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Layer-transferred MoS$_2$/GaN PN diodes

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Electrical and optical characterization of two-dimensional/three-dimensional (2D/3D) p-molybdenum disulfide/n-gallium nitride (p-MoS$_2$/n-GaN) heterojunction diodes are reported. Devices were fabricated on high-quality, large-area p-MoS$_2$ grown by chemical vapor deposition on sapphire substrates. The processed devices were transferred onto GaN/sapphire substrates, and the transferred films were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM). On-axis XRD spectra and surface topology obtained from AFM scans were consistent with previously grown high-quality, continuous MoS$_2$ films. Current-voltage measurements of these diodes exhibited excellent rectification, and capacitance-voltage measurements were used to extract a conduction band offset of 0.23 eV for the transferred MoS$_2$/GaN heterojunction. This conduction band offset was confirmed by internal photoemission measurements. The energy band lineup of the MoS$_2$/GaN heterojunction is proposed here. This work demonstrates the potential of 2D/3D heterojunctions for novel device applications. © 2015 AIP Publishing LLC.

Molybdenum disulfide is the most widely studied of the two-dimensional layered transition metal dichalcogenides (TMDs). Mechanically exfoliated MoS$_2$ films have been utilized to fabricate flexible and transparent devices,$^{1-4}$ photodetectors,$^{5,6}$ and transistors.$^{7-12}$ Mechanical exfoliation of MoS$_2$ flakes onto bulk semiconductors circumvents the issue of lattice mismatch that might inhibit direct growth of MoS$_2$ and other 2D films onto lattice mismatched substrates. However, stable, substitutional doping of mechanically exfoliated flakes and the scalability of the device fabrication on these flakes is poor. Chemical vapor deposition (CVD) of MoS$_2$ has been reported using a variety of Mo and S precursors including MoO$_3$,$^{13-15}$ Mo$_6$S$_8$ powder,$^{17}$ sulfur powder and MoO$_2$. These growth methods result in non-continuous films, often in the form of triangular MoS$_2$ domains the largest of which are on the order of hundreds of microns. Large area films achieved by these growths rely on these domains coalescing into a polycrystalline layer.

The development of CVD growth of large-area MoS$_2$ grown on sapphire substrates with Mo metal and S powder precursors was previously reported.$^{19}$ This growth process was improved by changing the sulfur precursor to MoS$_2$ powder and increasing the growth temperature. The resulting films were single crystal and exhibited epitaxial registry with respect to the sapphire substrate.$^{20}$ P-type conductivity in MoS$_2$ was demonstrated by adding a thin layer of Nb to the Mo metal precursor.$^{21}$

More recently, heterojunction devices utilizing two dimensional (2D) and bulk, traditional “3D” semiconductors (SiC$^{22}$ and Si$^{23-27}$) have been explored. These 2D/3D heterojunctions represent an area of opportunity for the expansion of the functionality 3D semiconductors. For example, in the case of wide band gap semiconductors like GaN, SiC, and ZnO, p-type doping has proven challenging due to the high activation energy of holes. Lattice mismatch between wide and narrow band gap materials provides another constraint for integrating dissimilar semiconductors. The integration of 2D, layered, p-doped semiconductors like MoS$_2$ with wide band gap materials could provide an avenue towards achieving high-performance, bipolar devices that were otherwise unattainable due to the aforementioned obstacles.

Direct growth of high-quality, large-area, p-doped MoS$_2$ has been reported on hexagonal basal plane semiconductors like wide band gap SiC.$^{22}$ However, our previous attempts at direct growth of MoS$_2$ on GaN resulted in decomposition of GaN due to the high growth temperature and the constraints introduced by our growth method. We combined the advantages of growth of high-quality, large-area, p-doped MoS$_2$ films on sapphire with the ability to transfer these films onto arbitrary substrates, allowing for the study of a wide range of 2D/3D heterostructures. We report here on the electrical and optical characterization of heterojunctions formed by thin film transfer of high-quality, CVD-grown, large-area, p-doped MoS$_2$ and n-doped GaN.

Nb-doped MoS$_2$ was grown using the growth process detailed in the previous work from our group. The Mo/Nb metal precursor used to obtain degenerately doped, p-type MoS$_2$ was deposited by sputtering (AJA Orion RF/DC Sputter Deposition Tool) the metals onto c-plane sapphire substrates. A 0.2 nm layer of Nb was sandwiched between 2.5 nm layers of Mo, and the Mo/Nb-coated sapphire substrates were placed in a small quartz tube (1 cm inner diameter) with 8.0 mg of MoS$_2$ powder as a sulfur source. The tube was pumped down by mechanical pump and sealed. The samples were heated at 1100°C for 4.5 h and then cooled at a rate of 0.5°C/min as described in Ref. 20. The resulting film was approximately 10 nm thick and expected to exhibit a doping concentration of $3 \times 10^{20}$ cm$^{-3}$ and a hole mobility of 8 cm$^2$/V s, as reported in Ref. 21. The GaN templates onto which the p-MoS$_2$ films were transferred were obtained from Lumilog and were n-type.
doped (ND = 3 × 10^{18} \text{ cm}^{-3}). An additional 200 nm of lightly doped n-type GaN (ND = 7 × 10^{17} \text{ cm}^{-3}) was grown by molecular beam epitaxy on the GaN/sapphire templates to reduce band-to-band tunneling leakage in the transferred p-MoS2/n-GaN diodes (atomic force microscopy (AFM) image shown in Figure 1(a)). Figure 1(b) shows a 2 \mu m × 2 \mu m AFM image of p-MoS2 transferred to GaN. The root mean squared (RMS) roughness of the MoS2 after transfer to GaN was 1.95 nm. On-axis X-ray diffraction spectra of the transferred p-MoS2 films on GaN/sapphire template are shown in Figure 1(c). This indicates that the structural quality of MoS2 was not significantly degraded by the film transfer process. The spectra of the transferred MoS2 films showed the (002) family of peaks of 2H-MoS2. Comparison with on-axis XRD spectra prior to film transfer (not shown here) indicates that the structural quality of MoS2 was not significantly degraded by the film transfer process.

The following details the film transfer process used to fabricate MoS2/GaN PN diodes. Devices were fabricated on as-grown degenerately p-doped MoS2 on sapphire utilizing ultraviolet stepper lithography (i-line). Ni/Au/Ni contacts were electron beam evaporated to form Ohmic contacts to MoS2. Isolation mesas were dry-etched using inductively coupled plasma/reactive ion etching (ICP/RIE) with BCl3/Ar chemistry. The sample was spin-coated with a layer of polymethylmethacrylate (PMMA) and soaked in a NH4OH + H2O2 + H2O solution at 80°C. Oxygen bubbles at the edges of the film detach the PMMA/MoS2 film from the sapphire substrate on which it was grown, causing the film to float to the surface of the solution. The detached film was removed from the solution to a DI water bath, rinsed with DI water and picked up with a GaN substrate. The PMMA layer was removed with acetone. Contact to the n-GaN layer was formed by indium dot (Figure 2).

Vertical current-voltage (J-V) characteristics of the MoS2/GaN heterojunction diode were measured by applying bias to the Ni/Au/Ni contacts on p-MoS2. The room temperature J-V characteristics showed 9 orders of magnitude rectification at ±2 V and exhibited an ideality factor of approximately 2 in the exponential region before series resistance became dominant. This indicates that transport in the MoS2/GaN heterojunction diode is likely dominated by recombination current (Fig. 3).

Figure 4 shows the capacitance-voltage (C-V) characteristics of the MoS2/GaN diode. The C-V characteristic was measured with bias applied to contacts on p-MoS2 and was consistent with that of a reverse-biased p-n junction. A doping concentration of 7 × 10^{17} \text{ cm}^{-3} was extracted from the C-V measurement. This concentration was consistent with the expected doping based on secondary ion mass spectrometry. The 1/C^2 characteristic determined from the C-V exhibited a linear dependence on applied voltage, and the extracted built-in voltage of the MoS2/GaN heterojunction was 1.5 V. We used the assumption of band gap narrowing in MoS2 due to degenerate doping from Ref. 22 (Eg = 950 meV) and used the Joyce-Dixon approximation to determine the position of the Fermi level in p+-MoS2. The conduction band offset, ΔEC, is determined by

\[ \Delta E_C = qV_{bi} - E_g - \Phi_p + \Phi_n, \]

where ΔEC is the conduction band offset, Eg is the band gap of MoS2 considering the band gap narrowing, Φp is the
Fermi level position in p-MoS₂, and \( \Phi_n \) is the Fermi level position in GaN. The extracted conduction band offset from the electrical characterization of typical MoS₂/GaN heterojunction diodes was 230 meV.

Internal photoemission (IPE) measurements were used to determine the conduction band offset of the MoS₂/GaN heterojunction. A Xe lamp was used for optical excitation, and the resulting photocurrent was measured with an electrometer. Photocurrent was normalized to the flux variation of the lamp to rule out its contribution as the source of an onset. Zero-bias was applied to the junction, and incident photon energy was varied from 1.2 to 2.5 eV. According to Ref. 27 and Fowler’s hypothesis,²⁸ photocurrent from the excitation of electrons from the valence band and their subsequent emission over a barrier should exhibit a quadratic dependence on incident photon energy. This yield corresponds to the electrons emitted per photon absorbed. Figure 5 shows the square root of the photo-yield as a function of the incident photon energy. Photo-yield, \( Y \), is given by

\[
Y = A(h\nu - E)^2, \tag{2}
\]

where \( A \) is a constant, \( h\nu \) is the energy of the incident photon, and \( E \) is the total energy an electron in the valence band of MoS₂ requires to be excited from the valence band of MoS₂ to the conduction band of GaN. The extrapolation of the linear fit of the square root of photo-yield current to the energy axis shown in Figure 5 indicated a photon energy threshold of 1.46 eV. This is the energy required for the photo-excited electron to complete the process of excitation from the valence band to emission over the barrier.

We again extract the conduction band offset between MoS₂ and GaN using the onset determined by IPE measurements. We kept the assumption of band gap narrowing in degenerately p-doped MoS₂ and the calculated Fermi energy. In this case, the conduction band offset was given by

\[
\Delta E_C = E_0 - (E_{g,\text{MoS}_2} + \Phi_p), \tag{3}
\]

where the \( E_0 \) refers to the energy threshold determined by IPE. The conduction band offset of the MoS₂/GaN heterojunction determined by optical measurements was 170 meV. The measurement apparatus introduced an error of ±50 meV.

Electrical and optical measurements of the MoS₂/GaN heterojunction exhibit satisfactory agreement. Our work
suggests that 2D/3D heterojunctions can be treated electrically using theory developed for traditional heterojunctions, no Fermi level pinning or other effects are evident, and more significantly, the interface between MoS$_2$ and GaN showed no out-of-plane bonds are formed. Figure 6 shows the band diagram of MoS$_2$/GaN with a conduction band offset of 0.23 eV, based on electrical measurements. The characterization of this junction illustrates the utility of exploring 2D/3D heterojunctions to elucidate their utility for extending the functionality of existing semiconductors. MoS$_2$/GaN is appropriate as a base/collector diode in a heterojunction bipolar transistor.

We reported the electrical and optical characterization of MoS$_2$/GaN diodes formed by film transfer. The diodes exhibited excellent rectification. A conduction band offset of 230 meV was extracted from electrical characterization of the junction by C-V measurement. Optical characterization of the junction by IPE measurement exhibited a conduction band offset of 170 meV. Electrical and optical characterization of the junction exhibited sufficient agreement, and the band diagram of the heterojunction was proposed with most of the band offset in the valence band.

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