Atomic-Scale Carving of Nanopores into a van der Waals Heterostructure with Slow Highly Charged Ions

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ABSTRACT: The growing family of 2D materials led not long ago to combining different 2D layers and building artificial systems in the form of van der Waals heterostructures. Tailoring of heterostructure properties postgrowth would greatly benefit from a modification technique with a monolayer precision. However, appropriate techniques for material modification with this precision are still missing. To achieve such control, slow highly charged ions appear ideal as they carry high amounts of potential energy, which is released rapidly upon ion neutralization at the position of the ion. The resulting potential energy deposition is thus limited to just a few atomic layers (in contrast to the kinetic energy deposition). Here, we irradiated a freestanding van der Waals MoS2/graphene heterostructure with 1.3 keV/amu xenon ions in high charge states of 38, which led to nanometer-sized pores that appear only in the MoS2 facing the ion beam, but not in graphene beneath the hole. Reversing the stacking order leaves both layers undamaged, which we attribute to the high conductivity and carrier mobility in graphene acting as a shield for the MoS2 underneath. Our main focus is here on monolayer MoS2, but we also analyzed areas with few-layer structures and observed that the perforation is limited to the two topmost MoS2 layers, whereas deeper layers remain intact. Our results demonstrate that in addition to already being a valuable tool for materials processing, the usability of ion irradiation can be extended to mono- (or bi)layer manipulation of van der Waals heterostructures when the localized potential energy deposition of highly charged ions is also added to the toolbox.

KEYWORDS: 2D material modification, ion beam surface modification, monolayer precision, van der Waals heterostructure

Since the discovery and realization of the first known two-dimensional (2D) material in 2004,1 active research has led to the synthesis and preparation of a large number of 2D atomic crystal structures with extraordinary properties. Apart from well-known graphene, transition-metal dichalcogenide (TMD) monolayers are especially attractive for application as atomically thin semiconductors that, for example, provide flexibility unattainable with their bulk competitors. Besides profiting from the outstanding properties of individual 2D materials, the application potential of 2D materials can be extended by combining them into van der Waals heterostructures.2−5 Stacking of atomically flat layers allows for development of devices benefiting from the composition of properties found in the individual 2D crystals. The high conductivity in graphene in combination with the semiconducting molybdenum disulfide (MoS2), for instance, can be used to fabricate flexible and transparent memory devices.5,6 Another example, utilizing the high optical absorption of monolayer MoS2 with a direct electronic band gap in combination with graphene as the channel material, allows scalable fabrication of phototransistors.6

Overall, one major focus so far has been on the synthesis of 2D materials,7−10 while processing and modifying them postgrowth11−14 is only now emerging as a way toward new applications for 2D crystals and their heterostructures. Ideally, precise surface sensitive techniques that allow structural
Tailoring of individual layers while preventing damage in the substrate would be needed, as it is often the support that governs the defect formation in 2D materials. Heavy ions, in general, and focused ion beams, in particular, have been used since the 1970s for milling patterns into surfaces for industrial use and are still a powerful toolkit for modern applications. Unfortunately, these methods often damage the underlying substrate through the buildup of an extended collision cascade. Slow ions in high charge states avoid this problem because they carry large amounts of potential energy (determined by the sum of ionization energies), the majority of which is released within a shallow area in the surface when the charged projectile undergoes deexcitation. The released energy is transferred preferentially to the target’s electronic subsystem, leading to a high degree of electronic excitation and ionization. This leads in the end to atomic motion and nanostructure formation on the surface without creating additional ionization and electronic excitation in the substrate along the ion’s path (in contrast to, for example, swift heavy ions).

In this study, we irradiate MoS2/graphene heterostructures with highly charged xenon ions and observe nanometer-sized pores exclusively in the MoS2 layer if it faces the ion beam. The remaining potential energy after the transmission through the first layer is not sufficient to perforate a single layer of graphene, which, as seen in atomic resolution scanning transmission electron microscopy (STEM) images, stays without observable damage. Moreover, when the graphene faces the ion beam first, no damage is observed in the MoS2 underneath. Although protective shielding from electronic excitation induced damage of MoS2 by graphene was shown before in a transmission electron microscopy (TEM) experiment, it has not been reported in the context of highly charged ion (HCl) irradiation and it has a different origin in our case of HClIs. This protection likely stems from the high electron mobility which leads to rapid screening of the excitations that we have shown before. In contrast, individual freestanding single layer MoS2 can be perforated using HClIs, similar to our graphene-supported samples. Our analysis of sample areas containing few-layer MoS2 on graphene shows that under the conditions used here, in such a system the HCl perforation is limited to two layers. Overall, our results clearly reveal the extreme surface sensitivity of HClIs, establishing them as the ideal tool for material property tailoring of van der Waals heterostructures down to monolayer precision.

**RESULTS AND DISCUSSION**

Our experiment is schematically depicted in Figure 1. Figure 2a illustrates that the irradiation with 1.3 keV/amu Xe58+ ions (at a fluence of $1 \times 10^8$ ions/cm²) leads to the perforation of a 2D van der Waals MoS2/graphene heterostructure similar to what has been reported for a freestanding MoS2 membrane. All presented microscopy images were recorded with the Nion UltraSTEM 100 aberration-corrected STEM instrument at an acceleration voltage of 60 kV using the medium-angle annular dark field (MAADF) detector. Each pore is a result of a single-ion impact, which follows from the low probability (<10⁻⁷) of double impacts at this low fluence. The pore size corresponds to a sputtering yield of ~340 at/ion, which clearly follows from the ion’s potential energy deposition and not from direct knock-on, as sputtering in that case would be more than 2 orders of magnitude lower (~2 at/ion). A magnification of...
the image (Figure 2b,c) reveals the pore to be only in the topmost MoS$_2$ layer. Beneath the pore, the still intact hexagonal structure of graphene is visible (c). Thus, even in the presence of a highly conductive support such as graphene, charge exchange in between the membranes is not sufficient to resupply charges in the MoS$_2$ on the time scale of lattice disintegration. Even small pores remain and do not get repaired by surrounding contaminations, which might be important in view of future applications. In total, we analyzed 68 pores in MoS$_2$ from two different samples after HCl irradiation with the help of atomic resolution STEM, and determined a mean pore radius of 3.2 ± 1.0 nm, in agreement with pores found earlier in individual freestanding MoS$_2$ layers irradiated under similar conditions.$^{12}$ Pores appearing along grain boundaries$^{29}$ or created due to electron irradiation during imaging were excluded from the analysis. The width of ±1.0 nm given here stems from a Gaussian distribution width (standard deviation) of evaluated pore radii, while the error of the mean amounts to only 0.14 nm. For radius evaluation we determine the area of the pores by their contrast (image analysis) and calculate the radius from a circle with the same area as the pores are not always exactly circularly shaped. Note that at the electron beam energies we used the damage cross section is smallest, and we took care to minimize exposure as much as possible during imaging. From the comparison of the pore density with the ion fluence we can conclude that the pores are ion induced rather than electron induced and their size stays constant during imaging.

In general, we distinguish between two mechanisms possibly leading to the observed perforation of a semiconducting thin membrane, both induced by the high electronic perturbation the HCl brings into the system. The first one is a local charge build-up as a consequence of charge removal combined with too low electron mobility to compensate the missing charges within the time scale of lattice vibrations. This may play a role for defect creation in band gap materials such as MoS$_2$. It leads to repulsive forces between ionized target atoms and eventually to a rupture of the material (a process termed as "Coulomb explosion").$^{30}$ Alternatively, structural weakening of the lattice can follow from perturbations in the electronic structure, caused by excitation of electrons from bonding valence states to antibonding states in the conduction band. If these excitations survive long enough and stay localized (e.g., forming self-trapped excitons),$^{31}$ the excitation energy can be transferred to target atoms leading to desorption of atoms and ions.$^{32}$ Bond weakening due to such a mechanism was recently identified as the reason for defect formation during low-energy electron irradiation.$^{33}$

In our experiment we cannot rule out either one of the defect mechanisms a priori, but similarities to processes induced by electron irradiation might be pointing toward the second process. We note that a major difference would be observable in the ejected fragments after pore formation: An enhanced yield of positively charged secondary ions would be a strong indication for the Coulomb explosion model, while neutral fragments at thermal energies would be expected from a desorption driven process. However, such fragments following from HCl irradiation of monolayer MoS$_2$ have so far not been reported.
In the following, we discuss the high sensitivity of perforation to the first or first two surface layers achievable by the irradiation with slow HCIs. Figure 3a shows a bilayer MoS$_2$ (BL-MoS$_2$) on graphene after HCI irradiation. (Some bi- and fewlayer areas are inevitably grown during chemical vapor deposition of MoS$_2$ on a SiO$_2$/Si substrate.) In Figure 3a, a pore in both MoS$_2$ layers, is visible with a remaining monolayer MoS$_2$ (ML-MoS$_2$) area around the pore. Again, the graphene underneath the pore stays without observable damage. In contrast, Figure 3c shows a pore in triple-layer MoS$_2$ (TL-MoS$_2$) on top of graphene. For such samples, pores were observed only within two MoS$_2$ layers leaving the third layer and graphene intact (compare zoom-in in Figure 3d).

Hence, we conclude that the majority of potential energy of a highly charged 1.3 keV/amu Xe$^{38+}$ ion is deposited within the first two layers and as a consequence the remaining energy is not sufficient to create a pore in the third MoS$_2$ layer. Further, we expect that addressing exclusively just one of the layers within a multilayer MoS$_2$ sample becomes feasible when tuning the ion’s kinetic energy and/or charge state.

As a counter experiment, the stacking order was reversed (graphene facing the ion beam). The resulting images after 1.3 keV/amu Xe$^{38+}$ ion irradiation are shown in Figure 4. This time, no perforation is visible in either the graphene or in the MoS$_2$ layer. Although surprising, this finding is consistent with earlier work on freestanding graphene. Because the potential energy deposition of the HCI proceeds only above and within the first layer, electronic excitations are now created predominantly in graphene. This results in carrier mobilities of up to $\mu \approx 10,000$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature enable prompt charge resupply and prevent Coulomb explosion. Also, as a semimetal, strong electronic excitations (more precisely excitation densities) created in the graphene are highly mobile, and the energy can be dissipated before lattice movement sets in. Consequently, the perforation of the MoS$_2$ monolayer beneath the graphene is now completely suppressed. The large field of view images shows no ion-induced defects in any of the layers. To check for the presence of both layers in all observed images, a fast Fourier transform (FFT) was performed as it allows detecting the presence of both 2D crystals (Figure 4e,f).

In Figure 4d, spots following from MoS$_2$ are marked with red circles, while the graphene lattice leads to spots marked via blue circles in the image. An intact hexagonal structure of the monolayer MoS$_2$ can be revealed from the same STEM images after sequentially filtering the image for contamination (diffuse scattering in d) and graphene (on top of the sample). To conclude these observations, graphene protects the monolayer MoS$_2$ underneath against irradiation damage as it is able to mitigate the induced ionization. Note that direct knock-on damage induced by the heavy Xe projectile is expected to lead to about 1−4 sputtered atoms per layer.28 For graphene, such point defects may heal out while the sample is transported (in ambience) to the STEM instrument and even in MoS$_2$ point defects can be substituted by oxygen or even hydrocarbides.40,41 Furthermore, such small defects would be almost impossible to distinguish from intrinsic or electron-irradiation induced damage. Therefore, we consider pores with radii $>1$ nm as “damage” (in contrast to smaller “defects”) and layers with only point defects and/or substituted defects as “defects”. Note that single point defects affect the electronic properties of a 2D material while we consider here carving or perforation of the heterostructure.
Recently, it was shown that radiolysis driven beam damage in monolayer MoS\textsubscript{2}, induced by and observed in TEM, can be reduced through a single layer of graphene on top of the membrane or even avoided when encapsulating MoS\textsubscript{2} in two graphene sheets.\textsuperscript{25} As we derive a similar behavior for our ion beam experiments, we want to put our work into context. It is well-known that for semiconductors like MoS\textsubscript{2}, atom displacement via direct knock-on is not the only damage mechanism during TEM imaging. Even if the former can be avoided by setting the electron beam energy below the displacement energy threshold, as in experiments reported in ref \textsuperscript{25}, damage with a significantly large cross section still occurs and is associated with bond weakening and subsequent lattice disintegration. Hence, it is concluded that it is rather a high density of electronic excitation as a result of energy transfer into the electronic system which leads to target atom displacement in MoS\textsubscript{2}, in contrast to a simple momentum transfer in a knock-on collision. The underlying mechanism for the effective shielding of the membrane through a graphene sheet in TEM is not fully understood. For electron irradiation experiments, however, the energy deposition in either layer of a heterostructure is virtually the same as the stopping in one layer leads to perforation in case of MoS\textsubscript{2} at the front, but keeps graphene intact in cases where graphene is at the front. In our case, it is the layer order, which is crucial for the protective shielding of layers in a van der Waals heterostructure from HCI induced potential sputtering. Consequently, the HCI\textsuperscript{2} potential energy deposition is strongly depth dependent; i.e., the very first layer absorbs the majority of potential energy of the ion. The energy take-up from the first layer leads to perforation in case of MoS\textsubscript{2} at the front, but keeps graphene intact in cases where graphene is at the front. This is consistent with earlier findings on HCI irradiation of individual layers. For as-grown bilayer MoS\textsubscript{2} (on graphene) the interlayer coupling is expected to be much higher than for the transferred MoS\textsubscript{2}/graphene heterostructure and thus the potential energy can be distributed over two layers. Still, we observe no perforation of a third layer. This layer dependence of perforation is in stark contrast to electron based experiments in TEM. The shielding of graphene is for HCIs a consequence of energy absorption from the ion rather than energy transfer from the excited MoS\textsubscript{2} layer to graphene.

To elucidate the interlayer coupling between graphene and MoS\textsubscript{2}, we performed density functional theory (DFT) calculations of a commensurate graphene/MoS\textsubscript{2} slab containing 3 × 3 MoS\textsubscript{2} and 4 × 4 graphene unit cells. Electron densities are strongly located within the respective layers, with a minimal shift of the graphene density toward the MoS\textsubscript{2} layer (Figure 5). While these results are obtained within a ground-state approach, they highlight the comparatively weak coupling between the adjacent layers in van der Waals heterostructures. For a more quantitative analysis, we compare the band structure of the 2D heterostructure with those from isolated graphene and MoS\textsubscript{2} layers. We find nearly no difference (see Supporting Information Figure 1 and note the scale in Figure 5 (right)), showing strong electronic separation not only concerning electron densities but also individual eigenstates and lower lying conduction bands. Avoided crossings emerge between Mo-dominated bands of MoS\textsubscript{2} and \( p_z \) bands of graphene (see zoom-in in Supporting Information Figure 1), with a splitting of roughly 50 meV. Finally, we estimate electronic transport between the two layers by a tight-binding approach: we parametrize separate graphene and MoS\textsubscript{2} tight-binding models from DFT orbitals and couple them using an empirical interlayer coupling coefficient \( \gamma_{IL} = 100 \text{ meV} \) between the layers chosen to reproduce the splitting in the band structure as obtained from DFT (zoom-in in Supporting Information Figure 1). We find that the intralayer conductance within graphene or MoS\textsubscript{2} is at least 2 orders of magnitude larger than the interlayer conductance (compare Supporting Information Figure 2), even in the case of ideal defect-free layers. Consequently, charge transport from the graphene to the MoS\textsubscript{2} layer is not efficient enough to resupply the missing charges or adsorb electronic excitations induced by the ion neutralization. Due to the small interlayer conductance, we observe pores in the MoS\textsubscript{2} layer on top of graphene when the ion beam first faces the semiconductor. In the opposite case (reversed stacking order), however, electronic excitations are predominantly introduced in graphene in which the missing charges can be rapidly resupplied within the plane due to the large intralayer conductance. Consequently, the MoS\textsubscript{2} layer beneath remains intact.

Figure 5. Isosurface plot of the electron density in the MoS\textsubscript{2}/graphene system (left) and charge density projected onto the z-axis (middle). The difference in electron density for the coupled MoS\textsubscript{2}/graphene system from charge densities calculated for the individual monolayers is negligibly small (right).
CONCLUSIONS

To summarize, we showed that the irradiation of a MoS2/graphene van der Waals heterostructure with slow HCIs results in the perforation of one or two MoS2 layers when the ion beam faces the semiconducting MoS2 before its impact on graphene. A mean pore radius of 3.2 ± 1.0 nm for 1.3 keV/amu Xe ions is extracted from atomic resolution STEM images, a finding well in agreement with pores observed in freestanding monolayer MoS2 despite the presence of a single layer graphene support. A tight-binding approach shows an intralayer conductance of 2 orders of magnitude larger than the conductance in between the layers, resulting in an insufficient charge transport from graphene to the MoS2 monolayer. When the stack order is reversed (graphene on top), MoS2 remains undamaged. Further, the exclusive perforation of only up to two layers within multilayer MoS2 (on graphene) emphasizes the high-surface sensitivity accessible with HCI irradiation and moreover leads to the assumption to reach true monolayer precision once a careful choice of irradiation parameters (lower kinetic energy) is made. Therefore, carving of nanostructures by slow HCIs is one of the very few methods in a plethora of material modification techniques which truly delivers surface sensitivity down to atomic precision. Moreover, as each pore is created by a single ion, the method presented here provides more control over the damage formation. This is in stark contrast to irradiation of van der Waals heterostructures with highly energetic electron beams for which to some extend all layers are damaged, and the effect does not depend on the order of layers. Structuring of monolayers with pores on the nanometer scale without damaging the substrate or additional layers underneath becomes especially interesting for a large variety of van der Waals heterostructures. Well-defined perforated MoS2 “masks”, for instance, can further be used for metal cluster deposition within the pores of an efficient optical absorber (MoS2) and already being well connected to the conductor such as graphene beneath may serve as an optically as well as electronically addressable quantum dot. Moreover, MoS2 and its hybrids with metal(-oxides) grown at the specific pore sites are in particular known as catalysts for electro/photocatalytic hydrogen evolution reactions, and are considered for photocatalytic CO2 reduction. MoS2-based heterostructures might present the requested scalable and low-cost materials adered by evaporating a droplet of isopropanol. Then, a droplet of potassium hydroxide (KOH) was dispersed on the substrate to etch the oxide layer and detach the grid from Si substrate, leaving MoS2/graphene on the grid. Finally, the TEM grid was rinsed in water and 2-propanol. Atomic-resolution STEM images were acquired using an aberration corrected Nion UltraSTEM100 operated at an acceleration voltage of 60 kV, with a pressure of 2 × 10−5 mbar at the sample. A medium angle annular dark field (MAADF) detector in the annular range of 60−200 mrad was used to record the images. For image processing the Nion Swift software (Gaussian blur in Figure 4a, as well as all FFTs) and ImageJ for coloring the image with the look-up table Plasma were applied. When done carefully, damage caused by the electron beam and the ion beam can be easily distinguished during STEM imaging. While the latter is straight away visible, electron-beam induced damage starts by creation of sulfur vacancies that during continuous imaging merge first into line defects and finally transform to pores. This process takes several minutes during continuous irradiation. The average pore-radii induced by ion irradiation were calculated by measuring the area $A = \pi r^2$ ($N = 68$), assuming a circular shape for the pores. For filtering the contaminations in Figure 4b,c we used FFT and masked spatial frequencies to be excluded before back transformation (inverse FFT).

DFT and Transport Calculations. We performed density functional theory (DFT) calculations of approximately commensurate 4 × 4 graphene and 3 × 3 MoS2 layers using the VASP software package. A Monkhorst−Pack k-point grid of 15 × 15 × 1 was used. Layer separation of 4.8 Å was obtained from a Grimme D3 van der Waals relaxation. We find no strong dependence of the interlayer coupling on the spin−orbit interaction induced by Mo. Using the Wannier90 code, we obtained tight-binding parameters for the separate layers and then fitted a coupling strength of ~60 meV to reproduce the DFT splitting obtained from DFT in tight-binding. We then calculated the interlayer conductance of a 30 nm ribbon with periodic boundary conditions in the Landau−Büttiker approximation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c04476.

Band structure of MoS2/graphene heterostructure calculated from density functional theory and compared to individual band structure calculations for a monolayer MoS2 and a monolayer graphene separately; interlayer versus intralayer conductance in a MoS2/graphene heterostructure using a tight-binding approach (PDF)

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EXPERIMENTAL METHODS

Ion Beam Irradiation. Highly charged xenon ions were created in an electron beam ion source (EBIS) commercially available from Dreebit GmbH, Germany. An ion charge state of 38 with a potential energy of 0.3 keV/amu and kinetic energy of 1.3 keV/amu was selected via a Wien filter and applied for all experiments. Ion irradiation of the samples was performed under ultrahigh vacuum conditions (pressure below 3 × 10−9 mbar) and a low total fluence of 1 × 1010 ions/cm2 was applied to each sample to avoid multiple hits of the same area. After irradiation, samples were transferred through air to the STEM instrument (see below) and introduced again to UHV conditions.

Sample Preparation and Characterization. To fabricate the MoS2/graphene heterostructures, the MoS2 samples were synthesized on SiO2/Si substrates by CVD, as described in ref 46 and transferred onto commercially available graphene coated TEM grids from Graphenea, Inc., using a polymer free wet chemical method. To begin with, the TEM grid was placed on the MoS2 substrate and...
Author Contributions

J.S. and H.I. contributed equally to the work.

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