ABSTRACT: Production of defects under electron irradiation in a transmission electron microscope (TEM) due to inelastic effects has been reported for various materials, but the microscopic mechanism of damage development in periodic solids through this channel is not fully understood. We employ non-adiabatic Ehrenfest, along with constrained density functional theory molecular dynamics, and simulate defect production in two-dimensional MoS\(_2\) under electron beam. We show that when excitations are present in the electronic system, formation of vacancies through ballistic energy transfer is possible at electron energies which are much lower than the knock-on threshold for the ground state. We further carry out TEM experiments on single layers of MoS\(_2\) at electron voltages in the range of 20–80 kV and demonstrate that indeed there is an additional channel for defect production. The mechanism involving a combination of the knock-on damage and electronic excitations we propose is relevant to other bulk and nanostructured semiconducting materials.

KEYWORDS: Two-dimensional materials, transition-metal dichalcogenides, high-resolution transmission electron microscopy, defects

The emergence of two-dimensional (2D) materials\(^{17}\) attracted additional attention to the damage problem, as many of these systems proved to be radiation-sensitive materials\(^{2,18}\). At the same time, their very geometry, which enables one to identify single atoms, made it possible to quantify the damage at different voltages by directly counting missing atoms\(^{5,19}\) and imaging the development of the damage in the specimen with atomic resolution\(^{20–23}\). Nevertheless, the defect production channels mentioned above are difficult to differentiate,\(^2\) and the role of electronic excitations is not well understood. Currently, there is no quantitative microscopic theory describing the relation between the amount of energy deposited in the specimen through electronic excitations and damage creation in periodic solids. The lifetime of a core hole under electron beam. We show that when excitations are present in the electronic system, formation of vacancies through ballistic energy transfer is possible at electron energies which are much lower than the knock-on threshold for the ground state. We further carry out TEM experiments on single layers of MoS\(_2\) at electron voltages in the range of 20–80 kV and demonstrate that indeed there is an additional channel for defect production. The mechanism involving a combination of the knock-on damage and electronic excitations we propose is relevant to other bulk and nanostructured semiconducting materials.

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implemented in the GPAW code. (DFT) simulations. We used several computational ap-
ballistic energy transfer from the impinging electrons to the amount of damage created by the beam experimental data.

further carry out TEM experiments where we directly assess the formation of the TEM images. The simulations indicate that the excitation cannot be used to model electron scattering or electric where the energetic electron is approximated as a point source energetic electrons in the TEM, and it is close to the approach is justi-
the mass of an electron, negative charge, and the interaction with the electron/nuclei described by a modified hydrogen PAW potential. The details are given in SI. This approximation is justified by the small (∼10⁻² Å) de Broglie wavelength of the energetic electrons in the TEM, and it is close to the approach where the energetic electron is approximated as a point source electric field impulse. We stress that such an approximation cannot be used to model electron scattering or formation of the TEM images. The simulations indicate that the electron transfers a part of its kinetic energy to the electronic system of the target and leaves the system in a state mixture comprising a valence band excitation. The excitation is initially localized (Figure 1b), but it is spread over the whole system after a few fs. The energy deposition is rather small in this approach, as the PAW potential is too "soft" at small distances from the particle.

In order to investigate the time evolution of the excitation further and also account for a stronger perturbation of the electronic system by the electron impact, a separate set of ED simulations was performed. Exactly one electron was excited into the CBM with a localization length of about 1 Å (Figure 1c). Further details can be found in SI. The charge density difference for the excited state Δρ* = ρ* - ρ0 after an impact (c) Simulations where exactly one electron is excited with the excitation initially being localized on a sulfur atom. (d) The spatial extent of the excitation after 1.6 fs as described within the framework of ED.

Figure 1. ED simulations of a high-energy electron impact into a MoS₂ sheet. The electron is modeled as a classical particle with a precisely defined trajectory, which can give rise to electronic excitations in the target material, as schematically illustrated in (a). (b) The spatial extent of the electronic excitation created in the system immediately after the impact. (c) Simulations where exactly one electron was excited into the CBM with a localization length of about 1 Å. (d) The spatial extent of the excitation after 1.6 fs as described within the framework of ED.

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the excitation at the emerging vacancy site. The charge density difference can be analyzed in more detail by calculating the generalized inverse participation ratio \(GIPR\)\(^{10}\) for \(\Delta \rho^*\) defined as

\[
GIPR(t) = \sqrt{\int |\Delta \rho^*(\mathbf{r}, t)|^2 dV / \left[ \int |\Delta \rho^*| dV \right]^2}
\]  

(1)

As evident from Figure 2c, localization of \(\Delta \rho^*\) is substantial after 10 fs, when the recoil S atom is displaced by more than 0.6 Å. A decrease in the energy difference \(\Delta E^* = E^* - E_0\) where \(E^*\) and \(E_0\) are the excited- and ground-state energies, is related to the displacement of the atom, accompanied by the appearance of a defect state in the band gap of the material as the S atom moves out-of-plane. This is confirmed by static calculations of the density of states at different times during the displacement process shown in Figure 2d. As ED simulations are computationally too expensive to calculate \(T_d\) we used c-DFT MD to assess it. The initial kinetic energy was varied in order to find \(T_d\). An atom in the simulations was considered to be displaced when it moved at least 4.5 Å from its initial position and it has a velocity component still pointing away from the MoS\(_2\) sheet. Additionally, it was checked that the average force on the recoil atom is below 0.01 eV/Å. This situation is typically achieved for simulation times of about 400–600 fs (time step 0.2 fs). The conditions imposed on the recoil atom ensure that it will not come immediately back and fill the defect site.

The results are summarized in Table 1. For nonspin-polarized calculations, \(T_d\) for the ground state was found to be 7.1 eV in agreement with previous calculations.\(^7\) We also repeated calculations with account for spin-polarization and expectedly received lower values for \(T_d\) (by spin-polarization energy of an isolated atom). We stress, though, that the ground-state DFT MD cannot adequately describe the dynamics of the system associated with a spin flip, so that we list both non- and spin-polarized values. Table 1 also gives \(T_d\) when a core hole with an infinite lifetime is present at the recoil S atom. The details of simulations are given in SI. \(T_d\) also dramatically decreases, but as the actual lifetime of core holes is very short, just a few fs, as discussed above, this process cannot govern defect production, although it may still contribute to the creation of defects at the early stages of damage development, effectively lowering \(T_d\).

In the same simulation setup, we found a pronounced drop in the threshold to 4.8 eV, when one electron was in the excited state. \(T_d\) decreases further to 3.5 eV for the double excitation. This illustrates that initially delocalized electronic excitations localize on the incipient vacancy and have a dramatic effect on the behavior of the system when kinetic energy is transferred to one of the atoms.

Since displacement cross section data are available mostly for high (above 60 kV) voltages,\(^{7,59}\) we performed measurements of this quantity by directly analyzing high-resolution (HR)TEM images of MoS\(_2\) sheet obtained at voltages below \(U_{th}\). Figure 3a presents Cc/Cs-corrected HRTEM images of
Figure 3. (a) Cc/Cs-corrected HRTEM images of single-layer MoS$_2$ before and after exposure to the total dose of $1.5 \times 10^7$ electrons/nm$^2$ at an acceleration voltage of 20 kV. During irradiation, S vacancies appear. Fourier-filtered images from the red dashed framed area are given in the insets (solid frames). As an example, a vacancy in each filtered and raw image is marked by a cyan circle. $\Delta V$ gives the number of the produced vacancies. (b) The experimental (squares) and theoretical (curves) displacement cross sections $\sigma$ of S atoms in MoS$_2$, as calculated within the framework of the McKinley–Feshbach formalism with account for thermal vibrations and with different values of displacement threshold $T_d$ corresponding to the ground and excited states. The decrease in the excitation probability with increasing electron energy is accounted for within the framework of the Bethe theory. The total cross section with a $T_d = 1.5$ eV, which matches the experimental data reasonably well, is also shown.

The excitation can hypothetically be created by not only that same electron which displaces the atom but also by another electron. The lifetime of an excitation in a MoS$_2$ is about 1 ps, and therefore, one can expect that $\sigma^{tot}(E)$ can qualitatively describe the trends in the experimental observations. However, as evident from the dashed curves in Figure 3b, the decrease in the radiolysis cross section is too fast to provide a minimum on the total cross section curve. For the quantitative agreement, $T^{exc}$ should be lower than the calculated value, with the best fit yielding $T^{exc} = 1.5$ eV, yellow solid line. The lowering of the effective displacement threshold may be related to the contribution from core holes at the initial stages of damage development or multielectron excitations. The excitation can hypothetically be created by not only that same electron which displaces the atom but also by another electron. The lifetime of an excitation in a MoS$_2$ is about 1 ps, and therefore, one can expect that $\sigma^{tot}(E)$ can qualitatively describe the trends in the experimental observations. However, as evident from the dashed curves in Figure 3b, the decrease in the radiolysis cross section is too fast to provide a minimum on the total cross section curve. For the quantitative agreement, $T^{exc}$ should be lower than the calculated value, with the best fit yielding $T^{exc} = 1.5$ eV, yellow solid line. The lowering of the effective displacement threshold may be related to the contribution from core holes at the initial stages of damage development or multielectron excitations.

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our TEM experiments on single-layer MoS$_2$ sheets at electron voltages in the range of 20–80 kV are consistent with that picture. The mechanism we propose is relevant to other semiconducting materials and, in addition to beam-induced chemical etching, can be responsible for damage production in a wide range of materials at low electron voltages.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c00670.

Details of calculations and TEM experiments, along with additional TEM images of MoS$_2$ sheets before and after exposure to the electron beam. The estimates of energy deposition under typical imaging conditions in TEM experiments are also presented (PDF).

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∥Contributed equally to this work

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Supplementary Information – Formation of defects in two-dimensional MoS$_2$ in transmission electron microscope at electron energies below the knock-on threshold: the role of electronic excitations

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I. METHODS

A. Computational methods

*Quasi-classical electron impact simulations:*

Ehrenfest dynamics simulations based on the time-dependent density functional theory of a negative point particle impinging with 40 keV energy on 2D MoS$_2$ were carried out using the GPAW code. The charge of the projectile was set to -1, and its mass was set to 1/1836 amu, which corresponds to the mass of the electron. The PAW data set was modified taking the hydrogen dataset as a template, as detailed below. As the complete removal of the original valence state of hydrogen is not possible for technical reasons, the corresponding eigenvalue was moved up to the vacuum level. The simulations show no electron density around the particle.

The header of the modified setup file reads:

```xml
<?xml version="1.0"?>
<paw_setup version="0.6">
  <!-- Hydrogen setup for the Projector Augmented Wave method. -->
  <!-- Units: Hartree and Bohr radii. -->
  <atom symbol="e" Z="-1" core="0.0" valence="0"/>
  <xc_functional type="GGA" name="PBE"/>
  <generator type="scalar-relativistic" name="gpaw-0.4.2039">
    Frozen core: none
  </generator>
  <ae_energy kinetic="0.000000" xc="0.000000" electrostatic="0.000000" total="0.000000"/>
  <core_energy kinetic="0.000000"/>
  <valence_states>
    <state n="1" l="0" f="0" rc="0.900" e="-0.00002" id="H-1s"/>
    <state l="0" rc="0.900" e="-0.00001" id="H-s1"/>
    <state l="1" rc="0.900" e="0.00000" id="H-p1"/>
  </valence_states>
</paw_setup>
```

The sulfur PAW dataset still limited the simulation to impact parameters larger than
0.4 Å. The initial system was carefully relaxed using the maximum force criterion set to 0.001 eV/Å and 0.15 Å grid spacing. The time-dependent density functional calculations are performed on a coarser grid with a 0.25 Å spacing. A 4×4 unit cell was used for all calculations together with a gamma point centered 3×3 kpoint sampling according to the Monkhorst Pack grid. For the electron impact simulation, a time step of 0.05 attoseconds is chosen.

**Excited state evolution:**

The system was prepared in an excited state by placing electrons in a conduction band molecular orbital localized at a particular sulfur site. For that we made use of the dscf routines as implemented in GPAW (version 1.1.0). For the ”weights” keyword the index of the corresponding sulfur atom (here: 35) together with the weights of the projector functions (here: all) are specified. Additionally the excitation is then restricted to an energy window of 1 eV to simulate an excitation in the conduction band. Technically, this results in:

```python
from gpaw import GPAW
from gpaw import dscf
calc = GPAW(...)  # ground state calculation
exc = dscf.MolecularOrbital(calc, weights={35: [1,1,1,1,1]}, Estart=0.0, Eend=1.0)
dscf.dscf_calculation(calc_es, [[1.0, exc, 0]], atoms)
```

The evolution of the charge density was studied using Ehrenfest dynamics simulations. The accuracy settings are the same as in the electron impact ED calculation. The time step was adjusted to 5 attoseconds as a compromise between accuracy and simulation (wall) time. 10,000 time steps are performed corresponding to a simulation time of 50 fs.

**Atom displacement in excited MoS\(_2\):**

Ehrenfest molecular dynamics simulations based on time-dependent density functional theory were carried out using the GPAW code to demonstrate the long-living excitation and its localization under the displacement of the sulfur atom. The system was initially prepared in a delocalized valence-conduction band excited state. Then, the velocity of the sulfur atom is set to a value corresponding to the kinetic energy value transferred to it from the impinging electron. The evolution of the charge density of this excited system was calculated for 30 fs with a time step of 5 as.

**Displacement threshold calculations:**
For the systematic determination of the displacement threshold under different conditions (core hole, excited state) \textit{ab initio} Born-Oppenheimer molecular dynamics simulations were performed as implemented in the VASP code. An atom in the simulations was considered to be displaced when it moved at least 4.5 Å from its initial position and it has a velocity component still pointing away from the MoS$_2$ sheet. Additionally, it was checked that the average force on the recoil atom is below 0.01 eV/Å. This situation is typically achieved for simulation times of about 400 fs to 600 fs (time step 0.2 fs). The conditions imposed on the recoil atom assure that it will not come immediately back and fill the defect site.

The excited state in these displacement simulations was modeled by fixing the occupation number and performing constrained DFT cycles within the \textit{ab initio} MD simulation. The time step in these MD simulation run was set to 0.2 fs.

\textit{Core hole excitations:} MD simulations accounting for a core hole excitation were carried using the VASP code. Core hole excitations of the recoil atom were modeled by removing a 2p electron from the core of the “kicked” sulfur atom. The system was kept neutral by adding one electron to the system (to the conduction band in the pristine system). The system size and all other settings were the same as in the constrained DFT Born-Oppenheimer molecular dynamics simulations described above.

\section*{B. Experimental methods}

\textit{Sample preparation:} Molybdenum disulfate was exfoliated on silicon dioxide substrates with a thickness of 90 nm. With an optical light microscope and contrast, measurements were identified \cite{1}. Afterward, an Au Quantifoil TEM grid R 1.2/1.3 was placed on top of the monolayer and brought into contact by evaporation of a drop isopropyl alcohol between monolayer and grid. A solution of potassium hydroxide (KOH) was used to etch the SiO$_2$ surface to release the TEM grid with the monolayer. Residues of the preparation process are removed with double distilled water.

\textit{TEM imaging conditions:} All TEM images were acquired with the Cc/Cs-corrected Sub-Angstrom Low-Voltage Electron microscopy (SALVE) instrument which provides atomic resolution from 80 keV down to electron energies of 20 keV \cite{2}. The Cc and Cs values were
corrected to be in the range of -10 to -20 µm. Typical dose rates in the experiments were in the range of $10^5$ e-/nm$^2$. High-resolution images were recorded on a 2k x 2k GIF camera with exposure times of 1 s.

II. DAMAGE ACCUMULATION IN A SINGLE LAYER OF MOS$_2$ FROM THE ANALYSIS OF TRANSMISSION ELECTRON MICROSCOPY IMAGES

<table>
<thead>
<tr>
<th>Acceleration voltage [kV]</th>
<th>$N$</th>
<th>$\Delta V$</th>
<th>$\phi$ [$10^7$ e-/nm$^2$]</th>
<th>$\sigma$ [barn]</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>13474 281</td>
<td>3.9</td>
<td>5.3(4)</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>13818 282</td>
<td>4.2</td>
<td>4.9(4)</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>14781 227</td>
<td>1.7</td>
<td>9(1)</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>30947 604</td>
<td>1.7</td>
<td>11.6(5)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>27309 503</td>
<td>2.7</td>
<td>6.7(5)</td>
<td></td>
</tr>
</tbody>
</table>

TABLE I. Quantitative results for the damage-cross sections $\sigma$ for the different acceleration voltages. $N$ gives the number of sulfur atoms in the analysed area, $\Delta V$ is the number of the produced vacancies after a dose $\phi$. The values in the parenthesis give the confidence intervals and were taken as $\sqrt{N}$ for $N$, $\sqrt{\Delta V}$ for $V$ and 1% for the accumulated electron dose.

III. DETAILED EXPLANATION OF THE DISPLACEMENT CROSS SECTION CALCULATION

Figure 3 b) displays the comparison of the experimental data obtained in TEM and the displacement cross sections calculated from displacement thresholds determined in the first-principles calculations. The TEM data is plotted with the values and uncertainties summarized in Table 1 for different electron energies $E$ (grey squares). The ground state displacement cross section (blue solid line) for displacement threshold $T_d = 6.5$ eV is computed according to McKinley-Feshbach formula [3]

$$
\sigma_{el}(E, T_d) = \pi \left( \frac{Ze^2}{m_e c^2} \right)^2 \frac{1 - \beta^2}{\beta^4} \left\{ (\xi - 1) - \beta^2 \ln \xi + \pi \alpha \beta \left[ 2(\sqrt{\xi} - 1) - \ln \xi \right] \right\}, \quad (1)
$$
FIG. 1. Cc/Cs-corrected HRTEM images of two-dimensional MoS$_2$ before and after exposure (left/right panels) to the total dose of 1.5 $10^7$ electrons/nm$^2$ at various acceleration voltages. The images for (a) 80 kV, (b) 60 kV, (c) 40 kV are acquired in bright atom and for (d) 30 kV and (e) 20 kV in dark atom contrast. During irradiation, S vacancies appear. Fourier-filtered images from the red dashed framed area are given in the insets (solid frames). As an example, a vacancy in each filtered and raw image is marked by a cyan circle. $\Delta V$ gives the number of the produced vacancies. Scale bars are the same in all images.
where $\beta = v(E)/c$, $\alpha = Z/137$ with the atomic number $Z$ of the target atom and $\xi = T_m(E)/T_d$ with the maximum transferrable energy $T_m(E)$. The displacement cross section is averaged over the out-of-plane velocity distribution [4] to account for thermal vibrations of the target atoms within the Debye model (Debye temperature MoS$_2$ $\theta_{\text{Debye}} = 262.3$ K, ref. [5]). The displacement cross section determined within the same procedure for the excited state ($T_d = 3.5$ eV) is shown in red. In order to establish a comparison to a competing mechanism, the radiolysis cross section as determined by Susi et.al. is shown. Radiolysis by electronic excitation, however, cannot explain the interplay of knock-on damage and electronic excitation and the localization of the latter at a particular bond nor can it account for the drop of the displacement threshold at 20 keV with decreasing electron energy. The displacement cross section for lower displacement threshold ($T_d = 1.5$ eV) combined with the inelastic cross section according to Bethe theory [6] yield a better agreement and can account for this drop. The total displacement cross section as the sum of both contributions without and with account for electronic excitations is displayed in orange. The excitation probability determined by the inelastic cross section within Bethe theory is given by

$$\chi_{\text{Bethe}}^{\text{inel}}(E, E) = \frac{8\pi a_0^2 Z^2}{\beta^2} \frac{E_R}{\gamma m_e c^2} \left[ \ln \left( \frac{2\gamma m_e c^2 \beta^2}{E} \right) - \ln \left( 1 - \beta^2 \right) - \beta^2 \right] \times \zeta, \quad (2)$$

where $a_0$ is the Bohr radius, $E_R = 13.6$ eV the Rydberg energy, and $\gamma = 1/\sqrt{1 - \beta^2}$ denotes the Lorentz factor. The unknown parameter $E$, which quantifies the average energy transfer of the impinging electron to the electronic system of the target, can be estimated by a fit to the sulfur ionization cross section [7] as $E = 79.4$ eV. The magnitude of the inelastic cross section is summarized with the efficiency of the process to the parameter $\zeta$. The contribution of electronic excitations to the displacement cross section is than determined as

$$\sigma^{\text{es}}(E) = \sigma_{\text{el}}(E, T_d^{\text{es}}) \times \chi_{\text{Bethe}}^{\text{inel}}(E, E). \quad (3)$$

with $\zeta = 1.8 \cdot 10^{-11}$ for $T_d = 1.5$ eV.

IV. ENERGY DEPOSITION COMPARISON ELECTRON VS. LASER IRRADIATION

To show that energy deposition under TEM imaging conditions is much smaller than in the typical experiments when TMDs are subjected to laser irradiation and when struc-
tural changes in the sample are observed, we present here the relevant order-of-magnitude estimates.

The deposited power $W$ in the TEM experiments can be defined as:

$$W = I \cdot n_{\text{inel}} \cdot \langle E \rangle,$$

(4)

where $I$ is the total beam current ($I = 6 \cdot 10^{10} \text{ e}^-/\text{sec}$ in our experiments), $n_{\text{inel}}$ is the percentage of non-elastically scattered electrons ($n_{\text{inel}} \sim 10^{-2}$), and $\langle E \rangle$ is the average energy loss ($12 - 15 \text{ eV}$). In our experimental conditions $W$ is of the order of $10^{-9} \text{ W}$. At the same time, typical laser power (when the structure of the sample is changed) is at least 7 orders of magnitude higher (tens of mW) \cite{8, 9}.

It is also possible to estimate the energy deposition per area:

$$w = j \cdot n_{\text{inel}} \cdot \langle E \rangle,$$

(5)

where $j$ is the beam current density ($j = 10^5 \text{ e}^-/\text{nm}^2/\text{sec}$ in our experiments), $w \sim 10^{-15} \text{ W/nm}^2$. At the same time, assuming $W_{\text{laser}} \sim 10^{-2} \text{ W}$ and typical area of the spot of about $1 \mu\text{m}^2$, energy deposition per area would be $w_{\text{laser}} \sim 10^{-8} \text{ W/nm}^2$. Although it is assumed here that all energy is absorbed, the difference is also 7 orders of magnitude.

Another way to compare energy deposition is to look at the temperature raise under typical laser irradiation conditions and under electron beam in the TEM. It has been demonstrated \cite{10} that in graphitic atomically thin samples temperature raise due to the electron beam is about $10^{-3} \text{ K}$. At the same time, laser irradiation has routinely been used for annealing of MoS$_2$ samples \cite{9} or inducing phase transition in other dichalcogenides, MoTe$_2$ \cite{8}. In these experiments, temperature raised up to 700 K. The difference is nearly 6 orders of magnitude, so that even if we assume that the energy deposited by the electron beam is sufficient to raise temperature by about 1K, this would still be much lower than what occurs under laser irradiation.

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