Patterning Superatom Dopants on Transition Metal Dichalcogenides

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Supporting Information

ABSTRACT: This study describes a new and simple approach to dope two-dimensional transition metal dichalcogenides (TMDCs) using the superatom Co6Se8(PEt3)6 as the electron dopant. Semiconducting TMDCs are wired into field-effect transistor devices and then immersed into a solution of these superatoms. The degree of doping is determined by the concentration of the superatoms in solution and by the length of time the films are immersed in the dopant solution. Using this chemical approach, we are able to turn mono- and few-layer MoS2 samples from moderately to heavily electron-doped states. Moreover, we show that the superatom doping can be patterned on specific areas of TMDC films. To illustrate the power of this technique, we demonstrate the fabrication of a lateral p–n junction by selectively doping only a portion of the channel in a WSe2 device. Finally, encapsulation of the doped films with crystalline hydrocarbon layers stabilizes their properties in an ambient environment.

KEYWORDS: Transition metal dichalcogenide, superatom, chemical doping, lateral junction, encapsulation

In this letter we describe a new chemical strategy to chemically dope two-dimensional (2D) transition metal dichalcogenides (TMDCs) using a metal chalcogenide molecular cluster as the dopant. Metal chalcogenide molecular clusters are attractive building blocks for making new electronic materials because of their diversity and atomic definition.1,2 They can act as nanoscale building blocks (termed superatoms here), combining with C60 and other electron-poor building blocks to form superatomic solid-state compounds.3–5 The electronic states and the capability of doping can be easily tuned in superatoms by changing the metal atoms, the chalcogen atoms, and the capping ligands.5–7 Doping plays a vital role in electronic materials as an effective method to modulate the electrical properties of materials. Whereas traditional 3D semiconductors are doped by introducing atomic substitutions in the crystalline lattice,8 doping of 2D materials has been achieved through surface charge transfer. For instance, potassium metal,12 benzyl viologen,13 and silicon nitride (SiN₄)14 have been used to dope TMDCs such as MoS₂ and WSe₂ to the degenerate level. Here we explore how an electron-rich metal chalcogenide molecular cluster can be used as a tunable and controllable surface dopant for semiconductor TMDCs via charge transfer. To demonstrate the utility of this method, we fabricate a p–n junction by spatially confining the area of the WSe₂ that is doped. Lateral p–n junctions in WSe₂ have been created using electric field effects from multiple gate electrodes on the channel.15,16 We further find that we can passivate and stabilize the doped films from the ambient by covering them with a self-assembled hydrocarbon layer.

In this study, we used the electron-rich octahedral superatom Co₆Se₈(PEt₃)₆ as an electron dopant3 for MoS₂ and WSe₂. To study the doping process, we fabricated back-gated field-effect transistors (FETs) from mechanically exfoliated mono- or few-layer MoS₂ and WSe₂ with channel lengths of 1–2 μm.17 To create the devices we first exfoliated the TMDC layers to a Si substrate, whose surface is passivated with a 285 nm thick layer of thermally grown SiO₂ and then determined the exact number of MoS₂ and WSe₂ atomic layers by photoluminescence (PL) and Raman spectroscopy.18–20 We patterned source and drain electrodes on the TMDC films using e-beam lithography. We created Al/Cr/Au (40/5/40 nm) electrodes for MoS₂21 and Pd/Au (20/30 nm) electrodes for WSe₂.22 To dope the 2D semiconductor, we immersed the device into a toluene solution of Co₆Se₈(PEt₃)₆ (0.01–1 mg/mL) for 10 min, followed by rinsing with fresh toluene. Figure 1a displays a schematic of a superatom-doped device. Atomic force microscopy (AFM) strongly suggests that the molecular cluster is adsorbed on the surface of the van der Waals materials (Figure S1). For instance, the trilayer WSe₂ film was ~2 nm in thickness before
doping, and the surface roughness became ∼1 to 2 nm upon superatom adsorption, corresponding to the diameter of the superatoms. The electrical properties of FETs were measured at room temperature in a N$_2$-filled glovebox for each TMDC film, before and after superatom doping.

Figure 1b displays typical transfer characteristics for a trilayer MoS$_2$ back-gated FET before and after superatom doping. The as-prepared MoS$_2$ device exhibits n-type transistor characteristics with a large on/off current ratio (∼10$^5$) before doping. The carrier density of the pristine sample is estimated to be $2.0 \times 10^{12}$ cm$^{-2}$ at $V_g = 0$ V from the measured threshold voltage ($V_{th}$). Compare to this pristine device characteristic, the transfer characteristic of the channel after immersion in superatom solution exhibits remarkable changes. First, the conductance becomes more than a factor of 2 higher than that of the pristine one. Second, the transfer characteristic exhibits a weak n-type response to the gate voltage, without any apparent “off” current, indicating that the superatoms donate their electrons and heavily dope the MoS$_2$ film. The large number of carriers introduced by the superatoms at zero gate bias implies that charge transfer has occurred when the superatoms adsorb to the surface. We used Raman spectroscopy to determine if $A_{1g}$ mode of MoS$_2$ shows any change upon the superatom doping and to further understand the charge transfer, but we found that the laser interfered with the superatom adsorbates.

While the electron-rich superatom doping turns the pristine moderate n-type MoS$_2$ FET into heavily n-doped channel, similar chemical treatment also affects p-type WSe$_2$ FETs. Figure 1c displays how superatom adsorption affects the p-type WSe$_2$ layers. As shown in the black curve in this plot, the majority of WSe$_2$ FET devices with Pd source-drain contacts show typical p-type semiconductor characteristics before molecular cluster doping. Once the pristine device is immersed in the Co$_6$Se$_8$(PET$_3$)$_6$ solution, however, the transfer characteristics of WSe$_2$ exhibit strong electron transporting (n-type) behavior (red curve in Figure 1c). This change is consistent with injection of electrons into the WSe$_2$ layer from the molecular cluster. The shift in current–voltage characteristics at zero gate voltage implies that at equilibrium, the electron is transferred to the WSe$_2$ layer. We note that even after superatom doping, the current ($I_{ds}$) still depends strongly on the gate voltage with an excellent on/off characteristic (∼10$^5$). This is a strong contrast compared to previous chemical doping studies where doped WSe$_2$ devices exhibited degenerate doping with a suppressed on/off ratio. The difference between superatoms and these stronger dopants is in their redox potentials; the first redox potential of the Co$_6$Se$_8$(PET$_3$)$_6$ superatom (−0.4 eV, relative to the standard hydrogen electrode (SHE)) lies between the conduction band edge (−0.7 eV vs SHE) and the valence band edge (0.5 V vs SHE) of WSe$_2$. We therefore anticipate that superatoms donate electrons to WSe$_2$ to compensate hole carriers introduced by applied gate field in the WSe$_2$ FETs.

The device characteristics and the degree of doping are directly linked to both the time that WSe$_2$ is exposed to the superatom solution and the concentration of the superatom solution used for doping. When using a concentrated doping solution (1 mg/mL), the hole conductance of the WSe$_2$ decreases immediately, while the electron conductance increases over time and reaches a maximum value within 10 min of immersion time (Figure S2a). However, when using a lower doping solution concentration (0.1 mg/mL), the transfer
characteristics of a bilayer of WSe₂ maintains an ambipolar transport behavior, even for exposure times that saturate the doping level (Figure S2b). Similarly, the electron conductance increases as the concentration of superatom solution increases. Figure 1d depicts the linear relationship between the concentration of cluster dopants in solution and the 2D sheet carrier density ($n_{2D}$) of WSe₂ after cluster doping. This could be explained by an equilibrium between clusters on the TMDC surface and clusters in solution. When immersing the doped device (Figure S2b) in toluene solvent, the attached clusters dissociate from the surface, resulting in dedoping of WSe₂ (Figure S2c). These results demonstrate that we can controllably dope the WSe₂ films using electron-rich superatoms.

By combining this doping process with a lithographic mask, we can dope selected areas of a film of WSe₂. Using this local doping approach, we created a lateral p–n junction from a WSe₂ film. We first fabricated the mask from a few-layer hexagonal boron nitride (h-BN) flake. We exfoliated h-BN flakes with a thickness of ~10–30 nm on a silicon wafer with thermally grown SiO₂ on its surface. The deposited h-BN samples were patterned via e-beam lithography followed by inductively coupled plasma etching using a gas mixture of O₂ and CHF₃. We then transferred the patterned h-BN mask onto the target WSe₂ flake (4 nm thick) using a polypropylene carbonate-coated polydimethylsiloxane (PPC–PDMS) stamp. By positioning the patterned h-BN, we introduced dopants through the opening over the channel in the device. To complete the device we created the source and drain electrodes through the h-BN windows (Figures 2a and S3a).

Figure 2a shows a schematic and an optical image of the fabricated multiterminal device, including the fully h-BN-protected, partially h-BN-protected, and unprotected areas. This particular device made from a few-layer WSe₂ films exhibits the ambipolar transport characteristics. As shown in Figure 2b, the unprotected device is very electron-doped, compared to the fully h-BN-protected one, indicating doping by superatoms. It should be noted that the doping effect is less than the result shown in Figure 1c at the same concentration of cluster solution (1 mg/mL) because we use 4 nm thick WSe₂.
for this experiment. In addition, the current–voltage (I_d−V_d) curves for both devices are symmetric in both forward and reverse bias. Rectification ratios at all gate voltages are smaller than 15 at V_d = 1.5 V (Figure S3c,e). Using the selected-area doping method employing patterned h-BN encapsulation, we can create a lateral p–n junction device (indicated by dashed lines in the optical image in Figure 2a). Figure 2c displays the I_d−V_d characteristics of the junction at various gate voltages after doping. We observe a remarkable change of the I_d−V_d curve from symmetric to diode-like behavior at gate voltages ranging from 20 to 40 V (Figure 2d), yielding a rectification ratio of 3 orders of magnitude at V_d = 1.5 V. In addition, the ideality factor of the p–n junction is ~1.6, estimated from the I_d−V_d curve at V_g = 30 V.29 This value deviates from that of an ideal diode presumably due to recombination occurring at the WSe2/SiO2 interface. This diode behavior is similar to the previous result from heterojunction of monolayer WSe2 and MoS2.30 We also note that our observed rectification is more efficacious than the lateral MoS2 p–n junction formed by AuCl3 doping for the dark current.31 When the gate voltage is not in the range resulting in a p–n junction, the device forms a p–p junction (V_g < 0 V) or n–n junction (V_g > 40 V) (Figure 2e). In this case, the device exhibits rather symmetric I_d−V_d curves (Figure 2c) as expected from the band alignment diagram in Figure 2e.

As a control experiment, we built a device in which the WSe2 channel is fully covered by h-BN and measured its electrical properties before and after immersion in a solution of the dopant Co6Se8(PEt3)6. We find that h-BN is an efficient barrier to doping of the WSe2: the device characteristics are essentially unaffected by the doping process (Figure S3b), confirming our hypothesis that h-BN prevents surface charge transfer to WSe2.

We also tested the environmental stability of the doped WSe2 FETs as the superatoms are somewhat sensitive to ambient conditions.7 Figure S5a displays the change in the device characteristics when we exposed the doped device to ambient conditions. We observe that the p-type transport characteristics of the WSe2 are completely restored after ~11 h. We speculate that the ability of the superatom to donate electrons as a dopant disappears as it is oxidized in air.

To improve the lifetime of our molecular cluster-doped WSe2 FETs, we deposited a thin passivation layer of tetratetracontane (TTC, C_{44}H_{90}, Figure 3a).32 We selected TTC because it can be thermally evaporated at low temperature (~50 °C), as a passivation layer. The relatively low temperature process we used prevents damages to our devices that would arise from higher temperature processing.33 Figure 3b confirms that evaporation of the 150 nm thick layer of TTC does not affect the device characteristic of the doped WSe2. The doped WSe2 FET protected with a TTC layer maintains its original n-type semiconductor behavior after exposure to the ambient for 10 min, while the unpassivated device shows significant V_0 shift (from 18 to 37 V) over the same time period (Figure S5). For both devices, we extract the conductance value at gate voltage +60 V and plot it as a function of air exposure time in Figure 3c. Overall, we observe that TTC-passivated devices degrade much slower than unprotected ones.

In summary, we have demonstrated a new method to controllably dope MoS2 and WSe2 films. We find that the superatom Co6Se8(PEt3)6 is able to transfer electrons to the films. Upon doping, WSe2 layers change their semiconductor characteristics from hole transporting to electron transporting. As a demonstration of the power of this technique, we fabricated a p–n junction by doping a portion of the channel in the WSe2 device. We can use crystalline hydrocarbon layers to encapsulate the doped films and improve their ambient stability. This general method should be applicable to a variety of different TMDCs and superatoms with tailored electrochemical potentials.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b01152. Experimental methods, AFM characterization of the superatom-doped WSe2 device, and additional figures (PDF)

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**Notes**

The authors declare no competing financial interest.
Acknowledgments

Funding for this research was provided by the Center for Precision Assembly of Superstrectic and Superatomic Solids, an NSF MRSEC (Award Number DMR-1420634), by FAME, one of six centers of STARnet, a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the Air Force Office of Scientific Research (Award Number FA9550-14-1-0381). Use of the Shared Materials Characterization Laboratory (SMCL) and Nanofabrication Laboratory (NFL) made possible by funding from Columbia University. J.Y. thanks the Kwanjeong Educational Foundation for support. C.-H.L. acknowledges the support from Basic Science Research Program (NRF-2014R1A1A2055112) through the National Research Foundation (NRF) funded by the Korean Government Ministry of Education. D.B. was supported by a Banting postdoctoral fellowship from the Natural Sciences and Engineering Research Council of Canada (NSERC) and by a postdoctoral fellowship from Fonds de Recherche du Québec—Nature et technologies (FRQNT).

References

(24) A control experiment was conducted to check if the organic solvent would affect the device characteristics. It should be noted that the threshold voltage (Vth) does not show the noticeable change when the device was immersed in toluene up to 10 min, although the hole current is slightly decreased.
(25) The 2D electron sheet density of n-doped WSe2 devices can be estimated by n_{2D} = (qR_s)\cdot 4, where q is the electron charge, R_s is the sheet resistance at gate voltage +60 V, and μ is the field-effect mobility. The electron mobility was extracted from μ = (L/2WC_SV_{th})(dI_{DS}/dV_G), where L and W are the channel length and width and C_S is the gate oxide capacitance per unit area. The extracted values of μ are 0.15 cm²/V·s and 4.1 × 10^{-3} cm²/V·s, respectively, for the doped WSe2 with a concentrated (1 mg/mL) doping solution. Interestingly, the extracted mobilities for doped devices (in Figure 1d and S2b) showed similar values ~0.1 cm²/V·s, independent of the doping concentration.
(29) We calculated the ideality factor from the Shockley diode equation: I_D = I_0 \cdot \exp(V_D/V_T)^{1/m}, for V_D > 100 mV, where I_0 is the reverse bias saturation current and V_T is the thermal voltage (25.85 mV at 300 K). The ideality factor, m, is extracted from the slope by plotting ln(I_D) versus V_D at forward bias.
(33) We deposited hydrocarbons instead of applying the h-BN layer on top of the superatom-doped device because h-BN cannot serve as a passivation material due to the top-contacted device architecture.