WSe₂-contact metal interface chemistry and band alignment under high vacuum and ultra high vacuum deposition conditions

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Abstract

Contact metals (Au, Ir, and Cr) are deposited on bulk WSe₂ under ultra-high vacuum (UHV, \(1 \times 10^{-9} \text{ mbar}\)) and high vacuum (HV, \(5 \times 10^{-6} \text{ mbar}\)) conditions and subsequently characterized with x-ray photoelectron spectroscopy (XPS) to elucidate the effects of reactor base pressure on resulting interface chemistry, contact chemistry, and band alignment. Au forms a van der Waals interface with WSe₂ regardless of deposition chamber ambient. In contrast, Ir and Cr form a covalent interface by reducing WSe₂ to form interfacial metal selenides. When Cr is deposited under HV conditions, significant oxygen incorporation is observed resulting in the thermodynamically favorable formation of tungsten oxyselenide and a substantial concentration of Cr\(_2\)O\(_3\). Regardless of contact metal, WO\(_x\) (2.63 < \(x\) < 2.92) forms during deposition under HV conditions which may positively affect interface transport properties. Cr and Ir form unexpectedly large electron and hole Schottky barriers, respectively, when deposited under UHV conditions due to interfacial reactions that contribute to anomalous band alignment. These results reveal the true interface chemistry formed between metals and WSe₂ under UHV and HV conditions and demonstrate the impact on the Fermi level position following contact formation on WSe₂.

Introduction

As the scaling of Si-based electronic devices approaches its limit, alternative materials to Si are under investigation to permit extension of Moore’s law scaling. 2D materials, specifically transition metal dichalcogenides (TMDs, e.g. MoS₂, WSe₂), with atomic scale thickness, tunable bandgap (~0.7–2.2 eV), and comparable mobilities with existing Si metal-oxide-semiconductor (MOS) channels, have emerged as strong candidates to complement current Si-based device technology [1, 2]. TMDs are, in principle, ideal for the design of ultrashort channel field effect transistors (FETs) due to these novel properties which stem from their layered nature and set TMDs apart from Si, Ge, and III–V semiconductor materials.

Whereas MoS₂ has been widely studied as a potential channel material in TMD-based FETs [3–7], studies focused on WSe₂-based FETs are less prevalent. The electrical behavior of various contact metals on TMDs will vary significantly depending on the TMD, for instance MoS₂ favors n-type conduction while WSe₂ favors p-type conduction [8]. To date, reasonable performance has been achieved in WSe₂-based FETs with measured \(I_{ON}/I_{OFF}\) ratio > 10⁸ and mobility (\(\mu\)) of 2.1 \(\times\) 10⁷ cm² V⁻¹ s⁻¹ (at 5 K). However, the parasitic effects of contact resistance must be accounted for as substantial differences can arise between measured \(\mu\) (e.g. 100 cm² V⁻¹ s⁻¹) and intrinsic \(\mu\) (e.g. 500 cm² V⁻¹ s⁻¹) in WSe₂ based devices if contact resistance effects are overlooked [9–11]. Although WSe₂, among other TMDs, shows tremendous potential for the realization of a new class of low power devices, contact resistance (0.2 kΩ \(\mu\)m) [12] in TMD-based devices is an order of magnitude greater than what has been achieved in Si-based devices (0.01 kΩ \(\mu\)m) to date [8, 13, 14]. Ion implantation is commonly employed to reduce contact resistance in Si-based devices. Analogous doping schemes involving surface charge transfer [15, 16] or substitution [17] have been developed for TMDs, although doping effects degrade in air for many of these strategies. Alternative methods have been employed recently in TMD-based devices for reduced contact resistance and...
include but are not limited to a WO$_3$, hole injection layer [18], metallic edge contacts [12, 19], vacuum annealing [20], and metallic 2D top contacts [11, 21]. Contact resistances from 0.2 to 2 kΩ have been achieved in WSe$_2$-based FETs employing the strategies listed above. Perhaps the most promising advance is represented by the performance enhancement achieved via WO$_3$, hole injection layer as other strategies require processes such as large scale phase transformation or manually stacking exfoliated 2D materials for device structures are not commercially viable. Top contacts to TMDs offer a direct route to commercially viable device structures. Therefore, the contact metal must be carefully selected based on its work function ($\Phi$) to achieve the desired carrier injection into the TMD channel. Theoretically, carrier injection in an electronic device depends upon the Schottky barrier, or the difference between contact material and electron affinity of the TMD (in the case of an electron Schottky barrier) or ionization potential (in the case of a hole Schottky barrier).

However, many factors play a role in the chemical and electrical nature of the metal-WSe$_2$ interface, including the difference between contact material $\Phi$ and WSe$_2$, electron affinity (see Schottky–Mott model) [22] as well as the d-orbital interaction between the contact metal and W in WSe$_2$ [10, 23, 24]. Reaction products which form at the contact metal-TMD interface provide additional, often compositionally dependent, electronic states, which can reside in the TMD band gap and contribute to the complex mechanism of Fermi level pinning (FLP). In addition, gap states, and therefore FLP, are associated with the substantial concentration of defects common in geological and synthetic TMDs [25–28]. Kang et al predicts covalent bonding and ‘Ohmic interfaces’ between WSe$_2$ and Pd, W, and Ti [23]. However, experimentally determined n-type and ambipolar transport in WSe$_2$ FETs employing In and Ti as contact materials, respectively, disagree with density functional theory (DFT) predictions regarding analogous device architectures [10, 23, 15]. DFT models predicting the electronic properties and nature of the chemical bonding at various metal-WSe$_2$ interfaces limit material systems to a pure metal, defect free WSe$_2$, and a pristine metal-WSe$_2$ interface due to computational limitations, which is, of course, far from reality [8, 23].

Our recent work clearly demonstrates the dependence of contact composition and contact–MoS$_2$ interface chemistry on deposition chamber ambient, as reactions were observed between Ir, Cr, and Sc when deposited on MoS$_2$ under either high vacuum (HV, $5 \times 10^{-6}$ mbar—typical of cleanroom tools employed in device fabrication) or lower pressure ultrahigh vacuum (UHV, $1 \times 10^{-9}$ mbar) conditions [29]. Furthermore, significant oxidation of Cr and Sc was observed when deposited under HV conditions. McDonnell et al found that both the contact metal composition and the contact–MoS$_2$ interface chemistry differs drastically when Ti is deposited under UHV conditions compared with HV conditions [30]. Interface chemistry presumably plays a significant role in contact performance as significant improvements in contact resistance has been realized in MoS$_2$-based FETs via UHV contact deposition [4]. It is therefore not appropriate to rely solely on the presence of pristine metal–WSe$_2$ interfaces or a compositionally pure metallic contact, as is done in modeling. As a result, more realistic contact metal-TMD interface models, which consider the defective nature of TMDs and availability of background gas molecules at the TMD surface during metal deposition, in tandem with carefully designed experiments are essential to determine the optimal contact material and deposition conditions for superior TMD-based device performance.

To elucidate a more complete understanding of the true chemical and electronic interaction between contact metal and WSe$_2$, its dependence on deposition chamber ambient is explored for contact metals with vacuum work functions ranging from 4.5 to 5.3 eV, specifically Au, Ir, and Cr [3, 31, 32]. As noted previously, Cr is also often employed as an ‘adhesion layer’ for contacts in device fabrication [29]. XPS is employed to evaluate the contact composition, metal–(bulk)WSe$_2$ interface chemistry, and Fermi level (FL) shift resulting from metal deposition under different deposition chamber conditions. The potential implications of experimentally determined interface chemistry on metal–WSe$_2$ band alignment and transport across the interface are discussed.

Methods

Metal deposition under UHV and HV conditions and interface characterization

All WSe$_2$ samples originated from the same bulk crystal purchased from HQ Graphene [33]. The procedures employed for sample preparation, mounting, metal source outgassing, determining metal deposition rates (0.3–0.6 nm min$^{-1}$ depending on the metal), metal deposition under both HV and UHV conditions, and subsequent XPS analysis are identical to that employed for an analogous investigation of interface chemistry between Au, Ir, Cr, and Sc and bulk MoS$_2$ described elsewhere [29]. Exfoliation is performed under laboratory ambient conditions, as is typical in device fabrication. Under UHV conditions, metals were deposited via electron beam in a chamber, base pressure $\sim 1 \times 10^{-9}$ mbar, attached to a UHV cluster tool described in detail elsewhere [34]. Following metal deposition, samples were transferred, without breaking vacuum, to a separate chamber through a UHV transfer tube held at $1 \times 10^{-10}$ mbar where XPS was performed. Under HV conditions, metals were deposited in an elastomer-sealed Temescal BJD-1800 e-beam evaporator with base pressure $\sim 1 \times 10^{-6}$ mbar in the cleanroom facility [35]. Samples were then transferred ex situ as quickly as possible to the analysis chamber under UHV conditions for all XPS characterization (~5 min air exposure between removal
from cleanroom deposition tool and loading into UHV cluster tool. All Au, Ir, and Cr films were deposited on WSe2 with a target thickness of 1.5 nm.

The method by which the Au 4f, Ir 4f, and Cr 2p core level reference spectra were obtained is described elsewhere [29]. The W metal reference was obtained by sputtering 50 nm of W under an N2 flow of 30 sccm onto a Si(1 1 1) wafer cleaned in a 100:1 HF bath. The base pressure of the interconnected sputtering chamber is ~2 × 10⁻⁹ mbar. Prior to transferring the sample into the sputtering chamber for W deposition, the W target was outgassed for 1 h with identical parameters as those employed during deposition. Following outgassing, the chamber was pumped to a pressure of 2 × 10⁻⁹ mbar before moving the sample inside from UHV transfer tube. The sputtering tool is employed solely for the purpose of obtaining the W reference spectrum, and is attached to the same UHV cluster tool as was mentioned earlier. Prior to obtaining the W 4f reference spectrum, the W film obtained by sputter deposition was bombarded with Ar⁺ ions accelerated under 5 kV and 25 mA for a total of 30 min to ensure a clean, oxide-free surface. The reference W 4f spectrum was obtained in situ via XPS under UHV conditions immediately following Ar⁺ ion treatment. The corresponding O 1s and C 1s core level spectra were also obtained to confirm a clean W film within the photoelectron sampling depth.

Table 1. Binding energies of all chemical states detected in the W 4f/2 and Se 3d/2 core level spectra following Au, Ir, and Cr deposition on WSe2 under UHV and HV conditions.

|         | W 4f/2 binding energy (eV) | Se 3d/2 binding energy (eV) |
|---------|---------------------------|----------------------------|
|         | UHV                       | HV                         | UHV                       | HV                         |
| Au      | 32.58 (WSe2)              | 32.64 (WSe2)              | 54.83 (WSe2)              | 54.88 (WSe2)              |
|         | 35.25 (WO3)               |                            |                           |                            |
| Ir      | 32.05 (WSe2)              | 31.83 (WSe3)              | 54.50 (WSe2)              | 54.44 (WSe2)              |
|         | 32.29 (WSe2)              | 32.22 (WSe2)              | 54.73 (WSe2)              | 54.57 (WSe3)              |
|         | 35.09 (WO3)               |                            | 55.43 (IrSe3)             | 54.69 (IrSe3)             |
| Cr      | 31.32 (W0)                | 31.14 (W0)                | 54.35 (CrSe3)             | 54.05 (CrSe3)             |
|         | 32.40 (WSe2)              | 32.38 (WO3Se2)            | 54.65 (WSe2)              | 54.38 (WO3Se2)            |
|         |                            | 32.58 (WSe2)              |                            | 54.84 (WO3Se2)            |
|         |                            | 35.15 (WO3)               |                            |                            |

XPS instrumentation, parameters, and data analysis

XPS characterization of as-exfoliated WSe2 and WSe2 following metal deposition was performed via a monochromated Al Kα source and Omicron EA125 hemispherical analyzer with ±0.05 eV resolution. In addition, a takeoff angle of 45°, acceptance angle of 8°, and pass energy of 15 eV were employed during spectral acquisition. The analyzer was calibrated with Au, Ag, and Cu foils according to ASTM E1208 [36]. Spectra were deconvolved using AAnalyzer [37], a curve fitting software.

Results and discussion

We first consider the effects of reactor ambient upon interface chemistry between contact metals (Au, Ir, and Cr) and WSe2 via detailed analysis of appropriate core level spectra obtained by XPS prior to and following metal deposition under UHV and HV conditions. In addition, we employ thermodynamics to justify the chemical states observed in core level spectra.

All standard Gibbs free energy of formation (ΔGf) values are reported per selenium or oxygen atom. All electronegativities are reported according to the Pauling electronegativity scale. Interfaces at which the metal does not interact chemically with WSe2 will be referred to as ‘van der Waals’ interfaces. Interfaces at which reactions between deposited metal and WSe2 are detected will be referred to as ‘covalent’ interfaces. The binding energies of all reaction products detected in the W 4f and Se 3d core level spectra can be found in table 1. See the Methods section for details on photoelectron core level spectra acquisition.

Au–WSe2: van der Waals interface and dipole formation

Reactions between Au and WSe2 are not thermodynamically favorable. The persistence of WSe2 is far more energetically favorable than the reduction of WSe2 by Au to form AuSe as ΔGf,WSe2 = −132.0 kJ mol⁻¹, whereas the ΔGf,AuSe = −31.99 kJ mol⁻¹ [38]. The same presumably applies for other gold selenide stoichiometries. Figure 1(a) displays the Se 3d, W 4f, and W 5p/2 core level spectra obtained from bulk WSe2 following exfoliation and subsequent Au deposition under UHV and HV conditions.

Following exfoliation, the Se 3d5/2 and W 4f7/2 core levels are detected at binding energies of 55.08 and 32.85 eV, respectively, corresponding with a peak separation of 22.23 eV, typical of exfoliated, bulk WSe2 [28, 39]. Following Au deposition under UHV conditions, no new chemical states are detected in either the Se 3d or W 4f core levels. This indicates Au forms a van der Waals interface with WSe2, which has been predicted by DFT and verified in previous experiments [8, 23, 40]. Au deposition on WSe2 under HV conditions also results in a van der Waals interface. In contrast with Au deposition under UHV conditions, the formation of WO3 via WSe2 oxidation is observed, evidenced by the...
additional chemical state appearing at a binding energy of 35.25 eV in the corresponding W 4f core level spectrum. WSe₂ oxidation is thermodynamically favorable in the presence of gaseous oxidizing species typically present in the atmosphere (e.g. OH⁻, H₂O, CO⁻, CO₂) as ∆Gﾛ,WO₂ = −533.9 kJ mol⁻¹ and ∆Gﾛ,WO₃ = −764.1 kJ mol⁻¹, respectively [41]. Recently, DFT calculations predicted a particularly low kinetic energy barrier to oxygen adsorption on WSe₂ as a passivation mechanism under ambient conditions [42]. Addou et al and Park et al experimentally observed oxidation of WSe₂ domain edges, which are the most reactive sites within a WSe₂ domain [28, 43, 44]. Despite mild WSe₂ oxidation following Au deposition under HV conditions, the Se:W ratio remains virtually identical with that detected prior to and following Au deposition under UHV conditions (2:1:1). [The method employed in calculating stoichiometries reported here is discussed in further detail in the supporting information (stacks.iop.org/TDM/4/025084/mmedia).] The formation of WOₓ rather than WOₓSeₓ would result in complete loss of Se from WSe₂ and corresponding complete oxidation of W^{x+} formed from WSe₂ reduction. Any Se–Se or Se–O bonds resulting from the liberation of Se from WSe₂ via oxidation is below the limit of detection due to the significant difference between atomic sensitivity factors of the W 4f and Se 3d core levels (W 4f >> Se 3d, see Supporting Information). WOₓSeₓ formation would be evidenced by the appearance of chemical states in the W 4f, Se 3d, and O 1s core level spectra in addition to chemical states associated with bulk WSe₂ and WOₓ (see Cr–WSe₂ formed under HV conditions). A change in WSe₂ stoichiometry resulting from WOₓ formation via Au deposition under HV conditions is not expected and, if it occurs in this case, is below the detection limit of XPS.

The O 1s core level spectra obtained from the exfoliated WSe₂ surface and the Au–WSe₂ interface are displayed in figure 1(b). Oxygen-containing contaminants are below the XPS detection limit following exfoliation as there are no chemical states distinguishable from baseline noise in corresponding O 1s core level spectrum. A small concentration of oxygen related to adventitious species from background gases within the UHV cluster tool are detected following Au deposition. The doublet in the HV W 4f core level spectrum found
at high binding energy indicating the presence of WOx is accompanied by a chemical state in the O 1s core level spectrum detected at a binding energy of 530.79 eV, which is in agreement with previous XPS analysis of analogous WOx species [45].

Adventitious carbon is detected on all exfoliated samples as expected due to brief (~5 min), unavoidable air exposure following ex situ exfoliation and prior to loading into UHV. However, there are no carbon-related chemical states detected in any of the W 4f, Se 3d, Au 4f, Ir 4f, Cr 2p, or corresponding C 1s core level spectra which would suggest the formation of metal-carbon bonds of any kind. Our recent work demonstrated similar inert behavior of adventitious carbon at the metal-MoS2 interface [29] and therefore carbon at the metal-WSe2 interface will not be discussed further here. However, a typical procedure employed to fabricate TMD-based devices will involve exposing the channel material to air prior to patterning and metal deposition. Therefore, it is reasonable to assume the interface between metal and TMD channel will contain carbon, which could impact contact resistance.

The Au 4f core level spectra obtained from a Au reference film (~25 nm thick), and following Au deposition on WSe2 under UHV and HV conditions are displayed in figure 1(c). A single chemical state is detected in each of the Au 4f core level spectra following Au deposition under UHV and HV conditions at a binding energy of 84.00 eV in both cases, evidenced by the near perfect overlap with reference Au 4f spectrum when normalized (figure S1). This chemical state is indicative of metallic Au (Au–Au bonding) due to the asymmetric tail to the high binding energy side typical of core hole screening effects in metals [46, 47]. This also indicates Au forms a van der Waals interface with WSe2 regardless of deposition chamber ambient. Considering the attenuation of the W 4f and Se 3d core levels following Au deposition under UHV conditions, the thickness of the Au film is estimated to be 6 Å. This represents an estimate of the average film thickness. However, images obtained by atomic force microscopy (AFM) ex situ following Au deposition under UHV and HV conditions (figure S2) demonstrate Volmer–Weber (VW) type growth of Au on WSe2 regardless of deposition chamber ambient. These results are consistent with a similar study alternatively employing scanning tunneling microscopy (STM) to investigate Au growth on WSe2 [48]. Therefore, the estimate of Au thickness based upon the attenuation of the bulk WSe2 chemical states is not representative of the Au film morphology in the initial stages of growth on WSe2, specifically the height and diameter of Au clusters.

The binding energies of the Au 4f7/2 core level obtained from Au films deposited on WSe2 under UHV and HV conditions are 0.25 eV higher than that of the Au reference (83.75 eV). This suggests that the Au deposited under either UHV or HV conditions exhibits a smaller Φ than expected of bulk, polycrystalline Au, consistent with the size-dependent Φ of Au nanoparticles on a Si(111) substrate [49]. It is possible that a disagreement in the binding energies of reference Au and deposited Au indicates additional Au chemical states corresponding with reactions between Au and WSe2. However, when the Au 4f core level spectra obtained following Au deposition under UHV and HV conditions are shifted 0.25 eV to lower binding energy and normalized with the reference Au 4f core level spectrum (figure S1), there are no unique spectral features resolvable which would indicate a chemical state of Au other than Au0. Chemical state perturbation at the Au–WSe2 interface formed under UHV conditions, if present, is below the detection limit. However, the 0.25 eV Au 4f binding energy shift from reference Au and concomitant 0.25 eV shift to lower binding energy of the bulk WSe2 chemical states in the W 4f and Se 3d core levels following Au deposition under UHV conditions suggests an interface dipole forms upon deposition of an incomplete Au film (see table S1 for binding energies of initial bulk WSe2 chemical states). A similar interface dipole formation mechanism is predicted when Au is deposited on another layered material, GaSe [50]. Significant Schottky barrier height lowering has been reported when high Φ metal nanoparticles (e.g., Au, Pt) are present at the interface between a semiconductor and another substantially lower Φ metal contact (e.g., Ti) [51–53]. Therefore, the interface dipole mechanism between an incomplete coverage Au film (effectively Au nanoparticles) and WSe2 could be analogously employed in conjunction with a substantially lower Φ electrode metal (e.g., Ti, Sc) as a Schottky barrier lowering technique for electron contacts on WSe2-based devices.

Ir–WSe2 reactive high-Φ metal

Regardless of deposition chamber ambient, Ir reacts with WSe2 to form sub-stoichiometric tungsten selenide (WSex, x < 2) and corresponding IrSe, via reduction of WSe2. Figure 2(a) shows the Se 3d and W 4f core level spectra obtained following Ir deposition under UHV and HV conditions.

Following deposition under UHV conditions, the bulk WSe2 chemical states detected in the W 4f7/2 and Se 3d5/2 core level spectra at binding energies of 32.29 and 54.50 eV, respectively, have shifted 0.49 eV to lower binding energy from as-exfoliated WSe2. This indicates that interaction between Ir and WSe2 results in a FL shift towards the valence band maximum (VBM), which is expected as the FL of Ir (ΦIr = 5.27 eV) [31] should reside deep in the band gap of WSe2. The chemical state at high binding energy in the Se 3d core level spectrum obtained following Ir deposition under UHV and HV conditions indicates the formation of IrSe, at the Ir–WSe2 interface under either base pressure. The IrSe, and WSe2 chemical states in the Se 3d, W 4f, and Ir 4f core level spectra exhibit binding energies which are seemingly dependent upon the deposition chamber ambient. This could be related to the difference in Ir film thickness achieved under UHV and HV as well
as slight differences in reaction product stoichiometry. Reduction of WSe₂ to form sub-stoichiometric WSeₓ would result in a simultaneous reduction and oxidation of the W⁴⁺ and Se²⁻ chemical states in WSe₂, respectively. The additional chemical states detected in the W 4f and Se 3d core level spectra at binding energies of 32.05 and 54.73 eV, respectively (figure 2(a)), are in agreement with the proposed reaction mechanism.

Figure 2(b) displays the O 1s core level spectra obtained from as-exfoliated WSe₂ and following Ir deposition under UHV and HV conditions. Adventitious oxygen present in O–C and O–C–H adsorbrates is detected prior to Ir deposition due to the unavoidable brief duration of air exposure prior to loading into UHV. Following Ir deposition under UHV conditions, there are no chemical states detected in the O 1s core level spectrum below 532.0 eV that would indicate metal or chalcogen oxidation. However, following deposition under HV conditions, two additional chemical states appear with binding energies of 529.47 and 530.55 eV suggesting the formation of IrOₓ and WOₓ, respectively. Reduction of WSe₂ by Ir results in available W atoms free to react with residual oxidizing species. The electronegativity of Ir (2.20) is less than that of W (2.36) [54], which indicates iridium oxide should exhibit a chemical state in the O 1s core level spectrum with a lower binding energy than an analogous tungsten oxide species, consistent with the chemical states detected in this work. Formation of IrOₓ and WOₓ in the presence of excess oxidizing gases is thermodynamically favorable as the Gibbs free energy of formation under HV conditions, two additional chemical states detected in the O 1s core level spectrum at binding energies of 32.05 and 54.73 eV, respectively (figure 2(a)), are in agreement with the proposed reaction mechanism.

Figure 2(c) displays the Ir 4f core level spectra obtained from an Ir reference film (see Methods section for more details) and following Ir deposition on WSe₂ under both UHV and HV conditions. Both peaks comprising the reference Ir 4f doublet exhibit a significant degree of asymmetry, consistent with core-hole screening commonly observed in metallic species [46]. The intense asymmetric doublet detected with Ir 4f½/2 core level at a binding energy of 60.78 eV following Ir deposition under UHV and HV conditions indicates that metallic Ir (Ir–Ir bonding) comprises the majority of the deposited film. However, a chemical state in addition to metallic Ir is detected in the Ir 4f core level spectra following Ir deposition under HV conditions with a binding energy of 61.40 and 61.67 eV, respectively, indicating the formation of a small concentration of IrSeₓ. Unique to Ir deposition under HV conditions, a third chemical state is detected at high binding energy (62.59 eV) from the IrSeₓ state, indicating the formation of a small concentration of IrOₓ.

Thickness estimations using the attenuation of the total intensities of the Se 3d and W 4f core level spectra suggest that the thickness of the Ir film deposited under UHV conditions is 20 and 25 Å thick, respectively. This indicates Se diffusion into Ir in addition to Ir–Se interfacial bonding rather than Ir–Se bonding solely across the Ir–WSe₂ interface, similar to previous reports of sulfur out-diffusion when Ir is deposited on MoS₂ [29]. AFM images, which are discussed in greater detail in the Supporting Information, indicate Ir grows uniformly on WSe₂ regardless of deposition chamber ambient (figure S2). It is therefore reasonable to directly compare W 4f and Se 3d chemical state attenuation following Ir deposition under either base pressure to evaluate the Ir film thickness even at a thickness less than 2 nm. Intermetallic species comprised of the contact metal and chalcogenide at the metal-WSe₂ interface, such as IrSeₓ, in this case, may permit control of interface resistivity, similar to various silicides employed in MOSFET and CMOS technology [55]. The potential benefits of Ir and/or IrSeₓ present at the contact-TMD interface are discussed further in the Supporting Information.

**Cr–WSe₂: substantial oxidation of low-Φ metal and associated reaction products under HV**

The Se 3d, W 4f, and W 5pₓᵧ core level spectra obtained following Cr deposition on WSe₂ under both UHV and HV conditions are displayed in figure 3(a).

Bulk WSe₂ is detected in the W 4fₓᵧ/2 (32.40 [UHV] and 32.58 eV [HV]) and Se 3dₓᵧ/2 (54.65 [UHV] and 54.84 eV [HV]) core level spectra obtained following Cr deposition under both UHV and HV conditions despite reactions between Cr and WSe₂ in both cases. An asymmetric doublet is detected in the W 4f core level spectra following Cr deposition under HV conditions and Cr reference (see Methods section for details regarding the W reference). In addition, Se scavenging by Cr results in the formation of CrSeₓ regardless of deposition chamber base pressure, evidenced by the chemical states detected in the Se 3d core level spectra at binding energies of 54.35 (UHV) and 54.05 eV (HV). It is important to note that CrSeₓ is a member of the TMD family of layered materials with metallic transport properties and therefore CrSeₓ formation could be advantageous for charge transport across the interface [56]. Complete reduction of WSe₂ by Cr to form metallic W and CrSeₓ at the interface is thermodynamically favorable as ∆G°_{Cr,WSe₂} (~175.1 kJ mol⁻¹) [57], when Cr is deposited under HV conditions, intermediate WSeₓ (x < 2) that presumably forms as Cr scavenges Se is not stable in an atmosphere containing an excess of oxidizing gases (i.e. under HV or in air). As a result, reduced tungsten selenide (WSeₓ) oxidizes to form WOₓSeₓ, as indicated by the chemical states detected in the W 4f and Se 3d core level spectra following Cr deposition under HV conditions at binding energies of 32.38 and 54.58 eV, respectively. A decrease in binding energy of the WOₓSeₓ chemical state from that of bulk WSe₂ in the W 4f core level spectrum indi-
Cates a decrease in W oxidation state from WSe$_2$ (W$^{4+}$) to WO$_x$Se$_y$ (W$^{3+}$). It may be intuitive to expect an increase in W oxidation state resulting from oxidation of WSe$_x$ because O is significantly more electronegative than Se [54]. Cr reacting with Se atoms from WSe$_2$ will result in a reduced W oxidation state from W$^{4+}$ in WSe$_2$. In the event that each Se atom involved in the formation of CrSe$_x$ is not replaced by an oxygen atom during the formation of WO$_x$Se$_y$, it would be possible for W to undergo a net decrease in oxidation state from W$^{4+}$ in WSe$_2$ to W$^{3+}$ in WO$_x$Se$_y$. Cr exhibits a significantly smaller electronegativity (1.66) [54] than W. This suggests the Se$^{2-}$ chemical state in a CrSe$_x$ compound would appear at lower binding energy from an analogous WO$_x$Se$_y$ compound, which is consistent with the chemical states reported here. In addition, a nearly undetectable concentration of metallic W is converted to WO$_x$, evidenced by the chemical state at high binding energy (35.15 eV) in the W 4f core level spectrum obtained following Cr deposition under HV conditions. As was mentioned earlier, the formation of WO$_x$ is highly thermodynamically favorable.

Figure 3(b) displays the O 1s core level spectra obtained from exfoliated WSe$_2$ as well as WSe$_2$ following Cr deposition under UHV and HV conditions. Small concentrations of adventitious species, likely O–C and O–C–H, are detected in the O 1s core level spectrum between 532 and 535 eV following WSe$_2$ exfoliation. Concomitant chemical states corresponding with C–O and C–O–H are detected in the as-exfoliated WSe$_2$ C 1s core level spectrum (not shown here) between approximately 285 and 286 eV. This is expected due to unavoidable air exposure prior to introduction into UHV. Following Cr deposition under UHV conditions, oxygen is below the XPS detection limit. Photoelectrons originating from oxygen-based species initially present on the WSe$_2$ surface are no longer detectable due to attenuation by the Cr film. It is also possible that Cr reacts with adventitious species at the interface, however these reaction products are also below the limit of detection as there is no evidence of chromium carbide or chromium oxide in the UHV Cr 2p core level spectrum [58]. Following Cr deposition under HV conditions, a significant concentration of oxygen-based species are detected, including O–C–H (534.46 eV), O–C (532.95 eV), and WO$_x$Se$_y$ (531.1 eV), similar to the binding energy previously reported from an analogous tungsten oxycarbide (WO$_x$S$_y$).
chemical state in the O 1s core level spectrum [29]. A chemical state is also detected at 531.85 eV corresponding with the formation of Cr(OH)3 according to the intensities of the related chemical states corrected with appropriate atomic sensitivity factors, which is in reasonably close agreement with previous XPS analysis of a bulk Cr(OH)3 sample [59]. The most intense chemical state detected at 530.58 eV in the HV O 1s core level spectrum consists of a convolution of CrxOy and WOx chemical states. Transition metal oxide species can exhibit a range of binding energies between 528.0 and 531.0 eV depending on both the transition metal and its oxidation state [60].

There are substantial differences in Cr 2p core level spectra for different reactor base pressures. The Cr 2p core level spectra obtained from a Cr reference and following Cr deposition on WSe2 under UHV and HV conditions are displayed in figure 3(c). The reference Cr 2p3/2 and Cr 2p1/2 core levels (see Methods section for more details) exhibit binding energies of 574.10 and 583.41 eV, respectively, FWHMs of 0.92 and 1.45 eV, respectively, and significant degrees of asymmetry [61]. Following Cr deposition on WSe2 under UHV conditions, metallic Cr0 (Cr–Cr bonding) and CrSex are detected at binding energies of 574.05 and 575.74 eV [62], respectively. We only fit the Cr 2p3/2 core level spectrum obtained following Cr deposition under HV conditions due to parameter constraints in the fitting software. A much smaller concentration of metallic Cr is detected following Cr deposition under HV conditions coinciding with the formation of a substantial concentration of both CrxOy and Cr(OH)3 as evidenced by the chemical states detected at 575.99 and 577.21 eV, respectively, in the HV Cr 2p core level spectrum [56, 59, 60]. The four peaks which appear at higher binding energy from the CrxOy chemical state in the Cr 2p3/2 core level spectrum (each denoted by a downward pointing arrow) arise from multiplet splitting common in transition metal ions with unpaired d-electrons [59]. Multiplet splitting observed in the 2p core levels of various first row transition metal ions (Cr3+ in CrxOy in this case) is predicted theoretically [63] and the origins of which are discussed in further detail elsewhere [56, 59]. The binding energies of the chemical states associated with CrxOy and Cr(OH)3 are in much closer agreement with those of reference samples [59] when the four mul-

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**Figure 3.** XPS spectra of the (a) Se 3d, W 4f, W 5p3/2, and (b) O 1s core level spectra obtained from as-exfoliated WSe2 and following Cr deposition on WSe2 under UHV and HV conditions. (c) XPS spectra of the Ir 4f core level obtained from an Ir reference and following Ir deposition on WSe2 under UHV and HV conditions. The HV W 4f core level spectrum and associated fit data between 35 and 40 eV binding energy has been magnified (intensity × 5) to clearly display the WOx chemical state.
tiple peaks are included in fitting the Cr 2p spectrum obtained following Cr deposition under HV conditions compared with binding energies of the same chemical states when the multiplet peaks are omitted. In addition, the stoichiometry of CrO2.5 is reasonably close to Cr2O3, the most stable oxide of chromium, when multiple peaks are included in fitting the HV Cr 2p core level spectrum. If multiplet peaks are omitted from the HV Cr 2p spectrum, the stoichiometry of the chromium hydride species is far from Cr(OH)3, which is the most stable hydride of chromium. Cr(OH)3 is localized to the outermost surface as is evident when comparing normalized O 1s core level spectra obtained at two different take off angles (figure S3). The binding energy of the Cr(OH)3 chemical states in the O 1s and Cr 2p3/2 core level spectra are consistent with previous XPS analysis of a Cr(OH)3 reference sample and its formation has been observed in other transition metals via passivation upon air exposure [59]. The conversion of Cr to CrO2.5 is highly thermodynamically favorable as ∆Gf,CrO2.5 −353 kJ mol−1 and ∆Gf,Cr(OH)3 = −383 kJ mol−1 [41]. Unlike Sc, which completely oxidizes under HV conditions and following brief air exposure [29], Cr oxidation is not as thermodynamically favorable. This permits preservation of CrSe2 at the Cr-WSe2 interface despite substantial oxidation of remaining metallic Cr. The location of CrSe2 at the interface formed with WSe2 under HV conditions beneath metallic Cr, CrO2.5, and Cr(OH)3 serves as a kinetic barrier to oxidation.

**Implications of WO3 at the contact metal-WSe2 interface**

WO3 is detected at all metal-WSe2 interfaces formed under HV conditions investigated in this work. It is therefore necessary to consider the presence of WO3 at the metal-WSe2 interface as a typical device fabrication process will involve contact metal deposition under HV conditions. The binding energy exhibited by the W4+ chemical state in WO3 following Au, Ir and Cr deposition under HV conditions suggests x = 5 as these binding energies are between those previously detected from the W6+ and W4+ chemical states in WO3 and WO2, respectively [45]. In addition, WO3 detected at each metal-WSe2 interface exhibits O:W ratios between 2.6:1 and 2.7:1. Preferential WSe2 domain edge oxidation in the presence of excess oxidizing species has been predicted by DFT calculations and recently experimentally verified with STM and Scanning Tunneling Spectroscopy (STS) [44]. The same work theoretically predicted and experimentally verified metallic behavior at oxidized WSe2 domain edges. XPS obtained from WSe2 grown by chemical vapor deposition with oxidized edges indicates an O:W ratio between 2.6:1 and 2.7:1, consistent with oxygen deficient WO3 studied elsewhere [44] and also with WO3 detected in this work. WO3 detected in this work is expected to be metallic even considering the error associated with stoichiometry calculation by XPS (±0.2). Photoelectron spectroscopy has demonstrated, both previously [64] and in this work (see supporting information), the formation of shallow occupied gap states (figure S4(d)) and concomitant Fermi level shift towards the conduction band edge upon the formation of oxygen vacancies in WO3 (figure S4(a)). This results in metallic n-type conduction in amorphous WOx (a-WOx, x < 3), the structure and electronic properties of which are likely analogous with WO3 detected on WSe2 following metal deposition under HV conditions. We find that the surface of amorphous WO3 (a-WOx) exhibits an ionization energy (FL position) of 9.77 (6.90) eV, respectively, as indicated by ultra violet photoelectron spectroscopy (UPS) and XPS. However, generation of oxygen defects to form a-WOx (x < 3) results in a FL shift 0.20 eV towards the conduction band and corresponding appearance of additional chemical states at lower binding energy from the W6+ oxidation state in the W 4f core level spectrum (W5+, W4+) and higher binding energy from the intense oxide state in the O 1s core level spectrum. The high vacuum work functions of both a-WOx and a-WO3, we report here are in agreement with previous reports of WO3, serving as a p-type interlayer between channel and contact metal in WSe2-based devices [18]. In addition, the high vacuum work functions of a-WOx and a-WO3 indicate that both have potential to serve as Ohmic hole contacts in FETs employing a number of different TMDs as the channel material. In addition, the degree of p-type Fermi level shift in WSe2 can be controlled from <0.1 eV to >0.25 eV by varying WO3 coverage on the WSe2 surface (data not shown here). This work highlights the potential for enhanced hole transport in WSe2-based devices by hole injection (likely also applicable with other TMDs) via WO3 inserted at the contact-WSe2 interface. It also suggests predominant hole transport in WSe2-based devices could be a product of the interface chemistry formed between contact metal and WSe2 under HV conditions. A more detailed discussion of the expected band alignment and potential implications on electrical transport between a-WO3, a-WOx, and WSe2 can be found in the Supporting Information.

**Effects of interface and contact chemistry on metal-WSe2 band alignment**

Theories attempting to explain the FLP mechanism between a 2D semiconductor and metal include, but are not limited to, the formation of gap states by decaying metal wavefunction into the semiconductor [65, 66] and also by defects and/or disorder at the metal/semiconductor interface [67]. Regardless of the mechanism, the formation of interface gap states play a critical role in FLP between metal and semiconductor [32]. McDonnell et al found that defects present in MoS2 provide preferential conduction pathways across the metal-MoS2 interface [27]. It is therefore possible that the defective nature of TMDs plays a critical role in FL realignment upon metallization of a TMD. In addition, strong orbital hybridization of the transition metal in the TMD and contact metal near
the metal-TMD interface has been predicted by DFT [10, 32]. This facilitates charge redistribution across the interface and therefore influences the position of the pinned FL relative to the underlying bulk TMD. The Mo $d$-orbital contributes the majority of density of states near the conduction band minimum (CBM) of MoS$_2$ [32], hence the tendency for FLP near the MoS$_2$ CBM as strongest $d$-orbital overlap occurs there. Analogous FLP may occur in WSe$_2$ near the VBM as the $W$ $d$-orbital contributes the majority of the density of states near the VBM of WSe$_2$ [10].

Figure 4 displays representative band diagrams and corresponding FL position of as-exfoliated WSe$_2$ ($\Phi_{\text{initial}}$, purple) and subsequent FL shift following metal deposition under UHV conditions ($\Delta \Phi$, light blue). The position of the FL prior to metal deposition is determined from the valence band spectra (figure S4), which are discussed further in the Supporting Information. The degree of FL shift resulting from metal deposition is determined by the corresponding binding energy shift of the bulk WSe$_2$ chemical states in the W $4f$ and Se $5d$ core level spectra following metal deposition. A FL shift towards the VBM will be denoted as positive. The FL is positioned 0.97, 0.87, and 0.89 eV from the VBM within the band gap of WSe$_2$ prior to Au, Ir, and Cr deposition, respectively. Assuming bulk WSe$_2$ exhibits an ionization energy of 5.33 eV [68], these values indicate $\Phi_{\text{initial}}$ of 4.36, 4.46, and 4.44 eV prior to Au, Ir, and Cr deposition, respectively, and are consistent with n-type behavior [28]. The error associated with the Fermi level position following metal deposition is calculated to be ±0.11 eV (95% confidence interval). This is derived by considering the error propagation associated with assuming the magnitudes of the electron affinity and band gap according to previous work and also from deducing the Fermi level position prior to and following metal deposition by XPS.

Thus, Au deposition should result in a +0.77 eV (p-type) FL shift considering $\Phi_{\text{Au}} = 5.13$ eV [31], however a +0.27 eV shift is detected. Less severe band bending induced by Au deposition under either UHV or HV conditions is consistent with VW-type Au growth on WSe$_2$ results in Au clusters with significantly smaller $\Phi$ than expected of bulk, polycrystalline Au. Au nanoparticles on the order of 5 nm in diameter suspended on a Si(111) substrate can exhibit a $\Phi$ as small as 3.4 eV, with $\Phi$ approaching $\Phi_{\text{Au,bulk}}$ as particle size increases [49]. It is also possible that orbital hybridization near the interface accompanied by charge redistribution results in FLP and therefore an anomalously low $\Phi_{\text{Au}}$. The 0.53 eV electron Schottky barrier measured in this work is in relatively close agreement with previous DFT predictions of electron Schottky barrier magnitude for Au contacts to monolayer (0.58 eV) and bilayer (0.66 eV) WSe$_2$ [8]. Nonetheless, this highlights the complex nature of FL realignment even at a van der Waals interface.

Similar to Au, Ir causes p-type FL shift (+0.50 eV), 0.24 eV smaller than expected considering the initial FL position of WSe$_2$. Unlike Au, the binding energy of the chemical state corresponding with metallic Ir$^0$ in the Ir $4f$ core level spectra obtained following deposition under UHV conditions is in close agreement with that of the Ir reference. Therefore, additional gap states presumably arising from IrSe$_2$ contribute to the resulting FL position and larger than expected hole Schottky barrier for an Ir contact on WSe$_2$.

Contrary to the electron Schottky barrier expected for a pristine Cr contact on WSe$_2$ ($\Phi_{\text{Cr}} = 4.50$ eV [31]), Cr deposition under UHV conditions results in a +0.41 eV FL shift consistent with $\Phi = 4.92$ eV and a substantial hole Schottky barrier. It is possible that a mixture of metallic W ($\Phi_{\text{W}} = 4.55$ eV) [31] and Cr$_x$Se$_y$ ($\Phi_{\text{CrSe}} = 5.15$ eV) [68] present at the Cr-WSe$_2$ interface could result in a similar FL position. Although no Cr$_4$O$_7$ is detected following Cr deposition under UHV conditions, the electronic structure of chromium oxide varies substantially with composition [68–70] and therefore is likely to appreciably affect the FL position when Cr is deposited under HV conditions. Recently, n-type conduction has been reported for Cr contacts (HV) to multi-layer WSe$_2$-based devices in contrast with the band alignment obtained in this work between WSe$_2$ and Cr deposited under UHV conditions [71]. This highlights the need to understand the role of the interface on contact performance in TMD-based devices.

It is important to reiterate that experiments discussed here were performed on bulk WSe$_2$ crystals. However, single or few layer TMDs are most commonly employed as the channel material in device structures. The band structure of mono and few layer TMDs, and therefore the band alignment formed with various contact metals, can be quite different from that of the bulk analog. Monolayer (bilayer, bulk) WSe$_2$ exhibits a band gap of 2.2 (1.8, 1.3) ±0.1 eV as measured by STS [44]. Angle-resolved photoemission spectroscopy indicates the VBM of monolayer (bilayer, bulk) WSe$_2$ reside 1.8 (1.5, 1.1) eV from the Fermi level [72]. Error in photoemission measurements manifests in both the resolution of the spectrometer and also the method by which the VBM is extracted, typically on the order of ±0.03–

![Figure 4. Fermi level position of as-exfoliated WSe$_2$ samples (solid purple) and following Au, Ir, and Cr deposition under UHV conditions (dotted light blue) according to initial valence band spectra and WSe$_2$ core level shifts following metal deposition.](image-url)
0.04 eV [73]. Yeh et al. [72] report a spectrometer resolution of ±0.1 eV but none associated with the VBM extraction method employed. Therefore, an error of ±0.13 to ±0.14 eV associated with the ARPES derived VBM according to WSe$_2$ layer number is suspected. Together, these STM and ARPES measurements suggest a relatively unperturbed conduction band minimum (~0.3 eV offset from Fermi level) and increasingly large ionization energy and therefore bandgap with decreasing number of WSe$_2$ layers. The magnitude of electron Schottky barriers between the same contact metals deposited under analogous conditions as were studied in this work and mono or few-layer WSe$_2$ are therefore expected to be similar to those reported here. However, associated hole Schottky barriers are likely to be much greater in magnitude in the mono, bi-, and tri-layer cases due to substantial increase in associated ionization energy.

DFT predicts a direct proportionality between the degree of contact metal-TMD d-orbital overlap and interface transport properties [10, 23, 24]. Parameters such as interatomic distance and bond energy between contact metal and chalcogen are proposed as predictive factors for chemical and electrical properties of various metal-TMD interfaces. However, additional compounds arising from reactions in the vicinity of the interface will perturb orbital overlap further, resulting in different chemical and electrical interface properties. The FL shifts reported here provide evidence that interfacial reaction products in addition to the inherently defective nature of WSe$_2$ contribute to anomalous FL positions detected for various contact metals on WSe$_2$ and therefore must be considered in engineering low resistance Ohmic contacts.

**Conclusions**

This work elucidates variation in interface chemistry and contact metal chemistry with deposition chamber ambient for Au, Ir, and Cr deposited on WSe$_2$. In all cases, thermodynamics can reliably predict favorable metal-WSe$_2$ and metal-background gas reactions. Electronegativity trends are employed to correlate chemical states in complicated XPS spectra and accurately deduce chemical and stoichiometric properties of the metal-WSe$_2$ interface as well as the contact metal. Notably, Ir and Cr scavenge Se from WSe$_2$ to form interfacial intermetallics (IrSe$_x$, CrSe$_y$) and therefore a covalent interface with WSe$_2$ under both UHV and HV conditions, while Au forms a van der Waals interface irrespective of reactor base pressure. WO$_x$ forms at the metal-WSe$_2$ interface under HV conditions regardless of contact metal and likely improves interface transport properties due to the conductive nature of sub-stoichiometric tungsten oxide. Interfacial intermetallics likely generate gap states, contributing to FLP and unexpectedly large hole and electron Schottky barriers in the cases of Ir and Cr, respectively, deposited under UHV conditions. These results highlight the complex nature of the metal-WSe$_2$ interface chemistry, its dependence upon deposition chamber base pressure, and the implications it can have on band alignment between metal and WSe$_2$.

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**Supporting information**

Stoichiometry calculation method; Direct comparison of line shape exhibited by Au 4f core level spectra from reference Au and Au deposited on WSe$_2$ under UHV and HV conditions via normalization and binding energy shift; Variations in growth mechanism of Au, Ir, and Cr on WSe$_2$ with reactor base pressure as indicated by AFM images and corresponding RMS roughness values; Binding energies of W 4f and Se 3d core levels from as-exfoliated WSe$_2$ crystals; Angle resolved O 1s core level spectra (Cr deposition under HV); Expected band alignment between WO$_x$ and WSe$_2$ and implications on interface transport properties; Fermi level position prior to and following metal deposition under UHV conditions and its relation to the metal-WSe$_2$ interface chemistry.

**Conflict of interest**

The authors declare no competing financial interest.

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