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Material and device properties of superacid-treated monolayer molybdenum disulfide

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We study the effects of chemical treatment with bis(trifluoromethane) sulfonimide superacid on material and device properties of monolayer molybdenum disulfide grown by chemical vapor deposition. Our spatially resolved photoluminescence (PL) measurements and device studies reveal two key findings due to the chemical treatment: (1) noticeable transformation of trions to neutral excitons, and (2) over 7-fold reduction in the density of mid-gap trap states. Specifically, a combination of scanning Auger microscopy and PL mapping reveals that the superacid treatment is effective in passivating the sulfur-deficient regions. Published by AIP Publishing.

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Two-dimensional (2-D) transition metal dichalcogenides (TMDs) have potential for making a wide range of optoelectronic and electronic devices such as photovoltaics,1 photodetectors,2–4 and field–effect transistors (FETs).5–7 In all cases, the device performance strongly depends on the inherent material properties such as carrier mobility and minority carrier lifetime. However, structural disorders degrade these key material properties and the ensuing device performance. It is, therefore, essential to reduce the structural disorders during the synthesis or the post-synthesis steps using chemical treatments. The microelectronic industry has continually applied these strategies for reducing defects in semiconductor materials and their interfaces with dielectrics. Examples include passivation of interfacial defects by incorporating chlorine,8 hydrogen,9 or sulfur atoms.10,11

Many studies demonstrated the presence of high structural defects in 2-D TMD films prepared through mechanical exfoliation or chemical vapor deposition (CVD). Those structural disorders include various types of point defects, grain boundaries, and complex dislocations.12–14 Research is ongoing to develop effective chemical treatment methods for mitigating the detrimental impact of the structural defects on key material properties. Among those, Amani et al.15 has shown remarkable improvement in the quantum yield and the photoluminescence intensity for exfoliated and CVD sulfur-based TMDs via the chemical treatment using bis(trifluoromethane) sulfonimide (TFSI) superacid.15–17 They attributed the observed improvements to the reduction of sulfur-based defects, where a TFSI-mediated hydrogenation process causes the rearrangement of sulfur adatoms on the surface. However, more work needs to be done to quantify the effect of the superacid treatment on the density of defects in molybdenum disulfide (MoS2) films. In addition, from the work of Amani et al.,15 the surface passivation using superacid appears to be thermally stable, at least up to 300°C. This opens up the opportunity to investigate the effect of the superacid treatment on the interfacial properties between MoS2 and high-k dielectrics in a top-gated device configuration. Such device studies are currently missing in the literature.

In this work, we investigate the material and device properties of MoS2 upon treatment by TFSI superacid (Sigma-Aldrich). We observed noticeable transformation of trions to neutral excitons due to the superacid treatment. Scanning Auger microscopy (SAM) measurements reveal that the transformation of trions to excitons is more pronounced in regions with lower sulfur to molybdenum ration (S/M). Further, we fabricated top-gated FETs on as-grown and TFSI-treated CVD MoS2 films. Our electrical measurements indicate that the TFSI treatment improves the sub-threshold swing and reduces the density of mid-gap traps.

We initially used exfoliated flakes to optimize the chemical treatment process. We produced monolayer flakes through mechanical exfoliation of MoS2 bulk crystals (SPI Supplies). The monolayer flakes underwent TFSI treatments in a glovebox system with low oxygen and moisture levels below 10 ppm. This is to prevent the possible oxidation of the MoS2 films during the TFSI treatment. The enhancement of the PL intensity guided our experiments for finding the optimal treatment conditions. We found relatively weak dependence of the PL improvement on the concentration of the TFSI solution. In our experiments, we first dissolve 20 mg of TFSI in 1 ml of 1,2-dichloroethane (DCE) (Sigma-Aldrich), and further dilute it to ~2 mM. The samples were placed in a tightly sealed glass vial with 3 mL of TFSI solution, followed by heating the vials on a hot plate at 120°C for 10–20 min. The samples were then dried using nitrogen and baked on a hot plate at 100°C for 5 min. Using this process, we observed over 40-fold increase in the PL intensity of the exfoliated MoS2 flakes, measured at 20 μW laser excitation power (Fig. 1(a)).

The PL spectrum of MoS2 at monolayer thickness consists of charged trions and neutral excitons with overlapping emission energies18 (see supplementary material). Curve fitting using the Gaussian function is typically used for analyzing the PL spectra. It is, however, difficult to use this approach for analyzing a large amount of spatially resolved PL data. Bao et al. has shown the effectiveness of the
spectral median method for qualitative analysis of the spatial PL maps. The spectral median method is particularly useful to illustrate the relative population of the charged trions to the neutral excitons and to show the shift in the emission energy of those excitons. We have adopted this method for analyzing the spatial PL maps of the MoS2 flakes before and after the treatment with TFSI. In this method, the spectral median is defined at the energy that splits the PL spectrum into two regions with equal integrated intensities (see supplementary material).

Previous reports demonstrated the shift in the excitonic energies of the monolayer MoS2 upon increasing the laser excitation power. We made similar observation by studying the power-dependence of the PL spectrum (see supplementary material). This observation signals the increase in the relative emission of trions to neutral excitons possibly due to the significant increase in the non-radiative exciton-exciton interactions at a high excitation laser power density. In our chemical treatment studies, we used a laser excitation power of ∼200 µW with an estimated laser spot of ∼2 µm to create a discernable trion emission and subsequently examine their possible transformation mediated by the TFSI treatment. Many factors influence the population of charged trion states, including chemical doping and electrostatic doping. Further, the presence of sulfur vacancies in the lattice facilitates trion emission because of the enhanced local charge transfer at these defect sites. Our aim is to investigate the possible reduction of the charged and defect-bound trions in exfoliated and CVD MoS2 flakes upon TFSI treatment. The scatter plot in Fig. 1(b) shows the integrated intensity as a function of the spectral median for each position in the PL spatial maps of an exfoliated flake measured before and after the chemical treatment (Fig. S2 in supplementary material). This plot illustrates the shift in the spectral emission of MoS2 to higher energies upon TFSI treatment, thus qualitatively indicating the effectiveness of this chemical treatment for reducing the density of trions. Furthermore, we used the approach by Su et al. for analyzing the effect of the superacid treatment on various excitonic states in the PL spectra of the exfoliated flake (Fig. S3 in supplementary material). Our analysis shows the reduction of defect-bound excitons and also the reduction of charged trions upon treatment with TFSI superacid.

We now proceed to study the effect of the TFSI treatment on CVD MoS2. Large-area synthesis of high-quality TMDs is a necessary step for enabling a commercially viable technology based on these materials. Synthesis through CVD is a popular approach for growing monolayer MoS2 on SiO2/Si substrates. We produced monolayer MoS2 flakes on p+ silicon with the 285 nm SiO2 capping layer through CVD using molybdenum trioxide (6 mg) and sulfur (~100 mg) solid precursors at 850 °C. The details of the growth process are described in the supplementary material. Interestingly, our as-grown monolayer CVD MoS2 flakes exhibit about 10-fold stronger PL emission than the as-exfoliated flakes at a given excitation power. To understand the effect of TFSI superacid on the CVD flakes, the samples underwent a treatment process similar to the exfoliated flakes, described earlier. We found this recipe to give the highest PL enhancement for the CVD samples as well.

FIG. 1. (a) Enhancement of the PL intensity guided the optimization of the chemical treatment process. (b) The spectral median analysis reveals the transformation of trions to excitons upon TFSI treatment.
on these samples using atomic layer deposition (ALD) at 200 °C. A previous report indicates the thermal stability of the TFSI treatment at temperatures as high as 300 °C.16 Finally, the metal gate electrode was made through EBL patterning and lift-off of chrome/gold (Cr/Au, 10 nm/40 nm).

Fig. 3(b) shows the representative transfer characteristics of two devices on samples 1 and 2. We noticed that the TFSI-treated samples generally exhibit slightly better subthreshold swing than their as-grown counterparts. The TFSI and non-TFSI treated devices exhibit nearly similar drive currents, suggesting that those devices have comparable carrier mobility and contact resistance. Using the approach in Ref. 31, we estimated the carrier mobility and the contact resistance of both devices to be 12 cm²/V s and 1 kΩ.

We performed capacitance-voltage measurements to quantify the density of the localized gap states in these devices. The large size of the CVD flakes allows the fabrication of adequately large devices for making capacitance-voltage measurements. Figs. 4(b) and 4(c) show the corresponding capacitance-frequency characteristics of the devices on samples 1 and 2, respectively. Interestingly, the TFSI-treated device exhibits noticeably smaller frequency dispersion than the as-grown device, suggesting the effectiveness of the TFSI process in reducing the density of trap states. We used the equivalent device model shown in Fig. 4(a) to determine the density of localized gap states.32,33 In this model, C_it is the interface trap capacitance and is given by qD_it, where q is the elementary charge and D_it is the density of devices. The large size of the CVD flakes allows the fabrication of adequately large devices for making capacitance-voltage measurements. Figs. 4(b) and 4(c) show the corresponding capacitance-frequency characteristics of the devices on samples 1 and 2, respectively. Interestingly, the TFSI-treated device exhibits noticeably smaller frequency dispersion than the as-grown device, suggesting the effectiveness of the TFSI process in reducing the density of trap states. We used the equivalent device model shown in Fig. 4(a) to determine the density of localized gap states.32,33 In this model, C_it is the interface trap capacitance and is given by qD_it, where q is the elementary charge and D_it is the density of

TABLE I. Summary of Auger and PL measurements of the CVD flake in Fig. 2. The shift of the PL spectral median due to the chemical treatment is higher in the regions with lower S/Mo ratio.

<table>
<thead>
<tr>
<th>Point</th>
<th>S_Peak/Mo_Peak</th>
<th>ΔE (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11.7 ± 0.2</td>
<td>2 ± 0.3</td>
</tr>
<tr>
<td>B</td>
<td>10.7 ± 0.19</td>
<td>4.6 ± 0.5</td>
</tr>
<tr>
<td>C</td>
<td>10.96 ± 0.2</td>
<td>5.5 ± 0.8</td>
</tr>
<tr>
<td>D</td>
<td>10.8 ± 0.21</td>
<td>4.2 ± 0.6</td>
</tr>
</tbody>
</table>

FIG. 2. (a) The spatial analysis of the PL spectra using the spectral median method for a monolayer CVD MoS2 flake before and after the TFSI treatment process. (b) Shift in the excitonic energies due to the TFSI treatment is more pronounced near the intra-flake grain boundary, possibly due to the presence of high sulfur vacancy. (c) The SEM image of the CVD flake. The solid line shows the edge of the flake, and the dashed line represents the approximate location of the GB. (d) Auger spectra corresponding to four different locations on the flake, marked A, B, C, and D. The scale bars are 4 μm.
traps. The resistance in series with \( C_{it} (R_{it}) \) represents the trap resistance and is given by \( \tau_{it}/C_{it} \), where \( \tau_{it} \) is the time constant of the traps. We used two types of traps for fitting the capacitance data, namely, the mid-gap and the band-edge traps denoted by “M” and “B” subscripts in that model. The solid curves in Figs. 4(b) and 4(c) represent the fitted curves. Fig. 4(d) illustrates the corresponding density of mid-gap and band-edge trap states for the devices in Fig. 3(b). The fitting results show the reduction of the trap density for the TFSI-treated device. Theoretical studies suggest that sulfur vacancies in monolayer MoS\(_2\) manifest themselves through deep trap states in the energy gap. Therefore, we surmise that the smaller density of the mid-gap states in the TFSI-treated device is attributed to the passivation of sulfur-based defects by TFSI, which is consistent with our PL studies.

In summary, we have demonstrated the effectiveness of the chemical treatment using the TFSI superacid in passivating defects in sulfur-deficient regions. We analyzed the spatial PL data for both exfoliated and CVD monolayer MoS\(_2\) flakes using the spectral median method. The PL studies demonstrated the increase in the relative emission of neutral excitons to the charged trions upon TFSI treatment. The comparison of the electrical characteristics of the as-grown and the TFSI-treated top-gated FETs fabricated on CVD flakes indicates the effectiveness of TFSI treatment in reducing the density of the mid-gap traps.

See supplementary material for additional details on the CVD MoS\(_2\) synthesis, material and device characterization.

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A.A. and D.S. designed and carried out the experiments. P.Z. contributed to Auger measurements.