Structural Flexibility and Alloying in Ultrathin Transition-Metal Chalcogenide Nanowires

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ABSTRACT: Metallic transition-metal chalcogenide (TMC) nanowires are an important building block for 2D electronics that may be fabricated within semiconducting transition-metal dichalcogenide (TMDC) monolayers. Tuning the geometric structure and electronic properties of such nanowires is a promising way to pattern diverse functional channels for wiring multiple units inside a 2D electronic circuit. However, few experimental investigations have been reported exploring the structural and compositional tunability of these nanowires, due to difficulties in manipulating the structure and chemical composition of an individual nanowire. Here, using a combination of scanning transmission electron microscopy (STEM) and density functional theory (DFT), we report that TMC nanowires have substantial intrinsic structural flexibility and their chemical composition can be manipulated. Rotational twisting, axial kinking, and branching of an individual nanowire is consistently observed and junctions with well-ordered atomic structures can be fabricated. We also show that the density of states of these nanowires can be finely tuned via alloying either the chalcogen or the transition-metal elements, where the chalcogen alloying can be further controlled by the acceleration voltage of the electron beam during the fabrication. The results open up the possibility of tailoring the properties of TMC nanowires, paving the way for robust ultrasmall interconnects in TMDC-based 2D flexible nanoelectronics.

KEYWORDS: metallic nanowire, alloying, transition metal dichalcogenide, structural flexibility, junctions, chemical constituent manipulation

Truly one-dimensional (1D) structures in a 2D or 3D material matrix are of particular interest for their unexpected and extraordinary properties.1−9 Among all, transition-metal chalcogenide (TMC) nanowires are an important component for the fabrication of flexible nanoelectronics due to their authentic 1D nature and intrinsic metalliclicity.8,10−13 The robust metallicity of TMC nanowires originates from the strong p−d orbital hybridization between the chalcogen and metal atoms, where the metal atoms form octahedral units in a chain as the backbone of the nanowire and are capped by chalcogen atoms at the edge.6,11,12 Investigations of metallic TMC nanowires as ultrasmall conducting interconnects within a 2D electronic circuit are, therefore, complementary to the current intense study of semiconducting transition-metal dichalcogenide (TMDC) monolayers for the fabrication of planar field-effect transistors (FETs).14−16

Fabrication of TMC nanowires started in the 1990s. Early studies reported successful synthesis of Mo6X6 (X = S or Se) TMC bundled nanowires via different strategies, including dissolution of quasi-1D Li2Mo6Se6 crystals,17,18 physical vapor deposition (PVD),10 and sulfurization of Mo thin film.19 Synthesis of similar Mo6S9−xIx nanowire bundles were also reported in a facile one-step method.13,20 With the advent of research on TMDC monolayers, fabrication of isolated TMC nanowires within a TMDC 2D material matrix was recently achieved by electron-beam irradiation of TDLC monolayers as a first step toward integration of such nanowires in applications.7,21,22 Specifically, free-standing nanowires were fabricated within TMDC monolayers using transmission electron microscopy (TEM), but with limited control on the location of the nanowires due to the parallel illumination of the electron beam.21 The use of the focused electron beam of a scanning transmission electron microscope (STEM), on the other hand, led to the controlled sculpting of metallic MX (M = Mo or W; X = S or Se) TMC nanowire networks and junctions,8 which may inspire the creation of 2D functional devices.7 More recently, MoSe nanowires were fabricated using a TEM to create locally highly Se-deficient regions.22 All these fabrication methods create seamless connections between the
nanowires and the TMDC monolayers, which opens the possibility of large-scale patterning of subnanometer-wide wires inside a 2D electronic circuit. It is important to note that the MX nanowires fabricated using electron irradiation have the same atomic structure as the previously reported MX monolayers TMC nanowires created by chemical synthesis. Nevertheless, for
TMC nanowires to become more practical for diversified wiring purposes, a detailed study of the flexibility and robustness of the atomic structure of the nanowire is needed. Moreover, the possibility of fine-tuning the electronic properties of an individual nanowire is also essential for tailoring their properties. Up until now, the structural flexibility and chemical constituent variations of individual nanowires has not been investigated in detail, due to the difficulty in manipulating the atomic structure and chemical composition of individual nanowires during the synthesis.

In this paper, we directly manipulate the structure of individual TMC nanowires down to the single-atom level and explore their structural flexibility and alloying behavior using a precisely controlled focused electron beam in a STEM. We found that an individual nanowire can twist to accommodate different rotations, divert its axial direction by a kink, and branch to split into two nanowires. Well-ordered junction structures that connect multiple nanowires were fabricated for the first time. Alloyed MoS$_2$Se$_{1-x}$ and Mo$_x$W$_{1-x}$S nanowires were also successfully fabricated by sculpting their alloy monolayer counterpart or corresponding vertically stacked van der Waals heterostructures. Combining electron microscopy with density functional theory (DFT), we demonstrated the possibility of tuning the nanowire’s electronic properties by alloying Se or W atoms in a MoS nanowire through the reduced p–d orbital hybridization. Finally, we show that the alloying concentration of Se in a MoS nanowire can be further controlled by the acceleration voltage of the high-energy electrons during the sculpting process. Our results indicate that TMC nanowires are indeed a promising candidate for robust and versatile ultrasmall functional interconnects in 2D TMDC-based monolayer nanoelectronics.

RESULTS AND DISCUSSION

The fabrication procedure of an individual MoSe nanowire for the present investigations was reported in ref 8. Specifically, Figure 1A shows the STEM image of a MoSe nanowire twisting in the middle along the axial direction, which gives rise to different rotations in the upper and lower half of the nanowire. The angle between the two rotations is estimated to be $\sim 10^\circ$ by comparing with the simulated STEM image using a DFT-optimized model. Such large twist is consistently observed when three capping Se atoms in the same layer of the nanowire, defined as the atomic planes perpendicular to the axial direction as highlighted by the yellow and red dash lines in Figure 1A, are missing.

DFT calculations further confirm that the accommodation of large twist in the nanowire is assisted by Se vacancies presented in the nanowire. The deformation energy of twisting (see Methods) varies depending on the length of the nanowire models used in calculations. The nanowire model used in our calculation is composed of 9 unit cells, which is the typical length observed experimentally in the twisting structures. The deformation energy decreases as the number of Se vacancies in the same layer increase, as indicated in Figure 1E, which drops down to 0.28 eV when all three capping Se atoms are removed. This indicates that the twisting is easier to occur with the presence of Se vacancies, as observed in our experiments. It is worth noting that the twisting is elastic, where the twisting disappears without the pinning constriction at the two ends of the nanowire regardless of its length in our calculations. Such phenomenon suggests that the twisting structure may be caused by the different adaptive junctions connecting the two sides of TMC nanowire and the TMDC monolayer. More importantly, the presence of Se vacancies in this defect-assisted twisting structure has little effect on the metallicity of the nanowire, as shown by the density of state (DOS) of the twisted nanowire in Figure 1F, due to the intact connection of the backbone formed by Mo octahedral units (see the schematic in Figure 1G). These results suggest that MoSe (or MX) nanowires can accommodate large torsional distortions, which is further enhanced by the presence of Se vacancies while the conducting backbone retains its structural integrity. This phenomenon further provides an opportunity for defect engineering in these nanowires to enhance their mechanical stability.

Figure 1B shows a MoSe nanowire with a 60° kink in the middle of the nanowire. On the basis of the image intensity of each atomic site, we used DFT calculations to reconstruct an atomic model for the kink and simulated the STEM image based on the optimized model. The simulated image matches very well the experimental one, indicating the correctness of the atomic model of the kink structure. To further understand the formation of the kink, which can be used to change the axial direction of the nanowire, we provide a schematic diagram of the configurations of the basic units composing the backbone of the nanowire, as shown in Figure 1G. In this schematic diagram, we omit the capping Se atoms for clarity. The backbone of the nanowire can be considered as multiple octahedral units, as indicated by the different colored diamond-like models (projection of the octahedral unit) in Figure 1G. These octahedral units are stacked together along the same pair of the parallel facets in the octahedron (dashed triangles schematic of the inset in Figure 1G), as highlighted by the colored dashed lines, which defines the axial direction of the nanowire. Specifically, the kink forms when one of the octahedral units is mis-stacked onto the side facets other than the ones that are perpendicular to the axial direction, for instance, the interface between the purple and red unit in Figure 1G. The axial direction of the nanowire, therefore, changes by $\sim 60^\circ$ from its original direction due to the symmetry of the octahedral unit. Under this scenario, a nanowire with multiple kinks should be stable and achievable, i.e., the axial direction of a nanowire can be changed. Furthermore, DFT calculations verified that the metallicity is preserved in the kink structure, as shown by the DOS in Figure 1F. Such flexible feature in the axial direction without affecting the metallicity of the nanowire is of great importance for wiring purposes.

Figure 1C shows a branched nanowire, where an extra nanowire branched out from its parent nanowire with an angle of 42° with respect to the original axial direction. The connection region has a different atomic structure from the kink. The Mo octahedral unit is no longer preserved at the first layer of the branched nanowire, as illustrated by the atomic model in Figure 1C. However, the connection region is still metallic as indicated by the DOS (Figure 1F). By the careful programming of the scanning manner of the electron beam, different regions of monolayer MoSe$_2$ can be exposed to the electron irradiation in sequence, leading to a fine control of the nanowire structure during the e-beam sculpting. Figure 1D shows an “X” junction which connects four nanowires. Y-junctions have been reported previously, but with a complicated atomic structure that was not identified. We successfully fabricated junctions with much more simplified structures, which allows us to directly map out each atomic site and reconstruct the atomic model using DFT calculations, as
shown in Figure 1D. The junction has a symmetric structure where two nanowires in the upper and lower region merge and subsequently join together. The Mo atoms in the center of the junction form an irregular pentagonal ring with Se atoms capping the edges. Such configuration preserves the p–d orbital hybridization between the Se and Mo atoms in the center of the junction, which consequently remains metallic as verified by DFT calculations (Figure 1F). These results demonstrate that MoSe nanowires indeed maintain an intrinsic structural flexibility due to the versatility of the structure units, where various structural deformations and junctions of the nanowires that preserve their metallicity can be constructed for diversified applications.

To further diversify the properties of the nanowires, we explored the possibility of tuning the electronic properties of the nanowire by alloying either the chalcogen or the metal atoms. Since the formation of the nanowire is self-regulating under the electron beam, providing a sculpting material which contains both Se and S atoms (or Mo and W atoms) may lead to the formation of alloyed nanowires. Figure 2 shows two different types of materials for our sculpting experiments on alloyed nanowires. The first type is the alloyed MoS$_{2y}$Se$_{2(1−y)}$ and Mo$_x$W$_{1−x}$S$_2$ monolayers (0 < x < 1), where the S or Se and Mo or W atoms are covalently bonded in a hexagonal lattice. Here, x refers to the overall concentration ratio between the two different elements in the anion (cation) sites in the ternary 2D compounds. The second type is a vertically stacked bilayer van der Waal heterostructure of MoS$_2$ and MoSe$_2$ where the S and Se atoms are separated in two monolayers. We have successfully fabricated alloyed MoS$_x$Se$_{1−x}$ nanowires from these two types of structures since both of them serve as the reservoir for S/Se atoms during the formation of the nanowire. The alloyed Mo$_x$W$_{1−x}$S nanowire is fabricated in the alloyed monolayer and should also be achieved in any 2D structure that contains Mo and W atoms as a reservoir such as a vertically stacked MoS$_2$/WS$_2$ bilayer.

Figure 3 shows the atomic structure of the alloyed nanowires. Figure 3A shows an alloyed MoS$_x$Se$_{1−x}$ at 0° rotation. At this rotation angle, the projected image of the nanowire has three different atomic columns in each layer. These three atomic columns contain different atoms, i.e., one chalcogen atom, two Mo atoms, and one Mo atom sandwiched by two chalcogen atoms. One advantage of the Z-contrast imaging is that the image intensity is directly related to the atomic number of each imaged species. Since Se has a much higher atomic number than S, the incorporation of Se atoms in the chalcogen sites gives rise to distinguishable image intensity, as shown in the intensity profile (Figure 3E), which can be used to map out the Se locations in the alloyed MoS$_x$Se$_{1−x}$ nanowire by an atom-by-atom intensity quantification method. The simulated image using the atomic model shown on the right reproduces well the...
intensity of each atomic column in the experimental image (Figure 3A). The instantaneous chemical composition of the nanowire, based on this particular image, is determined to be MoS$_{0.79}$Se$_{0.21}$ through intensity quantification analysis. Note that this notation refers to the overall chemical composition of the entire nanowire rather than its unit-cell. Similarly, Figure 3C shows an alloyed Mo$_{0.76}$W$_{0.24}$S nanowire where the W atoms can be mapped out by the same technique. Moreover, a rotation is consistently observed during the lifetime of the nanowire. Figure 3B,D shows the alloyed nanowires at a 30° rotation angle. At this rotation angle, the projected structure has five nonoverlapping atomic positions, as shown in the atomic model, which facilitate and verify the mapping of individual Se or W atoms inside the alloyed nanowires. Such intensity quantification analysis of each imaged species is adopted to analyze the dynamic change of the alloyed concentration during the fabrication of the nanowire, as discussed later.

DFT calculations were carried out to study the changes in the DOS of the nanowire induced by alloying. We first explore the effect from single Se and W atom substituted in MoS$_{x}$Se$_{1-x}$ and Mo$_{x}$W$_{1-x}$S nanowires, respectively. To avoid interactions between neighboring alloying atoms, we constructed a long MoS nanowire model, which is composed of 12 unit cells, with only one S or Mo atom being replaced by a Se or W atom, written as MoS-1Se and MoS-1W, respectively, as shown in the atomic model in Figure 4A,B. As reported before, metallicity in MX nanowire originates from the p−d orbital hybridization between the chalcogen and the metal atoms.$^{11,10}$ We find that both Se and W alloying in MoS nanowires result in a reduction of the p−d orbital hybridization (Figure 4A,B), which substantially affects the structure of the DOS near the Fermi energy. In pristine MoS nanowire, the bond length between Mo and S atom in the same layer is ~2.49 Å, which increases to 2.62 Å for individual Se substitution and 2.51 Å for W. The projected DOS of the p-orbital of the single Se atom substituted in the MoS nanowire, as shown by Figure 4A, shows a reduction of the DOS in the same energy range as compared to the S atom in the same location. In contrast, the d-orbital of the Mo atoms surrounding the substitutional Se atom do not have much alteration in the DOS, as indicated by the projected DOS of the surrounding Mo atoms. We observed a
similar effect in nanowire with single W atom substitution, where the DOS of the projected d-orbital of W decreases as compared to the Mo atom in the same location in a pristine MoS nanowire. The projected DOS on the p-orbital of the S and d-orbital of the surrounding Mo atoms in the MoS nanowire is almost the same as the atoms in the same locations in the pristine nanowire (Figure 4B). Such reduction in hybridization may be due to the increased Mo−Se and W−S bond lengths, which is caused by the weaker interaction of the larger Se and W atoms inside the MoS nanowire. Consequently, we can increase the alloying concentration to alter the DOS structure near the Fermi energy in the nanowires. Figure 4C,D shows the total DOS structure of the alloyed nanowires with different concentrations, where the amount of DOS around the Fermi energy is different. The value of the DOS near the Fermi energy has a substantial effect on the electrical conductance of metals. For instance, partially substituting S with Se in the MoS$_{1−x}$Se$_x$ alloyed nanowires decreases the DOS near the Fermi energy, which corresponds to smaller conductivity. Thus, by manipulating the DOS near the Fermi energy via alloying the nanowires, we may achieve a fine-tuning of the electrical performance and different transport behaviors of the nanowire.

We further discovered that the Se alloying can be controlled by the energy (acceleration voltage) of the sculpting electron beam during the fabrication of the MoS$_{1−x}$Se$_x$ nanowires. It has been reported that the capping chalcogen atoms in MX nanowires can be easily removed by the high-energy electrons, while they can self-heal due to the low diffusion barrier of the chalcogen atoms traveling along the nanowire. Such self-healing mechanism provides the foundation for controlling the Se alloying concentration. In contrast, Mo/W atom replace-
ments are far less frequently observed during the fabrication of Mo$_x$W$_{1-x}$ alloyed nanowires, presumably due to the strong bonding between the cation atoms. We started the fabrication of the alloyed MoS$_{1/2}$Se$_{1/2}$ nanowire on the same parent material (vertically stacked MoS$_2$/MoSe$_2$ bilayer) vertically stacked heterostructure under 60 kV (first row) and 100 kV (second row), respectively. The overall composition of the starting bilayer material is MoSe, as indicated by the blue diamond symbol. The graph below summarized the evolution of the Se alloying concentration in the two nanowires as a function of time. The chemical composition of the nanowire is estimated frame-by-frame by direct intensity quantification analysis which determines the locations of the Se atoms, as discussed in the main text. Scale bars: 0.5 nm.

Figure 5. Acceleration voltage dependence of Se concentration in MoS$_{1/2}$Se$_{1/2}$ nanowires. Two rows on the top: snapshots of the sequential Z-contrast STEM imaging of the dynamical formation process of two different alloyed MoS$_x$Se$_{1-x}$ nanowires sculpted from a MoS$_2$/MoSe$_2$ bilayer vertically stacked heterostructure under 60 kV (first row) and 100 kV (second row), respectively. The overall composition of the starting bilayer material is MoSe, as indicated by the blue diamond symbol. The graph below summarized the evolution of the Se alloying concentration in the two nanowires as a function of time. The chemical composition of the nanowire is estimated frame-by-frame by direct intensity quantification analysis which determines the locations of the Se atoms, as discussed in the main text. Scale bars: 0.5 nm.

CONCLUSIONS

In conclusion, we systematically explored the structural flexibility of MX nanowires and the possibility to regulate their chemical constituents. We show that the MX nanowire can accommodate large torsional twist, change its axial direction via kinking, branch another nanowire from its original direction, and can join together to form multiple junctions. We also demonstrate that alloying the MX nanowires is possible, and the alloying can be used to tune the electronic properties of the alloyed nanowire to diversify their functionalities. Moreover, we have shown the possibility of controlling the concentration of the capping atoms in MX nanowires by tuning the acceleration voltage of the sculpting electron beam. All these features suggest that the MX nanowires are promising candidates for functional ultrasmall interconnect in future 2D nanoelectronics.
METHODS

STEM Z-Contrast Imaging. STEM Z-contrast imaging was performed on an aberration-corrected Nion UltraSTEM-100 operating at both 60 and 100 kV. The convergence semiangle for the incident probe was 31 mrad. Z-contrast images were collected for a half angle range of ~80–200 mrad. The dwell time for imaging is set to be 16 μs/pixel. The sequential Z-contrast imaging is set to be 1 frame/s, with a dwell time of 4 μs/pixel. All imaging was performed at room temperature.

DFT Calculations for Structural Optimization and Deformation Energy. DFT calculations were performed using the Vienna ab initio simulation package (VASP) with the core–valence interaction described by the frozen-core projector augmented wave (PAW) method. The exchange-correlation potential was described by the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE). All atoms are allowed to relax until the energy stored in a compressed elastic spring.

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Notes
The authors declare no competing financial interest.

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