Supporting Information

Complementary Hybrid Semiconducting Superlattices with Multiple Channels and Mutual Stabilization

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Preparation of substrates: The Si substrates used in this study were cut from p-type (100) Si wafers (Seyang Electronics) with resistivity $> 1 \, \Omega \text{cm}$. The Si substrates were initially treated with a chemical cleaning process that involved degreasing, HNO$_3$ boiling, NH$_4$OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water, and blow-drying with nitrogen to remove contaminants and grow a thin protective oxide layer on the surface. The flexible substrate was cut from polyimide (PI) films (Kolon CPI™). The PI substrate was cleaned with de-ionized water and ethanol and blown dry with nitrogen to remove contaminants.

Deposition of complementary hybrid superlattice thin films: ALD and MLD were used to deposit Al$_2$O$_3$ dielectric layers, ZnO nanolayers, and 4MP organic monolayers on the Si substrate within a homemade chamber. ALD and MLD procedures were conducted at low temperatures ($\sim 100 \, ^\circ\text{C}$), and Ar with a flow rate of 100 sccm served as a carrier and purging gas in both ALD and MLD. The Al$_2$O$_3$ dielectric layers were deposited onto the Si substrate using trimethylaluminium (TMA, Aldrich, 97%) and water (H$_2$O) as ALD precursors. Each ALD cycle consisted of 2 s exposure to TMA, 20 s Ar purge, 2 s exposure to H$_2$O, and 40 s Ar purge. 4MP organic monolayers were deposited using diethylzinc (DEZ, Aldrich, 97%) and 4-mercaptophenol (Aldrich, 97%) as MLD precursors. The MLD cycle consisted of 2 s DEZ exposure, 20 s Ar purge, 20 s 4MP exposure, and 200 s Ar purge. DEZ and 4MP were evaporated at 20 °C and 75 °C, respectively. ZnO nanolayers were deposited sequentially on the 4MP monolayers. Each ALD cycle consisted of 2 s DEZ exposure, 20 s Ar purge, 2 s H$_2$O exposure, and 40 s Ar purge. The thicknesses of the complementary hybrid superlattices were confirmed by ex-situ ellipsometry and AFM. The average thickness for each deposition cycle of Al$_2$O$_3$, 4MP, and ZnO was
approximately 0.09, 0.70, and 0.14 nm, respectively. Results from the ellipsometry measurements were in good agreement with the cross-sectional TEM images shown in Figure 1b.

**Fabrication of complementary hybrid superlattice devices:** A 15-nm-thick Al₂O₃ thin film was deposited on the Si substrate by ALD as a gate dielectric layer for FETs ($C_i=340 \text{ nFcm}^{-2}$, Figure S4 in Supporting Information). Subsequently, the superlattice thin films were deposited on Al₂O₃-coated Si substrates without breaking vacuum, followed by ex-situ patterning using photolithography for $500 \times 500 \mu\text{m}^2$ active channels of FETs. Finally, 70-nm-thick, aluminum (Al), four-probe contacts were vapor-deposited onto the active channel by thermal evaporation through a shadow mask under pressure of $\sim10^{-7}$ Torr. Channel length and width were $L_{ch}=300 \mu\text{m}$ and $W_{ch}=500 \mu\text{m}$, respectively, and the center-to-center distance between neighboring voltage probes was $D_{ch}=110 \mu\text{m}$. The MIS capacitor was fabricated on the 15-nm-thick Al₂O₃-coated Si substrate. The $500 \times 500 \mu\text{m}^2$ hybrid superlattice patterns were deposited on top of the 70-nm-thick Al electrodes. Then, the top metal electrodes were deposited as widely as the patterned semiconductor. Silver paste was then applied on top of each electrode for good electrical contact during capacitance-voltage ($C$-$V$) characterization. The single-quantum-well FET was prepared with a 4MP (0.7 nm)/ZnO (4 nm)/4MP (0.7 nm) channel structure and double-, triple-quantum-well FETs were fabricated by extra ALD-MLD to deposit one or two ZnO (4 nm)/4MP (0.7 nm) bilayer(s) on the single quantum well, respectively. Flexible superlattice FET employed polyimide substrate and 70-nm-thick Al gate electrode patterned with a shadow mask to replace the doped Si substrate.

**Characterization of complementary hybrid superlattice thin films and devices:** The hybrid superlattices were analyzed by JEOL JEM-ARM200F transmission electron microscopy (TEM) operated at 200 kV. Cross-sectional TEM specimens were prepared by a focused ion beam
(FIB) using a Helios NanoLab 600 apparatus. Carbon and platinum deposition were performed on the sample surface to protect the superlattice thin film from ion beam bombardment during the FIB process. Thin-film-crystallinity was measured by grazing incidence X-ray diffraction (GI-XRD) with a fixed incidence angle of 1°, measuring range from 20° to 70° for a 0.04° step, and scan speed of 3° per minute. GI-XRD was performed using a high-resolution X-ray diffractometer (Smartlab, Rigaku) with a HyPix-3000 detector and Cu-Kα (λ = 1.54 Å) radiation operating at 9 kW. The UV-VIS transmittance spectra of the superlattice thin film were obtained with a UV-VIS spectrometer (UV-VIS 8453, Agilent Technologies). The morphology of the thin films was collected by non-contact mode AFM (XE-100, Park Systems). Current-voltage (I-V) and capacitance-voltage (C-V) characteristics of the devices were measured using an Agilent 4155C semiconductor parameter analyzer and an Agilent E4980A Precision LCR meter, respectively, under ambient conditions. Temperature-dependent experiments were performed using liquid nitrogen (minimum at 90 K) in the dark under vacuum (~1.5 mTorr). Intensity of the LED used in the NBIS and PBIS test was measured using a digital lux meter (LX1010B).

**Technology computer-aided design (TCAD) simulations:** TCAD simulations were performed by incorporating band structure, the Schrödinger-Poisson model and tunneling model into Silvaco ATLAS-2D. The DOS masses for electron and hole carriers were assumed to be isotropic. The density-gradient theory stemming from the Schrödinger equation was used to calculate the quantum effect of FETs. The quantum transport model involves modification of semi-classical potential into quantum potential using the Bohm Quantum Potential method, with the drift-diffusion equation. The transfer characteristics for the FETs with 12 nm pure ZnO and hybrid superlattice channels were calculated using TCAD simulation and showed excellent fit to
the measured $I$-$V$ data, as shown in Figure S8. The physical parameters used to simulate the $I$-$V$ data are summarized in Table S2 and S3.

**Computational method:** All ab initio calculations were performed with the Vienna ab initio Simulation Package (VASP 5.4.1).\(^1\)\(^-\)\(^4\) We used the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with the projector augmented wave (PAW) method.\(^5\) Additionally, a Hubbard $U$ term was implemented to partially account for over-hybridization and localization of electron orbitals, and Hubbard potential of $U = 6$ eV was applied to the 3d orbital of Zn. A plane-wave cutoff energy of 500 eV was used. The DFT-D3 method proposed by Grimme et al.\(^6\)\(^,\)\(^7\) was used to study adsorption of 4MP molecules on the ZnO(001) surface while considering van der Waals interactions. The calculations for geometric optimization were carried out in periodically repeated surface (3 × 3) supercells with 2 × 2 $k$-point sampling. A seven-layer slab model was employed for ZnO(001), with layers separated by a 15 Å vacuum space in the z-direction to avoid interaction. In addition, the three top layers were allowed to fully relax, while the other layers were fixed to their optimized bulk positions. Lattice constants and internal atomic positions were fully optimized until the residual forces were less than 0.04 eVÅ\(^{-1}\). The schematics of our models are shown in Figure S1 in Supporting Information.
For investigation of accurate oxygen defect phenomena in 4MP/ZnO hybrid semiconducting superlattice, we preferentially explored the 4MP binding behaviors on the ZnO(001) surface, which is well-known to be the most stable surface. ZnO (001) surfaces have two Zn- and O-terminated surface types, as shown in Figure S1. Considering the partial charge of each atom in ZnO(001) and 4MP, the negatively charged S and positively charged C of 4MP can electrostatically interact with cationic Zn and anionic O sites of ZnO(001) surface, respectively. Therefore, we systematically investigated the 4MP binding configurations (hollow, bridge, and on-top) on the ZnO(001) surface via Zn-S and O-C chemical bonds, as shown in Figure S1. The results in Figure S1c reveal that all structural configurations converged to the energetically most stable configuration with hollow Zn-S and slight tilt on top of the O-C chemical binding configurations.

**Figure S1.** (a) Schematics for ZnO bulk and (001) surface structures. (b) Different 4MP binding sites on the Zn- or O-terminated ZnO(001) surface structure. (c) Hybrid 4MP/ZnO structure; red, gray, brown, white, and yellow colors represent O, Zn, C, H, and S, respectively.
Figure S2. Grazing incidence X-ray diffraction (GI-XRD) pattern of the triple-quantum-well superlattice on a glass substrate.
Figure S3. Atomic force microscopy (AFM) height images and cross-sectional profiles for the triple-quantum-well hybrid superlattice film.
Figure S4. The geometric capacitance of the 15-nm-thick Al₂O₃ gate insulator measured as a function of frequency. The inset schematically illustrates the capacitor with the 15 nm Al₂O₃ film.
[Gated four-probe (GFP) measurement and details of intrinsic mobility extraction]

For more accurate mobility extraction, we used gated four-probe (GFP) devices to suppress the effect of contact resistance $R_c$ in electrical characterization.\textsuperscript{9,10} As shown in Figure 1d, the field-effect transistors have four-point probe electrodes including two extra voltage tips V1 and V2 contacting one side of the channel pattern. The voltage drop $V_{4p}$ between the tips V1 and V2 was evaluated as $V_{4p}=V_2-V_1$ during FET characterization, where $V_1$, $V_2$, and $V_{gs}$ are V1-, V2-, and gate-to-source voltage, respectively. By measuring $V_{4p}$, the channel conductance $\sigma_{\text{channel}} = (I_{ds}/V_{4p}) \cdot (D/W)$ was estimated independent of contact resistance $R_c$. Now, we present equations to yield $R_c$-corrected intrinsic mobility $\mu_{4p}$ in a linear regime ($V_{ds} = 0.1 \text{ V}$; the output curves were given in Figures S5a and 5d) as shown below:

$$\mu_{4p} = \left( \frac{D}{W \cdot C_i} \right) \frac{\partial (I_{ds})}{\partial V_{gs}} = \frac{1}{C_i} \frac{\partial \sigma_{\text{channel}}}{\partial V_{gs}}$$ \hspace{1cm} [S1]

where $C_i$ is the geometric capacitance of the Al$_2$O$_3$ gate insulator (measured in Figure S4), and $W$, $L$, and $D$ are the channel width, channel length, and V1-to-V2 distance, which measured 500, 300, and 110 µm, respectively. Additionally, for more reliable extraction of mobility, a linear regression was applied with respect to $\sigma_{\text{channel}}$. As shown in Figures S5b and 5e, channel conductance $\sigma_{\text{channel}}$ of the devices was plotted with respect to gate overdrive voltage ($V_{gs}-V_{th}$), and $\partial \sigma_{\text{channel}}/\partial V_{gs}$ was estimated from the slope of the extrapolated $\sigma_{\text{channel}}$ line for $2 \text{ V} < V_{gs} - V_{th} < 3 \text{ V}$ to calculate $\mu_{4p}$ as shown in Equation S1.
Figure S5. Details of the gated four-probe measurement with temperature change. (a-c) Electrical characteristics of the hybrid superlattice transistor: (a) Output characteristics, (b) temperature-variable channel conductance ($\sigma_{\text{channel}}$) versus gate overdrive voltage ($V_{gs}-V_{th}$), and (c) Arrhenius plot of $\mu_{4p}$. (d-f) Electrical characteristics of the 12 nm pure ZnO transistor: (d) Output characteristics, (e) temperature-variable $\sigma_{\text{channel}}$ as functions of $V_{gs}-V_{th}$, and (f) Arrhenius plot of $\mu_{4p}$. Slopes of the dotted lines in (b) and (e) correspond with $\partial \sigma_{\text{channel}}/\partial V_{gs}$ in Equation S1.
We introduced a capacitance-voltage (C-V) depth profiling method with Equations S2 and S3 as previously reported by Lin et al. and Ambacher et al.\textsuperscript{11,12} Applying this method to the obtained C-V characteristics, the charge carrier concentration across the depth $z$ was extracted as

$$N_{CV} = \frac{2}{\varepsilon_0 \varepsilon q} \frac{d(1/C^2)}{dV}$$ \hspace{1cm} \text{[S2]}$$

depending on depth $z$

$$z(V) = \varepsilon_0 \varepsilon \left( \frac{1}{C(V)} - \frac{1}{C_i} \right)$$ \hspace{1cm} \text{[S3]}$$

where $q$ is the elementary charge, $C_i$ is the capacitance per unit area of the gate insulator, and $\varepsilon_0$ and $\varepsilon$ are the vacuum permittivity and relative permittivity of the semiconductor, respectively.

\textbf{Figure S6.} C-V depth profiling of the 12 nm pure ZnO semiconductor capacitor. (a) Schematic of the metal-insulator-semiconductor (MIS) capacitor based on the 12 nm pure ZnO semiconductor. (b) Total capacitance per unit area ($C$) versus bias voltage ($V$). (c) Depth profile of carrier concentration ($N_{CV}$) in the 12 nm pure ZnO semiconductor converted from (b).
Figure S7. TCAD simulation results for the 12 nm pure ZnO field-effect transistors (FETs). (a) Simulated free electron density distribution ($N_e$) along the out-of-plane direction of the device at $V_{gs} = 6$ V and (b) corresponding energy band diagram of the metal-insulator-semiconductor (MIS) structure in the transistor.
Figure S8. Measured and simulated transfer characteristics for (a) the 12 nm pure ZnO and (b) the single-, double-, and triple-quantum-well field-effect transistors.
**Figure S9.** Temperature-dependent gated four-probe measurement for single-quantum-well FET with a 4-nm-thick ZnO nanolayer. (a) Temperature-variable channel conductance ($\sigma_{\text{channel}}$) versus gate overdrive voltage ($V_{gs}-V_{\text{th}}$). (b) The intrinsic mobility ($\mu_{4p}$) plotted versus $T^{-1/4}$ in the temperature range of 300-90 K.
Figure S10. Summary of stability under diverse bias and illumination stresses for hybrid superlattice field-effect transistors (FETs). (a-c) Variation of transfer characteristics with time under (a) negative bias stress (NBS), (b) positive bias stress (PBS), and (c) positive bias illumination stress (PBIS). Time evolution of (d) threshold voltage shift ($\Delta V_{th}$) and (e) subthreshold swing shift ($\Delta SS$) under different stress conditions.
Figure S11. (a) Oxygen defect structure on (001) surface of pure ZnO and hybrid 4MP/ZnO. Red, gray, brown, white, and yellow colors represent O, Zn, C, H, and S, respectively. (b,c) Projected density of states (PDOS) on (b) the surface and (c) core oxygens of pure ZnO and hybrid 4MP/ZnO. Fermi levels are represented by black dashed lines.
Oxygen state related to defects was measured using X-ray photoelectron spectroscopy (XPS) analysis in both the 12-nm-thick pure ZnO thin film and the triple-quantum-well hybrid superlattice. The XPS peaks for O1s could be deconvoluted by three Gaussians curves, which centers were located at 529.9 eV, 531.4 eV and 532.5 eV, respectively. These three peaks could be interpreted by three kinds of oxygen state under different chemical environments in both films. The peak located at 529.9 eV (O1), which has maximum intensity and lowest binding energy, was attributed to the O$^{2-}$ ions in a wurtzite structure bonded with nearest Zn$^{2+}$ atoms. The peak located at 531.4 eV (O2) arose from oxygen atoms nearby oxygen vacancy. Finally, the peak at 532.5 eV could be assigned to the hydroxyl groups at the surface of films. The ratio of peak areas [O2/(O1 + O2)] could be used as a parameter of the relative quantity of oxygen vacancy in the films. The calculated results of the ratio [O2/(O1 + O2)] was 0.30 for pure ZnO and 0.12 for hybrid superlattice.

**Figure S12.** O1s XPS spectra for the 12 nm pure ZnO thin film and the triple-quantum-well hybrid superlattice.
Figure S13. Bending test of the hybrid superlattice field-effect transistors on a plastic substrate. (a) Evolution of transfer characteristics by bending cycles. (b-d) Variation of (b) two-probe field-effect mobility ($\Delta \mu_{2p}$), (c) subthreshold swing ($\Delta SS$), and (d) threshold voltage ($\Delta V_{th}$) as a function of bending cycle.
Figure S14. Transmittance spectra of the hybrid superlattice thin film. The inset indicates the schematic of the superlattice film on a quartz substrate.
**Table S1.** Comparison between electrical characteristics of typical field-effect transistor (FET) devices based on the hybrid superlattice and 12 nm pure ZnO channels.

<table>
<thead>
<tr>
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<th>Hybrid superlattice (triple quantum well)</th>
<th>12 nm pure ZnO</th>
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<tbody>
<tr>
<td>$\mu_{4p}$ (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>73</td>
<td>28</td>
</tr>
<tr>
<td>$I_{ON}/I_{OFF}$</td>
<td>$2.2 \times 10^6$</td>
<td>$1.4 \times 10^5$</td>
</tr>
<tr>
<td>$I_{OFF}$ (A)</td>
<td>$4.5 \times 10^{-12}$</td>
<td>$2.4 \times 10^{-11}$</td>
</tr>
<tr>
<td>SS (mVdecade$^{-1}$)</td>
<td>110</td>
<td>225</td>
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Table S2. Technology computer-aided design (TCAD) material parameters

<table>
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<tr>
<th>Parameter Symbol</th>
<th>Definition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{e,ZnO}$ (eV)</td>
<td>Bandgap energy of ZnO</td>
<td>3.2</td>
</tr>
<tr>
<td>$T_{ZnO}$ (nm)</td>
<td>Thickness of ZnO</td>
<td>4</td>
</tr>
<tr>
<td>$m^*_ZnO$</td>
<td>Electron effective mass of ZnO</td>
<td>$0.23m_0$</td>
</tr>
<tr>
<td>$N_{e,ZnO}$ (cm$^{-3}$)</td>
<td>Doping concentration of ZnO</td>
<td>$1 \times 10^{18}$</td>
</tr>
<tr>
<td>$\mu_{ZnO}$ (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>Electron mobility in conduction band of ZnO (single-/double-/triple-quantum-well transistor)</td>
<td>30/50/73</td>
</tr>
<tr>
<td>$E_{e,4MP}$ (eV)</td>
<td>Bandgap energy of 4MP</td>
<td>5.15</td>
</tr>
<tr>
<td>$T_{4MP}$ (nm)</td>
<td>Thickness of 4MP</td>
<td>0.7</td>
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**Table S3.** Electrical properties of the subgap density of state used in technology computer-aided design (TCAD). The TCAD simulation was performed under the condition that the subgap density of states of ZnO \((g_{\text{Ch}})\) and interface \((g_{\text{Dit}})\) were modeled to have one exponential function \((g_{TA})\) and one Gaussian function \((g_{DA})\), respectively. The formulas are as follows:

\[
\begin{align*}
N_{TA,Ch} & \quad (\text{cm}^{-3}\text{eV}^{-1}) \\
& \quad \text{Density of acceptor-like tail state of ZnO} \\
& \quad 4 \times 10^{18} \\
kT_{TA,Ch} & \quad (\text{eV}) \\
& \quad \text{Characteristic decay energy of acceptor-like tail state of ZnO} \\
& \quad 0.04 \\
N_{DA,Ch} & \quad (\text{cm}^{-3}\text{eV}^{-1}) \\
& \quad \text{Density of acceptor-like deep state of ZnO} \\
& \quad 3.2 \times 10^{17} \\
kT_{DA,Ch} & \quad (\text{eV}) \\
& \quad \text{Characteristic decay energy of acceptor-like deep state of ZnO} \\
& \quad 0.25 \\
N_{TA,Dit} & \quad (\text{cm}^{-3}\text{eV}^{-1}) \\
& \quad \text{Density of acceptor-like tail state of channel/insulator interface} \\
& \quad 4.1 \times 10^{13} \\
kT_{TA,Dit} & \quad (\text{eV}) \\
& \quad \text{Characteristic decay energy of acceptor-like tail state of channel/insulator interface} \\
& \quad 0.04 \\
N_{DA,Dit} & \quad (\text{cm}^{-3}\text{eV}^{-1}) \\
& \quad \text{Density of acceptor-like deep state of channel/insulator interface} \\
& \quad 3.8 \times 10^{13} \\
kT_{DA,Dit} & \quad (\text{eV}) \\
& \quad \text{Characteristic decay energy of acceptor-like deep state of channel/insulator interface} \\
& \quad 0.25
\end{align*}
\]

\[
g_{\text{Bulk}} (E) = g_{TA,Ch} (E) + g_{DA,Ch} (E) \\
= N_{TA,Ch} \exp \left(-\frac{E_c - E}{kT_{TA,Ch}}\right) + N_{DA,Ch} \exp \left(-\frac{(E_c - E)^2}{kT_{DA,Ch}}\right). \tag{S4}
\]

\[
g_{\text{Dit}} (E) = g_{TA,Dit} (E) + g_{DA,Dit} (E) \\
= N_{TA,Dit} \exp \left(-\frac{E_c - E}{kT_{TA,Dit}}\right) + N_{DA,Dit} \exp \left(-\frac{(E_c - E)^2}{kT_{DA,Dit}}\right). \tag{S5}
\]
Table S4. Sequential oxygen defect formation energies ($E_{V0}$) on the (001) surface of pure ZnO and hybrid 4MP/ZnO surfaces.

<table>
<thead>
<tr>
<th>Defect site</th>
<th>1st $E_{V0}$ (eV)</th>
<th>2nd $E_{V0}$ (eV)</th>
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<tr>
<td>ZnO_VO_core</td>
<td>4.689</td>
<td>-</td>
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<tr>
<td>ZnO_VO_surf</td>
<td>0.277</td>
<td>0.280</td>
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<tr>
<td>4MP/ZnO_VO_core</td>
<td>4.587</td>
<td>-</td>
</tr>
<tr>
<td>4MP/ZnO_VO_near</td>
<td>0.852</td>
<td>3.995</td>
</tr>
<tr>
<td>4MP/ZnO_VO_far</td>
<td>0.388</td>
<td>-</td>
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References


