

### Supportive Information:

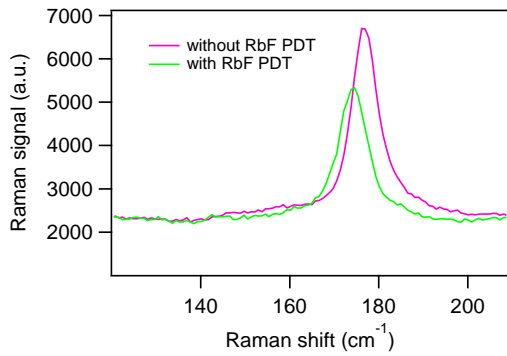


Fig. S1: Room-temperature Raman signal generated by a cw-laser with a wavelength of 532 nm and an excitation power of 3.5 mW. The Raman signal shows that the commonly observed A1 peak for CIGS shifts from 201  $\text{cm}^{-1}$  to 198  $\text{cm}^{-1}$  for the RbF treated layer. This A1 peak shift is expected for lower Ga/(Ga+In) ratios [21].

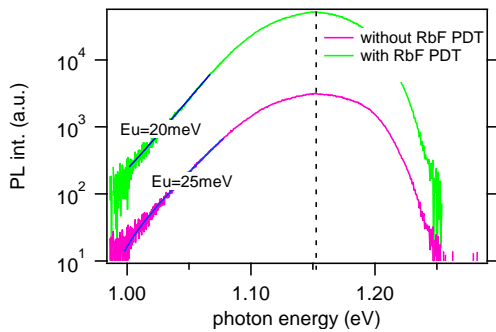


Fig. S2: room-temperature Photoluminescence signal generated by a cw-laser with a wavelength of 532 nm and an excitation power of 320  $\mu\text{W}$ . Since the measured PL signal is emitted from the material around the notch position [22], the energy of the peak position is close to the minimum band gap energy. Both samples show the same minimal band gap energy of 1.15 eV. The sub-gap tail energy, extracted from the exponential slope of the PL signal [19,12] is 25 meV for the non-treated layer and 20 meV for the RbF treated layer.

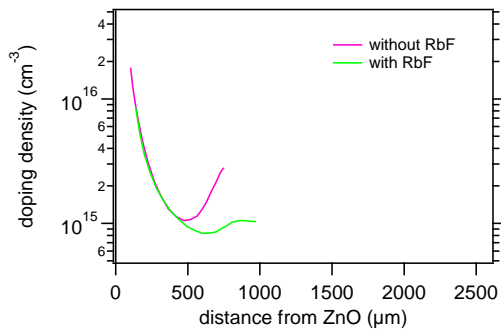


Fig. S3: Doping density versus space charge region depth derived from the Capacitance-Voltage curve recorded at room-temperature between -0.5V and +0.5V DC voltage and with a 1 kHz 20 mV AC voltage. The doping density can be calculated with the assumption that only shallow defects contribute to the capacitance as described in [17].

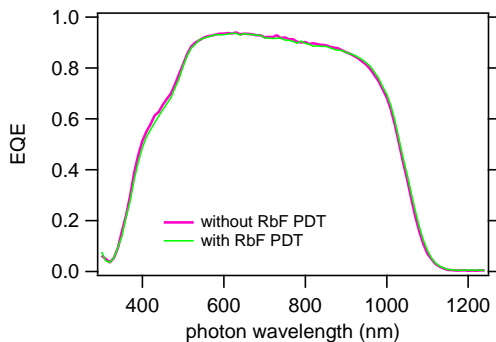


Fig. S4: The EQE measurements were conducted under white bias light with a chopper frequency of 78 Hz.

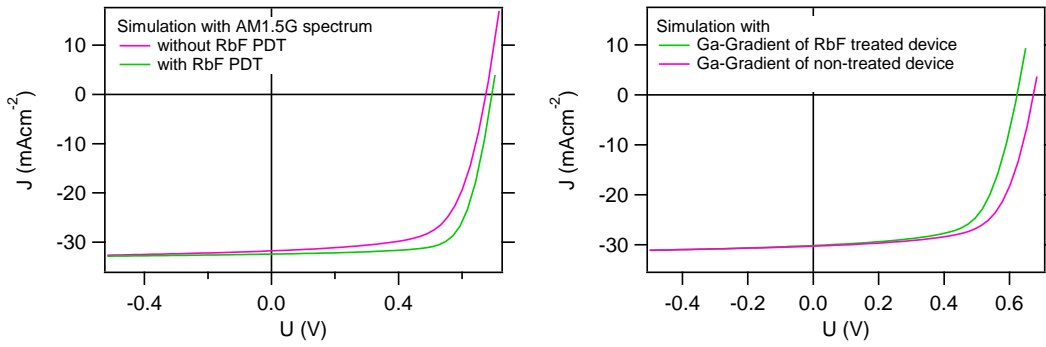


Fig. S5: Left: Simulated J-V curves using the same device models (including the same recombination rates) as used for the fitting of the IR-LED and UV-LED data with an AM1.5G illumination. The results reproduce well the experimental results in Fig. 7. Right: Influence of the Ga-Gradient. pink curve: Simulation of J-V curves (AM1.5G illumination) using the device model set-up (inclu. recombination rates and Ga-Gradient) for the non-treated device. green curve: Simulation using the device model setup-up for the non-treated device but the Ga-profile of the RbF treated device. The experimentally observed trend cannot be reproduced by only changing the Ga-profile.

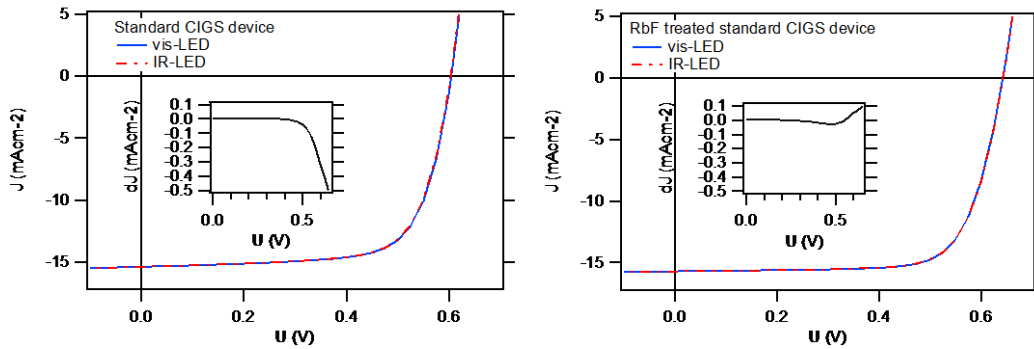


Fig. S6: experimental J-V curves recorded with visible and infrared LED illumination.

Tab. S1: Comparison of the experimental and simulated results

		tr-PL	C-V	SCAPS
No RbF	Doping	$4 \times 10^{15} \text{ cm}^{-3}$	$1 \times 10^{15} \text{ cm}^{-3}$	$1 \times 10^{15} \text{ cm}^{-3}$
	Lifetime	65 ns	x	10 ns
RbF	Doping	$5 \times 10^{15} \text{ cm}^{-3}$	$8 \times 10^{14} \text{ cm}^{-3}$	$8 \times 10^{14} \text{ cm}^{-3}$
	Lifetime	210 ns	x	67 ns