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$SnSe_2$ is currently considered a potential two-dimensional material that can form a near-broken gap heterojunction in a tunnel field-effect transistor due to its large electron affinity which is experimentally confirmed in this letter. With the results from internal photoemission and angle-resolved photoemission spectroscopy performed on $Al/Al_2O_3/SnSe_2/GaAs$ and $SnSe_2/GaAs$ test structures where $SnSe_2$ is grown on GaAs by molecular beam epitaxy, we ascertain a $(5.2 \pm 0.1)$ eV electron affinity of $SnSe_2$. The band offset from the $SnSe_2$ Fermi level to the $Al_2O_3$ conduction band minimum is found to be $(3.3 \pm 0.05)$ eV and $SnSe_2$ is seen to have a high level of intrinsic electron (n-type) doping with the Fermi level positioned at about 0.2 eV above its conduction band minimum. It is concluded that the electron affinity of $SnSe_2$ is larger than that of most semiconductors and can be combined with other appropriate semiconductors to form near broken-gap heterojunctions for the tunnel field-effect transistor that can potentially achieve high on-currents. *Published by AIP Publishing.* https://doi.org/10.1063/1.5016183

Currently, tremendous research focuses on different transistor designs for beyond-complementary metal–oxide–semiconductor (CMOS) technology. Among the latest designs, tunnel field-effect transistors (TFETs) are considered promising candidates since they offer a much improved on-off current ratio over a given gate voltage swing and low power consumption.[1–3] In contrast to thermionic emission of conventional CMOS operation, the TFET operation is based on band-to-band tunneling (BTBT) which can accommodate subthreshold slopes steeper than the intrinsic 60 mV/decade limit of the conventional CMOS. Only a few TFETs have been demonstrated with the sub-thermionic subthreshold slope, and most of them suffer much lower ON-currents than the CMOS counterparts. With the recent discoveries of two-dimensional (2-D) materials, the use of 2-D semiconductors has been proposed and demonstrated as TFET channel materials with supreme electrostatics and a much smaller tunneling width, which can subsequently improve the subthreshold slope and the on-state BTBT rate.[4–7] In one of the proposed 2-D TFET geometries, $SnSe_2$ has been selected amongst other 2-D materials because of its large electron affinity,[8] to be able to form a near-broken gap heterojunction that could, as a result, produce higher ON-current.[9–11] $SnSe_2$ has been grown by molecular beam epitaxy (MBE) on different layered semiconductor substrates[12,13] in the 1990 s and has received renewed interest recently[14,15] with the exploration of 2D layered materials. The electron affinity of $SnSe_2$ has been determined by ultraviolet photoemission spectroscopy (UPS) and the energy bandgap.[8,12] In this letter, we will experimentally ascertain in fact that $SnSe_2$ shows a large electron affinity that is inferred from its band alignment formed with a high-$k$ oxide. $SnSe_2$ was grown by molecular-beam-epitaxy (MBE) and was characterized by X-ray diffraction (XRD), angle-resolved photoemission spectroscopy (ARPES), Raman spectrum, and spectroscopic ellipsometry (SE). To facilitate the band offset measurement, high-k $Al_2O_3$ was used as the barrier of $SnSe_2$. The band alignment of $SnSe_2$ with $Al_2O_3$ was measured by internal photoemission (IPE) spectroscopy from which the work function and electron affinity are then deduced and confirmed. The results reported in this work are believed to possibly pave the way for further developments of TFETs using $SnSe_2$.

The schematic device structure and the IPE measurement setup[16] are shown in Fig. 1(a). The $n^+$ GaAs substrate (111)B was deoxidized in-situ under ultra-high vacuum ($4 \times 10^{-8}$ Pa) at 690 °C (for 3 min) and annealed under a flux of Se for 20 min, which provides a smoother growth surface.[17] After the substrate was cooled down and held at the growth temperature of 200 °C for 40 min, 63 layers (≈40 nm) of 1T-$SnSe_2$ were grown by simultaneous incidence of Sn and Se at a rate of 1/38 layer per second based on Reflection High-Energy Electron Diffraction (RHEED) oscillations. The beam equivalent pressures (BEPs) for Sn and Se, supplied by using Knudsen cells, are $2.67 \times 10^{-6}$ Pa ($2 \times 10^{-8}$ Torr) and $2.67 \times 10^{-4}$ Pa ($2 \times 10^{-6}$ Torr), respectively. After the growth, Se was incident on the surface during the cool down to encapsulate the $SnSe_2$ surface, preventing it from oxidation. The single phase and high

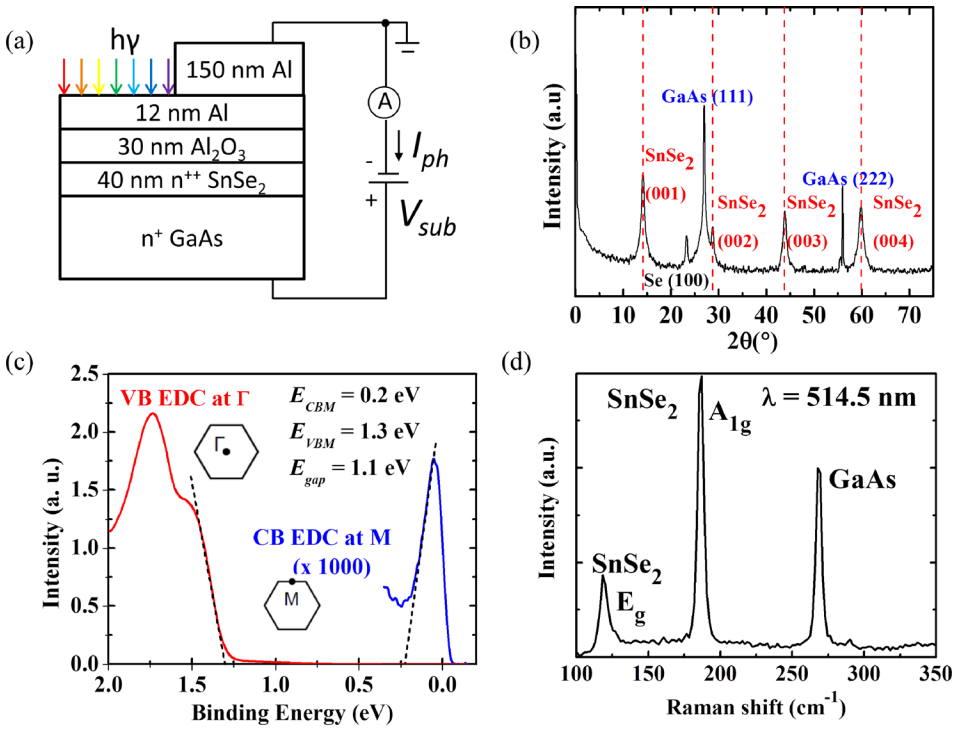


FIG. 1. (a) Schematic of the IPE measurement of the Al/$Al_2O_3$/$SnSe_2$/GaAs structure. (b) XRD of MBE Se capped $SnSe_2$ on GaAs (111) B. (c) ARPES EDCs at the Γ and M points of the surface Brillouin zone measured with He-Iα radiation. (d) Raman spectra of the Al/$Al_2O_3$/$SnSe_2$/GaAs structure.

crystallinity of MBE $SnSe_2$ are confirmed by XRD as shown in Fig. 1(b). By averaging the distance between the first order peak (001) of $SnSe_2$ and higher order peaks (002), (003), and (004) of $SnSe_2$, we obtain the c-spacing of 6.137 Å, which is identical to the reported c-spacing of 6.137 Å for bulk $SnSe_2$.[18] Although the Se cap is polycrystalline, the (100) peak of hexagonal selenium is observed at a 2Θ of 23.62°, which is close to the reported value of 23.52°.[19] The Se/$SnSe_2$/GaAs sample was then transferred to the atomic layer deposition (ALD) chamber, where the Se cap was desorbed at 300 °C prior to the deposition of 30 nm $Al_2O_3$ using trimethylaluminum (TMA) and $H_2O$ as precursors. 12 nm thick Al semi-transparent circles with a diameter of 100 $\mu$m were deposited through a shadow mask with the pitch of 200 $\mu$m, which brought into contact with 150 nm thick Al electrodes patterned by the same shadow mask. Another piece of the Se/$SnSe_2$/GaAs sample was de-capped in a separate high-vacuum system by heating to 250 °C for 30 min and subsequently measured by in-situ ARPES. The ARPES measurements were performed under ultrahigh vacuum (pressure $< 1.33 \times 10^{-8}$ Pa) at low temperatures (85 K to 100 K) using He-Iα photons ($h\nu = 21.2$ eV) with an energy resolution of 50 meV. Figure 1(c) shows ARPES energy distribution curves (EDCs) measured at the Γ and M points of the surface Brillouin zone. The valence band maximum (VBM) occurs at Γ, while the conduction band minimum (CBM) occurs at M. Extrapolating the linear part of the valence band (VB) and the conduction band (CB) EDCs to zero intensity[20] yields $E_{VBM} = 1.3$ eV and $E_{CBM} = 0.2$ eV, where $E_{VBM}$ and $E_{CBM}$ are the energies of the VBM and CBM, measured from the Fermi level, respectively. The large $E_{CBM}$ indicates a high level of intrinsic electron (*n*-type) doping. The corresponding indirect gap, $E_{gap}$, is deduced to have the value of 1.1 eV, which is in good agreement with recent reports.[14,21,22] Raman spectra were collected after the deposition of $Al_2O_3$ with a laser excitation wavelength of 514.5 nm at multiple locations, and the representative spectrum is shown in Fig. 1(d). The in-plane and the out-of-plane modes, $E_g$ and $A_{1g}$, are at 119.3 $cm^{-1}$ and 186.7 $cm^{-1}$, respectively, close to the values of 116 $cm^{-1}$ ($E_g$) and 185.5 $cm^{-1}$ ($A_{1g}$) as reported in Ref. 23, which were measured for bulk 1T phase $SnSe_2$, under the excitation of a 488 nm laser.

In the IPE measurements of the Al/$Al_2O_3$/$SnSe_2$/GaAs test structure, the incident photon energy is swept from 2.0 eV to 5.5 eV for each voltage ($V_{sub}$) applied between the GaAs substrate and the top Al electrode. Figure 2(a) shows the measured photocurrents as a function of the incident photon energy as $V_{sub}$ was stepped from −0.8 V to 0.6 V. The oxide flat band voltage ($V_{fb}$) is obtained using the voltage where the photocurrent switches sign near and above photoemission thresholds and found to be approximately 0.2 V. At voltages below $V_{fb}$, the measured photocurrents are negative as the electric field in the oxide points towards the $SnSe_2$ side and the photo-excited electrons from the degenerately doped *n*-type $SnSe_2$ CB near the $Al_2O_3$/$SnSe_2$ interface are injected into the $Al_2O_3$ conduction band and collected by the Al electrode. The band offset at the interface of $Al_2O_3$/$SnSe_2$ is extracted from the IPE quantity $Y^{\alpha}$, where $Y$ is the photon quantum yield defined as the number of emitted electrons normalized to the number of absorbed photons and α is a phenomenological parameter being equal to 1/3 for the photoemission from a semiconductor interface.[24] Experimentally, $Y$ is commonly presented by the ratio of the measured photocurrent to the incident light flux. In Fig. 2(b), the cube root of the yield $Y^{1/3}$ is plotted versus photon energy, and the band offset Φ at the interface of $Al_2O_3$/$SnSe_2$ is obtained from linear fitting of $Y^{1/3}$ to photon energy near the onset of the photoemission threshold, which has a ±0.05 eV uncertainty.[24] For $V_{sub} < V_{fb}$, $Y^{1/3}$ displays an optical feature at 3.8 eV which coincides at the same energy peak of the imaginary part of the dielectric function $\langle \varepsilon_2 \rangle$ of

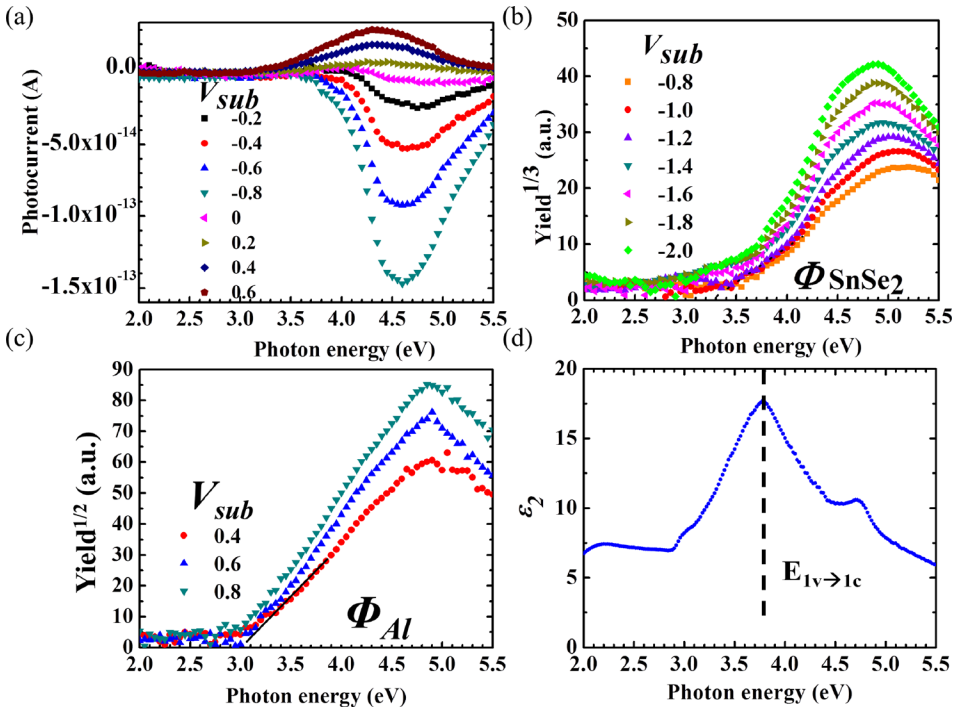


FIG. 2. (a) Photocurrent as a function of incident photon energy at different substrate biases from −0.8 to 0.6 V. The current switches direction at about 0.2 V, which is the flat-band voltage $V_{fb}$. (b) Cube root of the quantum yield as a function of incident photon energy at biases below $V_{fb}$ where the photoemission comes from the $SnSe_2$ layer. (c) Square root of the quantum yield as a function of incident photon energy at biases above $V_{fb}$, where the photoemission comes from Al. (d) The imaginary part of the pseudo-dielectric function of 40 nm $SnSe_2$ on the GaAs substrate measured by spectroscopic ellipsometry.

$SnSe_2$ which was measured by spectroscopic ellipsometry [Fig. 2(d)]. The 3.8 eV feature corresponds to the optical interband transition of $SnSe_2$ at $E_{1v\rightarrow1c}$[25] and therefore confirms that the photoemission shown in Fig. 2(b) originates from the $SnSe_2$ layer (not the GaAs substrate). We note a decrease in energy threshold as the electric field inside the oxide increases when applied $V_{sub}$ steps up from −1.2 V to −2.0 V. This observed threshold decrease is due to the well-known image force lowering effect.[24] When approaching to zero field (flat band) in the oxide, the thresholds are pinned at (3.3 ± 0.05) eV which is the *zero*-field band offset or the barrier height from the $SnSe_2$ Fermi level to the $Al_2O_3$ CBM. At voltages above $V_{fb}$, the band offset at the interface of Al/$Al_2O_3$ is also obtained from the IPE quantity $Y^{\alpha}$ and found to be (3.0 ± 0.05) eV, as shown in Fig. 2(c), where $\alpha$ is equal to 1/2 for the photoemission from a metal interface.[24] This band offset has a similar value and weak field dependence as seen in literatures,[26,27] which was explained by a possible interfacial dipole layer between the ALD $Al_2O_3$ and Al.[26]

The schematic band alignment of the Al-$Al_2O_3$-$SnSe_2$ structure now can be established and is shown in Fig. 3. On the Al side, the work function of Al (4.7 ± 0.1) eV results from the measured band offset of (3.0 ± 0.05) eV and the approximate 1.7 eV electron affinity of ALD $Al_2O_3$.[28,29] It is larger than the well-known Al work function of 4.25 eV,[30] which is possibly due to a negative dipolar layer at the Al-$Al_2O_3$ interface,[26] and might be reduced by 0.4 eV after annealing.[27] On the opposite side, the work function of $SnSe_2$ is (5.0 ± 0.1) eV, and the electron affinity of $SnSe_2$ is estimated to be (5.2 ± 0.1) eV. The matched electron affinity with UPS measurement results[8,12] and field dependence of the band offsets seen in Fig. 2(b) indicate a minimum of interfacial charge/dipole at the $Al_2O_3$-$SnSe_2$ interface. The difference between the work functions of Al and $SnSe_2$ is consistent with the measured flat band voltage of 0.2 V.

In this letter, we conclude that MBE-grown $SnSe_2$, currently considered as a potential 2-D material for advanced TFET applications, has a large electron affinity. The conclusion is drawn from the experimental results from the internal photoemission and angle-resolved photoemission spectroscopy performed on Al/$Al_2O_3$/$SnSe_2$/GaAs and $SnSe_2$/GaAs structures, respectively. Specifically, the *zero*-field band offset from the $SnSe_2$ Fermi level to the $Al_2O_3$ conduction band minimum was determined to be (3.3 ± 0.05) eV, and $SnSe_2$ is shown to have a high level of intrinsic electron (*n*-type) doping. The electron affinity of $SnSe_2$ was then derived to be approximately (5.2 ± 0.1) eV which is larger than most semiconductors, and therefore, it is expected that $SnSe_2$ will

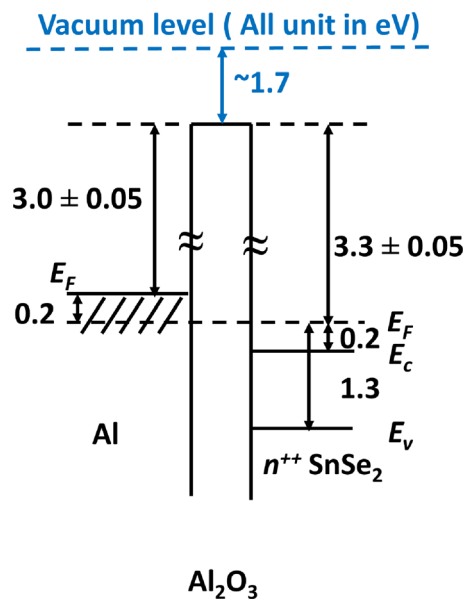


FIG. 3. The schematic band alignment of Al-$Al_2O_3$-$SnSe_2$ at the flat band condition. The values in black are measured by this work, and the value in blue is from the literature.

form the preferred near broken-gap heterojunctions with other semiconductors.

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