re_{ad-W}, Re_{ad-hex}, Re_{ad-Se}), where silver, green, and cyan atoms indicate W, Se, and Re atoms, respectively. (d) Band structure and projected density of states for the ionized Re dopant on a W site, including spin-orbit coupling. The density of states is projected onto the d -orbitals of the Re dopant atom, with the grey shading indicating the density of states for a WSe₂ formula unit 6.5 Å away from the dopant atom. (e) HRTEM image shows periodic atomic arrangement with some sites highlighted in the yellow

hexagons where Re_W are introduced in the WSe_2 lattice. The atomic arrangement of the unit cell (f) with and (g) without Re atoms, respectively. Simulated lattice spacing and corresponding fold symmetries for (h) Re-doped and (i) pristine WSe_2 are in a good agreement with experimental findings in Figure S9.

Low temperature scanning tunneling microscopy and spectroscopy (STM/STS) reveals several types of point defects in WSe_2 , one of which can be attributed to the Re impurity. Re-doped FOEL WSe_2 samples were prepared by growing WSe_2 monolayers on epitaxial graphene (EG) using similar growth conditions as samples on sapphire. A constant current overview STM image of monolayer WSe_2 is shown in Figure 3a. We can identify several point defects based on the close resemblance of their STM topographic contrast with defects previously identified and characterized extensively in CVD-grown WS_2 .^[55–59] Such defects include for instance Cr and Mo substituting for W,^[57] or oxygen substituting selenium, both at the top and bottom site.^[55,56] All of these defects are charge neutral and feature a low formation energy.^[57] Positively and negatively charged defects that exhibit a bright and dark contrast at positive sample bias (Fig. 3a) are more difficult to identify due to the presence of band bending (see Fig. S13) and hydrogenic states that obscure the chemical defect signature.^[58] Negatively charged defects do exist in nominally undoped WSe_2 and WS_2 , which we attribute in part to CH impurities at chalcogen sites.^[59] Positively charged defects on the other hand were exclusive to MOCVD WSe_2 samples and found in small abundance in nominally undoped samples and in very large abundance in Re-doped samples (see Fig. S13), suggesting that the positively charged defects correspond to ionized Re impurities. Tunneling spectroscopy identifies four dominant resonances close to the conduction band edge in the unoccupied spectrum, labelled A-D in Fig 3c. The energies of these states rigidly shift towards higher values in proximity to negatively charged defects and towards lower values in proximity to other positively charged defects (Fig. 3b), which can be explained by an electrostatic gating effect. The Re_W defect states A-D exhibit spatially distinct orbitals with three-fold symmetry, as shown in the dI/dV maps in Fig. 3d.

Figure 3.(a) STM topographic overview image of Re dopants in WSe_2 /graphene/SiC with one rhenium substituting tungsten defect (Re_W) outlined in black, $V_b = 1.4$ V, $I_t = 100$ pA. (b) STS of three Re_W defects in different local environments indicating a rigid shift of resonances with proximity to another positively

charged defect (pCD) or a negatively charged defect (nCD). (c) STS spectra along a line across a Re_W defect showing localized states just below the conduction band, which are labeled A-D. (d) Experimental dI/dV maps of the states A-D (e) Atom-projected density of states calculated with DFT shows the defect peaks associated with the Re dopant. For comparison, the grey shading indicates the local density of states of a WSe_2 formula unit $6.5 \text{ \AA}$ away from the dopant atom. (f) DFT-computed local density of states integrated over 20 meV energy windows at the positions of the identified defect peaks A-D.

To confirm the assignment of the positively charged defect as a Re atom at a W site, experimental STM and STS results were compared with DFT calculations. The defect peaks in the Re-atom projected density of states calculated with DFT (Figure 3e) and the shapes of the associated defect orbitals (Figure 3f) closely resemble the experimental findings. Like in the experimental STS spectra, the calculated density of states of Re_W^{1+} shows four dominant defect resonances at the Re dopant below the conduction band. Even though a direct quantitative comparison of the absolute defect state energies between experiment and theory is not possible on the DFT level, the relative energies of the defect states are reproducible. Most importantly, the corresponding defect orbitals displayed in Fig. 3f match the dI/dV images and retain the threefold symmetry of the original WSe_2 lattice. This implies that Re dopants in WSe_2 grown on epitaxial graphene tend to be ionized, unlike those in samples grown on *c*-plane sapphire (Fig. 2) which remain un-ionized.

To evaluate the electrical properties of pristine and doped FEOL WSe_2 on *c*-plane sapphire, the as-grown films were transferred onto 50 nm atomic layer deposition (ALD) Al_2O_3 substrates where back-gated field-effect-transistors (BGFETs) are constructed with a channel length (L_CH) of $1 \mu\text{m}$ and width (W) of $5 \mu\text{m}$.^[18] The transfer characteristics, drain current (I_DS) vs back-gate voltage (V_BG) at different drain voltage (V_DS), of pristine and lightly doped (0.07% and 0.5%) BGFETs (Figure 4 a-c) display similar ambipolar conduction where the presence of distinct n and p branches can be observed for $V_\text{BG} > 0$ and $V_\text{BG} < 0$, respectively.^[35,60,61] All three BGFETs demonstrate ON/OFF ratio $> 10^6$ and extracted carrier mobility from the peak transconductance method equals $1 \text{ cm}^2/\text{V}\cdot\text{s}$ which is highly underestimated due to the large Schottky barrier height that limits the ON-state current.^[62,63] Furthermore, device performance degrades as the doping concentration is increased up to 1.1% Re- WSe_2 . Highly doped (1.1%) samples exhibit an order of magnitude decrease in ON current and complete loss in gate modulation where the BGFET no longer acts as a semiconductor (Figure 4d). If Re acts as an n-type dopant in WSe_2 and donates an electron to the system, the n-branch current at $V_\text{BG} > 0$ must increase in all Re- WSe_2 FETs which do not coincide with our findings. We hypothesize that the observed phenomenon is a direct consequence of the large binding energy of the impurity state ($E_\text{b} = 200\text{-}300 \text{ meV}$) which cannot be activated thermally at room temperature.^[37,54] The impurity binding energy of layered materials is a strong function of the effective thickness where almost two orders of magnitude difference have been reported between bulk and monolayer 2D TMDCs by charge transition level (CTL) calculations and Keldysh formulation.^[64] As the thickness of Re- WSe_2 approaches monolayer level, the dielectric screening is reduced ultimately resulting in stronger Coulomb interaction between the donor nucleus and electron with higher E_b .^[37,54,64] Previous reports indeed demonstrate an increase in electron concentration in bulk Re- WSe_2 whereas FEOL Re- WSe_2 is monolayer in nature which further supports our hypothesis.^[33] Conventional, external dopant activation techniques such as high-temperature and laser-annealing methods can be used to ionize deep level dopants in extrinsic 2D TMDCs. Moreover, recent theoretical calculations demonstrate that encapsulation between high-k dielectrics might significantly increase the screening effect in the system resulting in a reduction of the large binding energy of impurity atoms.^[65] A combination of the aforementioned activities may be necessary toward achieving the desired performance of the extrinsic semiconductors and realize commercially available 2D electronic, magnetic, sensing, catalytic devices.

Figure 4. Electrical characterization of pristine and Re-doped FEOL WSe₂ back-gated field-effect-transistors (BGFETs) on 50 nm ALD Al₂O₃. (a)-(c) Transfer characteristics of BGFETs-drain current (I_{DS}) as a function of back-gate voltage (V_{BG}) at different drain voltages (V_{DS}) demonstrate ambipolar conduction in the pristine and lightly doped (0.07% and 0.5%) films. (d) At higher dopant concentrations (1.1%), device performance is degraded, and the semiconducting nature is lost.

Conclusion

We have developed a scalable, highly-controlled, uniform doping of FEOL and BEOL compatible 2D WSe₂ films with rhenium atoms via MOCVD. Detailed structural, chemical, and compositional analyses reveal successful incorporation of Re atoms into the host WSe₂ lattice where doping concentrations as low as <0.0001% can be easily achieved by having precise control over the partial pressure of the precursors. Our work shows a strong quasilinear dependence of doping concentration on the rhenium precursor flow rate and substitutional replacement of Re atoms at W site has been confirmed. Atomic-scale characterization along with DFT calculations demonstrates that Re atoms introduce discrete defect states in the band gap that lie near to the conduction band further implying the donor nature of the dopants. However, electronic transport properties of constructed FETs degrade as a function of doping concentration which may be attributed to the large binding energy of electrons due to less effective dielectric screening in monolayer 2D films. Activation of dopants will further require the development of a fundamental understanding of impurities in extrinsic monolayer 2D TMDCs by manipulating the dielectric environment between substrate and film interface.

Experimental Section

Gas source CVD growth of pristine and Re doped WSe₂ films. The films are synthesized in a custom-built vertical cold wall CVD reactor as previously reported elsewhere.^[7,18] The tungsten hexacarbonyl W(CO)₆ (99.99 %, Sigma-Aldrich) and dirhenium decacarbonyl Re₂(CO)₁₀ (98 %, Sigma-Aldrich) solid state sources are kept inside stainless-steel bubblers where temperature and pressure of the precursors are always held at 25 °C and 725 Torr, and 40 °C and 725 Torr, respectively. Hydrogen carrier gas flow is controlled through mass flow controllers and supplied to the bubblers to deliver W(CO)₆ and Re₂(CO)₁₀ into the reactor inlet. Hydrogen selenide (H₂Se) (99.99 %, Matheson) is introduced from a separate gas manifold to prevent the intermixing of the precursors. MOCVD growth of monolayer, epitaxial pristine and Re doped FEOL compatible WSe₂ films are carried out using a so-called three-step growth (nucleation, ripening and lateral growth) method on *c*-plane sapphire (Cryscore Optoelectronic Ltd, 99.996%) substrates at 800 °C and 700 Torr.^[7] Flow rate of H₂ gas through the W(CO)₆ bubbler is varied from 20 to 4.5 sccm at the different stages of the growth whereas H₂Se flow rate is always kept at constant 7 sccm. Re₂(CO)₁₀ is introduced during the lateral growth stage where the flow rate of H₂ through the bubbler is varied from 90 to 5 sccm. The synthesis

of BEOL compatible, pristine, and Re-doped WSe₂ is carried using a similar single step growth method on SiO₂/Si substrates (University Wafer, Silicon P/B (100)) with 300 nm wet thermal oxide, as previously reported.^[18] During the BEOL synthesis, the temperature and pressure of the reactor are kept at constant 450 °C and 700 Torr, respectively. Since, the BEOL growth conditions significantly differ from electronic-grade epitaxial films, the precursor flow rates are adjusted accordingly. H₂ gas flow rate through the W(CO)₆ bubbler is kept at constant 2 sccm whereas flow through the Re₂(CO)₁₀ bubbler is varied from 15 to 5 sccm. H₂Se flow rate is maintained at constant 9 sccm. In all cases, the substrates are cleaned prior to the growth with ultrasonication in acetone (10 min) and isopropyl alcohol (IPA) (10 min) followed by DI water rinse (5-7 times). Moreover, the rinsed substrates are dried with N₂ gun and transferred into a heated commercial Piranha solution (Nanostrip, KMG Electronic Chemicals) beaker (90 °C) for 20 min and DI water rinse (10-14).

Field emission scanning electron microscope (FESEM). Zeiss Merlin instrument with the accelerating voltage of 5 keV is used to collect the FESEM images of pristine and doped samples.

Atomic Force Microscopy (AFM). AFM measurements are performed in a peak force tapping mode using a Bruker Icon I tool.

Raman and Photoluminescence (PL) spectroscopy. Horiba LabRam HR Evolution VIS-NIR Raman system with a 532 nm laser at 0.4 mW power and 633 nm laser at 0.4 mW power are used to obtain Raman and PL spectra of the films.

X-ray photoelectron spectroscopy (XPS). A Physical Electronics Versa Probe II is used to obtain high resolution X-ray photoelectron spectroscopy data at high (<10⁻⁶ Torr) vacuum. A monochromatic Al K_α x-ray source (hν=1486.7 eV) with a 200 μm spot size irradiates the sample, and a hemispherical detector measures the kinetic energy and output of electrons. Additionally, an ion gun and floating electron neutralizer are used for charge neutrality. Spectra are taken for the W4f and C1s region at 29.35eV pass energy and 0.125eV energy step and charge corrected to C1s spectrum at 284.8 eV. To fit XPS spectra, Iterated Shirley background is used for Se whereas U 2 Tougaard background is used for Re and W, respectively.

In-plane X-ray diffraction (XRD). In-plane XRD measurements are performed using a Panalytical MRD diffractometer with 5 axis cradle employing Cu K_α radiation and filtering K_β radiation employing Ni filter.

DFT calculations. The formation energies of the neutral Re dopant at seven different sites in the WSe₂ lattice were computed using density functional theory (DFT) as implemented in the Vienna ab initio simulation package VASP.^[66] Calculations were performed in 4 × 4 and 5 × 5 supercells containing a single dopant atom each, with 20 Å vacuum spacing between layers. We performed calculations using projector-augmented wave potentials^[67,68] and treated the exchange-correlation using the Perdew-Burke-Ernzerhof (PBE)^[69] generalized gradient approximation functional. We employed a plane wave cutoff energy of 520 eV, and Methfessel-Paxton smearing^[70] with smearing energy width of 0.10 eV and Γ -centered Monkhorst-Pack k -point meshes^[71] for Brillion zone integration.

The formation energy $E^f[X]$ of a neutral point defect X is determined by DFT calculations using a supercell approach following $E^f[X] = E_{\text{tot}}[X] - E_{\text{tot}}[\text{pristine}] - \sum_i n_i \mu_i$, where $E_{\text{tot}}[X]$ and $E_{\text{tot}}[\text{pristine}]$ are the total DFT-derived energies of the supercell containing the defect X and the pristine supercell respectively, n_i is the number of atoms of species i added/removed, and μ_i is the corresponding chemical potential of the species. The values reported in Table S2 are referenced to hcp Re for μ_{Re} , and where required, either bcc W for μ_{W} (W-rich limit), or hexagonal (gray) Se for μ_{Se} (Se-rich limit). For selected sites, additional single-

point calculations were performed considering the effect of spin-orbit coupling on the system. Spin-orbit coupling was considered for all calculations of the electronic band structure and density of states.

Time-of-flight Secondary Ion Mass Spectroscopy (ToF-SIMS). SIMS data were acquired with a PHI NanoToF II. Spectra were collected with a 30 keV Bi_3^+ spectroscopy beam, rastered over an area of 100 x 100 microns. The best sensitivity to the species of interest (at m/e 182, 183, 186, 187) occurs in the positive ion spectrum. A mass range of 1850 AMU was scanned, with both electron and ion neutralization activated during acquisition of positive ion spectra. For each analysis location, 40 frames of data were acquired over a 22-minute interval, at an image resolution of 256 x 256 pixels. DC column currents were $\sim 700\text{pA}$, and the dose delivered during a spectral acquisition was about 8×10^{10} ions/ cm^2 . A bunched primary beam was used to maintain moderate mass resolution (~ 3500) during data collection. A stage bias of about 110 volts was required, and this could vary by ± 10 volts across the sample set. The contrast diaphragm was out during acquisition, and the energy slit was set for maximum bandpass. Sapphire substrates (1 x 1 cm, 0.5 mm thickness) were front-mounted and held to the stage at diagonal corner locations with Be-Cu spring clips. No masks or grids were applied to the analysis surface. Analytical chamber pressures were in the low 10^{-6} Pa range during data acquisition.

Scanning Tunneling Microscopy and Spectroscopy (STM/STS). STM/STS measurements were acquired at liquid helium temperature ($T < 7\text{ K}$) under ultrahigh vacuum ($p < 2 \times 10^{-10}$ mbar) with a Createc GmbH scanning probe microscope. An etched tungsten tip was prepared on a gold substrate and verified as metallic on the Au(111) surface. STM topographic measurements were carried out in constant current mode with the bias applied to the sample. STS measurements were taken using a lock-in amplifier at 683 Hz and modulation amplitudes between 5 and 15 mV for point spectra and maps, respectively. FEOL samples were prepared ex situ on epitaxial graphene on SiC substrate^[72] with a final 200 °C anneal in vacuum.

HRTEM and electron diffraction. As grown FEOL Re-WSe₂ (1.1% Re) are transferred onto gold quantifoil TEM grids by a PMMA-assisted technique.^[73] HRTEM images are acquired using a FEI Titan Cubed transmission electron microscope equipped with an image corrector in the image forming plan to correct the spherical aberration. The experiment was conducted at 80 keV accelerating voltage using a high-brightness gun (XFEG). The beam intensity is reduced through multiple lenses with the 150 μm C2 aperture to achieve approximately 150 pA screen current to reduce the possible electron beam damage. Acquired images are subjected to a Wiener filter^[74] to remove the effect of the amorphous contamination accumulated on the sample during imaging. Electron diffraction at selected area was performed at 2.1 MX magnification and 1.441 μm illumination area diameter recorded by the FluCam camera from the screen plane. Then, the diffraction pattern was processed using Digital Micrograph software and the DiffTools^[75] plug-in to locate the central spot and perform a rotation averaging at selected reflections.

STEM, Nanobeam diffraction, and EELS. Low and high magnification HAADF-STEM images were acquired with the same Titan Cubed microscope at 80 keV accelerating voltage and a 50 pA screen current approximately Nanobeam diffraction patterns were acquired using the FluCam camera after forming a sharp probe by reducing the beam convergence semi-angle to ≈ 1 degree and inserting the 10 μm C2 aperture. Core-loss EELS signal was collected using the Gatan's K2 SI direct electron detector at the M3 minor edges region of the Tungsten and Rhenium at electron dispersion 0.15 electron/channel. To ensure enough EELS signal at the minor edges' region, the spectrum was collected by summing 2000 frames at 0.1 sec/frame then the signal was smoothed, and the background was subtracted.

Fabrication of field-effect-transistors (FETs). The as-grown FEOL samples on *c*-plane sapphire were transferred onto 50 nm ALD Al_2O_3 on Pt/TiN/Si, respectively using a PMMA assisted method.^[73] E-beam lithography (Raith EBPG-5200) was used to construct back-gated FETs where the channels were isolated

using a SF₆/O₂ 30/10 sccm gas mixture for 30s in a Plasma-Therm Versalock 700 inductively coupled (ICP) plasma etch tool. The isolated channels were contacted with 40 nm Ni and 30 nm Au which were deposited in a Temescal e-beam evaporator tool under high vacuum (1×10^{-6} Torr).

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A. K. and J. A. R. conceived the idea, and J. A. R., B. S., N. B., S. D., J. M. R., and R. G. H. directed the research. A. K. carried out the MOCVD synthesis of extrinsic FEOL and BEOL WSe₂ films and conducted SEM, AFM, Raman, PL, and fabricated and measured the first set of FETs. A. V. performed XPS characterization and A. K. analyzed the XPS data. B.S. and K. A. C. conducted the STM/STS measurements and analyzed the data. DFT calculations are carried out by A.-M. Z. T. and the final set of FETs were fabricated by J. R. N. and measured by J. R. N. and A. K. V. B. carried out the ToF-SIMS measurements and A. B. performed in-plane XRD. H. E.-S. conducted the HRTEM, EELS and SEAD experiments. All authors contributed to analyzing and discussing the data. A. K. and J. A. R. wrote the paper with significant input from B. S., A.-M. Z. T., K. A. C., V. B., N. B., J. M. R., S. D., A. W.-B., and R. G. H.

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Conflict of Interest

Authors declare no conflict of interest

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