### **2D** Materials

PAPER

CrossMark

**RECEIVED** 2 February 2019

**REVISED** 28 March 2019

ACCEPTED FOR PUBLICATION 9 April 2019

PUBLISHED 6 June 2019

# Convergent ion beam alteration of 2D materials and metal-2D interfaces

Zhihui Cheng<sup>1</sup>, Hattan Abuzaid<sup>1</sup>, Yifei Yu<sup>2</sup>, Fan Zhang<sup>3</sup>, Yanlong Li<sup>3</sup>, Steven G Noyce<sup>1</sup>, Nicholas X Williams<sup>1</sup>, Yuh-Chen Lin<sup>1</sup>, James L Doherty<sup>1</sup>, Chenggang Tao<sup>3</sup>, Linyou Cao<sup>2</sup> and Aaron D Franklin<sup>1,4</sup>

Department of Electrical and Computer Engineering, Duke University, Durham, NC 27708, United States of America

<sup>2</sup> Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, United States of America

<sup>3</sup> Department of Physics, Virginia Tech, Blacksburg, VA 24061, United States of America

Department of Chemistry, Duke University, Durham, NC 27708, United States of America

E-mail: aaron.franklin@duke.edu

Keywords: MoS2, ion beam, metal-2D interface, contact engineering

Supplementary material for this article is available online

#### Abstract

Tailoring the properties of two-dimensional (2D) crystals is important for both understanding the material behavior and exploring new functionality. Here we demonstrate the alteration of MoS<sub>2</sub> and metal-MoS<sub>2</sub> interfaces using a convergent ion beam. Different beam energies, from 60 eV to 600 eV, are shown to have distinct effects on the optical and electrical properties of MoS<sub>2</sub>. Defects and deformations created across different layers were investigated, revealing an unanticipated improvement in the Raman peak intensity of multilayer MoS<sub>2</sub> when exposed to a 60 eV Ar<sup>+</sup> ion beam, and attenuation of the MoS<sub>2</sub> Raman peaks with a 200 eV ion beam. Using cross-sectional scanning transmission electron microscopy (STEM), alteration of the crystal structure after a 600 eV ion beam bombardment was observed, including generated defects and voids in the crystal. We show that the 60 eV ion beam yields improvement in the metal-MoS<sub>2</sub> interface by decreasing the contact resistance from 17.5 k $\Omega \cdot \mu$ m to 6 k $\Omega \cdot \mu$ m at a carrier concentration of  $n_{2D} = 5.4 \times 10^{12} \text{ cm}^{-2}$ . These results advance the use of low-energy ion beams to modify 2D materials and interfaces for tuning and improving performance in applications of sensors, transistors, optoelectronics, and so forth.

#### 1. Introduction

The advantageous electrical, mechanical, and optical properties of two-dimensional (2D) materials have attracted tremendous research seeking to integrate them into the next generation of transistors, optoelectronics, and sensors [1, 2]. One of the foremost bottlenecks to realizing these applications using 2D materials is the high metal-2D material contact resistance [3, 4]. Many methods have been explored to reduce the contact resistance, including doping the 2D surface, using different metals [5, 6], and innovating new fabrication processes [7]. In physically modifying 2D-metal interfaces, researchers have suggested a number of techniques such as ion beam bombardment [8], electron beam irradiation [9, 10], and plasma treatment [11, 12]. The actual impact of these often destructive processes on the 2D material has received limited attention and deserves further consideration based on the

© 2019 IOP Publishing Ltd

significant improvements they have been reported to offer for the metal-2D interface.

The use of energetic ion beams has been widely employed in controlled material processing [13, 14], where ion beams are used to sputter solid targets, selectively etch surfaces, implant ions, and alter material properties. The interaction of charged ions with surfaces of bulk materials was studied extensively for decades and is well understood [15-17]. However, the effect of low-energy ion beam bombardment on atomically-thin materials such as transition metal dichalcogenides (TMDs) remains largely unknown. The thinness of 2D materials and their large surfaceto-volume ratio allow ion beams to influence the entire atomic structure, thus significantly affecting material properties. Moreover, compared to other techniques, ion beams offer more degrees of control by changing the ion species, energy, flux, and angle of incidence.

In recent years, there have been demonstrations of the potential of ion beam technology to modify 2D



**Figure 1.** Experimental setup of the *in situ* convergent  $Ar^+$  ion beam source. (a) Schematic of the convergent ion beam source incorporated with an e-beam evaporator within an ultra-high vacuum (UHV) chamber. (b) Diagram showing the process of ions knocking out Mo and S atoms from the MoS<sub>2</sub> crystal.

materials [18, 19]. One historically prevalent application for ion beam technology is ion implantation for doping and researchers naturally attempted a similar approach for 2D materials by implanting ions of different species in films of graphene to manipulate their electronic properties [20-24]. Other works reported phase changes from semiconducting to quasi-metallic or insulating phases by changing the dose of a focused He<sup>+</sup> ion beam [25, 26]. Researchers have also used ion beams to engineer defects in different TMDs, allowing controlled alteration in electrical, mechanical and optical properties [27-29]. However, the understanding of ion beam use for physically tailoring the properties of 2D materials and consequently tuning the carrier transport across the contact interface is still deficient. First, most of the reports modify monolayer 2D crystals without considering multiple layers. Second, studies investigating the performance of 2D fieldeffect transistors (FETs) under ion irradiation generally show degradation after the ion beam modification [30, 31]. More importantly, no study has reported the use of convergent ion beams (with beam diameter on the order of centimeters) to modify the contact interface of 2D FETs.

In our previous study [32], we investigated the effect of ion dosage on the contact resistance of metal-MoS<sub>2</sub> interfaces using a broad ion beam source. In this work, we build upon our prior results by using a convergent ion beam source, which eliminates the chamber wall sputtering issue caused by the broad ion beam source (see supplemental note 1 for more details (stacks.iop.org/TDM/6/034005/mmedia)). We also experimentally investigate the impact of different ion beam energies on modifying monolayer to multilayer MoS<sub>2</sub> and their application in metal-2D contact interfaces. We first compare 2D materials before and after ion beam exposure using various characterization

tools, such as atomic force microscopy (AFM), photoluminescence (PL) spectroscopy, Raman spectroscopy, and cross-sectional scanning transmission electron microscopy (STEM). Then, we selectively modify the metal-2D contact interface using the convergent ion beam and study its impact on contact resistance. Subsequently, we present evidence of device performance improvement via controlled, ion-induced defects at the metal contact interface.

#### 2. Results and discussion

To better understand the ion beam modification technique, figure 1(a) depicts the experimental setup where the convergent ion beam source exclusively hits the substrate with negligible interaction with the chamber wall, confirmed by the x-ray photoelectron spectroscopy (XPS) study provided in supplementary note 1. The ultra-high vacuum (UHV) chamber houses an e-beam evaporator for in situ metal deposition after ion beam bombardment. The energetic ions (Ar<sup>+</sup>) impinging on the MoS<sub>2</sub> surface sputter away Mo and S atoms, with sulfur comprising the majority of the sputtered atoms due to its lighter atomic weight and higher density in the crystal lattice (figure 1(b)). We briefly introduce the mechanism of the ion source in supplementary note 1, in which we also compare the convergent and broad ion beam sources. The main parameters that were controlled in the experiments herein are the beam energy and current (ion flux) using an automated controller module.

#### 2.1. AFM analysis of the ion beam altered MoS<sub>2</sub>

In order to explore the impact of the  $Ar^+$  ion beam on  $MoS_2$  with various thicknesses, we used chemical vapor deposition (CVD) for its ability to produce large areas of thin films. Here, as shown in figure 2(a),



we selected regions of interest on one sample where monolayer (1L) to 4 layers (4L) MoS<sub>2</sub> can be seen. After exposing the sample to a 60 eV ion beam (beam voltage,  $V_b = 60$  V and beam current,  $I_b = 3$  mA) for 3 s, the thickness profile was mapped using AFM. Figure 2(c) shows the height profile of the line scan from figure 2(b) and suggests a uniform ~0.7 nm step height between each layer increment, from 1L to 2L to 3L. This step height is consistent with the materials without ion beam modification in supplementary figure 2, indicating that the 60 eV ion beam has a negligible etching effect. In contrast, a 200 eV ion beam ( $V_{\rm b} = 200 \text{ V}, I_{\rm b} = 3 \text{ mA}$ ) was used to expose the  $MoS_2$  in figure 2(d) for 3 s and a pronounced effect was observed. The height profiles in figure 2(f) represent the line scans in figure 2(e). The 1L to 2L step height after 200 eV ion beam is larger (~1.3 nm) than the same step after 60 eV ion beam (~0.7 nm), whereas the 2L to 3L step height remains similar. This height difference in 1L to 2L is attributed to a stronger etching effect on the monolayer and the underlying SiO<sub>2</sub> with the 200 eV ion beam. The capability of using the ion beam for etching is stronger at energies above 200 eV [33]. Optical images of the samples before and after ion beam exposure are compared in supplementary figure 3, where the 200 eV ion beam is shown to induce more color and contrast change.

### 2.2. PL and Raman mapping of ion beam altered MoS<sub>2</sub>

Both PL and Raman spectroscopy were used to map the altered flakes from figure 2. The 1L region in figure 3(a) has a bright PL signal before the 60 eV

ion beam exposure, as seen in figure 3(b), whereas the 2L to 4L regions are dark, consistent with the indirect bandgap of multilayer MoS2. After 60 eV Ar<sup>+</sup> ions are used, the 1L region turns dark (figure 3(c)), which suggests that the ion beam disrupts the crystal structure of 1L MoS<sub>2</sub>. Other studies have used TEM to show point defects, single line and double line defects after different energetic particle irradiation [28, 34]. In figure 3(f), we also compare the PL spectra for the 1L region inside the green box of figure 3(a), showing disappearance of the PL peak after ion beam exposure, which is consistent with the dark PL mapping signal in figure 3(c). In order to confirm whether the MoS<sub>2</sub> crystal structure still remains after 60 eV ion beam exposure, a stronger PL accumulation power was used and the result is provided in supplementary figure 4. The PL peak of  $MoS_2$  after 60 eV ion beam exposure can still be observed but with a significantly attenuated peak intensity (0.3% of the unaltered 1L  $MoS_2$ ). The remaining peak indicates that the crystal structure still remains but is significantly damaged.

The comparison of Raman mapping before and after the 60 eV ion beam exposure is shown in figures 3(d) and (e). Surprisingly, the 3L and 4L regions in figure 3(e) are brighter than the same region in figure 3(d). This unanticipated observation matches the Raman spectra in figure 3(g), where the  $A_{1g}$  peak intensity is 17.7% and 19% higher in the 4L and 3L regions, respectively. As visualized in figure 3(h), for the 2L region, the peak intensity remains similar whereas the 1L region shows a 10% drop. Note that the spectra have the same baseline as shown in



**Figure 5.** Photoluminescence and raman mapping of obe VAT on beam aftered MOS<sub>2</sub>. (a) Optical image of the MOS<sub>2</sub> with 1L to 4L in the same region. Scale bar, 5  $\mu$ m. Photoluminescence mapping of the region (b) before and (c) after ion beam exposure. Raman mapping of the region (d) before and (e) after ion beam exposure. (f) Photoluminescence spectra of the monolayer comparing the before and after ion beam exposure at the same L spot (green box in (a)). (g) Raman spectra of the films in the same regions for layers 1L to 4L. (h) Intensity change and (i) peak shift of  $A_{1g}$  and  $E_{2g}$  for different layers after ion beam exposure. The inset image shows an STM mapping of the altered 4L MoS<sub>2</sub> (I = 0.36 nA,  $V_s = -1$  V). Scale bar, 0.7 nm.

the 390 to 400 cm<sup>-1</sup> range. The lower Raman intensity of the 1L region correlates with the diminished PL peak in figure 3(f), indicating defects created onto the 1L surface. Presumably, similar defect creation should happen to the 2L, 3L, and 4L surfaces. However, the increased thickness can distribute the bombardment among the different layers. We argue that ion beam bombardment adds fewer defects (e.g. missing Mo-S bonds) per layer on multilayer than in the fully 1L region. Scanning tunneling microscopy (STM) was used to probe the 4L surface (see inset of figure 3(i)), showing that the MoS<sub>2</sub> crystallinity still remains. This largely intact crystallinity of the 4L MoS<sub>2</sub> surface is in contrast to the significantly diminished PL peak of 1L MoS<sub>2</sub>, supporting our previous argument that the defects spread throughout multiple layers rather than concentrating at the surface. More analysis of the STM image is provided in supplementary figure 5. The decrease of defects created among each individual layer facilitates the out-of-plane vibration mode, thus improving the  $A_{1g}$  intensity for multilayers.

Based on previous studies [27, 35-37], sulfur vacancies (SV) are expected to be created after the ion beam exposure. It has been well studied that SV can redshift the  $E_{2g}$  peak and blueshift  $A_{1g}$  on monolayer MoS<sub>2</sub>, as

the crystal vibration is interrupted by the abundant defects [38, 39]. For simplicity, the frequency of the vibrational mode can be explained by a harmonic oscillator  $\omega = \sqrt{\frac{K}{m}}$ , where  $\omega$  is the frequency, K is the restoring force constant, *m* is the total mass. The Raman peak shift can be explained by the relative change of restoring force constant and total mass. Consistent with previous reports [35, 40], the 1L region in figure 3(g) demonstrates a slight redshift in  $E_{2g}$  and blueshift in  $A_{1g}$ . However, for the first time, we observed that for multilayers (2–4L), the ion beam exposure causes redshift in  $A_{1g}$  as well as  $E_{2g}$  peaks. This new observation is attributed to the interaction between the ion beam and the multilayer crystal. Specifically, the defects created between adjacent layers may dampen the interlayer coupling and decrease the restoring force constant while the total mass remains relatively unchanged, as proven by the STM image for altered 4L MoS<sub>2</sub>. This relative change of K and m eventually decreases the frequency (redshift). The increased peak shift versus increased thickness in figure 3(i) indicates that as the  $MoS_2$  thickness increases, the m decreases less and K increases more. This result reveals new information on how interlayer defects can impact the vibrational frequency. Since the creation of defects in multilayer crystals is more complex than in monolayers,



Figure 4. Photoluminescence and Raman mapping of 200 eV Ar<sup>+</sup> ion beam altered MoS<sub>2</sub>. (a) Optical image of the MoS<sub>2</sub> with 1L to 7L in the same region. Scale bar, 5  $\mu$ m. Photoluminescence mapping of the region (b) before and (c) after ion beam exposure. Raman mapping of the region (d) before and (e) after ion beam exposure. (f) Photoluminescence of the monolayer comparing the spectra before and after the ion beam exposure at the same 1L spot (green box in (a)). (g) Raman spectra of the films in the same regions for layers from 1L to 7L. (h) Intensity change and (i) peak shift of A<sub>1g</sub> and E<sub>2g</sub> for different layers after ion beam exposure.

a more extensive study is needed to quantify the sulfur vacancies for these multilayer 2D materials.

The detailed Raman and PL studies for the 200 eV ion beam alteration of MoS<sub>2</sub> are provided in figure 4. On one region of the sample, we can find 1L to 7L  $MoS_2$ , as shown in figure 4(a). Similar to the 60 eV exposure, we compare the PL and Raman spectra before and after ion beam exposure for four layers with the 5-7L spectra plotted in supplementary figure 6. As expected, the PL signal of the 1L area disappeared in figures 4(c)and (f) after the ion beam exposure because of the higher energy of 200 eV. Even with higher accumulation power, the PL peak remains absent, as shown in supplementary figure 4. The vanished PL indicates the etching effect of 200 eV ion beam and further corroborates the increased 2L-1L height difference in figure 2(f). Raman mapping after ion beam exposure in figure 4(e) shows obvious dimming in intensity compared to figure 4(d). This drop in Raman intensity is expected as a higher ion beam energy can induce more defects across different layers. For 3L and 4L regions, the 200 eV ion beam results in a similar redshift of  $A_{1g}$ and  $E_{2g}$  peaks, as with the 60 eV exposure but with a larger magnitude, comparing figures 3(i) and 4(i). This increased magnitude stemming from the higher energy bombardment is based on an increase in defects

and intralayer deformation across different layers. This intralayer and interlayer damage will disrupt the interlayer coupling and reduce the restoring force constant, thus redshifting both the in-plane  $(E_{2g})$  and vertical vibration  $(A_{1g})$  [41]. For 1L and 2L regions, the 200 eV ion beam is strong enough to cause the peaks to be fully attenuated. The greatly reduced peak intensity across the 1L to 4L area confirms the increased number of defects created in the MoS<sub>2</sub> crystal. As the layer number increased to 7L, the loss in intensity and magnitude of the redshift drops (figures 4(h) and (i)), consistent with our expectation that thicker MoS<sub>2</sub> can bear more ion damage compared to 1L and 2L MoS<sub>2</sub>. The fact that the  $A_{1g}$  signal of 4L MoS<sub>2</sub> drops to a similar intensity of 1L before the ion beam exposure does not mean that the 4L region is thinned down to 1L. The reason behind this observation is that the  $E_{2g}$  peak of 4L after ion beam exposure represents a sharp left shift compared to the 1L  $E_{2g}$  peak prior to ion bombardment. The dark PL mapping in figure 4(c) analysis confirms the absence of 1L MoS<sub>2</sub>.

We also compare the longitudinal acoustic (LA) peaks before and after ion beam exposure in supplementary figure 7. Longitudinal acoustic modes are phonon modes at the M point of the Brillouin Zone, abbreviated as LA(M). It has been suggested that defect



**Figure 5.** Cross-sectional STEM analysis of 600 eV ion beam modified MoS<sub>2</sub> film. (a) Mechanically exfoliated, unaltered 15L MoS<sub>2</sub> flake. Scale bar, 4 nm. The same flake after (b) 25 s and (c) 50 s of 600 eV ion beam exposure. Scale bars in (b) and (c) are 5 nm. (d) and (e) High magnification image of (a) and (b) comparing the atomic defects and disorder. Scale bars in (d) and (e) are 2 nm.

density can activate the LA(M) at ~227 cm<sup>-1</sup> [40]. However, in our experiments, we have not observed the peaks of LA(M) before or after the ion beam exposure across different thicknesses of MoS<sub>2</sub>. The second order of LA(M) is 2LA(M) at ~454 cm<sup>-1</sup>, which disappeared after 200 eV ion beam bombardment but remained after 60 eV ion beam. This observation further confirms that a 200 eV ion beam can induce greater structure damage than a 60 eV beam.

#### 2.3. Cross-sectional STEM analysis of altered MoS<sub>2</sub>

In order to analyze the atomic deformations caused by the convergent ion beam, cross-sectional STEM was used. A 10nm (15L) flake was mechanically exfoliated onto a 300 nm SiO<sub>2</sub>/P<sup>++</sup> Si substrate, as shown in figure 5(a). Using poly(methyl methacrylate) (PMMA) as an etching mask, different regions of the same flake were irradiated with a 600 eV ion beam  $(V_{\rm b} = 600 \text{ V}, I_{\rm b} = 36 \text{ mA})$ , as described in the Methods section and illustrated in supplementary figure 8. To make the effect of the ion beam more pronounced across different layers, the beam voltage and current were increased to 600 eV and 36 mA with a prolonged exposure time of 25 s and 50 s. Cross-sectional STEM images after 25s and 50s ion beam exposure are presented in figures 5(b) and (c). Comparing the unexposed region (figure 5(a)) to the one exposed for 25 s (figure 5(b)), defects and deformations can be seen across different layers. The thickness decreased

from 10 nm (15L) to 4 nm (5L-6L) after ion beam exposure—an etch rate of approximately 1L per 2.5 s. However, this etch rate changes with the thickness of the materials, as is evident from comparing the results of 25 s and 50 s exposure. After the 50 s exposure, the 2-3L region still partially remains. Surprisingly, some interlayer delamination in the MoS<sub>2</sub> crystals is also observed, as shown in figure 5(c). In addition, small and large gaps appear horizontally between different regions and vertically between different layers. These new effects could have profound implications for metal-2D material interfaces and other applications such as intercalation and sensing devices. In order to atomically compare the unexposed and exposed layers, the higher magnification STEM images in figures 5(a)and (b) were studied in figure 5(d) and (e). An ordered and uniform atomic structure is present across different layers of the unaltered  $MoS_2$  (figure 5(d)), whereas the 25s exposed region shows apparent disorder and defects, indicated as arrows in figure 5(e). The gaps highlighted in figure 5(e) are likely caused by S atom vacancies, while distinguishing missing Mo atoms is more difficult, especially in bottom layers. Examining the remnants of the topmost layers in figure 5(e) reveals structural disorder, leaving no distinguishable MoS<sub>2</sub> crystal lattice. Also of note is the different direction of S atoms (compared to the uniform line up in figure 5(d)) imposed on the atomic diagram as a representation of the possible structural



**Figure 6.** Alteration of metal-MoS<sub>2</sub> contact interface using Ar<sup>+</sup> ion beam. (a) Diagram of the *in situ* Ni evaporation process carried out immediately after ion beam exposure. Schematics of (b) the metal contact region of a non-modified device (prior to lift-off) and (d) a modified device (prior to lift-off). (c) AFM image of a set of devices fabricated on a single MoS<sub>2</sub> crystal region. Scale bar, 2  $\mu$ m. (e) and (f) Comparison of *I*–V characteristics for 60 eV altered versus unaltered contact 2D FETs. (g) Extraction of *R*<sub>c</sub> using the transfer length method (TLM). (h) Comparison of the effect of different ion beam energies on device performance. The ion beam exposure conditions are as follows (60 eV, 3 mA, 3 s), (200 eV, 3 mA, 3 s) and (600 eV, 36 mA, 3 s).

transformation (crystal plane shifting). To obtain higher resolution images and also minimize the impact of the electron beam, a further study using, for instance, 80 keV STEM is needed to characterize the interlayer atomic defects and achieve a better understanding of the possible atomic/structural transformation.

Phase or structural transformation has been demonstrated by electron beam irradiation [42, 43], laser beam [44] and electrostatic [45] methods. First principle calculations have also shown that the combination of strain, vacancies, and electronic excitations created by an electron beam can lead to a phase transition [46]. The structure transformation induced by an Ar<sup>+</sup> ion beam merits further investigation into its mechanism and implications on physical, chemical and electrical properties. For example, the interlayer defects can be used for new photonic [47] and memristor [48] applications that rely on the out-of-plane interlayer transport.

#### 2.4. Modification of metal-2D material interface

After characterizing the ion beam modification of  $MoS_2$  using different beam energies, the  $Ar^+$ ion beam was used to modify the contact interface between  $MoS_2$  and Ni contacts. Contact resistance is a frequently studied subject, especially for transistors based on 2D materials [49–52]. Based on the Raman and PL mapping data in figures 3 and 4, it was decided to use relatively thick flakes in order to avoid disrupting the crystal structure in 1L and 2L  $MoS_2$ . We exfoliated and transferred a 5 nm (7L)  $MoS_2$  flake onto a 10 nm  $SiO_2/p^{++}$  Si substrate and used the device fabrication technique described in the Methods section. Of special note is that we only exposed the contact region, keeping the channel region intact, by using PMMA as a mask. Moreover, in order to avoid variation for the purpose of comparing device performance, we fabricated the devices with and without ion beam modified contacts on the same MoS<sub>2</sub> flake. The same ion source is used as in the previous experiments. It is worth stressing that immediately after ion beam modification, the *in situ* e-beam evaporator was used to deposit the contact metal (figure 6(a)), protecting the modified region from other reactive species. Figures 6(b) and (d) are schematics of the two contact interfaces. 40 nm of Ni was used as the contact metal. After characterizing the devices in N<sub>2</sub> at room temperature, we found that the devices with 60 eV ion beam modification outperform the unaltered devices, as shown in figure 6(e). From the output curves in figure 6(f), the modified devices also show improvement in the low  $V_{\rm DS}$  region, where carrier injection at the contact dominates the current output. At  $V_{\rm DS} < 0.5$  V, The *I*–V curves of the device with ion beam have a larger slope than the unmodified device, indicating a smaller contact resistance. As  $V_{\rm DS}$  increases, the current output depends more on the channel properties, thus limiting the improvement of  $I_D$  at  $V_{DS} = 3$  V. The I-V characteristics of devices with longer channel lengths are depicted in supplementary figure 9. We

calculated the total resistance of these devices at  $V_{\rm DS} = 0.5$  V and plotted  $R_{\rm tot}$  in figure 6(g). Using the transfer length method (TLM), we detected an  $R_{\rm C}$  improvement from  $17.5 \,\mathrm{k\Omega} \cdot \mu \mathrm{m}$  to  $6 \,\mathrm{k\Omega} \cdot \mu \mathrm{m}$  at a carrier density of  $n_{\rm 2D} = 5.4 \times 10^{12} \mathrm{ cm}^{-2}$ . The relationship between contact resistance and  $n_{\rm 2D}$  is further analyzed in supplementary figure 10, showing contact performance improvement at different  $n_{\rm 2D}$ . This improvement of contact performance is attributed to the defects facilitating greater carrier injection [32, 53, 54].

The impact of different ion beam energies on the contact interface was also investigated. We plot  $I_{\rm D}-V_{\rm GS}$ curves of devices built on exfoliated flakes of ~7 nm but with different exposure conditions in figure 6(h). Compared to the 60 eV ion beam, 200 eV ion beam exposure tends to degrade the contact performance. As the ion beam energy increases to 600 eV, the device performance degrades even further. These results are consistent with the amount of damage and disorder created by the higher energy ions, as detailed in figure 5. Clearly, there is a tradeoff between damaging the MoS<sub>2</sub> to increase carrier injection and the resultant degradation in lateral carrier transport from contact to channel. Though higher energy ion beams show little promise for improving the metal-MoS<sub>2</sub> interface, we can utilize their etching capability to create edge contacts to thin layers (1-2L) of 2D materials [55]. Other applications such as sensing, intercalation and physical modification of 2D materials can also benefit from these findings.

#### 3. Conclusion and outlook

We have uncovered the effects of different ion beam energies on  $MoS_2$  using a variety of characterization techniques. The 200 eV ion beam is shown to degrade the optical properties, while 60 eV ion beams can improve carrier transport across the contact interface. The impact of  $Ar^+$  ion beam bombardment across different layers of  $MoS_2$  is particularly interesting, as visualized in Raman mapping and STEM images. The 60 eV ion beam shows promise for improving carrier injection in metal-2D material interfaces, whereas 200 eV and 600 eV ion beams degrade the contact performance.

#### 4. Methods

## 4.1. Growth of MoS<sub>2</sub> flakes by chemical vapor deposition

The MoS<sub>2</sub> flakes were grown using a chemical vapor deposition (CVD) process reported previously [56– 58]. Typically, 1 g sulfur powder (Sigma-Aldrich) and 15–30 mg MoO<sub>3</sub> (99.99%, Sigma-Aldrich) source materials were placed upstream and at the center of a tube furnace, respectively. The substrates (heavily doped Si substrate with 300 nm SiO<sub>2</sub>) were placed downstream in the tube. Typical growth

was performed at 750 °C for 10 min under a flow of argon gas at a rate of 100 sccm at ambient pressure.

#### 4.2. Convergent ion beam

In a custom-designed ultra-high vacuum (UHV) chamber (LAB Line, Kurt J. Lesker Company), the sample was exposed to an ion beam source (KDC40, KRI) under a pressure of  $2 \times 10^{-4}$  torr (base pressure:  $2 \times 10^{-8}$  torr) to modify the 2D material (MoS<sub>2</sub>). KDC40 is a gridded ion source that uses a direct-current (DC) discharge to generate ions and comes with a 4 cm diameter, 3-grid defocused dished molybdenum ion optics. The ion beam profile at the substrate is on the order of a few centimeters diameter, which is more focused than the profile of a gridless (broad) ion source but much more divergent than a focused ion beam (FIB). KDC40 generates 60–1200 eV, 2–100 mA ion beams at typical argon gas flow of 4–6 sccm.

### 4.3. Raman and photoluminescence characterization

Raman and PL mapping were carried out by Horiba Labram HR800 system with a 532 nm laser. Unless otherwise specified, all experiments were performed at room temperature. The PL accumulation power and time are included in supplementary figure 4.

#### 4.4. Scanning tunneling microscopy

The scanning tunneling microscopy (STM) measurements were carried out in an ultra-high vacuum (UHV) STM system (Omicron RT-STM). Similar to the previously reported annealing process for 2D MoS<sub>2</sub> [59, 60], the sample was annealed at 300 °C for 3 h in the UHV chamber with a base pressure of  $4.0 \times 10^{-10}$  torr. The STM used a chemically etched tungsten tip. All the STM images were obtained at room temperature.

### 4.5. Cross-sectional scanning transmission electron microscopy

An FEI (Thermo-Fisher) Quanta 3D dual beam was used to prepare cross-sectional TEM samples. A 250 nm coating of electron beam deposited Pt was deposited over the device followed by a 2  $\mu$ m ion beam Pt deposition. Initial lift-out was performed with a 30 kV Ga beam while final thinning was performed at 16 kV to reduce damage. The final polish of 48 pA at 5 kV was performed at ±4° to limit further damage. The STEM images were collected using a probe corrected FEI Titan operated at 200 kV. The beam convergence angle was set to 20 mrad, and collection angles > 50 mrad were used to obtain the Z-contrast high-angle annular dark-field (HAADF) images.

#### 4.6. Device fabrication

After  $MoS_2$  growth, the substrate was coated with poly(methyl methacrylate) (PMMA) and electronbeam lithography (EBL) was used to pattern the source/drain contacts. For the baseline field-effect transistors (FETs) without ion beam modification, 40 nm of Ni was then deposited in the contact regions, followed by lift-off in acetone. The second set of FETs with ion beam modification in the contact region was then fabricated on the same  $MoS_2$  flake. EBL once again was used to form the contact pattern in PMMA. The convergent ion beam was used to bombard the contact region. Then, 40 nm of Ni was deposited in the contact regions in the same UHV chamber without breaking the vacuum. Devices were electrically characterized in ambient.

#### Supplementary information

Supplementary note 1 and figure 1: Comparison of convergent ion beam and broad ion beam.

Supplementary figure 2: AFM analysis of the  $MoS_2$  without ion beam modification.

Supplementary figure 3: Optical images comparing the impact of ion beam alteration.

Supplementary figure 4: PL using different accumulation power and time.

Supplementary figure 5: STM mapping altered 4L MoS<sub>2</sub>.

Supplementary figure 6: Comparison of 1-7L MoS<sub>2</sub> before and after 200 eV ion beam for 3 s.

Supplementary figure 7: Longitudinal Acoustic peaks analysis for 200 and 60 eV ion beam modification.

Supplementary figure 8: Process flow for obtaining cross-sectional STEM in figure 5 of the main text.

Supplementary figure 9: I-V characteristics of devices in figure 6(c) of the main text with different channel lengths.

Supplementary figure 10: Analysis of contact resistance versus carrier density.

#### Acknowledgment

We acknowledge the assistance of Robert Garcia and Rohan Dhall from North Carolina State University Analytical Instrumentation Facility (AIF) in obtaining the cross-sectional STEM images. This work was supported in part from a National Science Foundation Grant ECCS-1508573. This work was performed in part at the Duke University Shared Materials Instrumentation Facility (SMIF), which is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), which is supported by the National Science Foundation (Grant ECCS-1542015) as part of the National Nanotechnology Coordinated Infrastructure (NNCI). YY and LC acknowledge the support of ECCS-1508856 from the National Science Foundation. FZ, YL and CT acknowledge the support from the U.S. Army Research Office Grant W911NF-15-1-0414.

#### Author contributions

ZC and ADF designed all the experiments. ZC completed all device fabrication and characterization. YY and ZC conducted the PL and Raman mapping. YY is responsible for CVD growth of MoS<sub>2</sub>. FZ and YL performed the STM scan with samples prepared by ZC and HA. ZC and HA also completed the AFM scan. ZC, HA, and YY analyzed and interpreted the data, with input from all authors. All authors commented on the manuscript.

#### **ORCID** iDs

Zhihui Cheng b https://orcid.org/0000-0003-1285-0523

Steven G Noyce https://orcid.org/0000-0002-2953-7560

Chenggang Tao <sup>(b)</sup> https://orcid.org/0000-0002-6609-0219

AaronDFranklin@https://orcid.org/0000-0002-1128-9327

#### References

- [1] Novoselov K *et al* 2016 2D materials and van der Waals heterostructures *Science* **353** aac9439
- [2] Cao W et al 2018 2D layered materials for next-generation electronics: opportunities and challenges *IEEE Trans. Electr. Devices* 65 4109–21
- [3] McDonnell S *et al* 2014 Defect-dominated doping and contact resistance in MoS<sub>2</sub> ACS Nano 8 2880–8
- [4] Giubileo F *et al* 2017 The role of contact resistance in graphene field-effect devices *Progr. Surf. Sci.* **92** 143–75
- [5] Das S et al 2012 High performance multilayer MoS<sub>2</sub> transistors with scandium contacts Nano Lett. 13 100–5
- [6] Kang J et al 2012 A computational study of metal-contacts to beyond-graphene 2D semiconductor materials IEEE Electron Device Meeting (IEDM) p 17.4
- [7] Liu Y et al 2018 Approaching the Schottky–Mott limit in van der Waals metal–semiconductor junctions Nature 557 696– 700
- [8] Tapaszto L et al 2008 Tuning the electronic structure of graphene by ion irradiation Phys. Rev. B 78 233407
- [9] Teweldebrhan D *et al* 2009 Modification of graphene properties due to electron-beam irradiation *Appl. Phys. Lett.* 94 013101
- [10] Komsa H-P et al 2012 Two-dimensional transition metal dichalcogenides under electron irradiation: defect production and doping Phys. Rev. Lett. 109 035503
- [11] Ho Y-T et al 2016 Contact resistance reduction on layered MoS<sub>2</sub> by Ar plasma pre-treatment Silicon Nanoelectronics Workshop (SNW) (IEEE) pp 52–3
- [12] Zhu J et al 2017 Argon plasma induced phase transition in monolayer MoS<sub>2</sub> J. Am. Chem. Soc. 139 10216–9
- [13] Nastasi M et al 1996 Ion-Solid interactions: Fundamentals and Applications (Cambridge: Cambridge University Press)
- [14] Bernas H 2009 Materials Science with Ion Beams vol 116 (Berlin: Springer)
- [15] Czanderna A W et al 2006 Beam Effects, Surface Topography, and Depth Profiling in Surface Analysis vol 5 (Berlin: Springer)
- [16] McGuire G 1978 Effects of ion sputtering on semiconductor surfaces Surf. Sci. 76 130–47

- [17] Ditchfield R and Seebauer E 2001 Semiconductor surface diffusion: effects of low-energy ion bombardment *Phys. Rev.* B 63 125317
- [18] Li Z and Chen F 2017 Ion beam modification of twodimensional materials: Characterization, properties, and applications Appl. Phys. Rev. 4 011103
- [19] He Z et al 2018 Defect engineering in single-layer MoS<sub>2</sub> using heavy ion irradiation ACS Appl. Mater. Interfaces 10 42524–33
- [20] Bangert U *et al* 2013 Ion implantation of graphene: toward IC compatible technologies *Nano Lett.* **13** 4902–7
- [21] Willke P *et al* 2015 Doping of graphene by low-energy ion beam implantation: structural, electronic, and transport properties *Nano Lett.* **15** 5110–5
- [22] Cress C D *et al* 2016 Nitrogen-doped graphene and twisted bilayer graphene via hyperthermal ion implantation with depth control *ACS Nano* **10** 3714–22
- [23] Friedman A L et al 2016 Electronic transport and localization in nitrogen-doped graphene devices using hyperthermal ion implantation Phys. Rev. B 93 161409
- [24] Nanda G et al 2015 Defect control and n-doping of encapsulated graphene by helium-ion-beam irradiation Nano Lett. 15 4006–12
- [25] Fox D S et al 2015 Nanopatterning and electrical tuning of MoS<sub>2</sub> layers with a subnanometer helium ion beam Nano Lett. 15 5307–13
- [26] Naitou Y and Ogawa S 2016 Anderson localization of graphene by helium ion irradiation Appl. Phys. Lett. 108 171605
- [27] Ma Q et al 2013 Controlled argon beam-induced desulfurization of monolayer molybdenum disulfide J. Phys.: Condens. Matter 25 252201
- [28] Iberi V et al 2016 Nanoforging single layer MoSe<sub>2</sub> through defect engineering with focused helium ion beams Sci. Rep. 6 30481
- [29] Stanford M G et al 2016 Focused helium-ion beam irradiation effects on electrical transport properties of few-layer WSe<sub>2</sub>: enabling nanoscale direct write homo-junctions Sci. Rep. 6 27276
- [30] Bertolazzi S *et al* 2017 Engineering chemically active defects in monolayer MoS<sub>2</sub> Transistors via ion-beam irradiation and their healing via vapor deposition of alkanethiols *Adv. Mater.* 29 1606760
- [31] Ochedowski O et al 2013 Radiation hardness of graphene and MoS<sub>2</sub> field effect devices against swift heavy ion irradiation J. Appl. Phys. 113 214306
- [32] Cheng Z et al 2016 Modifying the Ni–MoS<sub>2</sub> contact interface using a broad-beam ion source IEEE Electr. Device Lett. 37 1234–7
- [33] Laegreid N and Wehner G 1961 Sputtering yields of metals for Ar<sup>+</sup> and Ne<sup>+</sup> ions with energies from 50 to 600 eV J. Appl. Phys. 32 365–9
- [34] Komsa H-P et al 2013 From point to extended defects in two-dimensional MoS<sub>2</sub>: evolution of atomic structure under electron irradiation Phys. Rev. B 88 035301
- [35] Ghorbani-Asl M et al 2017 Two-dimensional MoS<sub>2</sub> under ion irradiation: from controlled defect production to electronic structure engineering 2D Mater. 4 025078
- [36] Ma Q et al 2014 Postgrowth tuning of the bandgap of singlelayer molybdenum disulfide films by sulfur/selenium exchange ACS Nano 8 4672–7

- [37] Chen Y et al 2018 Tuning electronic structure of single layer MoS<sub>2</sub> through defect and interface engineering ACS Nano 12 2569–79
- [38] Molina-Sanchez A and Wirtz L 2011 Phonons in single-layer and few-layer MoS<sub>2</sub> and WS<sub>2</sub> *Phys. Rev.* B **84** 155413
- [39] Lee C *et al* 2010 Anomalous lattice vibrations of single-and few-layer MoS<sub>2</sub> *ACS Nano* 4 2695–700
- [40] Mignuzzi S et al 2015 Effect of disorder on Raman scattering of single-layer MoS<sub>2</sub> Phys. Rev. B 91 195411
- [41] Wang D et al 2017 Engineering two-dimensional electronics by semiconductor defects Nano Today 16 30–45
- [42] Lin Y-C et al 2014 Atomic mechanism of the semiconductingto-metallic phase transition in single-layered MoS<sub>2</sub> Nat. Nano 9 391
- [43] Sutter E et al 2016 Electron-beam induced transformations of layered tin dichalcogenides Nano Lett. 16 4410–6
- [44] Kappera R et al 2014 Phase-engineered low-resistance contacts for ultrathin MoS<sub>2</sub> transistors Nat. Mater. 13 1128
- [45] Zhang F et al 2019 Electric-field induced structural transition in vertical MoTe<sub>2</sub>-and Mo<sub>1-x</sub>W<sub>x</sub>Te<sub>2</sub>-based resistive memories *Nat. Mater.* 18 55
- [46] Kretschmer S et al 2017 Structural transformations in twodimensional transition-metal dichalcogenide MoS<sub>2</sub> under an electron beam: insights from first-principles calculations J. Phys. Chem. Lett. 8 3061–7
- [47] Liu Y et al 2018 Enhancement of out-of-plane charge transport in a vertically stacked two-dimensional heterostructure using point defects ACS Nano 12 10529–36
- [48] Ge R et al 2017 Atomristor: nonvolatile resistance switching in atomic sheets of transition metal dichalcogenides Nano Lett. 18 434–41
- [49] Schulman D S et al 2018 Contact engineering for 2D materials and devices Chem. Soc. Rev. 47 3037–58
- [50] Allain A *et al* 2015 Electrical contacts to two-dimensional semiconductors *Nat. Mater.* **14**1195
- [51] Léonard F and Talin A A 2011 Electrical contacts to one-and two-dimensional nanomaterials *Nat. Nano* 6 773
- [52] Cheng Z et al 2018 Contacting and Gating 2D Nanomaterials IEEE Trans. Electr. Device 65 4073–83
- [53] Smith J T *et al* 2013 Reducing contact resistance in graphene devices through contact area patterning *ACS Nano* **7** 3661–7
- [54] Liu D et al 2013 Sulfur vacancies in monolayer MoS<sub>2</sub> and its electrical contacts Appl. Phys. Lett. 103 183113
- [55] Cheng Z et al 2018 Immunity to scaling in MoS<sub>2</sub> transistors using edge contacts (arXiv:1807.08296)
- [56] Lee Y H et al 2012 Synthesis of large-area MoS<sub>2</sub> atomic layers with chemical vapor deposition Adv. Mater. 24 2320–5
- [57] Najmaei S et al 2013 Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers Nat. Mater. 12 754
- [58] Yu Y et al 2016 Engineering substrate interactions for high luminescence efficiency of transition-metal dichalcogenide monolayers Adv. Funct. Mater. 26 4733–9
- [59] Mills A et al 2016 Ripples near edge terminals in MoS<sub>2</sub> few layers and pyramid nanostructures Appl. Phys. Lett. 108 081601
- [60] Zhang F et al 2018 Atomically resolved observation of continuous interfaces between an as-grown MoS<sub>2</sub> monolayer and a WS<sub>2</sub>/ MoS<sub>2</sub> heterobilayer on SiO<sub>2</sub> ACS Appl. Nano Mater. 1 2041–8