Synthetic Lateral Metal-Semiconductor Heterostructures of Transition Metal Disulfides

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ABSTRACT: Lateral heterostructures with planar integrity form the basis of two-dimensional (2D) electronics and optoelectronics. Here we report that, through a two-step chemical vapor deposition (CVD) process, high-quality lateral heterostructures can be constructed between metallic and semiconducting transition metal disulfide (TMD) layers. Instead of edge epitaxy, polycrystalline monolayer MoS₂ in such junctions was revealed to nucleate from the vertices of multilayered VS₂ crystals, creating one-dimensional junctions with ultralow contact resistance (0.5 kΩ·μm). This lateral contact contributes to 6-fold improved field-effect mobility for monolayer MoS₂, compared to the conventional on-top nickel contacts. The all-CVD strategy presented here hence opens up a new avenue for all-2D-based synthetic electronics.

Functional heterostructures are indispensable building blocks for modern electronics and optoelectronics. With recent advancement in flexible and deformable electronics, an emerging requirement arises in thinning down the host materials in these heterostructures to fulfill such targets. Two-dimensional (2D) transition metal dichalcogenide (TMD) layers, as a class of inorganic van der Waals (vdW) materials, can be potential candidates for building such ultrathin heterostructures. Diverse TMD layers, as well as other 2D materials, have been isolated and combined into heterostacks, termed vdW heterostructures, to serve as tunneling transistors, light-emitting diodes, photodetectors, and photovoltaic cells. Moreover, the lattice-structure similarity of all TMDs, combined with their tunable electronic properties, has enabled them to epitaxially stitch and integrate in the 2D plane, forming lateral heterostructures of ultimate thinness and comparable functionalities to their vdW heterostructure analogues.

While significant progress has been made recently in the chemical vapor deposition (CVD) of edge-epitaxy lateral TMD heterostructures and superlattices, most of the prior works focused on semiconductor-semiconductor junctions that have diode-like rectifying properties. It remains an open question whether such edge-epitaxy schemes can be extrapolated to other types of lateral heterostructures, one of which, being a key component in modern electronics and optoelectronics, is the metal-semiconductor TMD junctions. Although fundamental understandings on such one-dimensional (1D) “Schottky” junctions are still limited, they have been predicted to have unique depletion profiles that contributes to ultralow-resistance contacts, a property greatly desired for high-performance 2D electronics. However, CVD growth of lateral metal-semiconductor TMD heterostructures is still challenging because of the chemical instability of metallic TMDs, and the unknown surface/edge energetics of both, leading to either in-phase alloying, vertical stacking, or coplanar stitching. It is hence imperative to uncover, understand, and finally control their growth behaviors to achieve desirable configurations of metal-semiconductor TMD heterostructures.

Here we take VS₂ and MoS₂, the representative metallic and semiconducting TMDs, respectively, as an example to demonstrate that CVD techniques can be used to synthesize and stitch the two complementary materials to form lateral heterostructures. Interestingly, polycrystalline monolayer MoS₂ in such junctions was revealed to nucleate from the vertices of multilayer VS₂ crystals, rather than epitaxially grow from their...

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edges. The obtained lateral VS₂−MoS₂ heterostructures exhibit remarkable contact properties with Schottky barrier height as small as ∼30 meV, contributing to a 6-fold improved field-effect mobility for monolayer MoS₂, compared to conventional on-top nickel contacts. This opens up an avenue for all-TMD-based synthetic 2D electronics.

Figure 1a,b shows the atomic models of VS₂ and MoS₂ that crystallize in 1T and 2H phases, respectively, whose electronic structures are schematically illustrated in Figure 1c,d. Although VS₂ is a metal and MoS₂ is a semiconductor by nature, they have similar sulfur–metal–sulfur sandwiched layers and close in-plane lattice periodicities of ∼0.32 nm. This offers the possibility that the two TMD materials can be parallally stitched with minimal strain at the 1D interface. In our experiment, the construction of such lateral junctions involves two sequential steps: synthesis of VS₂ nanosheets and growth of MoS₂ nanosheets. This two-step CVD process offers precise control for an abrupt transition from presynthesized VS₂ to the second-step grown state (0.15 nm) (Figure S3g). This can be directly seen, MoS₂ tends to grow outward from and encompass the pregrown VS₂ nanosheets. This two possible growth mechanisms mediated either by the edge or the surface of the pregrown VS₂ nanosheets.

The CVD of individual VS₂ and MoS₂ nanosheets was performed at first, whose methodologies are similar to our previous reports (see Figure S1 and S2 for more details). As shown in Figure 2a, the VS₂ nanosheets manifest unique half-hexagonal shapes and uniform optical contrast, which can be associated with homogeneous thicknesses of 5−7 nm (Figure S3c), as measured by atomic force microscopy (AFM). We note that although the VS₂ prepared by such CVD methods is slightly nonstoichiometric, its 1T-phase framework persists along with the high electrical conductivity, hence exerting no influence on the construction of metal-semiconductor heterostructures with MoS₂. The morphology of MoS₂ nanosheets, on the other hand, is different from that of VS₂ in that the grain structures are more complicated with triangular and polygonal outlines (Figure 2b), and the sheet thickness can be down to monolayer (Figure S3f).

With the optimized growth of individual VS₂ and MoS₂ nanosheets, their 2D heterostructures can be readily achieved by the two-step growth process. Figure 2c shows a typical optical image of the lateral MoS₂−VS₂ heterostructure. As can be seen, MoS₂ tends to grow outwards from and encompass the pregrown VS₂ nanosheet, tuning the optical contrast of VS₂ from purple to blue (Figure 2c). Sharp optical contrast is observed between VS₂ and MoS₂ along the edges of VS₂, indicating that the MoS₂ grown in the second step laterally stitches to VS₂. The parallel stitching was further evidenced under higher spatial resolution by AFM (Figure S3), SEM (Figure 2f) and transmission electron microscopy (Figure S4) studies, together with more detailed discussions in the Supporting Information.

One significant feature for the VS₂ region after MoS₂ growth is the higher surface roughness (2.3 nm) compared to its as-grown state (0.15 nm) (Figure S3g). This can be directly observed in the SEM image of the lateral heterostructure (inset in Figure 2f), showing nanosized dots on VS₂ surface that indicates formation of nanoparticles. Further Raman and photoluminescence characterizations (Figure 2g,h) reveal signals of multilayered, particulate MoS₂ on the VS₂ region. Such granular rather than layered growth of MoS₂ on VS₂ surface can be attributed to the surface roughening of VS₂ under a high-temperature oxidative atmosphere (Figure S3d). Nevertheless, the sharp switching of MoS₂ morphologies divided by the VS₂ edges suggests an effective decoupling of the MoS₂ growth on and surrounding the VS₂ flakes.

The commonly observed star shapes of MoS₂ surrounding VS₂ flakes is a strong indication that the MoS₂ rims are not single crystalline (Figure S5). This is in contradiction with an edge epitaxy behavior where the surrounding MoS₂ should have had its lattice orientationally aligned with the internal VS₂ crystals. Second harmonic generation (SHG) imaging was then
employed to uncover the domain orientations and the grain boundaries (GBs) within MoS₂. Figure 3a is the optical image of a lateral MoS₂—VS₂ heterostructure being characterized. Corresponding SHG images of the total intensity, as well as the y- and x-polarized SHG emissions, respectively, from the heterostructure. Orientation distribution of surrounding MoS₂ domains. Arrows indicate armchair orientations of corresponding domains. (f) Schematic illustration of a possible stitching growth mechanism of MoS₂ initiated from the vertices of a presynthesized VS₂ flake. Blue lines mark the intermediate growth fronts.

As such, the orientation distribution of surrounding MoS₂ domains was calculated and plotted in Figure 3e, explicitly revealing the polycrystalline nature. Arrows were superposed on the image to mark out the armchair directions of MoS₂, which surprisingly point from the nearest VS₂ vertices to the outmost vertices of the corresponding MoS₂ domains. The GBs, on the other hand, were found to originate from VS₂ vertices and orientationally bisect neighboring two arrows. We note that such grain structures are commonly observed in all the lateral MoS₂—VS₂ heterostructures (Figure S6), confirming a universal growth mechanism. While the mirror-symmetric GBs can be explained by kinetic models that consider the interplay between growth front and GB propagation, the above SHG results suggest that the star-shaped MoS₂ in our case is due to multicenter nucleation from the VS₂ vertices, instead of epitaxy from VS₂ edges. For this, a schematic model is proposed in Figure 3f illustrating the nonepitaxial growth of MoS₂ surrounding VS₂, in consistency with all the observed grain structure characteristics.

Although the VS₂ flakes become rougher after MoS₂ growth, their resistances were found to show negligible changes compared to as-grown ones (Figure 4b and Table S1). This allows us to exploit them as the lateral contacts to monolayer MoS₂ for field-effect transistor (FET) applications. Figure 4c compares the output characteristics of MoS₂ devices with VS₂ and Ni contacts, both of which exhibit linear I_DS−V_DS relationships, indicating their Ohmic-like contact behavior. Remarkably, with the same V_G and V_DS applied, the I_DS for the VS₂-contacted device are consistently 6 times higher than that of the Ni-contacted counterpart. In terms of their transfer characteristics (Figure 4d), the two devices show nearly identical threshold voltages (~35 V), subthreshold swings (2.5 V dec⁻¹), and on/off ratios (10⁶). This indicates that the two MoS₂ channels are essentially the same in the doping level and the density of gap states, and the improved on-state currents for the VS₂-contacted device can be exclusively attributed to the decreased contact resistance. As expected, the field-effect mobility (μ_FE) for the VS₂-contacted device reaches as high as 35 cm² V⁻¹ s⁻¹, at least six time higher than that of the Ni-contacted counterpart (5.5 cm² V⁻¹ s⁻¹).

![Figure 4](https://example.com/figure4.png)

Figure 4. Electrical characterizations of the lateral VS₂—MoS₂ heterostructures. (a) Schematics showing monolayer MoS₂ field-effect transistors (FETs) with the lateral VS₂ contacts (upper) and vertical Ni contacts (lower). (b) I_DS−V_DS characteristics of a typical VS₂ electrode before and after MoS₂ growth. (c) I_DS−V_DS characteristics of MoS₂ devices with VS₂ and Ni contacts, with V_G ranging from 0 to 50 V. (d) I_DS−V_G characteristics of both types of devices in linear (dashed) and logarithmic scales (solid), respectively. (e) Schottky barrier heights (Φ_p) of VS₂- and Ni-contacted MoS₂ devices, as a function of V_G. Dashed arrows indicate flat-band Φ_p. (f) Contact resistances for MoS₂ FETs with VS₂ and Ni contacts, at different V_G.
Temperature-dependent electrical measurements (Figure S7) were then performed to extract the Schottky barrier heights (Φ_b) of both types of MoS_2 devices. Figure 4e compares their extracted Φ_b at different V_G. Whereas the flat-band Φ_b for conventional Ni–MoS_2 contacts is ~163 meV, similar to previously reported values, the Φ_b for our lateral VS_2–MoS_2 contacts is as small as 30 meV, which is one of the lowest barrier heights that outperforms many low-work-function metal contacts. Furthermore, contact resistances (R_C) of the two typical devices were extracted from four-probe measurements (Figure S8) and plotted in Figure 4f. The R_C for lateral VS_2–MoS_2 contacts was found to be ~20 Ωμm at V_G = 50 V, which is more than ten times smaller than that of Ni–MoS_2 contacts (8640 Ωμm). Note that on-top metal contacts generally result in R_C of several kΩμm. Evidently, the lateral contact scheme based on our VS_2–MoS_2 heterostructures dramatically lowers the contact resistance and effectively boosts the performance of MoS_2 FETs, close to that with phase-engineered 1T-MoS_2 and 1T’-MoTe_2 contacts.

In summary, we have successfully demonstrated the growth of lateral MoS_2–VS_2 heterostructures using a two-step CVD strategy. We found that the latter growth of MoS_2 surrounding the presynthesized VS_2 flakes was mediated by the VS_2 vertices rather than the edges, leading to polycrystalline MoS_2 rims that laterally stitch the VS_2 flakes. Such coplanar VS_2 contacts were proven by electrical measurements to offer a low-barrier 1D interface to the semiconducting MoS_2 monolayer, improving the field-effect mobility and contact resistance by nearly 1 order of magnitude, as compared to the conventional on-top metal contacts. We postulate that the all-CVD strategy presented herein will open up an avenue for TMD-based synthetic 2D electronics in a straightforward, scalable and cost-effective way.

**ASSOCIATED CONTENT**

Supporting Information The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07806.

Experimental details and supporting figures (PDF)

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Notes

The authors declare no competing financial interest.

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