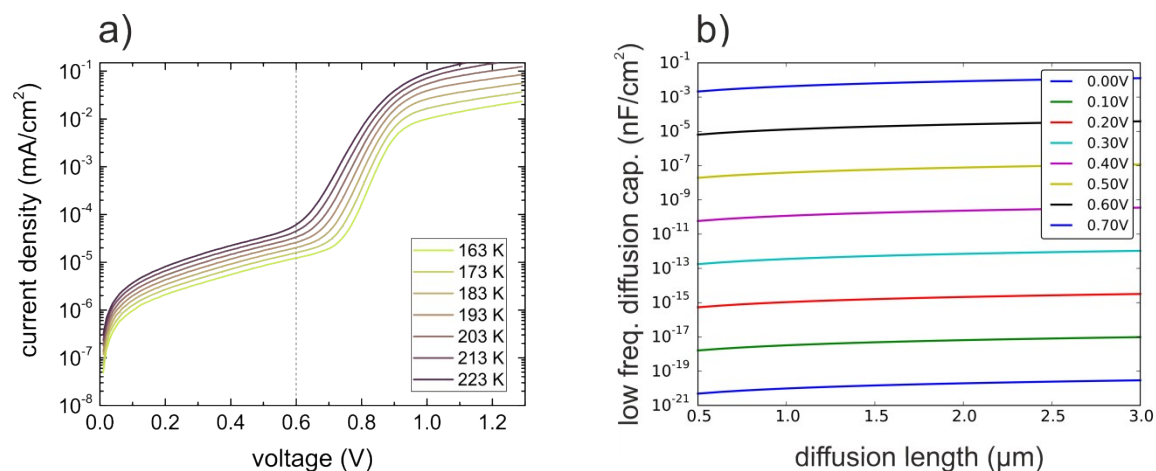
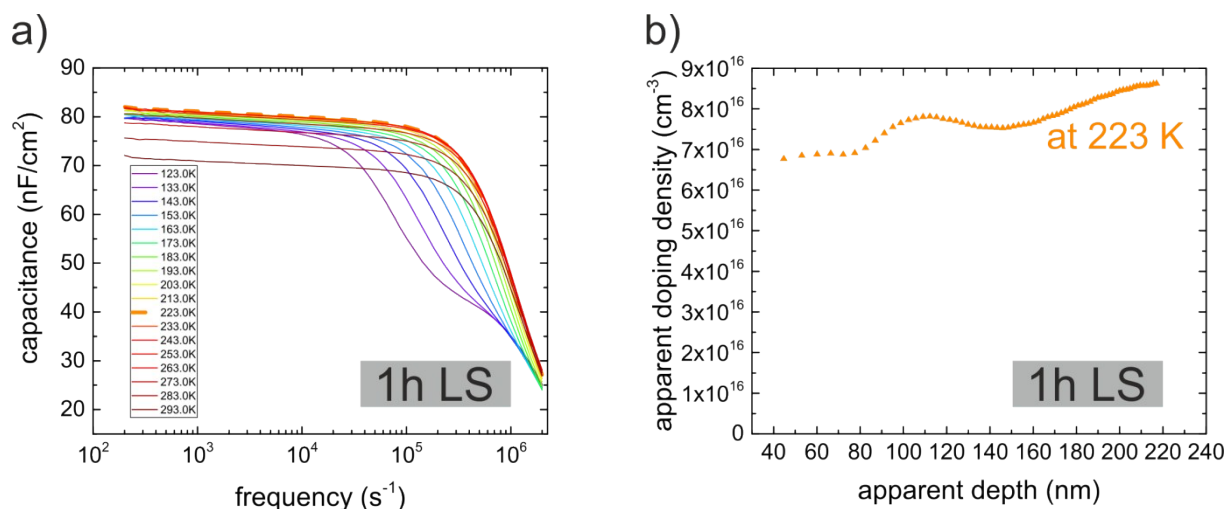


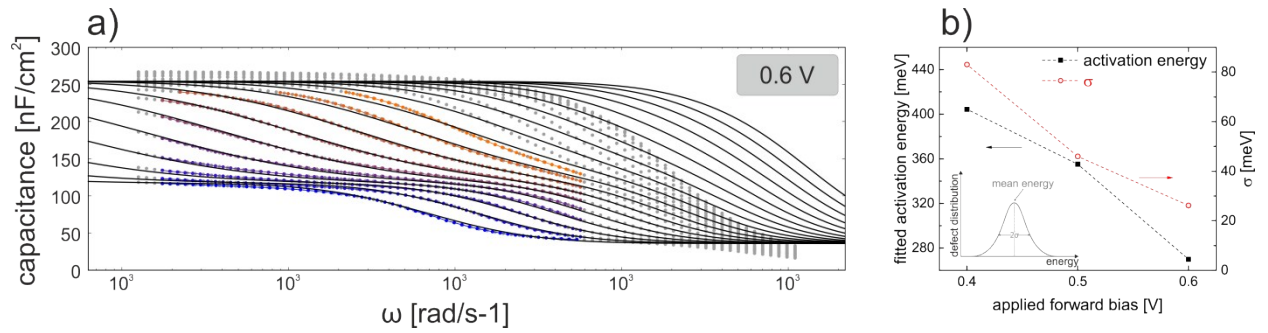
1. Supplementary figures



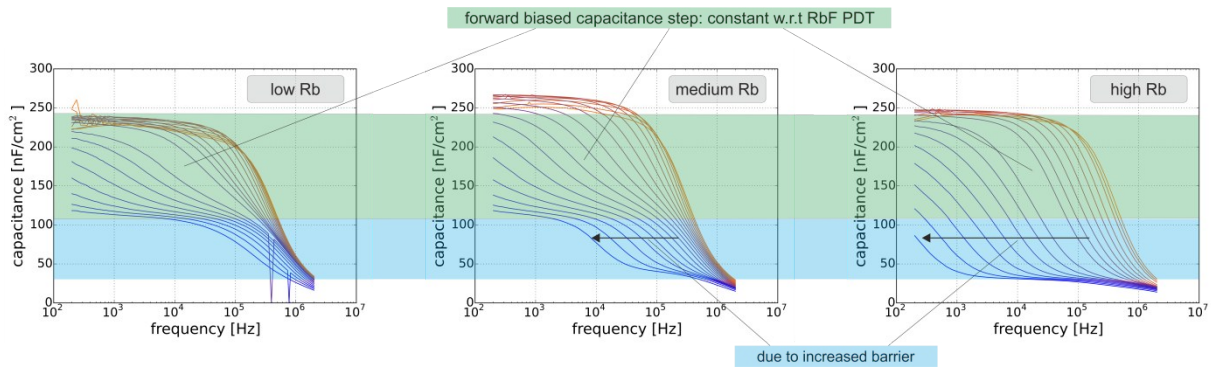
Supplementary Figure 1 – Current density - voltage characteristics at temperatures, where the additional forward biased capacitance step is observed (a). Vertical black line indicates the maximal dc bias voltage used during admittance measurements. Clearly, no onset of the diode current is observed up to this voltage and the current is limited by the shunt resistance. The calculated diffusion capacitance as a function of diffusion length and bias voltage according to Eqn. Fehler! Verweisquelle konnte nicht gefunden werden. is shown in (b). According to these calculations the contribution of the diffusion capacitance can be neglected.



Supplementary Figure 2 - Capacitance spectrum in the light soaked state under 0V bias (a). The relaxation process is visible for temperatures above 263 K. The measured apparent doping profile at 223 K is not influenced by the relaxation process (b). A mean apparent doping density of roughly 8e16 cm⁻³ is observed, which is used as input for the doping density for the CIGS front layer (see Fehler! Verweisquelle konnte nicht gefunden werden.).



Supplementary Figure 3 – a) Fitted capacitance spectrum (solid lines) to experimental data (colored circles). Grey circles represent experimental data, which was not used for fitting. A good fit for the high temperature forward biased capacitance step between 125 and 250 nF/cm² is obtained resulting in a mean activation energy of 270 meV and a standard deviation of 26 meV of a Gaussian defect distribution (see inset in b)). **b)** Mean defect energy and width σ of the Gaussian defect distribution with respect to the applied forward bias voltage during the admittance measurements. Clearly, the extracted parameters depend on the applied voltage. The mean activation energy and width of the defect distribution σ shift to higher values with lower applied forward bias voltages. A reason could be that with lower bias voltages only the tail of the defect distribution is probed and therefore higher activation energies are obtained. Additionally, the band bending is stronger with lower bias voltages leading to a higher spread of energies, which are detectable with admittance spectroscopy. Consequently, a higher σ value is observed.



Supplementary Figure 4 – Capacitance spectra measured from 123 K – 323 K under 0.6V forward bias voltage with different RbF PDT treatments (see reference [29] for details). The low temperature capacitance step (marked by the blue area) can be assigned to an injection barrier [29]. In contrast, the forward biased capacitance step is independent of the Rb amount and is thus not assigned to a barrier.