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High-Throughput Electrical Potential Depth-Profiling in Air

Kevin J. Rietwyk*, David A. Keller, Koushik Majhi, Adam Ginsburg, Maayan Priel, Hannah-Noa Barad, Assaf Y. Anderson and Arie Zaban*

Dr. K. J. Rietwyk, D. A. Keller, Dr. K. Majhi, A. Ginsburg, M. Priel, H.-N. Barad, Dr. A. Y. Anderson and Prof. A. Zaban

Department of Chemistry and Center for Nanotechnology & Advanced Materials, Bar-Ilan University, Ramat Gan 52900, Israel
Email: krietwyk@gmail.com, arie.zaban@biu.ac.il

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The operation of thin-film electronic devices is dictated by the band alignment at the interfaces of the various layers. While a number of methods for measuring the depth profile of the electrical potential at interfaces have emerged, these are typically arduous to perform and involve the use of ultra-high vacuum, complicated sample preparation and/or suffer from poor resolution. Here we present a method to directly map the depth profile of the electrical potential at an interface in air by growing a sample with an intentional thickness gradient and correlating the surface potential, measured using (macroscale) scanning Kelvin probe, to the thickness at each point. Our approach is non-destructive and rapid, is ideal for large substrates and films grown with an inherent thickness gradient. It enjoys very high depth (2 nm) and energy resolution (5 meV), comparable to other methods. In this work we develop and demonstrate the method on FTO|TiO₂|Co₃O₄ all-oxide junctions and show a depletion width of only 8.6±3.8 nm in the Co₃O₄ layer.

1. Introduction
Thin film electronics is a rapidly growing technology that offers a range of device functionalities not possible with conventional metal-oxide-semiconductor technology such as printable, flexible and transparent electronics\textsuperscript{[1–3]}. The technology relies on the careful arrangement of individual layers of materials that perform a specific function such as light emission or absorption, charge carrier transport, selective carrier blocking and electrical contacts. These layers can be considered as building blocks but the resulting device function/performance is dictated by the energetics of the interfaces between the layers. Knowledge of the depth profile of energetics at the interface is paramount to understanding the operation of thin film devices and two key methods for measuring this have matured. One involves a stepwise growth of a film onto a substrate with concurrent photoemission or Kelvin probe analysis performed in ultra-high vacuum with interconnected deposition and analysis chambers\textsuperscript{[4–6]} and the other, is to cleave or mill and polish a complete device and measure the work function across the cross-section using a scanning Kelvin probe force microscopy (KPFM) in air,\textsuperscript{[7–12]} or nitrogen atmosphere to minimise oxygen and humidity\textsuperscript{[13,14]} (if the measurement atmosphere was unstated in the paper it was presumed air). The stepwise approach using photoemission is more common and offers detailed electronic and chemical analysis with high surface sensitivity\textsuperscript{[15]} of ~5-10 nm (laboratory based light source) but can be slow and cumbersome to perform, especially when the substrate is heated during the deposition and subsequently cooled to room-temperature for analysis. As such studies are so laborious, often only several depositions are characterised for a single sample, limiting the accuracy of this approach. In contrast, the cross-section methodology provides the electrostatic potential profile of the device in a single measurement but has enjoyed limited success since sample preparation is complicated and can induce damage, while the characterisation is performed perpendicularly to the growth of the layer and may be distorted by longitudinal effects\textsuperscript{[10]}. Additionally, the spatial resolution is limited by the size of the tip\textsuperscript{[9]}, typically of the
order of \( \sim 30-50 \) nm which prevents measurement of band bending at interfaces at these length scales and is a significant drawback for the technique\(^8\).

In a recent roadmap on optical energy conversion\(^{16}\) the “Development of faster and more accurate experimental methods for… determining band offsets at hetero-interfaces” was identified as a future need for discovery of disruptive materials suitable for new photovoltaic devices. One approach is to employ a high-throughput (combinatorial) protocol, in which library samples are fabricated to contain variations in material properties across the library such that each point of the sample is unique; a number of reviews have been published on high-throughput material science.\(^{17–21}\) An example of a library would be a thin film grown with a thickness gradient; each point of the sample would have a distinct thickness. A line-scan analysis of some material property across this library would reveal how this property varied with thickness. Applying a combinatorial approach to depth-profiling, Siol \textit{et al.}\(^{22}\) have developed a system that utilises orthogonal gradient in the film thickness and other deposition parameters (such as temperature). Although offering considerable exciting opportunities, the data analysis could prove to be exceedingly challenging and this protocol cannot easily be adopted by other researchers since it requires a considerable initial investment. We propose a different solution to improving the rate of depth profiling junctions.

Here we describe a novel, high-throughput method for depth profiling the electrical potential at interfaces that combines the strengths of the aforementioned methods. Our approach is to monitor the change in the work function (measured in the dark) using (macroscale) scanning Kelvin probe (SKP) for a large substrate (7 cm \( \times \) 7 cm) before and after depositing an additional layer (adlayer) with an intentional thickness gradient. We correlate spatial changes in the work function with the
thickness of the adlayer at each point in order to achieve depth profiling of the work function and hence directly map the band bending at the interface. This approach can be seen as a hybrid of the two aforementioned approaches. Similar to the stepwise growth method, we deposit a single layer and then analyse the resulting interface, but due to the thickness gradient with drastically more data-points per deposition (13 times more in this paper) reducing the number of depositions required to characterise a single junction. The characterisation itself more closely matches the cross-section method since both correlate the surface potential (typically measured in air) to the depth from the interface to develop an understanding of internal band bending; with a key advantage of our approach being the avoidance of possibly detrimental longitudinal and cleaving/mill effects common to the cross-section method. In order to analyse the large datasets, we also developed a fitting algorithm that utilises the solution to the 1D Poisson’s equation to calculate the depletion width and carrier concentration in each layer; two material/device parameters that are often non-trivial to determine.

To demonstrate the capabilities of this method we investigate the band alignment of the TiO$_2$|Co$_3$O$_4$ interface which has recently garnered significant attention in low-cost, all-oxide solar cells$^{[23-27]}$ since both TiO$_2$ and Co$_3$O$_4$ are abundant, non-toxic and chemically stable. For these solar cells TiO$_2$ acts an n-type window layer and Co$_3$O$_4$ as a p-type absorber with FTO as one the electrodes. Furthermore, our group has already reported on the optical and structural properties of the constituent layer as well as the photovoltaic performance of these devices in recent publications, allowing us to focus on the electronic characterisation$^{[23-25]}$.

2. Results
Figure 1 summarises the principle of our depth profiling approach. Typically, the work function of the substrate is measured and then an adlayer is deposited with an intentional thickness gradient across the substrate using pulsed laser deposition (PLD). Immediately after the adlayer is deposited (and cooled if necessary) the sample is removed from vacuo and measured in the Kelvin probe. The first scan is a line scan across the thickness gradient which is performed within 10 minutes of exposing the sample to air to minimise its impact. This line scan is repeatedly performed for 25-30 minutes across the same points in order to observe changes in the work function due to prolonged exposure to air and verify if the changes are consistent for different adlayer thicknesses; the results of which will be addressed in the discussion. A scan across the entire surface is then performed in a square grid of at least $26^2$ points to ensure there are no inhomogeneities in the region of the first scan. Next, we measure the optical transmission and reflection over the visible range, in a grid of 13×13 points across the sample (ensuring that one line of points from this grid overlaps with the work function line scan) and then calculate the optical absorptance of the adlayer at each point. A thickness map is produced using either Beer-Lambert’s law or optical modelling. The work function from the first scan is interpolated to overlay the corresponding line thickness profile using an inverse distance interpolation\cite{28} with 5 points and power 2. Finally, the work function and thickness data are curated and plotted against each other as shown in the example given in Figure 1b. This process is repeated for multiple depositions on additional substrates to achieve an appropriate thickness range to map out the band bending of the adlayer, as shown in Figures 2 and 3. It is worthwhile mentioning that the Kelvin probe measures the contact potential difference, the difference in the sample and tip work functions (\( \text{CPD} = \phi_S - \phi_T \)) and the sample work function is corrected for a tip work function $\phi_T = 4.22 \text{ eV}$.
Figure 1. a) Schematic depicting the lateral measurement of the Kelvin probe across a FTO|TiO₂ substrate with a strongly exaggerated Co₃O₄ adlayer grown in the PLD with the natural thickness gradient. b) Plot of the work function against Co₃O₄ thickness for a single sample, with a fit calculated using the 1D solution to the Poisson’s equation. This is intended only as an example. c) The evolution of the band diagram of the TiO₂|Co₃O₄ junction with increasing Co₃O₄ thickness, illustrating the evolution of the work function shown in b) and including the variables mentioned in the text. For clarity, the various energies were labelled only as their corresponding potentials in accordance with the single electron model i.e. V instead of qV where q is the elementary charge.

Figure 1c shows a schematic of the evolution of the band bending at the TiO₂|Co₃O₄ interface with increasing Co₃O₄ thickness (starting from zero thickness) and illustrates how changes in the band bending will affect the measured work function. Upon deposition of the adlayer, new electronic states are available to the charge carriers in the substrate and occupation of the states is governed by a common Fermi-level. To induce equilibrium, charge may cross the interface, in accordance with thermodynamics, and reside near the junction of the two layers, resulting in a
spatially varying electric field in this region in either or both materials, known as band bending. In the case of the TiO$_2$|Co$_3$O$_4$ interface, the work function increases due to both upward band bending in the TiO$_2$ and downward band bending in the Co$_3$O$_4$. The thickness of the adlayer at which the work function remains constant marks the end of the space charge (depletion) region and is the depletion width of the adlayer, $Z_P$. The change in the work function over this spatial range is due to the built-in potential of the junction which is the sum of band bending in both the TiO$_2$ and Co$_3$O$_4$ layers $V_{BI} = V_N + V_P$. By plotting the work function versus the layer thickness, as shown in Figure 1b, the adlayer depletion width and the built-in potential are determined from the thickness at which the potential no longer changes. Both of these parameters are crucial in determining the performance of a conventional photovoltaic device because it is the corresponding electric field that dissociates the optically excited electron/hole pair that produces the photocurrent.

Since it is non-trivial to confidently define the depletion width “by-eye”, a robust fitting algorithm has been developed. For the fit we will use the very well-known solution to the 1D Poisson’s equation (that can commonly be found in elementary semiconductor textbooks) to describe the electrostatic potential as a function of distance from the interface, given by:

$$V(z) = \begin{cases} \pm \frac{qN}{2\varepsilon\varepsilon_0} (z - z_d)^2 + V_{Bulk}, & 0 \leq z \leq z_d \\ V_{Bulk}, & z > z_d \end{cases},$$

where the sign is positive for upwards and negative for downwards band bending, $q$ is the elementary charge, $z_d$ is the depletion width of the layer, $\varepsilon\varepsilon_0$ is permittivity of the layer, $N$ is the dominant ionised dopant concentration and $V_{Bulk}$ is the work function for a thick film. By using
this formula we make some assumptions commonly employed in describing junction energetics. We assume that the depletion approximation holds i.e. that under equilibrium no free carriers exist in the depletion region of either layer and that immediately outside of these regions the net charge density is zero. It is also assumed that there is a single dominant ionised dopant that is homogenously distributed throughout each layer and that there are no localised interface charges. A detailed description of the algorithm is provided in the supplementary information. It is important to note that by using a line of best fit we mitigate slight differences in the work function values between samples within each dataset. Furthermore, the capability to determine the carrier concentration without the need of having to form ohmic contacts, specific contact geometries or the application of magnetic fields (Hall-effect measurements) is particularly advantageous. This analysis approach and has recently been demonstrated by Rojas et al.[29] to be effective for organic semiconductors interfaces.

Having described our analysis methodology we will now present the experimental data before performing a detailed analysis. Figure 2 shows a plot of the work function of Co₃O₄ layers deposited onto FTO|TiO₂ substrates versus the Co₃O₄ thickness for layers grown at 25 °C, where various colours and shapes correspond to different samples. The work function at zero thickness is the mean TiO₂ work function of 4.39 eV. For the Co₃O₄ layer grown at 25 °C, there is an observed increase in the work function as the thickness increases, until ~10 nm, after which the work function remains constant at ~5.31 eV up to the measured range of 340 nm (only up to 250 nm is shown). The drastic increase in the work function at low thicknesses is attributed to charge transfer between TiO₂ and Co₃O₄; with electrons transferring from the TiO₂ to the Co₃O₄ layer causing downwards band bending in the TiO₂. The region where the work function is constant corresponds to thicknesses at which the surface is far enough from the interface that we are no
longer measuring the changes in the work function due to the band bending in either layer. This work function corresponds to the ‘bulk’ case.

Figure 2. Band bending at the TiO$_2$|Co$_3$O$_4$ interface. Work function of Co$_3$O$_4$ deposited at 25 °C onto FTO|TiO$_2$ substrates versus the Co$_3$O$_4$ thickness. The work function measurements were performed within 10 minutes of exposing the sample to air. Different marker shapes/filling indicate different sample libraries. The solid line is a fit using the 1D solution to the Poisson’s equation as described in the text to attain the depletion width of $z_p = 8.6 \pm 3.8$ nm.

At this point, it is worth addressing what may appear as a discrepancy in the data for the various samples in Figure 2, in particular, the sample represented by green triangles. Upon initial observation it appears as if the data fails to follow the trend of the other datapoints and the line of best fit. However, the data is most likely exhibiting experimental uncertainty since all the datapoints fail within an acceptable error of the line of best of fit, less than 3 nm and 35 meV and as such would be inappropriate to remove. Importantly, the line of best fit does not change significantly if this data is removed whilst performing the fitting algorithm (the depletion width
increases by 1 Å and the bulk work function reduces by 10 meV), which highlights the stability of the algorithm. As a further check, we have repeated the analysis for the data in Figure 2, with only the single datapoint corresponding to the greatest thickness for each of the samples revealing a slight change. The depletion width increased by 2.2 nm to 10.8 nm with a reduction in the 0 nm thickness work function from 4.49 to 4.40 eV, giving an overall built-in potential of 0.87 V. This analysis is the equivalent of performing the stepwise growth method and the similarity in the results provides credence to our methodology. Details of both aforementioned analyses are provided in the supplementary information.

Figure 3 shows a plot of the work function TiO₂ layers deposited onto commercial FTO substrates versus the TiO₂ thickness. The rapid reduction in the work function from 4.68 eV (FTO work function) to 4.50 eV is as expected for electron transfer from TiO₂ to FTO. Due to the high level of doping of the FTO layer, compared with the TiO₂, we can assume that there is negligible change in the Fermi-level position in the FTO upon deposition of TiO₂ i.e. no band bending in the FTO layer and Equation 1 describes the band bending in the TiO₂ solely.
Figure 3. Band bending at the FTO|TiO$_2$ interface. Work function of TiO$_2$ deposited onto FTO substrates versus the TiO$_2$ thickness. Different shapes indicated different sample libraries. The solid line is a fit using the 1D solution to the Poisson’s equation as described in the text to attain the depletion width of 20.1±7.3 nm.

We begin the detailed analysis by first considering the FTO|TiO$_2$ interface. From the fit of the data in Figure 3 we derive 0.15 eV for the band bending, a depletion width of 20.1±7.3 nm, and by applying a dielectric constant of 4.0 (from the optical modelling of the TiO$_2$ layers, UV-Vis data) we attain a donor concentration of $N_D = 1.5 \times 10^{17} \pm 1.3 \times 10^{17}$ cm$^3$ for the TiO$_2$. The upwards band bending in the TiO$_2$ for this interface has been reported in the literature$^{[30]}$ and although it should impede electron transfer to the FTO, this interface has been employed in a number of high efficiency solar cells of various geometries. In fact, perovskite based solar cells made within our group, using similarly prepared TiO$_2$ on the same commercial FTO, have achieved 16% efficiency$^{[31]}$.

Let us now consider the energetics of the TiO$_2$|Co$_3$O$_4$ interface. From the fit of the data in Figure 2 a depletion width of 8.6 nm and built-in potential of $V_{BI} = 0.78$ V (5.27-4.49 V) was determined for the Co$_3$O$_4$ layer. The built-in potential is the sum of the band bending in each layer $V_{BI} = V_N + V_P$, using this relationship, Equation 1 and the conservation of charge $N_A z_P = N_D z_N$, it is straightforward to calculate the hole concentration in the bulk Co$_3$O$_4$ layer $N_A = 8.2 \times 10^{17}$ cm$^3$, the TiO$_2$ depletion width $z_N = 46.0$ nm and the amount of band bending in each layer: 0.74 and 0.04 eV in TiO$_2$ and Co$_3$O$_4$, respectively. We have assumed a dielectric constant of Co$_3$O$_4$ of 12.9 from literature$^{[32,33]}$ and that the TiO$_2$ layers grown in the spray and PLD are electronically comparable and this is supported by the similarity in the work functions. The work function of
the PLD TiO$_2$ reduces to 4.43 eV after two weeks in air, which is within error of the 4.39 eV for sprayed TiO$_2$. Based on the results and analysis presented in this paper it is trivial to draw a band diagram of the FTO|TiO$_2$|Co$_3$O$_4$ layers with accurate accounts of the band bending at each interface, given in Figure 4.

Figure 4. Detailed band diagram of the FTO|TiO$_2$|Co$_3$O$_4$ structure. The ionisation energy of Co$_3$O$_4$ was measured using air-photoemission and the band gaps of TiO$_2$ and Co$_3$O$_4$ were determined from Tauc plots reported elsewhere.$^{[23,34]}$ For the band diagram we used the 1.5 eV optical band gap for Co$_3$O$_4$. Although a ~0.8 eV band gap for Co$_3$O$_4$ has been reported, it is sensitive to the fabrication method and we have no evidence of it in our samples, unlike the 1.5 eV gap$^{[27,35]}$. All values are in units of eV unless otherwise specified and are based on the relevant fits in Figures 2, 3 and corresponding analysis.

3. Discussion

The above analysis provides some crucial insights into the operation of TiO$_2$|Co$_3$O$_4$ photovoltaic devices and shortcomings of the Co$_3$O$_4$ layers presented here as an absorber. Such devices exploit
the band bending in the Co$_3$O$_4$ layer to dissociate optically excited electron/hole pairs and promote charge collection with free electrons transporting to the FTO and holes to a back contact. Although Co$_3$O$_4$ has a near ideal band gap of 1.5 eV and demonstrates a very high optical absorption, for our films the high carrier concentration in the material, greater than that of TiO$_2$, leads to a very narrow depletion region of only $8.6 \pm 3.8$ nm and a weak electric field with a maximum of only $5 \times 10^5$ V cm$^{-1}$. Due to the poor mobility of carriers typically observed in Co$_3$O$_4$, it is crucial to have the depletion width span the entire layer, however, growing the layer only 8.6 nm thick would greatly restrict the number of photons that would be absorbed. A straightforward method to improve device performance would be to grow a thicker Co$_3$O$_4$ layer with a lower carrier concentration to provide a suitable band bending profile, possibly via controlling the oxygen content during the film growth$^5$.

The methodology we have developed in this paper overcomes the major shortcomings of the two methods outlined in the introduction. By characterising samples with a thickness gradient we drastically enhance the number of data-points attained per sample, compared with the stepwise method, from 1 to 13 in the case presented here. From the six samples measured in Figure 2 we measured 78 data-points (some are off the plot axis) an order of magnitude more points than typically observed in reports using the stepwise method! Our use of multiple substrates has an additional benefit that since our method is non-destructive it allows for parallel measurements to be performed and/or extra layers to be deposited to form complete devices, while having overlapping data-points between samples provides a measure of reproducibility. Also, by performing measurements in air we avoid the necessity of a vacuum analysis chamber which allows for more rapid characterisation of samples without significant limitations on the sample size. In contrast to the cross-section approach, we measure the surface/interfaces of interest as
grown without any polishing or milling of the measured surface which may affect the measured work functions. Finally, one of the key benefits of our approach is that it can be performed with low-cost instrumentation common to many laboratories that characterise photovoltaic devices, namely a Kelvin probe and UV-Vis optical scanner.

Let us now discuss the spatial and energy resolutions of this depth-profiling method, beginning with the instrumental resolution. Kelvin probe enjoys both high energy and depth resolutions of 1 meV\(^{[36-38]}\) and 1-3 atomic layers (~1 nm),\(^{[39]}\) respectively, with a lateral resolution determined by the tip size of 2 mm, although smaller tips are available. However, a standard deviation of ~5 meV for the contact potential difference (CPD) was commonly observed for measurements performed at a single position for the samples reported here. To test the variation between samples three \(\text{Co}_3\text{O}_4\) films were grown at ~400 nm whilst rotating the substrate during the growth in order to minimise the thickness gradient. CPD line scans were measured and the largest standard deviation within a single sample was 12 meV with a standard deviation of 25 meV across all the samples. The work function of the tip is ascertained by measuring the CPD of a gold sample followed by an absolute measurement of the work function of the sample using air-photoemission. Over the span of a year this gives a work function of 4.22 eV with a standard deviation of 35 meV. This is within the range of the resolution of the air photoemission instrument, 30-50 meV\(^{[40]}\) as stated by the manufacturer, which defines the resolution of the absolute work functions. The knowledge of the absolute work function is not necessary for determining the depletion width and the uncertainty in this value only affects the offset in the work function axis of the plots given in Figures 2 and 3 and the values given in the band diagram.
Having considered the resolution of the instrumentation, it is now possible to discuss the resolution of our depth-profiling approach. For this discussion we will ignore the impact of surface roughness and the uncertainty in determining the thickness i.e. we assume smoothly varying and absolutely known thicknesses. The ability to resolve depth using our approach is defined by the local thickness gradient of the adlayer under the lateral probing area (2 mm diameter of the tip) i.e. the amount the thickness of the adlayer varies within the lateral probing area. This varies across each sample and between each sample due to the shape of the plasma plume during PLD film growth. For example, in the case of the sample represented by diamonds in Figure 2, at thicknesses 1.9, 8.7 and 26.7 nm we calculate the variation in the thicknesses under the tip to be 0.3, 0.7 and 0.6 nm. To summarise, performing depth profiling via exploiting an adlayer with a thickness gradient using Kelvin Probe, a depth resolution of less than 2 nm can be achieved. However, since the work function of the adlayer depends on the thickness, in the case of thicknesses less than the depletion width, we also need to consider the impact of the depth resolution on the ultimate energy resolution. The corresponding energy resolution is determined by the product of the variation of the thickness and electric field strength or the derivative of the work function with depth. For the 1.9 nm thickness data point, where the resolution is lowest because the electric field is strongest, this is 4 meV. From this analysis it is clear our depth profiling methodology can boast very high depth and energy resolutions and that the overall accuracy of this approach is limited by the sample and measurement conditions.
Figure 5. Evolution of the contact potential difference (CPD) for prolonged exposure to air for a TiO$_2$|Co$_3$O$_4$ sample. Time zero is defined at the time of the first work function measurement on the sample. The data was least squares fitted with $CPD = 442 \times \exp(-0.0144 \times t) + 699$ to permit one to project to the time when the sample was removed from vacuo at $t = -10$ minutes.

Now, a few remarks about performing our depth-profiling method in air. We will focus the discussion on the TiO$_2$|Co$_3$O$_4$ samples and not the FTO|TiO$_2$ sample, since the impact was larger on the former. As mentioned earlier, it takes less than 10 minutes to get the sample from the PLD deposition chamber into the Kelvin probe to begin CPD measurements but once there, the CPD at each point analysed is measured over a period of ~30 minutes in order to observe changes in the work function due to prolonged exposure to air. Figure 5 shows the change in work function with respect to time for TiO$_2$|Co$_3$O$_4$, where time $t = 0$ is taken to be the moment of the first CPD measurement. For each position measured on each sample an exponential fit of $CPD=C+A\times\exp(Bt)$, was performed, where $A$, $B$ and $C$ are constants determined from a least squares fit. From these equations it is trivial to extrapolate to time $t = -10$ minutes, and to calculate how much the CPD varied from the point of first measurement to when the samples...
were first exposed to air. It is important to note there were no obvious correlations between changes in the CPD and the adlayer thickness. The average CPD change of all points on all the samples TiO$_2$|$\text{Co}_3\text{O}_4$ was $-63\pm25$ meV. In principle it would be easy to apply a correction to each point on a point-by-point basis, sample-by-sample basis or based on the overall average, to the data presented in Figure 2. However, we have made no such attempt at this stage since we have yet to perform a detailed study and confidently show that such a fit is appropriate and that the work function values are unaffected by the repeated measurement. It is worthwhile to remind the reader at this point that the cross-section depth-profiling method is typically performed in air without any such correction.

4. Conclusion

In this paper we have detailed a new methodology for rapidly measuring the electrostatic potential of interfaces. Using scanning Kelvin probe and the intentional thickness gradient of films grown by PLD we correlated changes in line scans of work function with the thickness of the adlayer at 13 points in order to directly map the band bending at interface with the substrate. In order to fit this data we have developed a robust algorithm to provide a direct measure of the depletion width and built-in potential, as well as, facilitates the calculation of the carrier concentration of the adlayer. We explained how our method enjoys both very high depth resolution and energy resolution of only 2 nm and a 5 meV. To demonstrate the capabilities of our methodology we explored the band alignment of the FTO|$\text{TiO}_2$|$\text{Co}_3\text{O}_4$ all-oxide solar cell subset. By performing our depth profiling method on the FTO|$\text{TiO}_2$ junction we showed that the TiO$_2$ experiences upward band bending of 0.15 eV, has a depletion width of $20.1\pm7.3$ nm and an acceptor concentration $N_D = 1.5\times10^{17} \pm 1.3\times10^{17}$ cm$^3$. In the case of the TiO$_2$|$\text{Co}_3\text{O}_4$ junction, a depletion width of $8.6\pm3.8$ nm was measured with a built-in potential of 0.78 V. From further
analysis we calculated the band bending in the Co$_3$O$_4$ to be only 0.04 compared to 0.74 eV in TiO$_2$, due to a higher dominant carrier concentration in the former of $N_A = 8.2 \times 10^{17}$ cm$^3$. Using this information, we were able to develop a detailed band diagram of the FTO|TiO$_2$|Co$_3$O$_4$ solar cell subset.

5. Experimental Section

Substrates:
The substrates used are a commercial glass (with dimensions of 72 mm × 72 mm) coated with a transparent conducting oxide film, fluorine-doped SnO$_2$ (FTO, TEC15 from Hartford Glass Co.), with a sheet resistance of 15 Ω/square. The substrates were washed with soap, ethanol, and thoroughly rinsed with de-ionized water. Work function maps of six FTO substrates were measured throughout the course of this study and the mean and standard deviation of the work function values are 4.71 and 0.051 eV, respectively.

TiO$_2$ spray pyrolysis deposition:
For TiO$_2$ window layers, an ethanol precursor of TiO$_2$ was made from 0.20 M titanium tetra isopropoxide and 0.40 M acetylacetone$^{[41]}$. Subsequently, the precursor was sprayed through a spray nozzle (Spraying Systems Co.) in conjunction with a CNC x-y-z scanner to produce either a linear thickness gradient along the x-axis (ranging from 140 to 290 nm) or a homogenous thickness of ~200 nm via multiple spray cycles on an FTO substrate placed on a 450 °C hot-plate.

TiO$_2$ pulsed laser deposition:
TiO$_2$ adlayers were deposited by a commercial pulsed laser deposition (PLD) system (Neocera) using a KrF excimer laser (248 nm) and a commercial TiO$_2$ target (Kurt J. Lesker, 99.9% pure). The thin films were deposited without masks to provide an intentional non-linear gradient
thickness profile with a substrate temperature of 300 °C in a partial O₂ pressure of \(7 \times 10^{-3}\) Torr. The energy fluence of the laser was 1.8 Jcm\(^{-2}\) (~75 mJ per pulse) and fired with repetition rate of 8 Hz for 4000, 20000, 80000 pulses to generate the necessary thickness range. The target–substrate distance was 57 mm.

**Co\(_3\)O\(_4\) PLD deposition:**

Co\(_3\)O\(_4\) layers were deposited using the aforementioned PLD, and a commercial Co\(_3\)O\(_4\) target (Kurt J. Lesker, 99.9% pure). The thin films were deposited without masks, at 25 °C with differing number of pulses (from 500 to 160 000) to generate samples with the necessary thickness range. The thin films were deposited in a partial O₂ pressure of \(3.1 \times 10^{-2}\) Torr. The energy fluence of the laser was 1.2 Jcm\(^{-2}\) (~50 mJ per pulse) and fired with repetition rate of 2-6 Hz. The target–substrate distance was 77 mm.

**Electrical Characterisation:**

The work function and the ionization energy of the sample were measured under ambient conditions using a SKP microscope combined with an air photoemission system (ASKP150200, KP Technology Ltd.)\(^{[40]}\). The tip was stainless-steel with a 2 mm diameter and was frequently calibrated against a gold reference sample, for which, the absolute work function was measured at the time of calibration using air photoemission. The mean work function of the tip, over the course of about a year, was 4.22 eV with a standard deviation of 0.035 eV, indicating the high consistency of the tip and excellent precision of both the Kelvin probe and air-photoemission measurements. Samples were measured in the dark immediately after extraction from *vacuo* to minimise the impact of illumination and air exposure, respectively. All electrical characterisations were performed in a room in which the temperature 21 ± 3 °C. The humidity
was measured frequently throughout the course of year and the mean relative humidity was 42% with a standard deviation of 12% due to seasonal changes but with considerably less variations within and between days.

**Optical Characterisation:**

The optical transmission and reflection of films were measured with an optical-fibre compatible CCD array spectrometer (USB4000, Ocean Optics) to obtain the optical absorbance over the visible range, as described elsewhere\textsuperscript{[42]}. These measurements were used to calculate the Co$_3$O$_4$ film thickness using Beer-Lambert’s law. The absorption coefficient at 700 nm, $\alpha = 4.95 \times 10^6$ was used for Co$_3$O$_4$ films grown at 25 °C, which was determined using a Helios 600 (FEI) scanning electron microscope to measure the cross section and thickness of the Co$_3$O$_4$ samples. There was excellent agreement between the measured and calculated thickness over the range of 70 to 235 nm, with an average discrepancy of only 5%. The TiO$_2$ thickness and dielectric constant were determined by fitting the optical data using the Fresnel equation with the licenced software CODE by W. Theiss. In the case of thin films <30 nm thick, the optical response was often too low to accurately determine the thickness profile from the optical analysis and an average of thickness profiles of a thicker sample appropriately scaled based on the number of pulses during the deposition was employed.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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References

[1] M. A. M. Leenen, V. Arning, H. Thiem, J. Steiger, R. Anselmann, *Phys. Status Solidi A* 2009, 206, 588.

[2] Y.-H. Kim, J.-S. Heo, T.-H. Kim, S. Park, M.-H. Yoon, J. Kim, M. S. Oh, G.-R. Yi, Y.-Y. Noh, S. K. Park, *Nature* 2012, 489, 128.

[3] A. Facchetti, T. J. Marks, Eds., *Transparent Electronics: From Synthesis to Applications*, John Wiley & Sons, Ltd, Chichester, UK, 2010.

[4] E. A. Kraut, R. W. Grant, J. R. Waldrop, S. P. Kowalczyk, *Phys. Rev. Lett.* 1980, 44, 1620.

[5] M. T. Greiner, Z.-H. Lu, *NPG Asia Mater.* 2013, 5, e55.

[6] K. J. Rietwyk, Y. Smets, M. Bashouti, S. H. Christiansen, A. Schenk, A. Tadich, M. T. Edmonds, J. Ristein, L. Ley, C. I. Pakes, *Phys. Rev. Lett.* 2014, 112, DOI 10.1103/PhysRevLett.112.155502.

[7] C.-S. Jiang, F. S. Hasoon, H. R. Moutinho, H. A. Al-Thani, M. J. Romero, M. M. Al-Jassim, *Appl. Phys. Lett.* 2003, 82, 127.

[8] Q. Chen, L. Mao, Y. Li, T. Kong, N. Wu, C. Ma, S. Bai, Y. Jin, D. Wu, W. Lu, B. Wang, L. Chen, *Nat. Commun.* 2015, 6, 7745.
[9] C.-S. Jiang, M. Yang, Y. Zhou, B. To, S. U. Nanayakkara, J. M. Luther, W. Zhou, J. J. Berry, J. van de Lagemaat, N. P. Padture, K. Zhu, M. M. Al-Jassim, Nat. Commun. 2015, 6, 8397.

[10] A. Guerrero, E. J. Juarez-Perez, J. Bisquert, I. Mora-Sero, G. Garcia-Belmonte, Appl. Phys. Lett. 2014, 105, 133902.

[11] T. Usunami, M. Arakawa, S. Kishimoto, T. Mizutani, T. Kagawa, H. Iwamura, Jpn. J. Appl. Phys. 1998, 37, 1522.

[12] S. Ikeda, T. Shimada, M. Kiguchi, K. Saiki, J. Appl. Phys. 2007, 101, 094509.

[13] J. Lee, J. Kong, H. Kim, S.-O. Kang, K. Lee, Appl. Phys. Lett. 2011, 99, 243301.

[14] P. Narchi, J. Alvarez, P. Chrétien, G. Picardi, R. Cariou, M. Foldyna, P. Prod’homme, J.-P. Kleider, P. R. i Cabarrocas, Nanoscale Res. Lett. 2016, 11, DOI 10.1186/s11671-016-1268-1.

[15] S. Tanuma, C. J. Powell, D. R. Penn, Surf. Interface Anal. 2011, 43, 689.

[16] S. V. Boriskina, M. A. Green, K. Catchpole, E. Yablonovitch, M. C. Beard, Y. Okada, S. Lany, T. Gershon, A. Zakutayev, M. H. Tahersima, V. J. Sorger, M. J. Naughton, K. Kempa, M. Dagenais, Y. Yao, L. Xu, X. Sheng, N. D. Bronstein, J. A. Rogers, A. P. Alivisatos, R. G. Nuzzo, J. M. Gordon, D. M. Wu, M. D. Wisser, A. Salleo, J. Dionne, P. Bermel, J.-J. Greffet, I. Celanovic, M. Soljacic, A. Manor, C. Rotschild, A. Raman, L. Zhu, S. Fan, G. Chen, J. Opt. 2016, 18, 073004.

[17] M. L. Green, I. Takeuchi, J. R. Hattrick-Simpers, J. Appl. Phys. 2013, 113, 231101.

[18] R. Potyrailo, K. Rajan, K. Stoewe, I. Takeuchi, B. Chisholm, H. Lam, ACS Comb. Sci. 2011, 13, 579.

[19] I. Takeuchi, J. Lauterbach, M. J. Fasolka, Mater. Today 2005, 8, 18.

[20] H. Koinuma, I. Takeuchi, Nat. Mater. 2004, 3, 429.
[21] K. Rajan, *Annu. Rev. Mater. Res.* **2008**, *38*, 299.

[22] S. Siol, P. Schulz, M. Young, K. A. Borup, G. Teeter, A. Zakutayev, *Adv. Mater. Interfaces* **2016**, *3*, 1600755.

[23] B. Kupfer, K. Majhi, D. A. Keller, Y. Bouhadana, S. Rühle, H. N. Barad, A. Y. Anderson, A. Zaban, *Adv. Energy Mater.* **2015**, *5*, n/a.

[24] K. Majhi, L. Bertoluzzi, D. A. Keller, H.-N. Barad, A. Ginsburg, A. Y. Anderson, R. Vidal, P. Lopez-Varo, I. Mora-Sero, J. Bisquert, A. Zaban, *J. Phys. Chem. C* **2016**, *120*, 9053.

[25] K. Majhi, L. Bertoluzzi, K. J. Rietwyk, A. Ginsburg, D. A. Keller, P. Lopez-Varo, A. Y. Anderson, J. Bisquert, A. Zaban, *Adv. Mater. Interfaces* **2016**, *3*, n/a.

[26] B. Wang, Y. Cai, W. Dong, C. Xia, W. Zhang, Y. Liu, M. Afzal, H. Wang, B. Zhu, *Sol. Energy Mater. Sol. Cells* **2016**, *157*, 126.

[27] C. Lohaus, J. Morasch, J. Brötz, A. Klein, W. Jaegermann, *J. Phys. Appl. Phys.* **2016**, *49*, 155306.

[28] D. Shepard, ACM Press, *1968*, pp. 517–524.

[29] G. A. Rojas, Y. Wu, G. Haugstad, C. D. Frisbie, *ACS Appl. Mater. Interfaces* **2016**, *8*, 5772.

[30] S. Rühle, D. Cahen, *J. Phys. Chem. B* **2004**, *108*, 17946.

[31] L. Gouda, R. Gottesman, S. Tirosh, E. Haltzi, J. Hu, A. Ginsburg, D. A. Keller, Y. Bouhadana, A. Zaban, *Nanoscale* **2016**, *8*, 6386.

[32] K. V. Rao, A. Smakula, *J. Appl. Phys.* **1965**, *36*, 2031.

[33] C.-S. Cheng, M. Serizawa, H. Sakata, T. Hirayama, *Mater. Chem. Phys.* **1998**, *53*, 225.

[34] H.-N. Barad, A. Ginsburg, H. Cohen, K. J. Rietwyk, D. A. Keller, S. Tirosh, Y. Bouhadana, A. Y. Anderson, A. Zaban, *Adv. Mater. Interfaces* **2016**, *3*, DOI 10.1002/admi.201500789.
[35] L. Qiao, H. Y. Xiao, H. M. Meyer, J. N. Sun, C. M. Rouleau, A. A. Puretzky, D. B. Geohegan, I. N. Ivanov, M. Yoon, W. J. Weber, M. D. Biegalski, *J. Mater. Chem. C* 2013, 1, 4628.

[36] W. Melitz, J. Shen, A. C. Kummel, S. Lee, *Surf. Sci. Rep.* 2011, 66, 1.

[37] I. D. Baikie, P. J. Estrup, *Rev. Sci. Instrum.* 1998, 69, 3902.

[38] I. D. Baikie, S. Mackenzie, P. J. Z. Estrup, J. A. Meyer, *Rev. Sci. Instrum.* 1991, 62, 1326.

[39] E. Kopatzki, H.-G. Keck, I. D. Baikie, J. A. Meyer, R. J. Behm, *Surf. Sci.* 1996, 345, L11.

[40] I. D. Baikie, A. C. Grain, J. Sutherland, J. Law, *Energy Procedia* 2014, 60, 48.

[41] S. Rühle, A. Y. Anderson, H.-N. Barad, B. Kupfer, Y. Bouhadana, E. Rosh-Hodesh, A. Zaban, *J. Phys. Chem. Lett.* 2012, 3, 3755.

[42] A. Y. Anderson, Y. Bouhadana, H.-N. Barad, B. Kupfer, E. Rosh-Hodesh, H. Aviv, Y. R. Tischler, S. Rühle, A. Zaban, *ACS Comb. Sci.* 2014, 16, 53.
A novel methodology for depth profiling the electrical potential at interfaces that can be performed in air is presented. The approach is non-destructive, rapid and enjoys high spatial and energy resolution. In this work we develop and demonstrate the method on FTO|TiO$_2$|Co$_3$O$_4$ all-oxide junctions and show a depletion width of only 8.6±3.8 nm in the Co$_3$O$_4$ layer.

**Band alignment**

K. J. Rietwyk*, D. A. Keller, K. Majhi, A. Ginsburg, M. Priel, H.-N. Barad, A. Y. Anderson and A. Zaban

**High-Throughput Electrical Potential Depth-Profiling in Air**
Supporting Information

High-Throughput Electrical Potential Depth-Profiling in Air

Kevin J. Rietwyk*, David A. Keller, Koushik Majhi, Adam Ginsburg, Maayan Priel, Hannah-Noa Barad, Assaf Y. Anderson and Arie Zaban*

Supplementary information

The algorithm used for the fitting of the work function vs thickness data is summarised as a flow chart in Figure S1 and will be described here briefly. Firstly, the work function vs thickness data for one side of a junction is curated with increasing thickness. Beginning with a thickness from 0 nm to the thickness of the 5th data-point a least square fit, using a modified Levenberg-Marquardt algorithm native to Sci-lab, is performed for the equation \( V(z) = A(z-B)^2 + C \), where A, B and C are fitting parameters. For the remainder of the thickness range, \( V(z) = C \). The sum of squared residuals (SSR) is calculated over the entire range, then the thickness is increased by 1 Å and the process is repeated until the fit is performed for the entire thickness range of the data. The fit with the least SSR is selected and the potential at zero thickness is compared with work function of the corresponding data-point. If the difference is less than the tolerance \( V_{tol} = 0.1 \) eV, then the fit is employed as the line of best fit for the data, if not, additional weighting is applied to the zero thickness data-point and the whole process is repeated until the difference is sufficiently small. The reason for this check is to ensure the fit at low thickness accurately describes the data and this is necessary because there are often fewer data-points at these thicknesses and as a consequence less weighting; the intentional increase in the weighting is to correct this feature (if necessary).
Figure S1. Flowchart of the work function/thickness data fitting algorithm.

Figure S2 shows a plot of the work function of Co$_3$O$_4$ layers deposited onto FTO|TiO$_2$ substrates versus the Co$_3$O$_4$ thickness for layers grown at 25 °C, similar to Figure 2 in the main text except with the removal of the green triangle datapoints. The fit of the data with Equation 1 in the main text provides a remarkably similar fit with a depletion width $Z_P = 8.7$ nm and work function at zero thickness and in the bulk of the Co$_3$O$_4$ of 4.49 and 5.25 eV, respectively. Therefore, by removing the datapoints for the sample represented by the green triangles the change in the fit of the data is an increased depletion width of 1 Å with a reduction in the bulk work function by 10 meV.
Figure S2. Work function of Co$_3$O$_4$ deposited at 25 °C onto FTO|TiO$_2$ substrates versus the Co$_3$O$_4$ thickness, similar to Figure 2 in the main text, except with the removal of the green triangle datapoints. The work function measurements were performed within 10 minutes of exposing the sample to air. Different marker shapes/filling indicate different sample libraries.

Figure S3 shows a plot of the work function of Co$_3$O$_4$ layers deposited onto FTO|TiO$_2$ substrates versus the Co$_3$O$_4$ thickness for layers grown at 25 °C, using only the datapoint corresponding to the greatest thickness of each sample, which is the equivalent of performing the stepwise growth depth profiling method. In the case the fit is slightly better and gives a depletion width $Z_P = 10.8$ nm and work function at zero thickness and in the bulk of the Co$_3$O$_4$ of 4.40 and 5.27 eV, respectively, with the former in close agreement with the work function of the TiO$_2$ substrate of 4.39. The difference between this fit and the fit of Figure 2 is an increase of 2.2 nm in the depletion width and reduction 0.09 eV in the zero thickness work function resulting in an increase of the calculated dominate carrier concentration for Co$_3$O$_4$ of only 6%.
Figure S3. Work function of Co$_3$O$_4$ deposited at 25 °C onto FTO|TiO$_2$ substrates versus the Co$_3$O$_4$ thickness using only the datapoint corresponding to the greatest thickness of each sample. The work function measurements were performed within 10 minutes of exposing the sample to air. Different marker shapes/filling indicate different sample libraries.