Into chemical depths

With chemical depth profiles, it's possible to analyse thin layers, such as in solar cells, for their chemical composition from top to bottom. This lets scientists and engineers check whether the materials used are present in the desired order and purity. Empa researchers have developed an instrument which can create the chemical depth profile of very thin layers quickly and with high resolution.

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Layers at the micro- and nanoscale are growing in popularity in research and industry thanks to their unique physical properties. They find applications, for instance, as polymer films in organic electronics, in food packaging and also in photovoltaics. Experts at Empa and other research institutes are designing prototypes of innovative solar cells made of various organic and inorganic materials. These cells are only a few micrometres thick but even so achieve the same or even better efficiency than conventional solar cells made of silicon. In addition, thin-film solar cells are significantly lighter, which expands the number of places where they can be used, and they require less material in their production.

To make sure that sunlight is converted into the largest amount of electricity, the films are generally very complex and built up of a wide range of materials. Producing these multilayer films precisely, reliably and in a reproducible manner means that the design and chemical composition of the individual layers must be checked on a regular basis. Instruments which create a chemical depth profile are thus required. Empa's Mechanics of Materials and Nanostructures Laboratory in the city of Thun has developed such an instrument.

Fast – and at the same time with high resolution

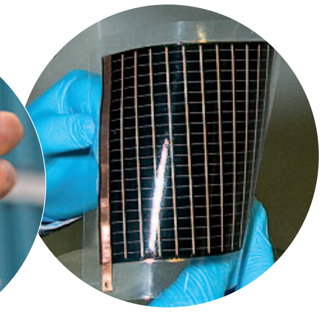
The plasma profiler, as the instrument is called, combines mass spectrometry with a glow discharge. The latter uses a plasma in the noble gas argon to release and ionise atoms and molecules from the solid sample under analysis, and this at an ambient pressure of only a few millibar. The resulting ions then make their way into the mass spectrometer, which determines the chemical composition of the thin layers.

"The combination of glow discharge and mass spectrometry isn't really anything new", remarks Empa researcher James Whitby, who co-developed the instrument. "The time-of-flight mass spectrometer we use, however, enables a very fast measurement without the need for us to limit the masses over which we can measure. That's something which has been unavailable until today." The importance is that the time-of-flight mass spectrometer analyses all the ions at the same time including very large ones, for example those from polymers, even when the layers are very thin. The depth resolution is approximately five nanometres.

A development on the road to marketability

The initial work on the plasma profiler started roughly eight years ago. Development of the instrument then continued within the scope of a project financed by the Swiss Commission for Technology and Innovation CTI. Besides Empa, Tofwerk AG was involved. That company, headquartered in Thun, specialises in time-of-flight mass spectrometers. Further European universities and industrial partners then joined the effort for a follow-up project which was part of the EU 6th Framework Programme. In all, three prototypes were built. Besides the first instrument in Thun, today there is also a plasma profiler at the University of Oviedo in Spain and another located at one of the industrial partners, HORIBA Jobin Yvon SAS in Paris, which is also already marketing the commercial version of the instrument.

The Empa researchers in Whitby's team have worked primarily on the fundamental aspects. "We've invested a great deal of time in understanding and mastering the instrument", elaborates Whitby. "That's because an analysis instrument is useful only when we can correctly interpret its 'output'." How must the samples be pre-



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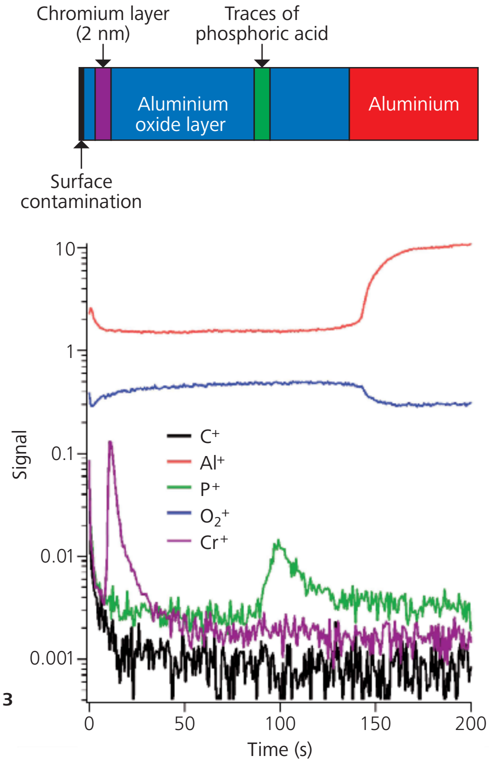

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pared? Which ambient pressures are optimal? At which frequencies must the plasma be excited? Which materials leave which "fingerprints" in the mass spectrometer? All these questions need to be answered if the instrument is to deliver reliable and reproducible results.

An instrument with many talents

The plasma profiler offers a wide range of advantages, just one being pulsed excitation. Metastable argon atoms – which are especially numerous in the plasma during the afterglow, in other words in the short time after the pulse – ionise the sample material "gently" and thus simplify the mass spectrum from molecular materials. In addition, the pulsed excitation preserves the sample material so even substances such as glass, which would be damaged by continuous excitation, are now "analysable". Even so, this isn't enough. Thanks to the time-of-flight mass spectrometer, the instrument not only measures positively charged metal ions but also negatively charged anions, for example halogens like fluorine and chlorine, something not so easy when used in combination with other mass spectrometers. Because the plasma profiler employs radio-frequency excitation, non-conductive samples can also be analysed. That's something that until now was impossible with commercially available instruments which combine mass spectrometry with a glow discharge, but nonetheless is important when studying organic polymers.

Thus, this multi-talented machine has a correspondingly wide range of applications. One example is the study of corrosion processes, such as on cultural assets but also in the automobile and aerospace industries. It's also possible to perform chemical analyses with nanometre precision on coatings for medical implants and dielectric mirrors, which reflect only a portion of the light spectrum and are used, for instance, in lasers.

Instrument for 3D profiles

The plasma profiler is on the road to commercialisation. The Empa team is already working on further projects. For example, they're developing an instrument which shows results at high resolution not only into the depths of a sample but also laterally, that is, to the side. With it they can create 3D chemical maps of complex, multicomponent materials. //

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Thin layers are studied for a variety of applications such as in photovoltaics. Producing them precisely, reliably and in a reproducible manner means that the design and chemical composition of the individual layers must be checked on a regular basis.

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The plasma profiler analyses samples and creates chemical depth profiles even from very thin layers and does so with high resolution. The glow discharge takes place in the chamber at left in the photo (the sample holder is not visible in this closed position); on the right is the mass spectrometer (along with its power supply).

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Depth analysis: an extremely thin chromium layer (violet, 2 nanometres thick) was embedded within an aluminium oxide layer (blue, 230 nanometres thick). The peak shows with high resolution where the chromium layer is located. The strong signal at the start of the measurement results from surface contamination with carbon.