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Accelerated screening of oxide semiconductors by combinatorial spray deposition and high-throughput analysis

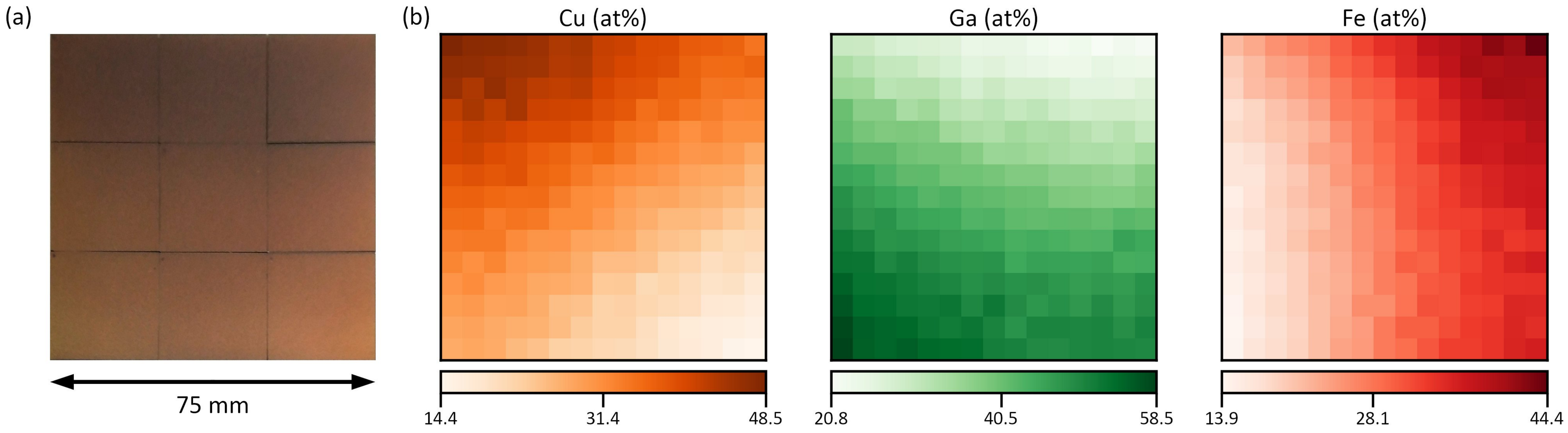

Fig. 1

(a) Photo of a combinatorial Cu-Ga-Fe-O film deposited on 3×3 soda-lime glass substrates.

(b) Normalized mole fraction maps of the elemental gradients obtained by energy dispersive spectroscopy (EDS) measurements with standardless quantification of the as-deposited film. The values of the colour bars are the minimum, the mean, and the maximum mole fraction.

INTRODUCTION

Combinatorial and high-throughput methods are instrumental for the development and deployment of approaches which target autonomous operation, e.g., Material Acceleration Platforms or make use of large data sets, e.g., machine learning. To this end, spray pyrolysis has shown to be a well suited deposition technique, facilitating the synthesis of thickness and composition gradients. Here, we present an electronically controlled multiple-pump system which enables us to deposit two-dimensional composition gradients with control over the spatial distribution. As a proof of principle, the Cu-Ga-Fe-O system is investigated in terms of opto-electronic properties. Binary oxides of this system tend to crystallize in delafossite and spinel structures which are promising candidates for the application in photovoltaics and photo-electrochemical watersplitting. Specifically, the dependency of the optical band gap on the crystal structure and the composition of the materials is examined.

RESULTS

Composition

As depicted in Fig. 1 b, the combinatorial film holds a wide variety of unique stoichiometries which relate to over 200 different materials, i.e., pixels. Back-to-back experiments validate the robustness of the deposition method with a repeatability in the composition of around 97%.

Crystal structure

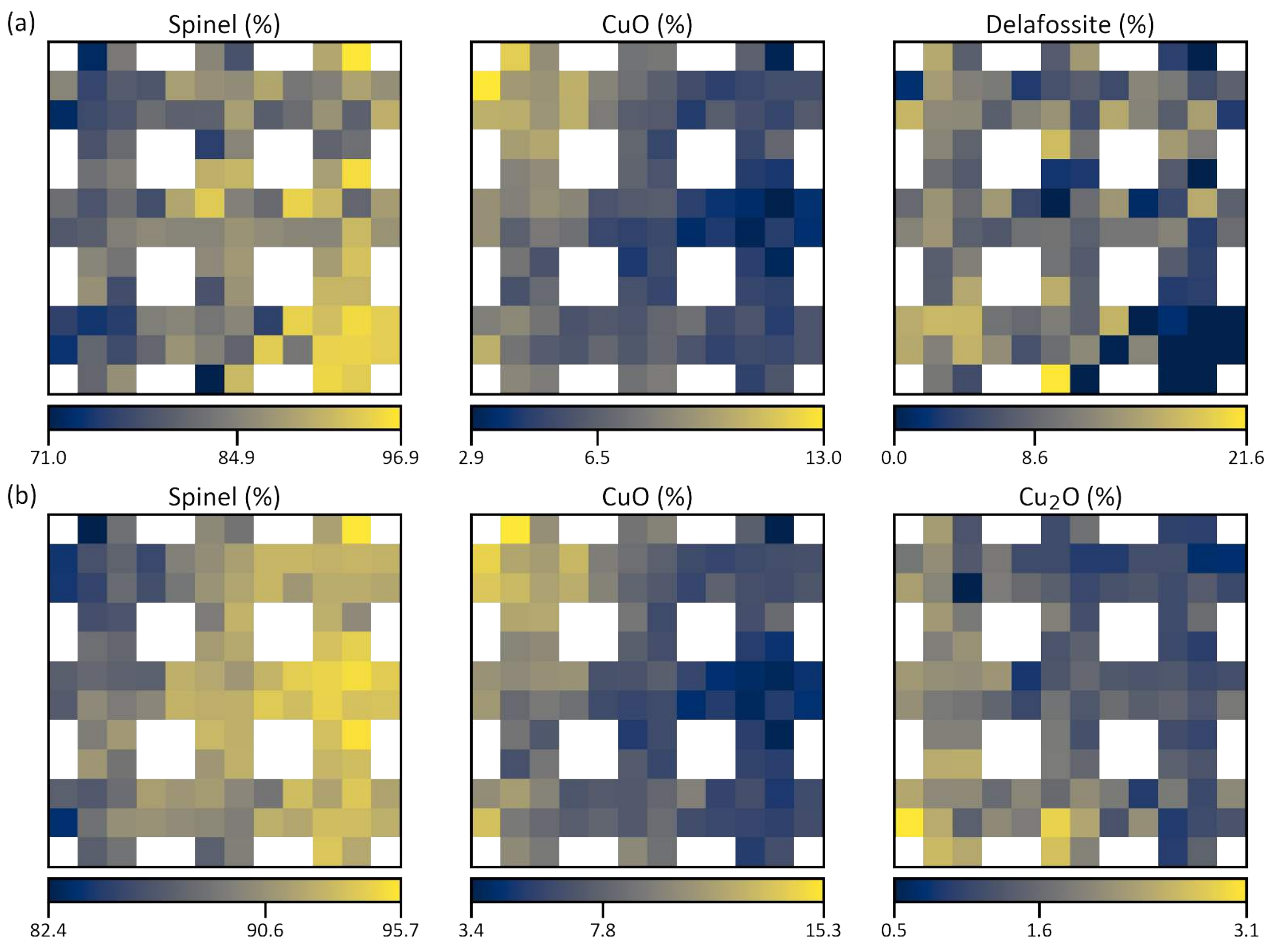

Fig. 2 Normalized structure maps from a quantification based on a composition-restricted model, (a) considering spinels* CuO, Cu_2O, and delafossites**, and (b) without considering delafossites as possible compounds. The values of the colour bars are the minimum, the mean, and the maximum relative amount of the structure.

* $CuFe_2O_4$, $CuGa_2O_4$, Fe_3O_4, $FeGa_2O_4$
** $CuFeO_2$, $CuGaO_2$

Thickness

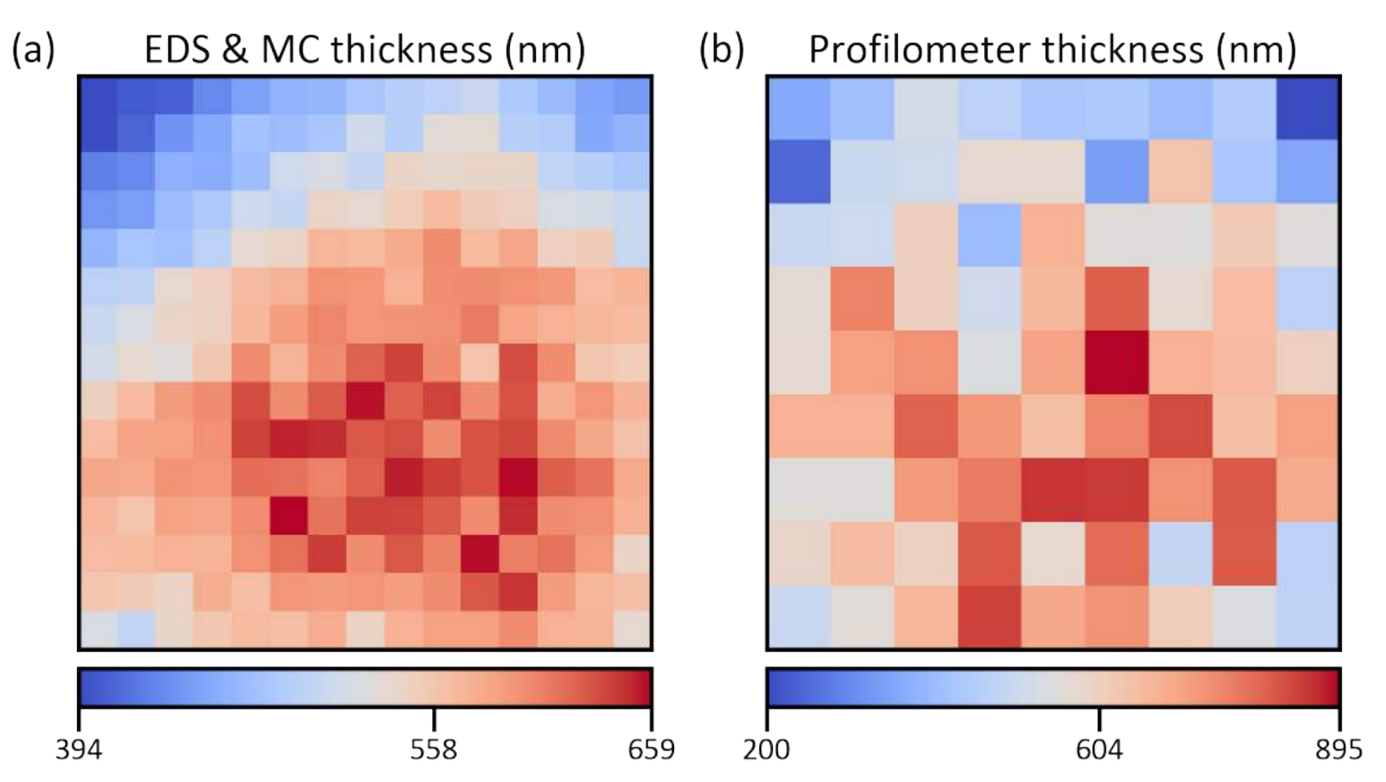

Fig. 3 Thickness maps of the as-deposited film, (a) calculated based on Monte-Carlo (MC) simulations of EDS measurements, and (b) measured using a tactile profilometer on a sample which was partially covered during the deposition. The values of the colour bars are the minimum, the mean, and the maximum thickness.

Band gap

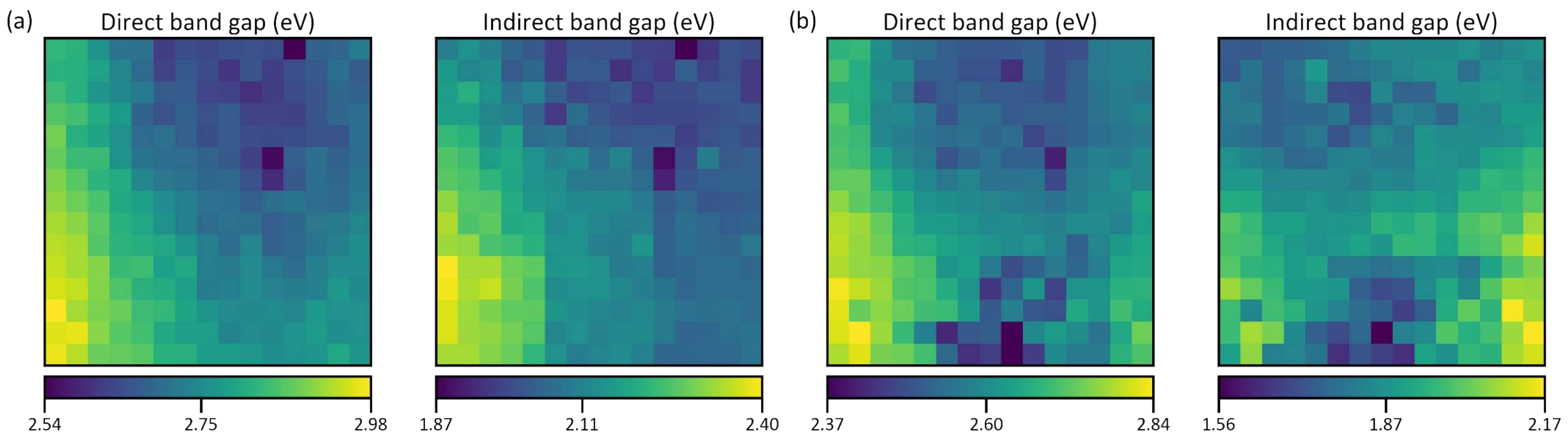

Fig. 4 Maps of direct and indirect band gaps evaluated using the Tauc method (a) for the as-deposited film, and (b) for the same film after annealing at 550 °C for 2 h under N_2. The values of the colour bars are the minimum, the mean, and the maximum band gap energy.

EXPERIMENTAL

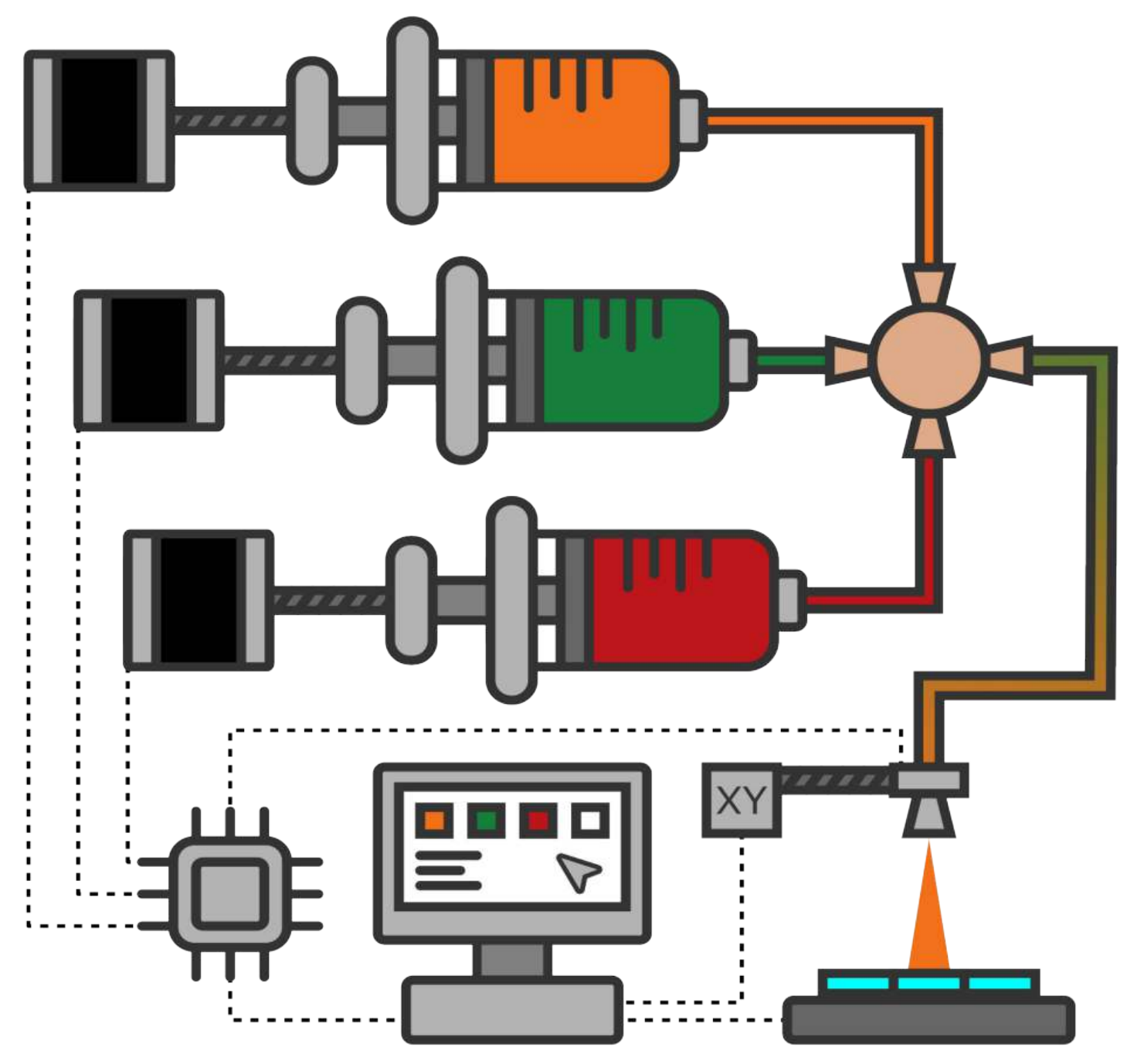

Fig. 5 Illustration of the employed combinatorial spray pyrolysis system with three custom-built syringe pumps which are controlled by a single-board computer. The solutions are mixed at a four-way connector and fed into the nozzle of the spray coater.

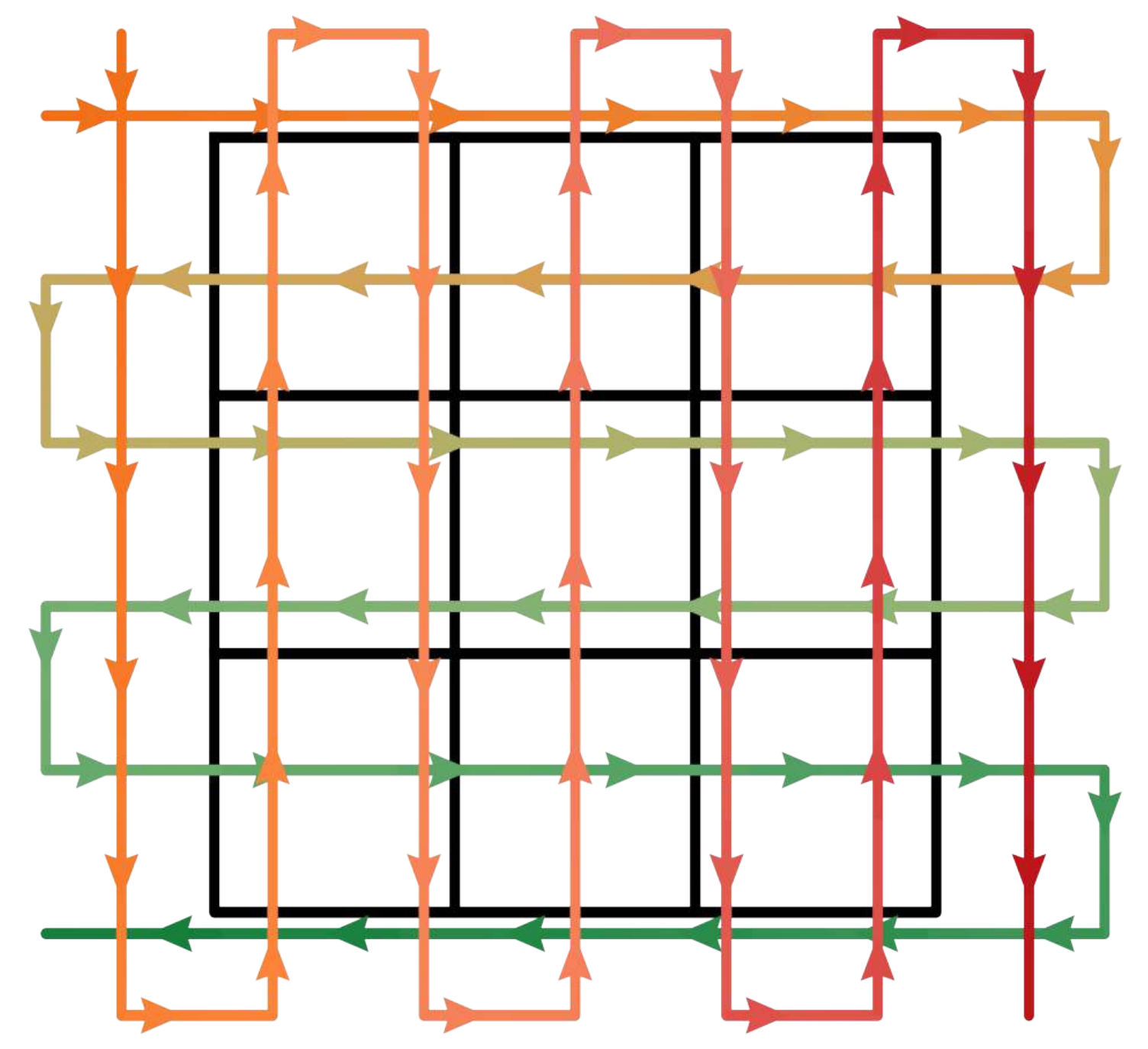

Fig. 6 Combinatorial spray pattern which alternates between a vertical Cu-Ga gradient (orange to green) and a horizontal Cu-Fe gradient (orange to red). The number of displayed scan lines is reduced from 25 and 27, resp., in order to simplify the illustration.

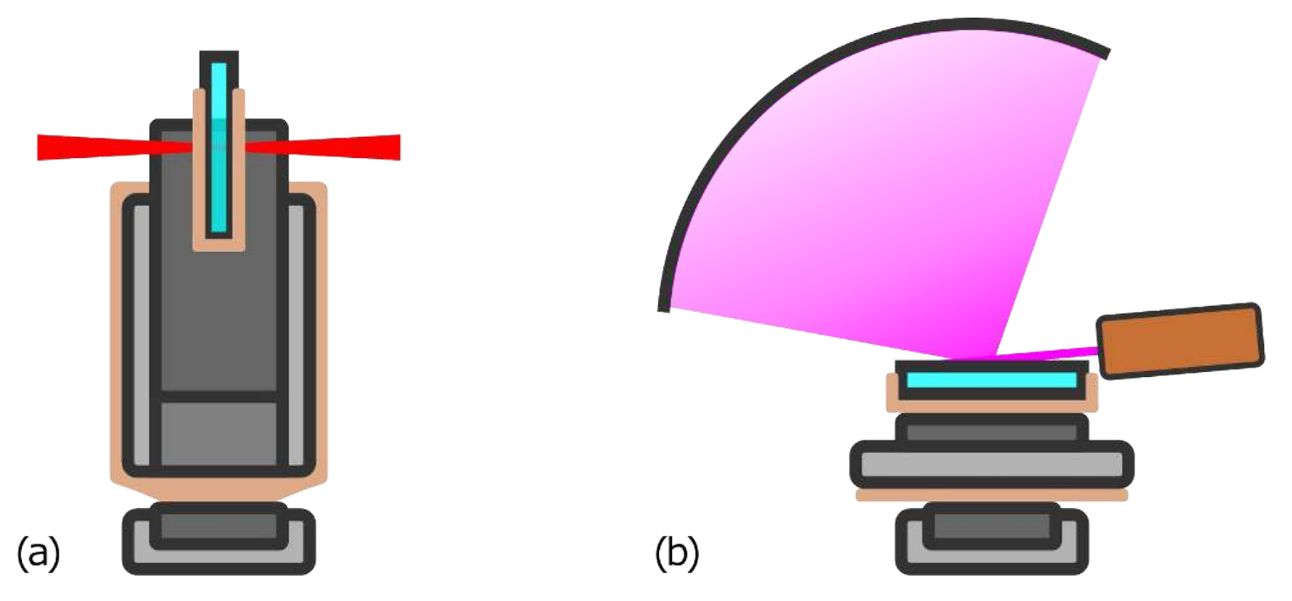

Fig. 7 In order to enable semi-automatized measurements of the combinatorial film, custom sample positioning systems for (a) a fourier-transform spectrometer and (b) an x-ray diffractometer were developed. Piezo-actuated linear and rotation stages are used for accurate positioning.

OUTLOOK

Combinatorial device measurements

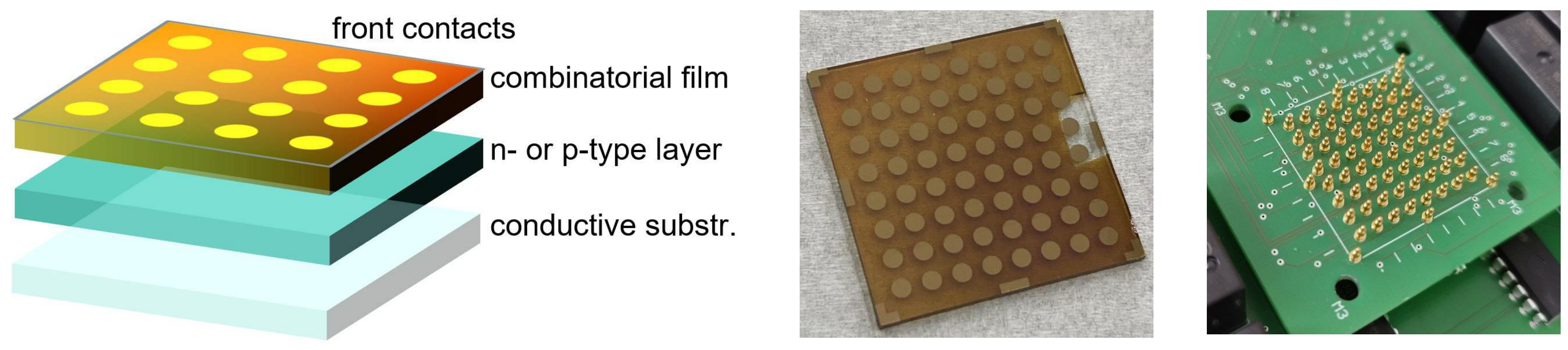

Fig. 4 A device design and measurement setup for combinatorial photovoltaic analysis are currently under development. It will allow to characterize 64 cells in a single run.

Increased data density through ML

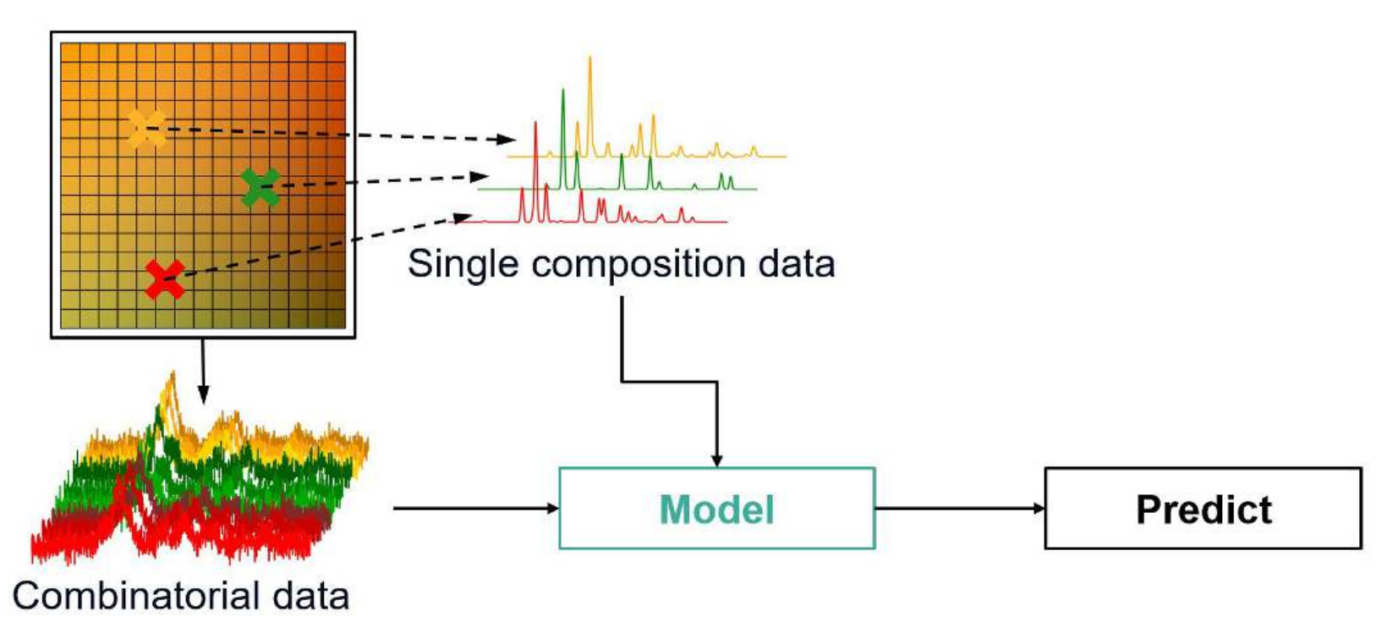

Fig. 9 The combinatorial characterization is limited in measurement complexity because of the high-throughput (HT) design. But the combination of the HT results with more elaborate analysis of selected compositions through machine learning (ML) has the potential to increase the overall data density.

CONCLUSION

The combinatorial spray pyrolysis yields a variety of materials with distinct compositional, structural, and optical properties for a fraction of the time and human labour costs in comparison to conventional approaches. Together with the (semi-)automatized characterization methods, a platform for high-throughput screening of oxide semiconductors is created. The investigated Cu-Ga-Fe-O combinatorial film consists mainly of spinel phases mixed with CuO, Cu_2O and/or delafossite phases, has a varying thickness in the range of 400–650 nm, and direct and indirect bandgaps of 2.5–3.0 eV and 1.9–2.4 eV, respectively. Finally, the presented platform can be deployed for optimizing or tuning opto-electronic properties. But the real potential lies in generating material libraries which are used to drive machine learning algorithms that enable to find novel structure-property relationships.