Impact of N-plasma and Ga-irradiation on MoS2 layer in molecular beam epitaxy

Pawan Mishra¹, Malleswararao Tangi¹, Tien Khee Ng¹, Mohamed Nejib Hedhili², Dalaver H. Anjum², Mohd Sharizal Alias¹, Chien-Chih Tseng³, Lain-Jong Li³, Boon S. Ooi¹ a)

¹Photonics Laboratory, Computer, Electrical, and Mathematical Sciences and Engineering (CEMSE), King Abdullah University of Science & Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia
²Imaging and Characterization Laboratory, King Abdullah University of Science & Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia
³Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, KSA

Recent interest in two-dimensional (2D) materials has resulted in ultra-thin devices based on the transfer of transition metal dichalcogenides (TMDs) onto other TMDs or III-nitride materials. In this investigation, we realized p-type monolayer (ML) MoS2, and intrinsic GaN/p-type MoS2 heterojunction by the GaN overgrowth on ML-MoS2/c-sapphire using plasma-assisted molecular beam epitaxy. A systematic nitrogen plasma (N²⁺) and gallium (Ga) irradiation studies are employed to understand the individual effect on the doping levels of ML-MoS2, which is evaluated by micro-Raman and high-resolution X-Ray photoelectron spectroscopy (HRXPS) measurements. With both methods, p-type doping was attained and was verified by softening and strengthening of characteristics phonon modes $E_{2g}^{\nu}$ and $A_{1g}$ from Raman spectroscopy. With adequate $N_2^+$-irradiation (3 min), respective shift of 1.79 cm⁻¹ for $A_{1g}$ and 1.11 cm⁻¹ for $E_{2g}^{\nu}$ are obtained while short term Ga-irradiated (30 sec) exhibits the shift of 1.51 cm⁻¹ for $A_{1g}$ and 0.93 cm⁻¹ for $E_{2g}^{\nu}$. Moreover, in HRXPS valence band spectra analysis, the position of valence band maximum measured with respect to the Fermi level is determined to evaluate the type of doping levels in ML-MoS2. The observed values of VBM are reduced to 0.5, and 0.2 eV from the intrinsic value of ≈1.0 eV for $N_2^+$- and Ga-irradiated MoS2 layers, which confirms the p-type doping of ML-MoS2. Further p-type doping is verified by Hall effect measurements. Thus, by GaN overgrowth, we attained the building block of intrinsic GaN/p-type MoS2 heterojunction. Through this work, we have provided the platform for the realization of dissimilar heterostructure via monolithic approach.

a) Author to whom correspondence should be addressed. Electronic mail: boon.ooi@kaust.edu.sa
The recent investigations reveal that the dissimilar heterojunctions formed by TMDs and III-nitrides provide the route for novel devices in the area of optoelectronic, electronics, and water splitting applications. 1-4 In addition, 2D materials such as graphene, boron nitride nanosheets and layered transition metal dichalcogenides (TMDs) were investigated as potential buffer layers for the epitaxial growth of III-V semiconductors on foreign substrates.5-8 Use of TMDs, in particular, layered-MoS2 as a buffer layer attracts the potential interest of researchers to address the issues such as large lattice and thermal expansion mismatch for the growth of GaN.9,10 Recently, GaN epitaxy on layered-MoS2 flakes was demonstrated using high temperature (~1000 °C) growth process of metal-organic chemical vapor deposition (MOCVD).5

In contrast to MOCVD process, molecular beam epitaxy (MBE) has the advantage of low growth temperature and ultra-high vacuum with a low partial pressure of oxygen (~10⁻¹¹ Torr). Yamada et al. demonstrated GaN epitaxy using MBE on bulk MoS2.11,12 In their work, they investigated the effect of nitrogen plasma (N₂⁺) and Ga-irradiation on the surface morphology of overgrown GaN. However, the effect of N₂⁺- and Ga-irradiation on the 2D layered-MoS2 in high to ultra-high vacuum (UHV) environment has not been explored. Focusing on MoS2, the tunability of doping,13-17 optical,18-20 and structural,21 properties of the layered-MoS2 has been reported by employing the plasma (O₂⁺ or N₂⁺) irradiation. However, in most of these studies, ~150 Torr of the background utilized during plasma irradiation, whereas in plasma-assisted MBE (PAMBE), low background ~10⁻⁶ Torr can be used for tuning the properties of layered-MoS2. Here, we present the demonstration of p-type monolayer (ML) MoS2, by N₂⁺- and Ga-irradiation under UHV conditions using PAMBE, and subsequently demonstrated the intrinsic GaN/p-type MoS2 heterojunction by GaN overgrowth.

We deposited layered-MoS2 on the c-sapphire substrates using CVD, details published elsewhere.22 The N₂⁺- and Ga-irradiation were performed using VEECO GEN930 PAMBE system at a substrate temperature of 450 °C. Active nitrogen species (N₂⁺) were provided by using a Veeco Uni-Bub radio
frequency plasma N₂ source supplied through inert gas purifier fed with high purity N₂ gas (99.9999 %). N₂ plasma conditions i.e. RF power 300 W, N₂ flow rate 1 sccm were used. Ga was evaporated by standard dual filament Knudsen cell with beam equivalent pressure (BEP) value of 6 × 10⁻⁸ Torr. The realization of p-type MoS₂ through N₂⁺- and Ga-irradiation were confirmed by using Raman spectroscopy and HRXPS analysis. For analyzing the optical quality of ML-MoS₂ samples post MBE processes, photoluminescence (PL) spectroscopy was used. Further GaN growth on ML-MoS₂\('sapphire was implemented in PAMBE by using two step 450 °C/700 °C growth temperatures. Further, aberration corrected high angle annular dark field (HAADF) high-resolution scanning transmission electron microscopy (HR-STEM) cross-section analysis was used to characterize GaN/MoS₂ interface. Cross-section specimen preparation method and operational details for HRSTEM are described in our previous work.²³ For micro-PL and micro-Raman spectroscopy we used 473 and 325 nm laser sources equipped in Horiba Aramis system. The high-resolution X-Ray photoelectron spectroscopy (HRXPS) studies were carried out with a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα x-ray source (hv = 1486.6 eV) operating at 150 W, a multichannel plate, and a delay line detector under a vacuum of 7.5 × 10⁻¹⁰ Torr. The samples were mounted in floating mode in order to avoid differential charging. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination which was taken to be 284.8 eV. Single magnetic field (0.58 T) Hall effect measurement system was used to determine sheet carrier concentration of samples at Room Temperature (RT).

Fig. 1(a) shows Raman spectrum of the pristine-MoS₂ and N₂⁺-irradiated layered-MoS₂ samples. The
pristine-MoS$_2$ exhibits characteristic phonon modes i.e. in-plane $E_{2g}^1$ and out-of-plane $A_{1g}$ modes at $\sim 385.3$ cm$^{-1}$ and $\sim 405$ cm$^{-1}$ respectively which stem from the monolayer of pristine-MoS$_2$. Relative to pristine ML-MoS$_2$, the shift of $1.79$ cm$^{-1}$ (for $A_{1g}$) and $1.11$ cm$^{-1}$ (for $E_{2g}^1$) towards higher and lower wavenumber value, respectively obtained for the 3 min $N_2^*$-irradiated ML-MoS$_2$. Such relative shift of phonon modes in the opposite direction has been predicted to be caused by p-type doping in ML-MoS$_2$. As pristine ML-MoS$_2$ prone to have S vacancies, hence the incorporation of N atoms is favorable during $N_2^*$-irradiation. Therefore, enhancement of compressive strain with increasing N incorporation in ML-MoS$_2$ occurs, due to smaller atomic radii of N atoms as compared to that of sulfur (S) atoms, and hence promoting softening of $E_{2g}^1$ phonon mode. Whereas, for n-type doping, softening of $A_{1g}$ phonon mode, thus shifts towards lower wavenumber has been reported.

Further enhancement in carrier concentration has been identified by increase in the peak intensities ratio i.e. $I(A_{1g})/I(E_{2g}^1)$ (from 2.11 to 2.24) for $N_2^*$-irradiated samples as shown in Fig. 1(b). For mulilayered-MoS$_2$, and ML-MoS$_2$ such increase in the $I(A_{1g})/I(E_{2g}^1)$ value has been attributed to the increasing the carrier density for p- as well as n-type of doping. Such increase in intensity ratio is due to the suppressed in-plane movement of the Mo–S atom and thus suppressing $E_{2g}^1$ under enhanced compressive strain due to the N incorporation. However, with increasing $N_2^*$-irradiation time, FWHM of $E_{2g}^1$ also, increases from 5.63 (for pristine-MoS$_2$) to 11.09 (for 3 min $N_2^*$-irradiation) as shown in Fig. 1(b). Such increase in the FWHM points towards the increase in the doping level as well as defects generation.

Figs. 2(a-c) shows the Mo 3d, Mo 3p$^{3/2}$/N 1s, and S 2p XPS spectra for the pristine and $N_2^*$-irradiated (for 1 and 3 min) ML-MoS$_2$. Mo 3d$^{5/2}$, Mo 3p$^{3/2}$, and S 2p$^{3/2}$ peaks show shifts toward lower binding energies for $N_2^*$-irradiated ML-MoS$_2$ samples. In particular, Mo 3d$^{5/2}$ peak for pristine ML-MoS$_2$ obtained at 229.8 eV, after the $N_2^*$-irradiation for 3 min shift of 0.2 eV towards lower binding energy is obtained. In addition, the Mo3p$^{3/2}$/N 1s region shows the existence of N 1s peak at binding energy $\sim 398.7$ eV after $N_2^*$-irradiation of ML-MoS$_2$ confirming the formation of N-Mo bonds as shown
5

in Fig. 2(b) and thus confirming p-type doping. From the valence band spectra (Figs. 2(d-f)), we obtained valence band maximum (VBM) of pristine ML-MoS$_2$ is 1 eV, which is in consistence with previous value in literature.$^{4,32}$ For N$_2^*$-irradiated MoS$_2$ samples for 1 min (3 min), the binding energy of VBM is 0.9 (0.5) eV.

It is found that the VBM decreases with increasing N$_2^*$-irradiation time and hence confirming enhancement of p-type doping in layered-MoS$_2$ as predicted by the analysis of Raman spectroscopy results.$^{33}$ As CVD grown pristine-MoS$_2$ has n-type semiconducting behavior because of S vacancies and thus realization of p-type doping is quite challenging especially in the case of mono or bilayer MoS$_2$. Using our approach of N$_2^*$-irradiation we demonstrated a reduction in $E_{V-E_F}$, which shows a change in polarity of the carriers. Further increment in the carriers without significant physical damage to the layered-MoS$_2$ will remain a process optimization challenge, which may be addressed by adopting the low brightness mode of nitrogen plasma irradiation for a longer time.

Further, we investigated the effect of Ga-irradiation on ML-MoS$_2$. Fig. 3(a) shows Raman spectroscopy of pristine-, Ga irradiated, and 2-step i.e. Ga-irradiation for 30 sec (step 1)\ N$_2^*$-irradiation for 1 min (step 2) treated ML-MoS$_2$ samples. Similar to N$_2^*$-irradiated MoS$_2$, softening in $E_{2g}^{1}$ phonon mode by 0.93 cm$^{-1}$\ (2.83 cm$^{-1}$) obtained for Ga-irradiated (2-step treated) MoS$_2$ sample as shown in Fig. 3(a). In addition,
uplift in the $I(\text{A}_{1g})/I(\text{E}_{2g})$ values i.e. 2.46 and 2.31 obtained for Ga-irradiated (30 sec) and two-steps treated sample respectively, as compared to that of 2.11 for pristine ML-MoS$_2$. Also, increase in FWHM as shown in Fig. 3(b) after Ga-irradiation shows enhancement in doping as well as possible degradation of ML-MoS$_2$.

FIG. 3. (a) Raman spectroscopy of pristine-, Ga irradiated, and 2-step i.e. Ga-irradiation (step 1), N$_2^*$-irradiation (step 2) treated ML-MoS$_2$ samples (b) Intensity ratio of characteristic phonon modes, i.e. $I(\text{A}_{1g})/I(\text{E}_{2g})$ and FWHM of $\text{E}_{2g}$ for Ga-irradiated MoS$_2$ samples. (c) Photoluminescence of N$_2^*$- and Ga-irradiated MoS$_2$ samples at room temperature.

Fig. 3(c) shows room temperature PL results of pristine, N$_2^*$-, and Ga-irradiated samples. PL intensity reduction with both methods has been observed which indicates structural degradation of MoS$_2$ layers. However, softening of $\text{E}_{2g}$ and enhancement of intensity ratio indicates towards p-type doping of ML-MoS$_2$ after N$_2^*$- and Ga-irradiation.

Fig. 4(a) shows Mo 3d$_{5/2}$ peaks shifted toward lower binding energies for Ga-irradiated samples relative to that of pristine ML-MoS$_2$. Fig. 4(b) shows Ga 2p for pristine ML-MoS$_2$ and Ga irradiated sample. The existence of Ga 2p$_{1/2}$, and Ga 2p$_{3/2}$ core levels at 1144 and 1117 eV, respectively, reveals the incorporation of Ga into MoS$_2$ post Ga-irradiation. It is important to point out that the short duration (30 sec) and use of low Ga flux beam equivalent pressure (BEP) of $6 \times 10^{-8}$ Torr during Ga-irradiation ensured no deposition of Ga adlayers on layered-MoS$_2$. Moreover, for Ga-irradiated MoS$_2$ the reduced
value of binding energy of VBM (0.2 eV) is obtained as shown in Fig. 4(c), which has similar trend obtained for N$_2$-irradiated samples and hence confirming realization of p-type ML-MoS$_2$.\textsuperscript{17, 34}

Such reduction in binding energy of VBM also confirms the absence of inelastic scattering of electrons at the surface of ML-MoS$_2$. In Ga-irradiated samples sulfur vacancies were occupied by Ga atoms and hence enabling the p-type behavior. Fig. 4(d) shows energy band diagrams of pristine ML-MoS$_2$ and p-type ML-MoS$_2$ realized by N$_2$- and Ga-irradiation in MBE. The reported electronic band gap of 2.15 eV for the ML-MoS$_2$ has been used in energy band diagram.\textsuperscript{32} For N$_2$- and Ga-irradiated MoS$_2$ samples, $E_F$-$E_v$ is 0.5 eV and 0.2 eV respectively. These values are comparable with that of other p-type TMDs and...
Further, the polarity change of carriers for treated samples was verified by Van der-Pauw Hall effect measurements having the sheet hole carrier concentration in the range of $2.64 \times 10^{12}$ to $5.74 \times 10^{13}$ cm$^{-2}$, which is consistent with the literature as shown in Figs. 4(e-f).

Subsequently, GaN/MoS$_2$ heterojunction was realized by an overgrowth of GaN on ML-MoS$_2$ using PAMBE, and retainability of MoS$_2$ layer after MBE processes was investigated. Fig. 5(a) shows a cross-section image of GaN/ML-MoS$_2$/c-sapphire using HAADF-HRSTEM. The interface between MoS$_2$ and GaN is observed to be not as sharp as the interface between sapphire and MoS$_2$ as described by the elemental profiles and mapping in Fig. 5(b) and respective inset. Observed interdiffusion in compositional mapping at MoS$_2$ and GaN interface attributed to the interaction of Ga and N$_2^*$ with layered-MoS$_2$, which validates the tuning of aforementioned doping properties of layered-MoS$_2$ in MBE.

In conclusion, we demonstrated p-type doping in the ML-MoS$_2$ in ultra-high vacuum MBE environment via N$_2^*$- and Ga-irradiation. Nondestructive Raman spectroscopy results revealed softening of $E_{2g}^1$ and uplift of $I(A_{1g})/I (E_{2g}^1)$ in irradiated samples and thus confirming p-type doping and increment of carrier concentration. The reduced ($E_F-E_V$) values i.e. 0.5 eV (0.2 eV) obtained in HRXPS analysis for N$_2^*$- (Ga-) irradiated sample, reveals p-type doping. Further, change of carrier polarity was observed in Hall effect measurements. HAADF-STEM results revealed the retainability of ML-MoS$_2$ even after MBE processes and showed the interaction between Ga and N atoms/active species with ML-
215 MoS$_2$. MBE based GaN on MoS$_2$ was demonstrated to realize GaN/p-MoS$_2$ heterojunction. Such 216 demonstrations pave the way for the realization of multiple quantum wells constituting III-nitrides as a quantum barrier and TMDs as a quantum well layer for application in optoelectronic and electronics devices.

This publication is based upon work supported by the King Abdulaziz City for Science and Technology (KACST), Grant No. KACST TIC R2-FP-008, and the King Abdullah University of Science and Technology (KAUST) baseline funding BAS/1/1614-01-01.

This manuscript was accepted by Appl. Phys. Lett. Click here to see the version of record.

...
(a) 

\[ \Delta \omega_{E_{2g}} = 2.83 \text{ cm}^{-1} \]

\[ \Delta \omega_{A_{1g}} = 1.51 \text{ cm}^{-1} \]

Intensity (a.u.)

Wavenumber (cm\(^{-1}\))

370 380 390 400 410 420 430

Ga-irrad. N-irrad.

0.93 cm\(^{-1}\)

Pristine-MoS\(_2\) sapphire

(b) 

Intensity ratio \([I(A_{1g})]/[I(E_{2g})]\)

FWHM (E\(_{2g}\))

Pristine Ga-(30 sec) 2-step

(c) 

Intensity (a.u.)

Wavelength (nm)

Prismatic

N (1 min)

N (2 min)

N (3 min)

Ga (30 sec)