Electronic Supplementary Information for

Revealing the TMA_2SnI_4/GaN band alignment and carrier transfer across the interface

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Contactless electroreflectance:

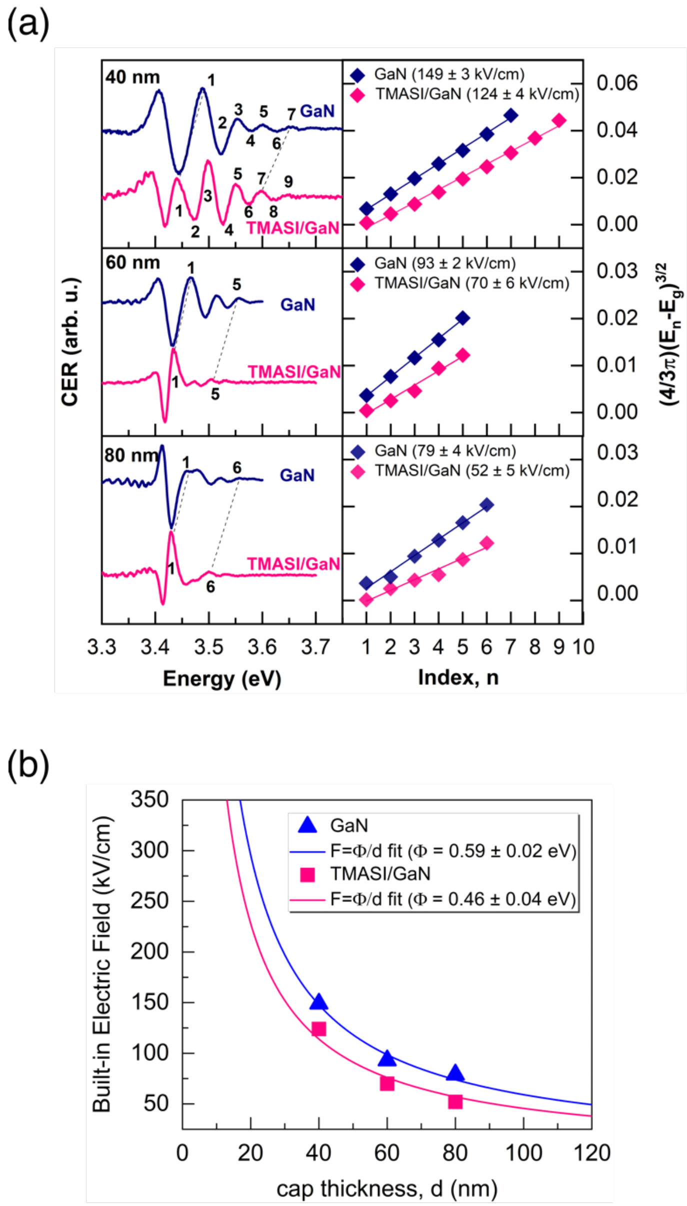

Figure S1 (a) CER spectra (left panels) and analysis of the built-in electric field (right panels) for reference GaN and TMA_2SnI_4\GaN:Si hybrids. (b) Evaluation of surface barrier height.

Figure S1 (a) shows CER spectra of the set of TMA_2SnI_4\GaN:Si samples with varying thickness (40, 60, 80 nm) of undoped cap in van Hoof structure. In each spectrum, a resonance corresponding to the GaN bandgap (approximately 3.45 eV) is succeeded by the FKO (numbered). Notably, for TMA_2SnI_4-coated structures, a reduction in the FKO period is evident, indicating a decrease in the built-in electric field's magnitude in the presence of perovskite. This observation aligns with the calculated values of the built-in electric field presented in the right-hand panels of Figure S1(a), obtained using equations (2) and (3) detailed in the main part of the manuscript. According to equation (4) ($\Phi_n=Fd$), the reduction in the built-in electric field for TMA_2SnI_4 covered GaN signifies a decrease in the surface barrier for electrons at the TMA_2SnI_4/GaN:Si interface. Figure S1(b) illustrates the determination of the surface barrier height by fitting the electric fields extracted from the CER experiment using the relation Φ_n=Fd. The obtained Φ_n values are (0.59 ± 0.02 eV) for reference GaN and (0.46 ± 0.04 eV) for TMA_2SnI_4/GaN:Si interface.

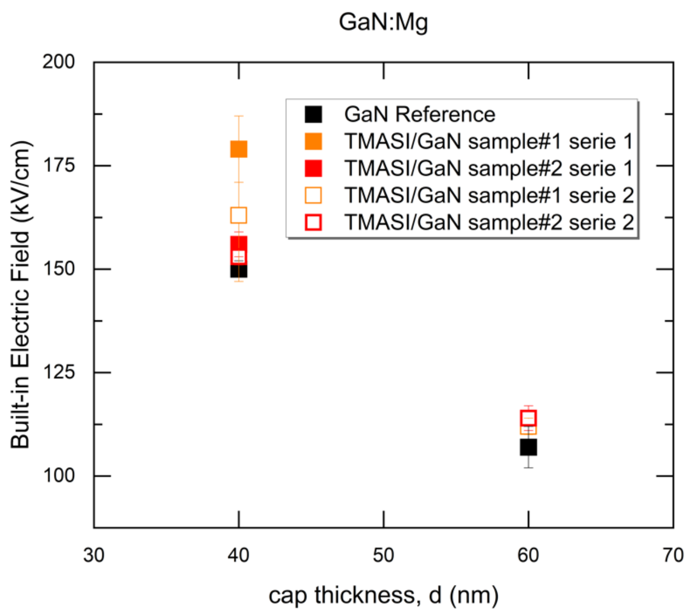

Figure S2 Built-in electric fields obtained for two series of TMA_2SnI_4/GaN:Mg samples.

Figure S2 presents values of built-in electric fields acquired from CER spectra measured for two series of reference GaN:Mg substrates and TMA_2SnI_4/GaN:Mg hybrids. As evident within the range of experimental uncertainties, consistent values of the built-in electric field were obtained for investigated cap thicknesses, demonstrating the repeatability of the observed phenomena.

X-ray photoelectron spectroscopy

The surface electronic and chemical properties were examined using X-ray photoelectron spectroscopy (XPS) with a monochromatic $Al_{K\alpha}$ (1486.6 eV) radiation source. Photoelectrons were collected by a hemispherical electron energy analyzer (Argus CU), with a 0.1 eV step size and a pass energy of 20 eV. The analyzer's optical axis was positioned at a 30° angle to the normal of the substrate surface. The Fermi level was calibrated using a clean Ag reference sample. All XPS measurements were performed at room temperature.

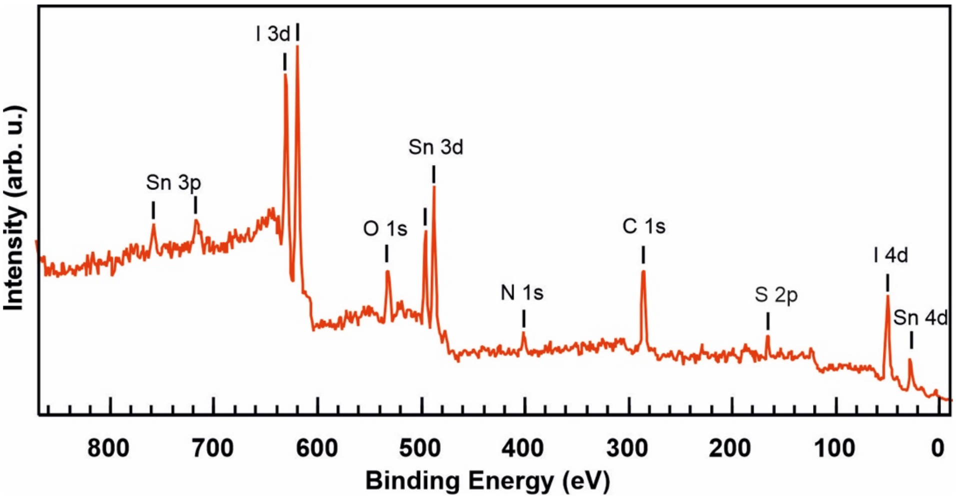

Figure S3 The XPS survey spectrum of TMA_2SnI_4 measured in the wide spectral range.

Figure S3 shows a wide XPS survey spectrum of TMA_2SnI_4 layer spin-coated on glass substrate confirming the presence of elements within the compound.

Steady-state photoluminescence:

300 nm TMA_2SnI_4 layer spin-coated on glass substrate was excited by a 532 nm CW laser with an excitation power of 250 μW. PL signal was detected with Avantes AvaSpec CCD detector.

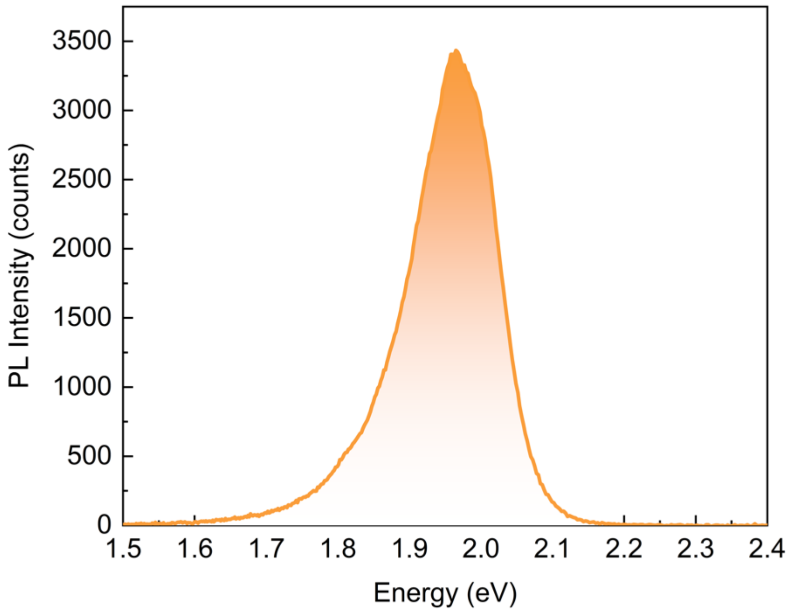

Figure S4 Room temperature PL spectrum of 300nm thick TMA_2SnI_4 layer.

Time-resolved photoluminescence:

The samples were excited by a 532 nm picosecond pulsed laser, operating at a repetition rate of 1 MHz and an average power density of approximately 0.4 W/cm². Photoluminescence (PL) decay at 600 nm was recorded using a system comprising a 0.3 m focal length monochromator and a time-correlated single photon counting module (Becker & Hickl SPC-150-NX) equipped with a PMC-150-04 detector.

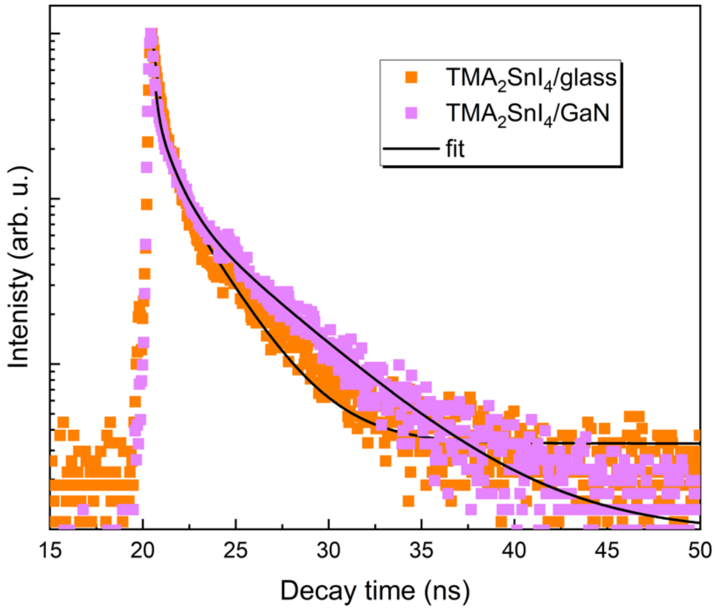

Figure S5 Time-resolved photoluminescence decays of TMA_2SnI_4/GaN and reference TMA_2SnI_4/glass structures.

Carrier dynamics on TMA_2SnI_4/GaN interface was investigated by time-resolved photoluminescence (TRPL). The TMA_2SnI_4 spin-coated on glass substrate was taken as a reference. As it can be seen in Figure S5, PL decays registered for both types of samples are similar. Measured curves were fitted with the following multi-exponential decays [1]:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right),$$

where A_1, A_2, A_3 are the amplitudes and τ_1, τ_2, τ_3 are the time constants related to band-edge, defect and charge transfer recombination mechanisms [1]. Time constants obtained from fitting procedure are shown in the table below. The PL decay of reference TMA_2SnI_4/glass structure was fitted with bi-exponential function, since no interfacial charge transfer is expected to occur [1]. Carriers' lifetimes obtained for TMA_2SnI_4 are consistent with those reported earlier [2]. As it can be noticed, time constants of TMA_2SnI_4/GaN are smaller than those obtained for TMA_2SnI_4/glass, suggesting the enhanced carrier recombination at the interface, what is expected for type II band alignment. However, it should be noted that within this range of time constants, we are approaching the detection limit of our experimental setup (130 ps).

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
TMA_2SnI_4/glass	0.395 ± 0.004	2.314 ± 0.042	-
TMA_2SnI_4/GaN	0.162 ± 0.009	0.930 ± 0.040	4.447 ± 0.099

References:

[1] Inorg. Chem. Front., 2022, 9, 4661-4670

[2] Dalton Trans., 2021, 50, 10261-10274