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Band offset and electron affinity of MBE-grown SnSe$_2$
Large-area SnSe₂/GaN heterojunction diodes grown by molecular beam epitaxy

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We report on the synthesis and properties of wafer-scale two-dimensional/three-dimensional (2D/3D) n-SnSe₂/n-GaN(0001) heterojunctions. The hexagonal crystal structure of crystalline SnSe₂ grown by molecular beam epitaxy was confirmed via in-situ reflection high-energy electron diffraction and off-axis X-ray diffraction. Current-voltage (I-V) measurements of SnSe₂/GaN diodes exhibited 9 orders of magnitude rectification, and the SnSe₂/GaN heterojunction barrier height was estimated to be 1 eV using capacitance-voltage measurements and internal photoemission measurements. Vertical electronic transport analyzed using temperature-dependent I-V measurements indicates thermionic field emission transport across the junction. This work demonstrates the potential of epitaxial growth of large area high quality 2D crystals on 3D bulk semiconductors for device applications involving carrier injection across 2D/3D heterojunctions. Published by AIP Publishing. https://doi.org/10.1063/1.4994582

Heterogeneous integration of two-dimensional (2D) and three-dimensional (3D) materials could enable device architectures that are not possible for conventional semiconductor heterojunctions. The absence of out-of-plane chemical bonds in 2D layered materials enables flexibility for epitaxy of 3D materials,¹² and can therefore enable combinations of materials for devices such as heterojunction bipolar transistors (HBTs), vertical tunneling devices,³ and hot electron transistors.⁴ The synthesis of 2D/3D heterojunctions has been investigated extensively using mechanically exfoliated 2D crystals transferred onto bulk crystals⁵–⁸ and wafer-scale chemical vapor transport⁹,¹⁰ or chemical vapor deposition¹¹–¹³ growth of 2D materials on epitaxial templates and molecular beam epitaxy (MBE). The method used in this work, MBE, offers some distinct advantages due to the ability to realize sharp interfaces, excellent control of background impurities, and powerful in situ characterization techniques.¹⁴,¹⁵ Previous work on MBE growth of metal dichalcogenides (MoS₂, HfSe₂, WSe₂, and SnSe₂) on 3D substrates has shown epitaxial registry between the 2D material and 3D bulk substrates.¹⁵–¹⁸

To date, band lineups for various heterojunctions between 2D and 3D materials have been proposed. For instance, type-I band alignment was demonstrated in n-MoS₂/p-Si,¹⁹ p-MoS₂/p-SiC,²⁰ and p-MoS₂/p-GaN.²¹,²² Unlike transition metal dichalcogenides, Sn has two oxidation states (Sn²⁺ and Sn⁴⁺) which give two stoichiometric phases, SnSe and SnSe₂. SnSe is an orthorhombic layered structure with p-type conductivity, while SnSe₂ is intrinsically an n-type semiconductor and is known to have two crystal structures. One is the 2H phase with D⁶h (P₆₃/mmc) symmetry and the other is the 1T phase with D₄d (P₃ m1) symmetry. The bulk 1T phase of SnSe₂ has been reported to have a direct energy bandgap of 1 eV (Refs. 25 and 26) with an electron affinity of 5 eV.¹⁸ This high electron affinity has been exploited to form type-III heterojunctions with black phosphorus²⁷ and WSe₂.¹⁸

In this paper, we report on the growth and electronic properties of SnSe₂/GaN heterojunctions. The combination of such a high electron affinity low bandgap material such as SnSe₂ with a wide bandgap material such as GaN presents a unique heterojunction combination that is not possible with the III-Nitride system alone. While the bandgap of InGaN can be tuned to be as low as 1 eV, lattice mismatch between InN and GaN (11%) makes it very challenging to grow high composition InGaN on GaN.

The epitaxial growth of SnSe₂ on GaN was performed in a Veeco GEN930 MBE system with a standard thermal effusion cell for Ga and Sn. A valve cracker source (with the cracker zone at 950 °C) was used to evaporate Se. The sample surfaces were monitored in-situ by reflection high-energy electron diffraction (RHEED) operated at 15 keV. The structural quality of the SnSe₂ films was evaluated through X-ray diffractometry (XRD) (Bruker, D8 Discover) and Raman spectroscopy (Renishaw) equipped with a 514 nm laser. The thickness of the SnSe₂ film was measured by X-ray reflectometry (XRR) (Bruker, D8 Discover). Atomic force microscopy (AFM) (Bruker Icon 3) was used to examine the surface morphology of the film. VESTA software was used to generate graphical illustrations of the SnSe₂ crystal structure.

Semi-insulating and n-type (0001) oriented GaN/sapphire substrates were used for the study. Pre-growth surface preparation included solvent cleaning followed by a 1 h 400 °C anneal under ultra-high vacuum conditions (~1 × 10⁻⁹ Torr). Samples were then loaded into the growth chamber (base pressure ~7 × 10⁻¹⁰ Torr) and exposed to the Ga polish procedure to remove gallium sub-oxides on the GaN surface prior to the growth. The procedure used is as
The RMS roughness was calculated to be 0.99 nm for a 4 SnSe$_2$ peaks are found to be at the theoretically expected substrate heater. attached to the continuous azimuthal rotation (CAR) substrate temperature was measured using a thermocouple X-ray reflection measurements to be 21 nm. Off-axis azimuthal scan [Fig. 1(f)] was done using a thick (SnSe$_2$ film. A full range of 360° mutual scan [Fig. 1(f)] was done using a thick (X-ray reflection measurements to be 21 nm. Off-axis azimuthal scan [Fig. 1(f)] was done using a thick (thick $(BEP)$ flux ratio (measured using a nude ion gauge with a tungsten filament) was maintained at $\sim 250$. The surface was covered with Se by opening the Se shutter for two minutes. Growth was then initiated by opening the Sn shutter. This procedure is qualitatively similar to that described previously for the growth of GaSe on GaN.14 Growth was carried out for 1 hour and terminated by closing all shutters and immediately cooling down the sample to room temperature.

For growth of SnSe$_2$, the Se:Sn beam equivalent pressure (BEP) flux ratio (measured using a nude ion gauge with a tungsten filament) was maintained at $\sim 250$. The surface was covered with Se by opening the Se shutter for two minutes. Growth was then initiated by opening the Sn shutter. This procedure is qualitatively similar to that described previously for the growth of GaSe on GaN.14 Growth was carried out for 1 hour and terminated by closing all shutters and immediately cooling down the sample to room temperature.

Figures 1(a)–1(d) show the RHEED patterns of the GaN substrate before growth and the SnSe$_2$ film after growth was completed, along the [1120] and [10T0] directions. The streaky RHEED patterns observed in both azimuthal orientations indicate 2-dimensional growth with azimuthally aligned to the GaN substrate ([1120] SnSe$_2$/[1120] GaN and [10T0] SnSe$_2$/[10T0] GaN). The RHEED spacing for the GaN and SnSe$_2$ patterns was found to have a ratio of 0.85, which matches the experimentally expected ratio (0.848) from bulk in-plane lattice constants of SnSe$_2$ ($a = 3.76$ Å) and GaN ($a = 3.189$ Å). We conclude that the hexagonal basal plane lattice for SnSe$_2$ and GaN materials is aligned along the same crystallographic direction despite their large lattice mismatch of 18%.

Figure 1(e) shows the on-axis (001)-oriented high resolution XRD spectrum of the SnSe$_2$/GaN structure, and the SnSe$_2$ peaks are found to be at the theoretically expected positions. No other phases were observed in the scan. The thickness of the crystalline SnSe$_2$ film was determined by X-ray reflection measurements to be 21 nm. Off-axis azimuthal scan [Fig. 1(f)] was done using a thick (>200 nm) SnSe$_2$ film. A full range of 360° scans (θ) for the SnSe$_2$ (101) plane and GaN (102) plane were done, and six peaks were found at the identical azimuth angles for both SnSe$_2$ and GaN, confirming that the two hexagonal unit cells are epitaxially aligned. This is in agreement with our conclusion from RHEED measurements.

Figure 2(a) shows the surface morphology of SnSe$_2$. The RMS roughness was calculated to be 0.99 nm for a 4 µm$^2$ region. As shown in Fig. 2(b), two characteristic Raman active modes for SnSe$_2$ at 112 (in-plane mode, $E_g$) and 186.27 (out-of-plane mode, $A_{1g}$) cm$^{-1}$ are present in the spectrum, which corresponds to 1 T phase SnSe$_2$ as reported for the MBE grown$^{18}$ and exfoliated bulk film.$^{7,29}$ The corresponding 1 T SnSe$_2$ crystal structure is shown in the inset of (b). The asterisk indicates the Raman modes at 419 and 570 cm$^{-1}$ for sapphire ($A_{1g}$) and GaN ($E_g$), respectively.$^3$

For electrical characterization of the SnSe$_2$/GaN heterojunction, Ti/Au/Ni contacts were evaporated using e-beam evaporation to form ohmic contacts to the SnSe$_2$. The contact to the n-GaN layer was formed by an indium dot. Inductively coupled plasma reactive ion etching (ICP-RIE) with BC$_3$/Ar chemistry was used for the device mesa isolation $(14 \times 14 \mu m^2)$. Hall measurements on SnSe$_2$ films on semi-insulating GaN substrates were found to exhibit n-type conductivity with a carrier concentration of $1.3 \times 10^{19}$ cm$^{-3}$ and an electron mobility of 4.7 cm$^2$ V$^{-1}$ s$^{-1}$.

To investigate vertical transport, n-type SnSe$_2$ films were grown on the MBE-grown n-GaN (100 nm–$10^{19}$ cm$^{-3}$ Si-doped) layer on n-GaN/Sapphire substrates. The structural and surface characteristics of these films were similar to the films (described earlier in this work) on insulating substrates. Vertical current-voltage characteristics of the n-SnSe$_2$/n-GaN isotype heterojunction diode were measured by applying a bias to SnSe$_2$ with respect to GaN [Fig. 3(a)]. The I-V characteristics at room temperature showed 9 orders of magnitude rectification at $\pm 1$ V and exhibited an ideality factor of 1.1 in the linear region of the semi-log forward bias curve. An optical microscopy image of the
SnSe₂/GaN diodes with metal contacts is shown in the inset of Fig. 3(a). Multiple devices were measured under the same conditions and showed identical I-V characteristics, indicating uniform electrical characteristics of large-area SnSe₂/GaN diodes (see supplementary material).

Capacitance-voltage (C-V) measurements showed typical C-V characteristics of a reverse-biased Schottky diode [Fig. 3(b)]. Since the SnSe₂ unintentional doping is significantly higher than the GaN doping density, the depletion region lies almost entirely in the GaN. Therefore, the relationship between capacitance and voltage can be approximated as $1/C^2 \approx 2/(qN_De_{GaN}\varepsilon_0) \times (V - V_{bi} - kT/q)$, where $q$ is the electron charge, $k$ is the Boltzmann constant, $T$ is the temperature, $N_D$ is the doping density in GaN, and $V$ is the reverse-bias voltage. The capacitance data yield a linear $1/C^2$ dependence on the voltage [inset of Fig. 3(b)], and the extracted built-in voltage of the SnSe₂/GaN heterojunction was 0.98 ± 0.02 V. A doping concentration of $2.1 \times 10^{18}$ cm⁻³ for GaN was extracted from the measurement (see supplementary material). The conduction band offset was determined using the expression, $\Delta E_c = qV_{bi} + (E_c - E_F)_{GaN} - (E_c - E_F)_{SnSe_2}$, where $E_c$ and $E_F$ are the conduction band edge and Fermi level, and the Fermi level positions in GaN and SnSe₂ were estimated using the Joyce-Dixon approximation. The extracted heterojunction barrier height was estimated to be 1 eV.

SnSe₂/GaN diodes were characterized using current-voltage-temperature (I-V-T) measurements in the temperature range of 100–400 K in steps of 50 K [Fig. 4(a)]. To determine the conduction mechanism, characteristic energy $(E_{00})$ can be used whether the transport is governed by thermionic emission (TE), thermionic field-emission (TFE), or field-emission (FE), where $E_{00}$ is defined from material parameters as $^{32,33}$

$$E_{00} = \frac{qh}{2} \left( \frac{N_D e_{GaN}}{\varepsilon_0 m_c^* m_0} \right)^2,$$

where $m_c^*$ is the electron effective mass for GaN, $\varepsilon_0 m_c^*$ the dielectric constant of GaN, $\varepsilon_0$ the vacuum permittivity, $m_0$ the electron rest mass, $N_D e_{GaN}$ the donor concentration of GaN, and $q$ the electronic charge. The calculated value of $E_{00}$ is 19.1 meV which is comparable to $kT$. Hence, the thermionic field emission (TFE) model was considered for the current transport mechanism. The current in TFE in the forward bias region is expressed as $^{34,35}$

$$I_{TFE} = \frac{AA^+ T^2}{kT} \sqrt{\frac{q\pi E_{00}(\phi_B - V - V_n)}{kT}} \times \exp \left[ \frac{qV_n}{kT} - \frac{q(\phi_B + V_n)}{E_0} \right] \exp \left( \frac{qV}{q\eta kT} \right) - 1,$$

where $V_n$ is $(E_{C,GaN} - E_{F,GaN})/q$, $\phi_B$ is the junction barrier height, $A$ is the diode area, and $A^+$ is the Richardson constant (26.4 A/cm² K² for GaN),

$$E_0 = E_{00}\coth \left( \frac{E_{00}}{kT} \right),$$

and $\eta$ is the ideality factor.
The values of the ideality factor ($\eta$) of the diode at different temperatures were extracted from the slope of the linear portion of $\ln(I)$ versus $V$ plot (see supplementary material) and are plotted in Fig. 4(b). $\eta$ closely follows the TFE curves for an $E_{00}$ of 15.8 meV, which is close to the theoretical value calculated above. The measured $E_{00}$ was used to fit the I-V-T data using the TFE model yielding the best fit with the barrier height of 0.84 eV, shown in Fig. 4(d). In addition, the barrier height lowering for TFE is estimated to be 0.08 eV using the expression,\[ \Delta \phi_B = \left( \frac{3}{2} \right)^{2/3} \frac{E_{00}^{2/3}}{kT} V_{bi}^{1/3}, \]

where $V_{bi}$ is the built-in potential. Therefore, taking into account the barrier lowering, the effective barrier height is 0.92 eV which is close to the value obtained from the C-V measurement.

The internal photoemission (IPE) measurement was also used to determine the heterojunction barrier height. Figure 5(a) shows measured photocurrent with an electrometer as a function of photon energy. Zero-bias was applied to the junction with an incident photon energy varying from 0.5 to 1.6 eV. The photo-yield was extracted from the quadratic dependence on incident photon energy,\[ \text{photocurrent} = \frac{1}{2} \frac{E_{00}^2}{kT} \coth \left( \frac{E_{00}}{kT} \right) \]

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