

GALLIUM OXIDE THIN FILMS DEPOSITED BY SPRAY PYROLYSIS WITH LOW CONTACT RESISTANCE TOWARDS INDIUM-TIN OXIDE AND THEIR IMPLEMENTATION IN HETEROJUNCTIONS WITH NICKEL OXIDE



Introduction

Gallium oxide (Ga_2O_3) is gaining significant attention as an ultrawide band gap semiconductor, offering promising potential for high-power and high-voltage electronic applications. However, the process of creating effective electrical contacts with Ga_2O_3 is particularly challenging. The material's wide band gap complicates the formation of low-resistance ohmic contacts, often necessitating the development of specialized metallization techniques and surface treatments.

Spray pyrolysis is a low-cost deposition technique, in which a precursor solution is atomized into a stream of droplets, which is directed onto a heated substrate. There the solvent evaporates and the precursor species undergoes a pyrolysis reaction to give the desired phase. Given an adequate solution chemistry and deposition parameters, CVD-like growth from the gas phase can be the dominant growth mechanisms, which leads to highly conformal and defect-free layers.

Gallium oxide preparation with spray pyrolysis

0.04 M Galliumacetylacetonate was dissolved in deionized water containing 3.5 M acetic acid. The optimized parameters (380°C substrate temperature, 1.2 ml/min flow rate, for more details see ref. [1]) yielded nanocrystalline $\beta\text{-Ga}_2\text{O}_3$. XPS-measurements found two oxidation states for Ga: the expected Ga(III) but also 15at.% of Ga(I), which leads to a slightly Ga-rich composition (Ga : O ratio of 44% : 56%). No carbon signal could be detected apart from surface contamination (Figure 1c).

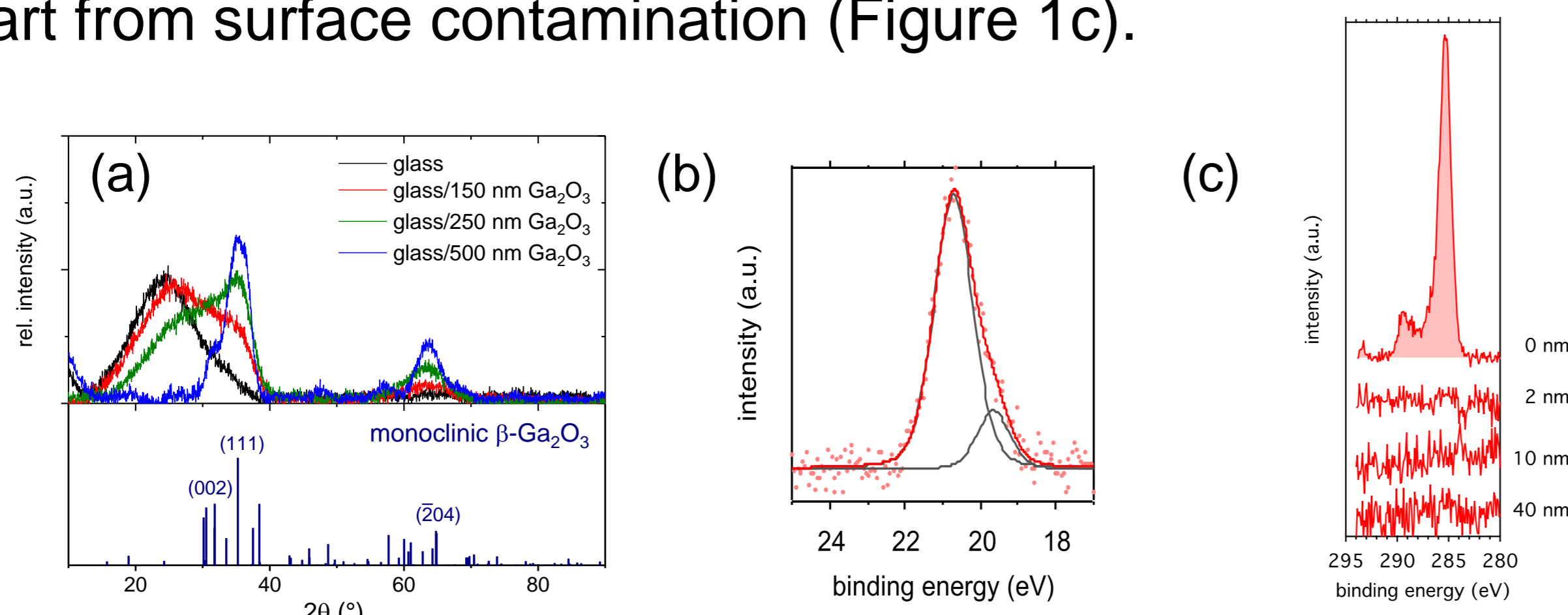


Fig 1. (a) XRD for glass/ Ga_2O_3 films, (b) Ga 3d XPS spectra, (c) C 1s XPS depth profiling.

Heterojunction Fabrication with sputtered NiO

ITO/ Ga_2O_3 stacks were further processed with sputtered NiO and Au to give p-n heterojunction devices. All layers were deposited without substrate heating at a substrate-to-target distance of ~9 cm. NiO was deposited using a NiO target (99.99% purity, AJA Int.), mounted on an RF magnetron source. A sputter power of 200 W and using 10 μbar pure Ar as process gas yielded a sputter rate of 0.11 nm/s. The deposition of the device contacts was carried out using an Au target (99.99% purity, Neyco) at 20 W and 2 μbar Ar pressure, resulting in a rate of 0.8 nm/s. The contacts were sputtered through a shadow mask, defining active device areas of 5.73 mm^2 and 10.43 mm^2 . The here presented heterojunctions had following thicknesses: ITO/ Ga_2O_3 (15nm)/NiO(20nm)/Au(100nm).

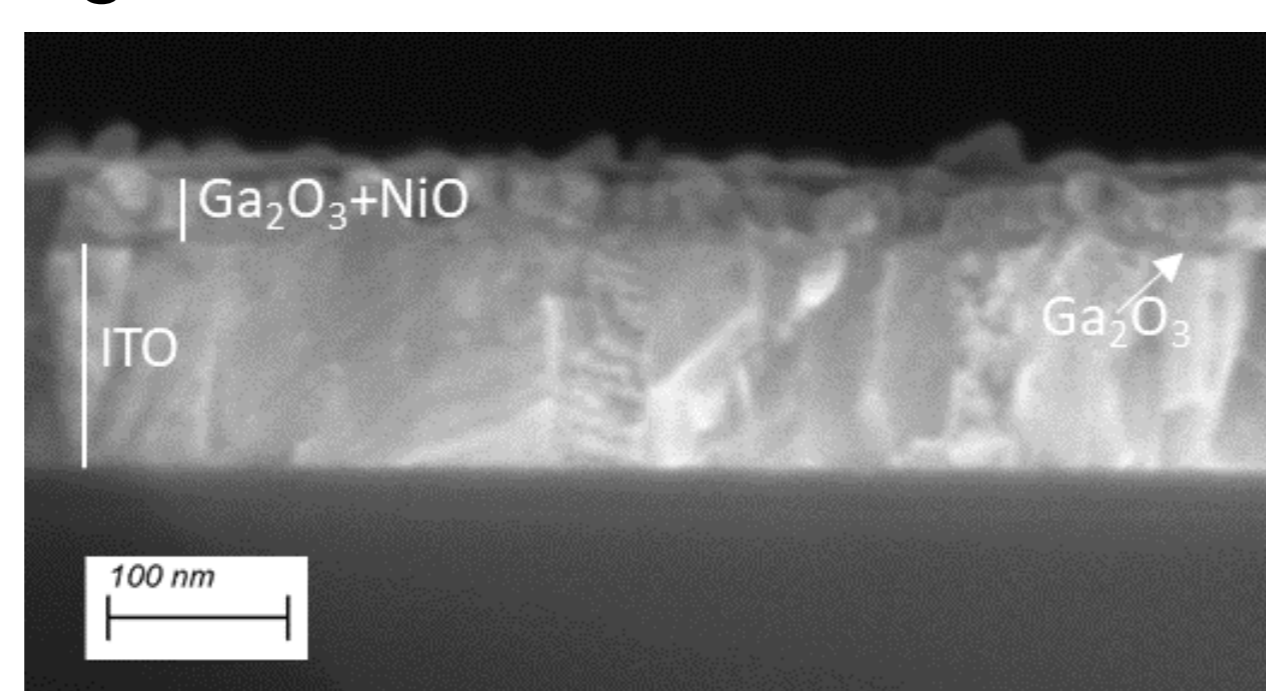


Figure 2. SEM cross section of the device.

Electronic properties of the layers

For the determination of the work function and ionization energy of the layers, Kelvin probe and ambient pressure photoemission spectroscopy were performed in air. The $\text{Ga}_2\text{O}_3/\text{NiO}$ junction is a wide-gap, type II heterojunction with a large CB offset and an even larger VB offset.

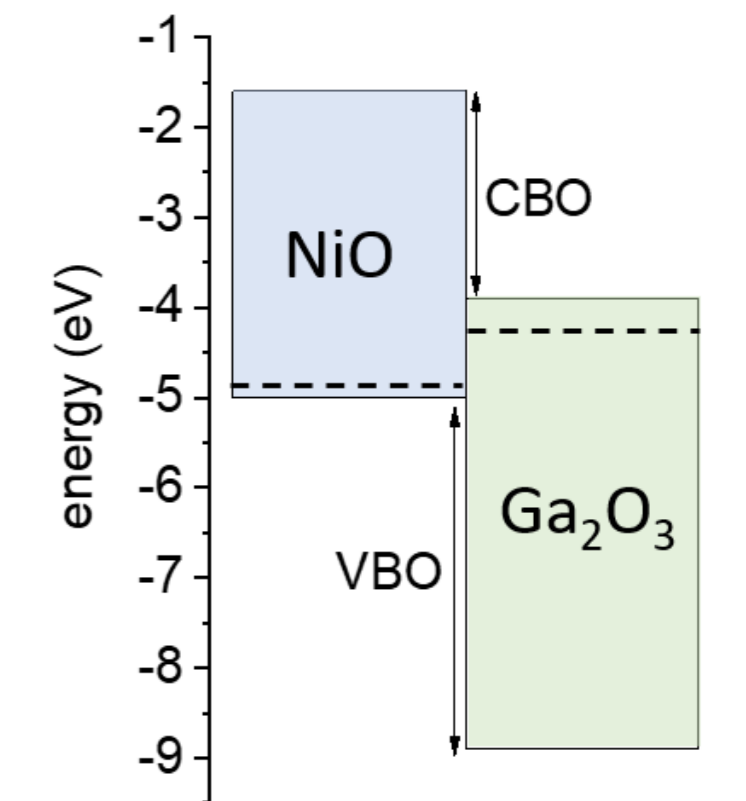


Fig. 3. Measured band alignment.

I-V characterization of the heterojunctions

The dark j-V shows large rectification (>1000 at $|V| = 0.5$ V), which demonstrates the formation of a high-quality n/p junction with a low turn-on bias of ~30 mV in the forward direction. The ideality factor n of the junction over five devices is $n = 1.6 \pm 0.2$ (measured over 5 devices). The temperature dependence of the dark j-V characteristics was measured in a range of 25 to 80 °C

and the ideality factor only slightly decreases with increasing temperature, as expected for the generation-recombination type of carrier transport. The parallel resistance was in the $\text{M}\Omega \text{ cm}^2$ range at ambient temperature for all measured devices.

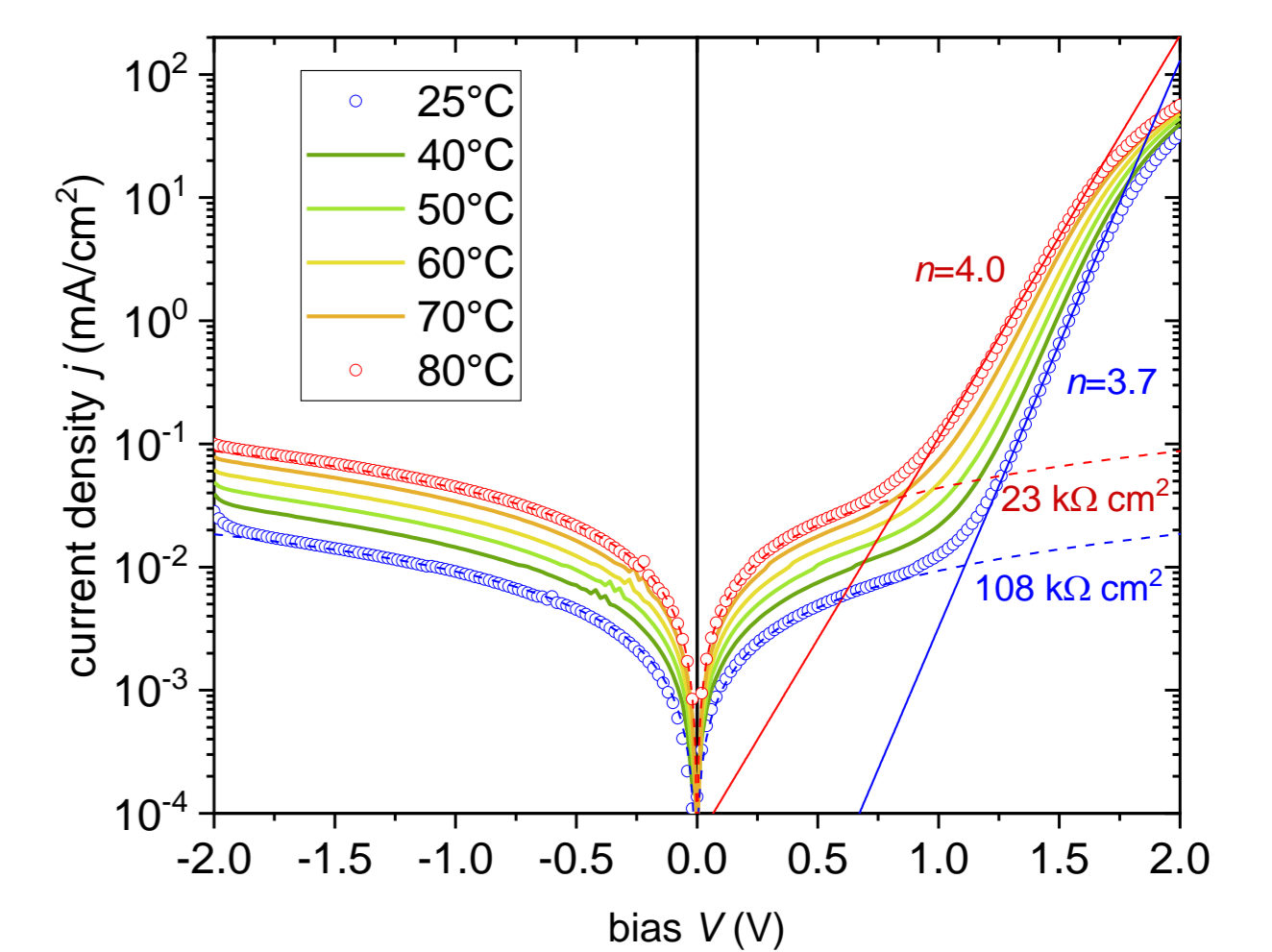


Fig. 4. Dark jV-measurements at different T.

The measurements also suggest that the ITO/ Ga_2O_3 junction has a low energy barrier for electrons, despite the large WF difference (0.6 eV) between ITO and Ga_2O_3 , which should block electron transport and result in low currents. The unimpeded transport may be explained by an interdiffusion of In, Sn and Ga at the interface, which was described in literature to occur at ITO/ Ga_2O_3 interfaces at temperatures higher 300°C, forming an Ohmic contact between the two layers [3,4]. It appears that the temperature during the deposition (380°C for 15 min plus 15 min to reach 250°C after the deposition) is sufficient for this effect to occur *in situ*.

Outlook – High throughput diode characterization

The spray pyrolysis process has been adapted to produce Ga_2O_3 layers with a thickness gradient by adjusting the spray pattern. Figure 5 shows the thickness distribution on a 7.5x2.5 cm^2 substrate, obtained by comparing SEM-EDX spectra with simulated Monte Carlo spectra for X-ray propagation [5]. These graded samples will be used to investigate the diode properties in dependence of the Ga_2O_3 thickness in a high-throughput manner. They will be coated with NiO and structured Au electrodes, creating an 8x8 cell array per 2.5x2.5 cm^2 area (see figure 6), which can be measured using our self-made solar cell platform and open-source COHESIVM software.

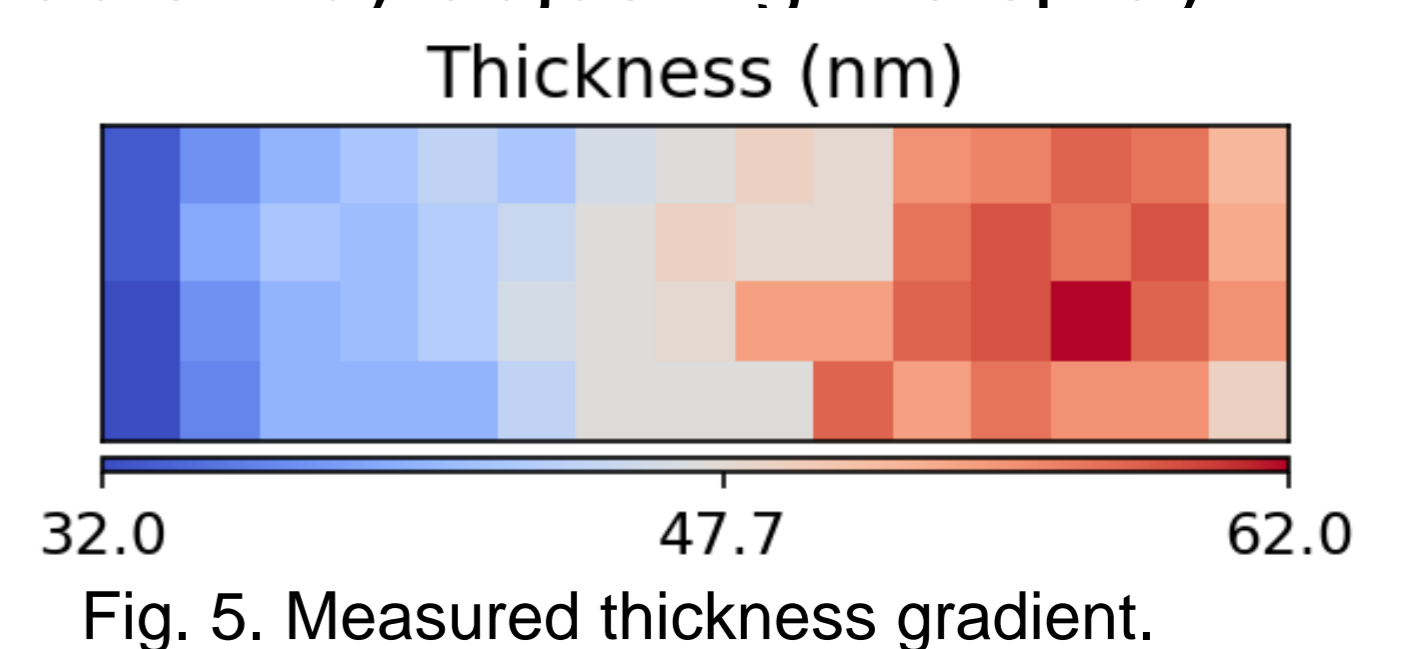
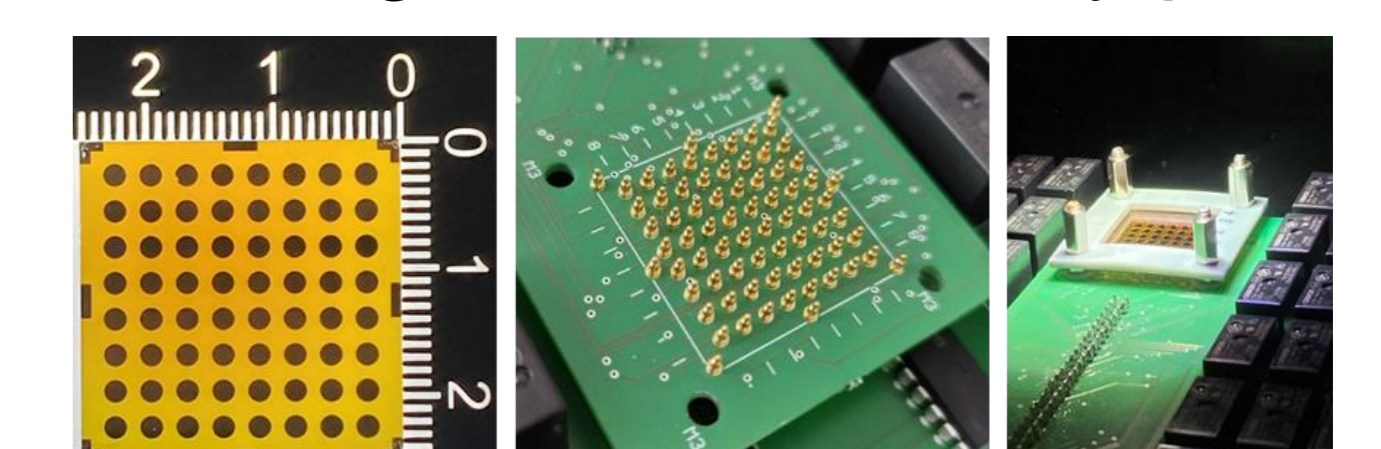


Fig. 5. Measured thickness gradient.



[6] Fig. 6. Our solar cell measurement platform.

References

- [1] N. Winkler, R. Adhi Wibowo, W. Kautek, G. Ligorio, E. J. W. List-Kratochvil and T. Dimopoulos, Journal of Materials Chemistry C, 2019, 7, 69–77.
- [2] T. Dimopoulos, R. A. Wibowo, S. Edinger, M. Wolf and T. Fix, Nanomaterials, 2024, 14, 300.
- [3] P. H. Carey IV, J. Yang, F. Ren, D. C. Hays, S. J. Pearton, A. Kuramata and I. I. Kravchenko, Journal of Vacuum Science & Technology B, 2017, 35, 061201.
- [4] X. Xia, M. Xian, F. Ren, M. A. J. Rassel, A. Haque and S. J. Pearton, ECS J. Solid State Sci. Technol., 2021, 10, 115005.
- [5] M. Wolf, G. K. H. Madsen and T. Dimopoulos, Materials Advances, 2023, 4, 2612–2624.
- [6] M. Wolf, <https://github.com/mxwalbert/cohesivm>

Acknowledgements

The work is funded by the Horizon Europe Project **SUNREY** (Boosting sustainability, reliability and efficiency of perovskite PV through novel materials and process engineering)

