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Type-I band alignment at MoS$_2$/In$_{0.15}$Al$_{0.85}$N lattice matched heterojunction and realization of MoS$_2$ quantum well

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The valence and conduction band offsets (VBO and CBO) at the semiconductor heterojunction are crucial parameters to design the active region of contemporary electronic and optoelectronic devices. In this report, to study the band alignment parameters at the In$_{0.15}$Al$_{0.85}$N/MoS$_2$ lattice matched heterointerface, large area MoS$_2$ single layers are chemical vapor deposited on molecular beam epitaxial grown In$_{0.15}$Al$_{0.85}$N films and vice versa. We grew InAlN having an in-plane lattice parameter closely matching with that of MoS$_2$. We confirm that the grown MoS$_2$ is a single layer from optical and structural analyses using micro-Raman spectroscopy and scanning transmission electron microscopy. The band offset parameters VBO and CBO at the In$_{0.15}$Al$_{0.85}$N/MoS$_2$ heterojunction are determined to be 2.08 ± 0.15 and 0.60 ± 0.15 eV, respectively, with type-I band alignment using high-resolution x-ray photoelectron spectroscopy in conjunction with ultraviolet photoelectron spectroscopy. Furthermore, we design a MoS$_2$ quantum well structure by growing an In$_{0.15}$Al$_{0.85}$N layer on MoS$_2$/In$_{0.15}$Al$_{0.85}$N type-I heterostructure. By reducing the nitrogen plasma power and flow rate for the overgrown In$_{0.15}$Al$_{0.85}$N layers, we achieve unaltered structural properties and a reasonable preservation of photoluminescence intensity with a peak width of 70 meV for MoS$_2$ quantum well (QW). The investigation provides a pathway towards realizing large area, air-stable, lattice matched, and eventual high efficiency In$_{0.15}$Al$_{0.85}$N/MoS$_2$/In$_{0.15}$Al$_{0.85}$N QW-based light emitting devices. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Group III-V semiconductors have been extensively studied due to their potential applications in high efficiency electronic and optoelectronic devices such as high electron mobility transistors, light emitting diodes, and laser diodes.$^{1–4}$ Alongside, group VI transition metal dichalcogenides (TMDs) in the form of MX$_2$ have recently emerged as an atomic layered material system with promising electronic and optoelectronic properties.$^{5–8}$ Among the TMDs, molybdenum disulfide (MoS$_2$) in a single layer form is of potential interest for such devices owing to its direct bandgap and its prominent transport properties.$^9,10$ Recent advances in the integration of group-III nitrides with TMDs for designing 2D/3D based optoelectronic devices. Furthermore, the growth of GaN on closely lattice matched TMDs.$^{14,15}$ Recently, we have reported the growth of GaN on single layer (SL)-MoS$_2$ and SL-WSe$_2$ with type-II band alignment.$^{22,23}$

In spite of the smaller in-plane lattice mismatch ($\approx 0.8\%$) of GaN with MoS$_2$, the type-II heterojunction formed by them can be solely utilized for electronic devices.$^{11–13}$ In contrast, optoelectronic devices formed by 2D/3D heterojunctions require a type-I band alignment which can be realized by using the group III-nitride alloys with higher bandgap as a constituent semiconducting layer of the 2D/3D heterojunction. Thus, In$_{x}$Al$_{1-x}$N with a low In composition (12%–18%) exhibiting higher bandgap (4.5 eV) and lattice matched to the MoS$_2$ layer with high contrast of the refractive index ($\approx 30\%$) may be employed to achieve the type-I 2D/3D junction. Hence, the determination of the band offset parameters (VBO and CBO) and the type of junction for epitaxially formed MoS$_2$/In$_{x}$Al$_{1-x}$N (or In$_{x}$Al$_{1-x}$N/MoS$_2$) heterointerfaces is necessary to provide a route towards the integration of group-III nitrides with TMDs for designing 2D/3D based optoelectronic devices. Furthermore, the (CVD) growth techniques, and layer transferred p-MoS$_2$ on GaN.$^{11}$ The band offset parameters (junction type: valence band offset—$\Delta E_v$ and conduction band offset—$\Delta E_c$) are measured for various heterojunctions.$^{18–21}$

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introduction of nitrogen plasma quenches the photoluminescence intensity due to plasma-induced damage, and thus, a modified epitaxial process was utilized.

In this study, CVD grown SL-MoS$_2$ on Si and In$_{0.15}$Al$_{0.85}$N/Si and MBE grown In$_{0.15}$Al$_{0.85}$N on Si and SL-MoS$_2$/Si and In$_{0.15}$Al$_{0.85}$N epilayers were used to determine the band offsets at the In$_{0.15}$Al$_{0.85}$N/SL-MoS$_2$ heterointerface. Later, the structural and optical properties of the designed In$_{0.15}$Al$_{0.85}$N/MoS$_2$/In$_{0.15}$Al$_{0.85}$N quantum well structure were studied.

The large area MoS$_2$ layers were prepared on Si(111) and In$_{0.15}$Al$_{0.85}$N/Si(111) substrates using a CVD system. The growth experiments of In$_{0.15}$Al$_{0.85}$N on Si and MoS$_2$/Si substrates were carried out using the Veeco GEN 930 plasma-assisted molecular beam epitaxy (PAMBE) system at a substrate temperature of 500°C. For In$_{0.15}$Al$_{0.85}$N growth, the nitrogen plasma source was operated with a flow rate of 0.5 sccm and a radio frequency (RF) power of 200 W. In and Al metals were evaporated using a standard Knudsen cell with the beam equivalent pressure (BEP) values of $\approx 1 \times 10^{-8}$ and $\approx 4 \times 10^{-8}$Torr. The crystallinity and composition of indium of the In$_{0.15}$Al$_{0.85}$N epilayer were investigated using a CuK$_\alpha$ High-Resolution X-ray Diffractometer (HRXRD). High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was utilized by operating a probe-corrected FEI Titan at an acceleration voltage of 300 kV. Using Horiba Aramis, room temperature (RT) Raman measurements were performed on In$_{0.15}$Al$_{0.85}$N and MoS$_2$ layers with the excitation line of the He-Cd laser of 325 nm and the cobolt laser of 473 nm, respectively. The respective inset shows a STEM cross-sectional image of the In$_{0.15}$Al$_{0.85}$N/MoS$_2$/Si heterojunction sample.

Micro-Raman spectroscopy was performed to investigate the optical quality and to ascertain the number of layers that accommodated in the CVD grown MoS$_2$ on Si and In$_{0.15}$Al$_{0.85}$N. Figure 1(d) (i–iv) Micro-Raman spectra of MoS$_2$/In$_{0.15}$Al$_{0.85}$N/MoS$_2$ and MoS$_2$/In$_{0.15}$Al$_{0.85}$N, the respective inset shows a STEM cross-sectional image of the In$_{0.15}$Al$_{0.85}$N/MoS$_2$/Si heterojunction sample.}

**FIG. 1.** (a) HRXRD 20–ω scans of on-axis and off-axis reflections acquired on the In$_{0.15}$Al$_{0.85}$N epilayer. (b) AFM surface morphology of the InAlN film. (c) Variation in the bandgap of the In$_{0.15}$Al$_{0.85}$N alloy with the Indium composition for bowing parameters $b = 0$ and 5 eV and with the in-plane lattice parameter (alternate X-axis), and the corresponding inset shows the PL spectra of In$_{0.15}$Al$_{0.85}$N. (d) (i–iv) Micro-Raman spectra of MoS$_2$/In$_{0.15}$Al$_{0.85}$N/MoS$_2$ and MoS$_2$/In$_{0.15}$Al$_{0.85}$N. The respective inset shows a STEM cross-sectional image of the In$_{0.15}$Al$_{0.85}$N/MoS$_2$/Si heterojunction sample.
of long wavelength optical phonons for In₀.₁₅Al₀.₈₅N is due to the condition that either mₐl < μ(In,N) or mₜ < μ(Al,N), where m is the mass and μ is the reduced mass. In contrast, the phonon modes of In₀.₁₅Al₀.₈₅N were not observed when the sample was excited with the 473 nm line, as shown in Fig. 1(d) (ii and iii), which is ascribed to the reduced resonant excitation effect. Moreover, as a consequence of this resonant effect, in Fig. 1(d) (iv), the intensity of E₂₉ and A₁g of MoS₂ observed to be extremely lower than E₂₃, InN-like, and AlN-like A₁g (LO) phonon modes of In₀.₁₅Al₀.₈₅N with 325 nm excitation. Thus, these results show the sustainability of the MoS₂ layer during the growth of In₀.₁₅Al₀.₈₅N. The inset of Fig. 1(d) shows the cross-sectional STEM image acquired at the In₀.₁₅Al₀.₈₅N/SL-MoS₂/Si heterojunction having a MoS₂ layer thickness of ≈0.8 nm, which is in good agreement with the thickness of the S-Mo-S single-layer. Thus, micro-Raman and STEM measurements confirm that the SL-MoS₂ is epitaxially grown on the lattice matched In₀.₁₅Al₀.₈₅N films and vice versa.

High-resolution XPS measurements were extensively employed to determine the valence band offset (VBO) of a heterointerface. To evaluate VBO at the MoS₂/In₀.₁₅Al₀.₈₅N interface, the energy difference between the Mo and In core levels from the MoS₂/In₀.₁₅Al₀.₈₅N (In₀.₁₅Al₀.₈₅N/MoS₂) heterojunction sample and the energy of core levels relative to the respective valence band maximum (VBM) of the MoS₂ and In₀.₁₅Al₀.₈₅N samples are required to be evaluated. Since the escape depth of photo-emitted electrons in HRXPS is significantly low, the overgrown MoS₂ (In₀.₁₅Al₀.₈₅N/MoS₂) layer of heterojunction sample MoS₂/In₀.₁₅Al₀.₈₅N (In₀.₁₅Al₀.₈₅N/MoS₂) has to be thin enough so that the electrons removed from both thin overgrown MoS₂ (In₀.₁₅Al₀.₈₅N) and underlying In₀.₁₅Al₀.₈₅N (MoS₂) layers can be easily probed. Furthermore, the surface area of MoS₂ is sufficiently large to carry out the XPS measurements. In particular, due to the non-continuity of the MoS₂ layer on Si and In₀.₁₅Al₀.₈₅N templates, the region of interest on MoS₂/Si and MoS₂/In₀.₁₅Al₀.₈₅N samples was selectively chosen within the spatial resolution of HRXPS. This was executed by comparing the intensity of Mo 3d and In 3d and Si 2p core-levels, which allowed us to collect the photoemission signal solely from MoS₂/Si and MoS₂/In₀.₁₅Al₀.₈₅N (In₀.₁₅Al₀.₈₅N/MoS₂), respectively. To determine the VBO, the core levels Mo 3d and In 3d were used for the analysis. The VBO for the MoS₂/In₀.₁₅Al₀.₈₅N heterojunction can be calculated by the method provided by Kraut et al., which is expressed as

\[
\Delta E_v = \left( E_{MoS_2/3d_{5/2}} - E_{VBM} \right) + \left( E_{MoS_2/In_{3d_{5/2}}} - E_{MoS_2/In_{3d_{5/2}}} \right) - \left( E_{In_{3d_{5/2}}} - E_{VBM} \right). \tag{1}
\]

From Fig. 2(a), the first term of Eq. (1) deduced by taking into account the position of the Mo 3d₅/₂ core-level referenced with respect to the VBM, which is measured to be 228.88 ± 0.15 eV. The valence band maxima (VBM) values are determined by extrapolating the linear leading edge of the valence band to the base level. In the peak deconvolution process, Voigt (mixed Lorentzian-Gaussian) line shapes were employed for fitting the Mo-S, S-Mo (trigonal prismatic, 

FIG. 2. (a) The Mo 3d core-level and valence band spectra collected on SL-MoS₂, representing the binding energy separation between the Mo 3d₅/₂ corelevel and VBM. (b) and (c) The spectra of In 3d and Mo 3d core-levels acquired on SL-MoS₂/In₀.₁₅Al₀.₈₅N and In₀.₁₅Al₀.₈₅N/SL-MoS₂ heterojunction samples. (d) In 3d core-level and valence band spectra obtained for the In₀.₁₅Al₀.₈₅N epilayer, providing the binding energy difference between In 3d₅/₂ and VBM. The peak positions of core-levels are shown in parentheses.
In0.15Al0.85N/Si to determine the electron affinity of constituent In0.15Al0.85N, respectively. Fermi level positions obtained from UPS analysis is 0.60 ± 0.15 eV.

The substitution of VBO (ΔEc) obtained from HRXPS analysis as described in Fig. 2 and electronic bandgap values of MoS2 (EgMoS2 = 2.15 eV)21 and In0.15Al0.85N (EgInAlN = 4.83 eV) eplayers in the following equation allow us to extract the conduction band offset (CBO) ΔEc of the MoS2/In0.15Al0.85N heterostructure.

\[ \Delta E_c = E_{\text{InAlN}} - E_{\text{MoS2}} \]  

Thus, from Eq. (2), the CBO (ΔEc) is determined to be 0.60 ± 0.15 eV. Furthermore, the measured CBO value is verified by Anderson’s affinity rule which is defined as the difference between the electron affinity values of constituent semiconductors of the heterojunction.39 In order to verify the CBO by employing the affinity rule to the MoS2/In0.15Al0.85N interface, the electron affinities of constituent materials are required. UPS measurements were performed on MoS2/Si and In0.15Al0.85N/Si to determine the electron affinity of constituent materials of the heterojunction. Figures 3(a) and 3(b) show the UPS spectra recorded on MoS2/Si and In0.15Al0.85N/Si. The electron affinities were measured using the following equation:

\[ \chi = h\nu_{\text{He-I}} - \Omega - E_g \]  

where \( h\nu_{\text{He-I}} \) is the photon energy of the He-I line, \( \Omega \) is the spectrum width, and \( E_g \) is the electronic band gap. The spectrum width (\( \Omega \)) is the energy separation between the VBM and cutoff energy of secondary electrons with a sharp photoemission onset as shown in Figs.3(a) and 3(b) for MoS2 and In0.15Al0.85N, respectively. Fermi level positions obtained from UPS are slightly shifted to higher binding energy than that of HRXPS, as the charging induced shifts are not corrected in UPS spectra. Thus, the electron affinity, energy separation between the vacuum level and CBM, values were determined to be 4.10 ± 0.10 and 3.50 ± 0.10 eV for MoS2 and In0.15 Al0.85N using Eq. (3). Hence, from Anderson’s affinity rule, the obtained CBO for the MoS2/In0.15Al0.85N heterojunction from UPS analysis is 0.60 ± 0.10 eV, which is in good agreement with the CBO value determined from HRXPS studies. Thus, obtained CBO and VBO facilitate the determination of the type of band alignment at the heterojunction. Thereby, the experimentally measured offset parameters from this study are represented as a schematic of the band alignment diagram in Fig. 3(c) which pertains to the type-I heterostructure.

Figure 4(a) shows the cross sectional high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image recorded across the stack of In0.15 Al0.85N/MoS2/In0.15Al0.85N layers which were prepared by FIB. This reveals that the thickness of the MoS2 well layer is ≈0.85 nm, while the thickness values of the top and bottom barrier layers are of ≈10 and ≈40 nm, respectively. Figure 4(b) shows the magnified STEM image of (a). Figure 4(c) displays the FFT image acquired on the In0.15Al0.85N barrier layer, which shows the wurtzite crystal structure with a c-oriented growth corroborated by the HRXRD measurements. Thus, the HAADF-STEM analysis is a clear evidence of the formation of a single layer MoS2 QW sandwiched between In0.15Al0.85N layers. Furthermore, the free exciton peak at ≈1.87 in μPL spectra as shown in Fig. 4(d) for the MoS2 QW is slightly blue shifted with respect to the PL peak at 1.84 eV of MoS2/In0.15Al0.85N. Here, we compare PL spectra of MoS2/In0.15Al0.85N and MoS2 QWs to rule out the peak shifts associated with the strain. Thus, the blue shift of ≈30 meV is attributed to the quantum size induced confinement effect. This observed blue shift is far less than the reported blue shift for MoS2 QDs,40 which can be due to the van der Waals epitaxy with reduced confinement effects in the QW structure. The peaks at 1.87 and ≈2.03 eV are the exciton resonances corresponding to the transitions from the conduction band to two spin-split valence sub-bands that originated from the broken inversion symmetry of the crystal lattice.41,42 The low intensity of PL for the QW is ascribed to the non-resonant excitation, which means that the In0.15Al0.85N barrier layers are not excited along with the MoS2 QW.43 However, our previous reports show the enormous quenching (100–150 times) of PL for nitrogen plasma irradiated MoS2 layers and 2D/3D heterojunctions.16,23 In this study, we preserved the PL signal of the QW with relatively high intensity (quenched by 5 times) and a comparable peak width of 70 meV by using the low nitrogen flow rate and low forward power of plasma source for the growth of In0.15Al0.85N barrier.
layers. The respective inset shows the Raman spectra for the QW sample having the phonon mode separation of 19.5 \pm 0.5 \text{cm}^{-1}, which clarifies that the MoS$_2$ QW is a single layer.

In conclusion, MoS$_2$ single layers were chemical vapor deposited on the PAMBE grown In$_{0.15}$Al$_{0.85}$N template to study the band alignment at the lattice matched MoS$_2$/In$_{0.15}$Al$_{0.85}$N heterointerface. We confirm that the CVD deposited MoS$_2$ is a single layer by means of micro-Raman phonon modes and STEM. The determination of band offset parameters at the MoS$_2$/In$_{0.15}$Al$_{0.85}$N heterostructure was carried out by utilizing the HRXPS and UPS measurements. We determine the valence band and conduction band offset values of 2.08 \pm 0.15 \text{eV} and 0.6 \pm 0.15 \text{eV}, respectively, with type-I band alignment at the MoS$_2$/In$_{0.15}$Al$_{0.85}$N heterostructure. Furthermore, we prepared a MoS$_2$ QW by growing the In$_{0.15}$Al$_{0.85}$N top barrier layer on the MoS$_2$/In$_{0.15}$Al$_{0.85}$N template. The blue shift in PL spectra with respect to the MoS$_2$ single layer confirmed that the MoS$_2$ well exhibits the quantum confinement effect. The PL properties of the QW were pre-

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