Effects of Proton Radiation-Induced Defects on Optoelectronic Properties of MoS₂

Brendan Foran, Colin Mann, Mark Peterson, Adam Bushmaker, Bo Wang, Jihan Chen, Sisi Yang, and Stephen B. Cronin

Abstract—We report on photoluminescence (PL) spectroscopy and transmission electron microscope imaging of suspended and substrate-supported flakes of the 2-D semiconductor MoS₂ before and after exposure to 100-keV proton radiation with fluences of \(6 \times 10^{13}\), \(6 \times 10^{14}\), and \(6 \times 10^{15}\) p/cm², respectively, and subsequent annealing. An indirect-to-direct bandgap transition is observed, which is preserved after annealing. This transition is accompanied by an unexpected increase in PL intensity after radiation exposure of multilayer samples, which is attributed to higher radiative efficiency of the direct-gap transition.

Index Terms—Proton radiation, semiconductor nanostructures, transition metal dichalcogenide.

I. INTRODUCTION

Progress in the area of 2-D semiconductors, such as MoS₂, has generated great interest in the electrical device research field due to potential use as a replacement of traditional semiconductors substrates for next-generation microelectronic and nanoelectronic devices and circuits, as they offer performance advantages such as high carrier mobility and tunable bandgap [2]. By evaluating radiation effects in the 2-D material MoS₂, we understand the response of devices fabricated from these materials operating in radiation environments, such as in particle accelerators and the space radiation environment. Radiation-induced displacement damage in semiconductors is particularly harmful for minority carrier devices such as optoelectronic components, diodes, and bipolar junction transistors (BJTs), where lattice defects can provide nonradiative decay pathways, greatly reducing the minority carrier lifetime. This is of particular concern for direct bandgap 2-D semiconductors, such as MoS₂, due to the interest in these materials for optoelectronic applications [3], [4]. Also, radiation-induced charging of insulators in close proximity to semiconductor materials can induce unintentional changes in the carrier density due to the field effect. This is concerning because 2-D semiconductors are typically supported on insulating substrates, for instance, when used as the channel material in field-effect transistors (FETs) [5].

In addition to environmental or otherwise unintentional radiation effects, energetic plasma surface treatments, which also create lattice damage, are sometimes used in the semiconductor industry for the processing of materials and devices. For example, plasma treatments are used to improve material surface wettability and bonding, surface functionalization, and material etching and doping. Notably, Lee et al. [6] found that plasma treatment can restore performance of MoS₂ FETs that have been degraded by wet processing or oxygen contamination.

Due to their small physical dimension, MoS₂ and other low-dimensional systems are highly susceptible to lattice defects, changes in individual molecular bonding or charge states of defects nearby or in contact with the device. This has been seen in carbon nanotubes with conductance changes caused by local defects in the surrounding material [7], [8], and also by direct chemical bond breaking/formation on the surface of the device [9], [10]. Furthermore, defects in or on the surface of semiconductors can manifest effects such as random telegraph noise, as is commonly observed in scaled deep-submicrometer silicon devices [11]–[13].

As more deeply scaled microelectronic and nanoelectronic technology utilizing novel low-dimensional materials are used in space systems, effects such as this will become more important.

There have been several studies of the effects of radiation on 2-D materials. Kim et al. [14] studied the effects of proton radiation on MoS₂ FETs and observed a substantial decrease in the conductance as well as shifts in the threshold voltage after irradiation. Zhang et al. [15] reported the effects of the X-ray irradiation on similar back-gated MoS₂ transistors, which resulted in decreased conductance and substantial shifts in the threshold voltage. Lee et al. [16] studied the effects of 662-keV \(\gamma\)-radiation on suspended MoS₂ micromechanical resonators and found that charges induced by the radiation caused a frequency upshift of 2% of the resonance frequency. The radiation hardness of MoS₂ FETs was investigated by Ochędowski et al. [17] with 1.14-GeV U\(^{28+}\) ions, and significant changes in the structural and electrical properties were observed by electrical characterization, atomic force
microscopy, and Raman spectroscopy. Tsai et al. [18] showed that trilayer MoS$_2$ metal–semiconductor–metal photodetectors exhibit high responsivity ($\sim$1.04 A/W) and photogain and are stable under 2-MeV proton illumination radiation indicating that they can be used in harsh environments. Finally, Zan et al. [19] demonstrated that electron beam radiation damage of MoS$_2$ flakes can be mitigated by encapsulation in graphene.

Few of these previous studies, however, have focused on the response of the measured photoluminescence (PL) spectra of the material after radiation. PL spectroscopy in an inexpensive, nondestructive, and simple technique for probing the electronic structure of a material, and can yield useful information about charge carrier dynamics such as the lifetime, decay mechanisms, band-edge energy, defect state presence and energy, and radiative recombination efficiency [20]. The evolution of defect states under exposure to high-energy radiation or extreme temperatures can then be used to identify the physical or chemical nature of imperfections that ultimately limit our ability to construct ideal devices.

In this paper, we used PL to characterize the influence of low-energy proton radiation on the band structure of 2-D MoS$_2$ and characterize lattice damage created by proton radiation using STEM imaging performed with an aberration-corrected microscope. This gives us the ability to obtain atomic resolution images of individual defects and direct measurement of defect character. Both suspended and substrate-supported MoS$_2$ are studied, for a variety of thicknesses. Postradiation annealing and subsequent PL measurements were performed to investigate the nature of the defects.

Fig. 1 shows the optical and scanning electron microscope (SEM) images typical of MoS$_2$ flakes measured in this paper. Samples were fabricated as follows: MoS$_2$ was first exfoliated onto transparent polydimethylsiloxane (PDMS) substrates. Flakes were then transferred using a dry transfer method [26] to 20-$\mu$m-wide suspended regions in a SiN membrane containing several holes approximately 2–3 $\mu$m in size, as shown in Fig. 1. MoS$_2$ samples imaged with STEM were transferred using the same technique to microscope compatible membrane substrates. PL spectra were collected from both suspended and nonsuspended regions of the MoS$_2$ using a Renishaw InVia microspectrometer using 532-nm wavelength light before and after proton irradiation. The laser was focused on the sample through a 100x, 0.75 NA objective, yielding a laser spot diameter of 860 nm. The incident laser power on the sample was 1 mW. No changes in PL spectra were observed during laser exposure. The thickness of the flakes was determined from optical microscope images and the energy of the indirect band emission peak in the PL spectra. The spatial dependence of the PL spectra was not measured. SEM) images were taken after all optoelectronic characterization, to avoid contamination and potential quenching of the MoS$_2$ PL.

The low energy accelerator facility [(LEAF), within the Physical Sciences Laboratories, The Aerospace Corporation] contains a 25–400-keV ion accelerator capable of producing proton beam currents from 10 pA up to 1 mA. The system can deliver proton fluences from $1 \times 10^9$ to $1 \times 10^{17}$ particles/cm$^2$. Redistribution subject to IEEE license.
and is shown in Fig. 2. This facility has been used in other testing for the space radiation environment, including solar cell structures [27], [28] and carbon nanotube films [29].

For the MoS₂ irrations, we irradiated at 100-keV proton energy for fluences of $6 \times 10^{13}$, $6 \times 10^{14}$, and $6 \times 10^{15}$ p/cm², respectively. A beam current of 1 μA at a flux of $\sim 10$ nA/cm² was used (100-cm² beam area). All proton radiation exposures were performed in a vacuum. The sample sees a total incoming power of 1 mW from the beam during irradiation. The low power and broad illumination area of the particle beam rule out sample heating during proton radiation exposure.

Proton ranges in MoS₂ and Si₃N₄ were calculated using the software program stopping and range of ions in matter (SRIM) [30]. For 100-keV protons, the projected ranges in MoS₂ and Si₃N₄ are 515 and 546 nm, respectively. For comparison, the layer spacing in MoS₂ is 0.62 nm. TRIM simulations and SRIM tables were run to calculate the vacancy densities, total ionizing dose (TID), and displacement damage dose (DDD) for various proton fluences in the device materials, and the results are listed in Table I. Mo, S, and total vacancies are the sum of direct proton knock-on (KO) events and also secondary KO events. Secondary KO events are rare due to the thin sample dimensions. For TID and DDD, the underlying Si₃N₄ material is included to capture effects possibly caused by substrate radiation response. Also, TID values for silicon are included for reference as a standard unit.

The TRIM simulation was run as a detailed calculation with full damage cascades for $10^6$ protons, yielding a total of 842 KO vacancies. The displacement energies $E_d$ were set to 7 eV for sulfur and 20 eV for molybdenum, from Komsa et al. [31]. The material layer thickness was set to 4 Å, and the defect density was measured at the first plane of interaction. The resulting monolayer defect density was then scaled by the lateral atomic density of layered MoS₂ material. The simulation was also run as a monolayer calculation, and the results were within 8% of the detailed calculation for KO vacancy density, however, the monolayer simulation does not explicitly list vacancy density broken out by atomic species.

Extrapolating lattice damage from [32], an estimated vacancy density of $1.7 \times 10^{13}$, $1.7 \times 10^{12}$, and $1.7 \times 10^{13}$ cm⁻², for 100-keV proton fluences of $6 \times 10^{13}$, $6 \times 10^{14}$, and $6 \times 10^{15}$ p/cm², respectively. These numbers were estimated by scaling the predicted vacancy densities from [32] by different fluences and different NIEL values for 100-keV protons versus 2-MeV protons in sulfur, which were obtained from SRIM tables. These vacancy densities are similar to the densities obtained with our own TRIM calculations listed in Table I. In addition to proton radiation, MoS₂ samples were exposed to $^{60}$Co radiation, to compare the effects of purely ionizing radiation with the mix of damage and ionization created by the proton radiation.

STEM images were collected on an FEI (TM) TITAN-Themos having a high brightness X-field emission gun/monochromator source and a DCOR spherical aberration corrector for the probe forming lens. An FEI NanoEx-i/v-MEMS sample holder was used to hold single and bilayer MoS₂ samples for lattice resolution STEM imaging using a 60-keV monochromated to 0.25-eV full-width at half-maximum to produce a 10-pA probe capable of STEM imaging to generate images that well resolved the projected “in-plane” Mo–S atom separation of 1.86 Å (these conditions have been shown to avoid beam-induced lattice damage which occurs at either higher beam energies or probe currents). Images of the MoS₂ lattice showed no damage accumulation after multiple imaging passes. Prior to imaging some areas of the pristine MoS₂ sample, the sample was heated to 350 °C for 10 min in the microscope’s vacuum (~ to test for removal of surface contamination effects. Heating did reduce beam-induced damage rates for higher beam currents (for example imaging at 50 pA).

III. RESULTS

Fig. 3 shows the PL spectra from monolayer, bilayer, trilayer, and four-layer MoS₂ flakes, from both suspended and substrate-supported regions. PL spectra are included for radiation doses of $6 \times 10^{13}$, $6 \times 10^{14}$, and $6 \times 10^{15}$ p/cm², along with the preradiation spectra and postannealing spectra. The samples were annealed after the $6 \times 10^{14}$ p/cm² proton exposure and PL spectra collection, and the $6 \times 10^{15}$ p/cm² proton exposure was subsequently performed. PL emission is more efficient from suspended regions of the MoS₂ flake [2]. Two PL peaks are observed in multilayered samples: a direct band transition at $\sim 1.85$ eV and an indirect band transition at 1.4–1.6 eV.

In all samples except suspended monolayers, PL intensity of the direct band transition peak increases with proton fluence to $6 \times 10^{14}$ p/cm² and then decreases for higher fluences. This is in contrast with the suspended monolayer data, which show a decrease in PL intensity with increasing proton fluence up to $6 \times 10^{14}$ p/cm². The increase in PL intensity measured from the suspended monolayer sample from $6 \times 10^{14}$ to $6 \times 10^{15}$ p/cm² is possibly due to the fact that the samples were annealed between these two fluence steps, as is stated earlier. All samples also exhibited a broadening of the direct transition PL spectra up to proton fluence of $6 \times 10^{14}$ p/cm², and all samples except the monolayer samples showed further broadening up to a proton fluence up to $6 \times 10^{15}$ p/cm². In addition to the observed increase in PL intensity from the direct bandgap transition, a decrease in intensity from
the indirect bandgap transition is observed. After postradiation annealing at 300 °C for 1 h in argon, the PL spectra resemble that of the pristine sample, with the exception that the indirect bandgap transition remains suppressed. The direct transition signal linewidth narrowed to be similar to that of the preradiation signal. In the monolayer sample, the linewidth...
the observed trends, although this is not expected. Further samples. Part-to-part variations may result in deviations from bandgap transition and increase in PL intensity for multilayer fluences showed similar trends, including the indirect-to-direct type was tested at all fluence levels and annealed. These cies) and are circled in the STEM image of irradiated MoS2.

PL spectra after annealing at 300 °C for 1 h. After irradiation, warranted by demonstrated annealing behavior observed in the samples were not heated in the STEM (or at any other time with PL spectroscopy and STEM, which was on the order of days. A few samples of each layer thickness and support type were tested at the lower dose levels (6 × 10^{14}–6 × 10^{15} p/cm²), and only one sample of each thickness and support type was tested at all fluence levels and annealed. These data are plotted in Fig. 3. Data from other samples at lower fluences showed similar trends, including the indirect-to-direct bandgap transition and increase in PL intensity for multilayer samples. Part-to-part variations may result in deviations from the observed trends, although this is not expected. Further study with larger sample numbers is needed.

No differences were observed in the PL spectra collected before and after the exposure to the 60Co gamma radiation. This could be due to the lower displacement damage created by gamma radiation; however, it is most likely due to the smaller radiation dose in general. For comparison, the TID deposited by the gamma radiation exposure was only 16.2 Mrads(Si), while the TID induced by the proton radiation is estimated to be 476 Mrads(Si), 4760 Mrads(Si), and 47600 Mrads(Si), for our proton fluences of 6 × 10^{13}, 6 × 10^{14}, and 6 × 10^{15} protons/cm², respectively.

Fig. 4(a) shows an averaged and filtered STEM image of the MoS2 lattice. The top right inset of Fig. 4(a) shows a zoomed-in view of image with lattice site atomic species assignment. Mo lattice sites are brighter than that of the S2 lattice sites due to Z-contrast (Z_{Mo} = 42, Z_{S} = 32). The inset of Fig. 4(a) (bottom right) shows a plot of intensity versus distance for a selected profile represented by the blue arrow in Fig. 4(a), showing a projected “in-plane” S2–Mo lattice site lateral distance of 1.86 Å.

Before STEM imaging, the sample was exposed to 6 × 10^{13} p/cm² proton radiation fluence, which generates an estimated defect density of ~3.23 × 10^{12} cm⁻². Irradiated MoS2 samples were not heated in the STEM (or at any other time after proton bombardment), to avoid annealing out defects as warranted by demonstrated annealing behavior observed in the PL spectra after annealing at 300 °C for 1 h. After irradiation, some suspected defect sites were observed (suspected S vacancies) and are circled in the STEM image of irradiated MoS2 plotted in Fig. 4(b).

IV. DISCUSSION

The observed indirect-to-direct gap transition with radiation exposure is likely caused by radiation-induced decoupling of the MoS2 layers [33]. Similar behavior was observed when MoS2 films were exposed to oxygen plasma [4]. The observed PL linewidth broadening is attributed to the formation of defect states and bound excitons [21], which collectively contribute to inhomogeneous broadening. It is notable that after annealing, the suppression of the indirect transition remains, yet the defect-associated linewidth broadening of the direct transition recovers. There could be several causes for this behavior. It is possible that defects associated with linewidth broadening are more easily annealed than those associated with layer decoupling. For instance, some defects, such as vacancies, cannot be healed by annealing. It is also possible that the layer decoupled morphology of the film is irreversible postradiation, even though the defects responsible for the creation of this morphology are annealed out.

In general, PL emission is less efficient from substrate-supported regions of MoS2 [2] than it is in suspended regions, due to substrate interactions which degrade radiative efficiency [34]. This is indeed observed in all data shown in Fig. 3. The response of the substrate-supported monolayer MoS2 film [Fig. 3(b)] is interesting, however, because the intensity increases after exposure to radiation, even though there is no indirect-to-direct transition possible. The film is already a monolayer, and exhibiting a direct transition, and thus one would expect the intensity to decrease after exposure to radiation, similar to the suspended monolayer sample [Fig. 3(a)].

It is possible that defect-mediated processes result in substrate decoupling, similar to the observed layer decoupling in multilayer films. This could result in the observed increase in PL intensity. Another possible explanation for the observed radiation-induced increase in PL intensity is defect-induced carrier depletion, which reduces substrate-induced doping and screening of excitons [21].

The MoS2 samples in this paper exhibit a lower radiation sensitivity than other optoelectronic materials found in the literature. For instance, one previous study investigated the effect of 1.5-MeV proton radiation on PL intensity from InGaAs/GaAs quantum well and quantum dot structures [35]. At a 1.5-MeV proton fluence of 6 × 10^{14} p/cm², significant degradation in PL intensity is observed; ~100× reduction in PL intensity for quantum dot structures, and a 10000× reduction in PL intensity for quantum well structures. In MoS2, 100-keV protons have a ~10× higher NIEL than 1.5-MeV protons in InGaAs, and thus, a larger amount of damage is created for a given fluence. For a total nonionizing dose (TNID) equivalent 100-keV proton fluence of 6 × 10^{13} p/cm², the effects of proton radiation are only beginning to become noticeable, with ~50% PL intensity degradation in monolayer samples (and an increase in PL intensity in multilayer samples). It is important to note that PL intensity reduction in response to displacement damage is strongly dependent on the initial starting material quality and minority carrier lifetime. Thus, it is possible that the MoS2 material had a low initial minority carrier lifetime and was, thus, relatively insensitive to radiation-induced defects. While our STEM studies did not identify any atomic defects in pristine samples, further analysis, and time-resolved PL studies are necessary for quantitative initial sample quality determination.

The observed low spatial frequency intensity fluctuations in the STEM image (Fig. 4) might be caused by residual surface contamination. These intensity fluctuations vary from image-to-image, indicating possible movement of the...
suspected surface contaminant layer, perhaps activated by energy deposited by the beam, or possibly slight changes in ripple structure that could also be resolved more easily in lower magnification (not atomic resolution) images.

Electron energy loss spectroscopy analysis after proton bombardment, repeated STEM analysis, and storage in plastic sample boxes showed contamination containing carbon and oxygen, and to a smaller extent silicon and nitrogen. This contamination may have originated from adsorbed contaminants picked up during storage or transfer, residues from the PDMS transfer process, or from hydrocarbon cracking and deposition in the microscope itself. In particular, all plastic boxes produce some level of direct proton Knock-On (KO) events and also secondary KO events. Secondary KO events are rare due to the thin sample dimensions.

TID and DDD are also listed for proton fluences, and were obtained using SRIM tables for both the sample material MoS₂, the underlying material for substrate supported samples, Si₃N₄, and Si for reference as a standard unit.

V. FUTURE WORK

Further study is needed to better understand these issues, for instance, thick, optically dense films might be treated using radiation to induce the indirect-to-direct bandgap transition, which might be useful for high quantum efficiency optoelectronic devices. This is in comparison to monolayer direct bandgap MoS₂ material, which is not optically dense. This paper also has implications for radiation-induced changes in electronic devices. The observed decrease in PL intensity with proton radiation in suspended monolayer films indicates the formation and/or enhancement of nonradiative recombination pathways for excited carriers, which might strongly affect bipolar devices such as BJTs and diodes. Finally, the radiation-induced change in electronic bandgap in multilayer films would also affect electronic device performance, perhaps by changing doping levels, metal contact work function alignment, and ON/OFF ratios.

Fig. 4. STEM images of (a) pristine and (b) defected monolayer MoS₂ region resolving individual Mo and S₂ crystal lattice sites. The image data from irradiated MoS₂ have not been filtered. Suspected S vacancy defect sites are circled.

TABLE I

<table>
<thead>
<tr>
<th>Ion Fluence (p/cm²)</th>
<th>MoS₂ Monolayer Vacancies/cm²</th>
<th>TID (Mrads)</th>
<th>DDD (MeV/g)</th>
</tr>
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<tbody>
<tr>
<td>H KO</td>
<td>Mo Vac</td>
<td>S Vac</td>
<td>sum Vac</td>
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<tr>
<td>6x10¹⁰</td>
<td>1.19 x10¹⁰</td>
<td>3.45 x10¹⁰</td>
<td>9.21 x10¹⁰</td>
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<tr>
<td>6x10¹¹</td>
<td>1.19 x10¹¹</td>
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<tr>
<td>6x10¹²</td>
<td>1.19 x10¹²</td>
<td>3.45 x10¹²</td>
<td>9.21 x10¹²</td>
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Predicted vacancies per unit area are listed for experimental 100 keV proton fluences, calculated using TRIM for a MoS₂ monolayer. Mo, S, and total vacancies are the sum of direct proton Knock-On (KO) events and also secondary KO events. Secondary KO events are rare due to the thin sample dimensions.

TID and DDD are also listed for proton fluences, and were obtained using SRIM tables for both the sample material MoS₂, the underlying material for substrate supported samples, Si₃N₄, and Si for reference as a standard unit.
allow for independent measurement of the minority carrier lifetime in the direct and indirect transitions, which would allow for better understanding of the observed indirect-to-direct bandgap transition. Electrical transport measurements on MoS$_2$ transistors before and after exposure to radiation would also give insight into degradation of parameters such as carrier mobility and interface trap density. Future work will also include spatial mapping of the luminescence intensity before and after radiation exposure, in order to test material homogeneity. Further sample substrate development may be necessary to pursue this line of study for the suspended regions, which are only 2 $\mu$m × 3 $\mu$m in size. Finally, Raman spectroscopy of peaks with shifts in the 150–350 cm$^{-1}$ range could provide another quantitative measure of the defect density in the materials after proton radiation exposure. This would be useful to correlate with our results from direct imaging of defects using electron microscopy.

VI. Conclusion

In this section, we have measured the effects of proton radiation on PL intensity and spectra from monolayer and few-layer MoS$_2$ flakes, and directly imaged the MoS$_2$ lattice with atomic resolution STEM imaging. We discussed band structure modification and carrier recombination processes affected by the radiation-induced lattice damage, which we understand by interpretation of the PL optoelectronic data and STEM images.

REFERENCES