EDAX FOCUS

Microstructural Characterization of Thin Film Photovoltaics Using Electron Backscatter Diffraction

Inside This Issue

Worldwide demand for electricity is growing and the driving force to develop new technologies and materials for alternative energy generation has been increasing due to economic, environmental, and political factors in recent years. Solar power is one such alternative being investigated through photovoltaic (PV) materials that convert sunlight into useable electrical energy. PV production has demonstrated significant growth rates, and this growth is expected to continue.

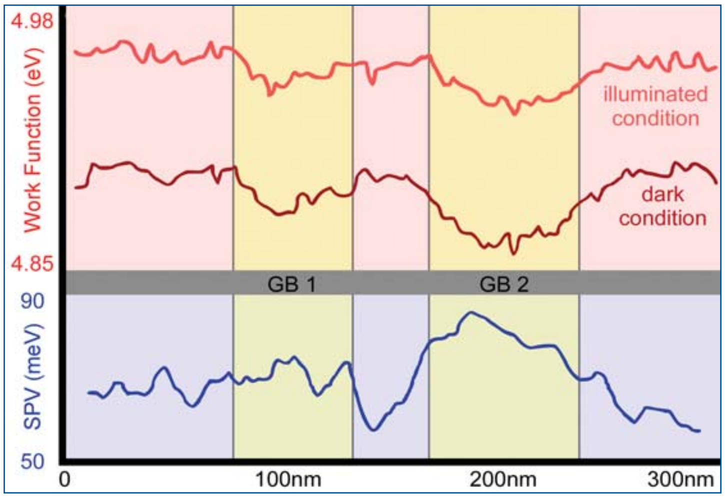

Figure 1 - Work function measurements on CGS film using Kelvin Probe Force Microscopy (red). The surface photovoltage (SPV) distribution is also shown (blue). Different grain boundary types are inferred from the differences in SPV behavior. Adapted from [6] with permission.

The majority of traditional solar cells are based on crystalline silicon. However the cost of this technology is still too high to compete with other means of power generation. One of the largest contributors to this cost is the silicon wafer used. Thin film photovoltaics are an alternative which use less material than traditional silicon solar cells and can be fabricated on a variety of lower cost substrates, including flexible low-mass and thin foil substrates that allow for potential new applications.

Two promising thin film materials are based on Cadmium Telluride (CdTe) and chalcopyrite-structured materials such as $Cu(In,Ga)Se_2$ (CIGS). These materials have near-optimal band gaps, high optical absorption, and good conversion efficiencies. Solar modules manufactured from these materials are commercially available. However the efficiencies of the commercial modules are lower than research-grade cells, indicating an area of potential improvement. Additionally these materials exhibit an unexpected characteristic. Both CdTe and CIGS devices are fabricated as polycrystalline thin films. Surprisingly these devices have higher efficiencies than their single-crystal counterparts, in direct contrast to Silicon and Gallium Arsenic (GaAs) devices [1]. This difference most likely arises from the role grain boundaries play in these materials.

Grain Boundaries

The grain boundaries present in polycrystalline materials are defects within the crystalline lattice that are expected to reduce photovoltaic performance through increased recombination rates. Grain boundaries can also act as localized accumulation sites for defect collection, which can lead to an improvement in crystal lattice quality within the interior of the grains and better photoelectric performance. Both structural and electronic grain boundary models have been proposed to explain the improved performance of these polycrystalline thin films materials. At the grain boundaries, periodicity of the atomic lattice is disrupted, free surface-like conditions occur, and the boundaries can become preferred sites for chemical diffusion and segregation. This can lead to the development of trapped localized electrical or polar charges that cause a region of depleted majority carriers (holes) in the vicinity of grain boundaries and a potential barrier for majority carrier transport. This condition has been verified with a variety of analytical techniques such as scanning capacitance microscopy (SCM) [2], scanning Kelvin probe

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EBSD NEWS

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microscopy (SKPM) [3], conductive probe atomic force microscopy (CP-AFM), and electron beam and ion beam induced current (EBIC and IBIC) [4] and cathodoluminescence (CL) imaging [5]. While majority carrier transport and photovoltaic-induced current is reduced in these regions, the presence of the depleted regions adjacent to grain boundaries can improve the separation and collection and recombination behavior of both majority and minority carriers, with holes flowing in one direction through the grain interiors and electrons flowing the other direction within grain boundaries.

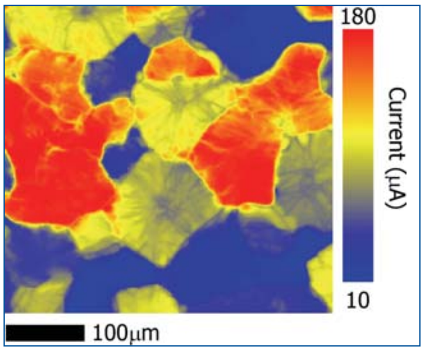

Figure 2 - Electron Beam Induced Current image taken at 53.5nA current illumination of CdTe film with a sample bias of 100V. Adapted from [4] with permission.

However not all grain boundaries are equal. Measurements of photoelectric behavior on individual grain boundaries show variations. Figure 1 shows work function measurements collected with KPFM across two grain boundaries in a CuGaSe2 (CGS) film (Adapted from Marrón et. al. [6] with permission). The red curves show the work functions under illumination and dark conditions. The blue curve shows the surface photovoltage (SPV) distribution. These two boundaries exhibit different SPV character, which suggest different types of grain boundaries. One type of grain boundary is a twin boundary, which can be described in terms of a coincident site lattice (CSL) model [7]. CSL boundaries describe orientation relationships where there is improved fit between adjacent grains, which can result in more complete bonding relative to a random grain boundary. This can lower grain boundary energy, and result in different electrical, diffusional, segregation, and transport properties. Twin boundaries are often referred to as $\Sigma 3$ CSL boundaries. For example, differences between $\Sigma 3$ twin boundaries and random boundaries in CIGS films have been observed with CL imaging [5]. Absolute values of CSL boundary properties vary between CdTe and CIGS films due to the difference in crystal structure, however the relative trends in electrical properties are still present [8]. Similar results have been shown with EBIC and IBIC [4]. In these measurements, induced current variations are seen at different grain boundaries. In addition, non-uniform response is observed between different grains, which could be related to the crystallographic orientation. Figure 2 shows an EBIC current map under high beam current illumination (Adapted from Baier et. al. [4] with permission). Not only are grain and grain boundary variations present, but the response near the grain boundary in one grain is affected by the current value of the adjacent grain as well. This suggests that both grain orientation and grain boundary structure details affect photovoltaic behavior. For example, high efficiency (18.8%) CIGS cells exhibited a (220)/(204) preferred orientation [9].

Figure 3 shows KPFM results from a CGS film where the relationship between local work function and crystallographic orientation has been identified (Adapter from Sadewasser et. al. [3] with permission). In this case, measurements were taken from a single grain of known orientation, and the facet surface orientations identified by measuring the angles between facets. Facets of similar orientation exhibit similar work functions, suggesting that the surface atomic configuration as defined by the crystallographic orientation helps determine the localized work function.

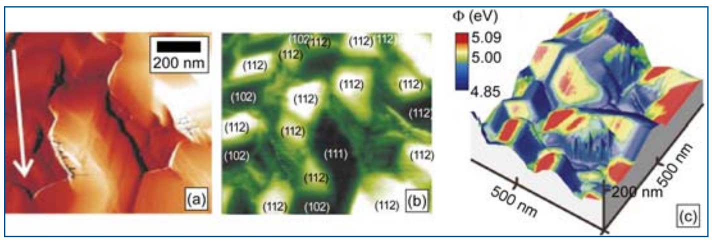

Figure 3 - Kelvin Probe Force Microscopy measurement of a CGS film showing (a) topographic image with facets. (b) Representation of the measured work function with crystallographic facets labeled. (c) 3D image combining topography and work function measurements. Adapted from [3] with permission.

The concept that grain boundaries, and different grain boundary types, can have both advantageous and adverse effects in solar cells is not new, nor the idea to engineer devices to increase the fraction of preferred boundaries [10]. This idea is related to the concept of measuring third level metrics (3LM), or the underlying microstructural features that govern film performance [11, 12]. Traditionally it has been difficult to measure the crystallographic grain boundary character of a material and therefore to correlate electrical properties with specific grain boundary structures. Transmission Electron Microscopy (TEM) has been used to characterize grain boundaries, but is limited by extensive sample preparation and the limited number of boundaries typically observed. X-Ray Diffraction does not measure crystallographic information in a

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spatially-specific manner required to resolve grain boundary information, but does provide information on preferred orientation, or texture. Electron Channeling Patterns (ECP) in a Scanning Electron Microscope (SEM) does not provide the necessary spatial resolution or automation for thin film measurements. A new analytical technique was required.

Electron Backscatter Diffraction (EBSD)

EBSD is an SEM-based characterization technique for measuring crystallographic orientation. An EBSD pattern from CdTe is shown in Figure 4. Information regarding orientation, phase, and strain can be extracted from these patterns. Orientation Imaging Microscopy (OIM) is the automated collection and analysis of EBSD patterns to create micrographs based on orientations and to quantitatively characterize the microstructure of a material.

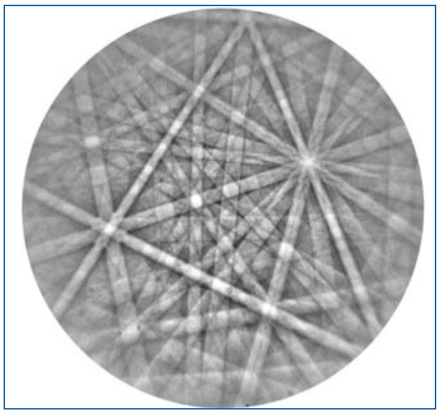


Figure 4 – EBSD pattern from CdTe thin film.

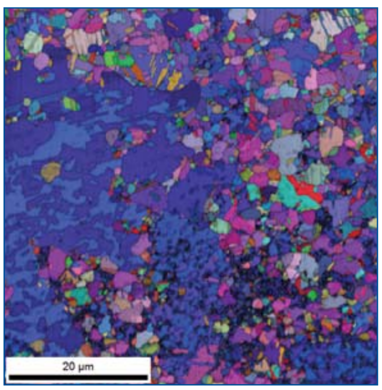
EBSD patterns are generated from approximately a 5nm x 15nm x 15nm volume of material interacting with the electron beam and producing diffraction patterns that are imaged with a low light digital camera. As such, EBSD patterns are sensitive to surface defects and oxide layers that may be present within this interaction volume. Additionally, EBSD pattern detection requires a line-of-sight view from the detector. Surface topography may inhibit this view and decrease collection efficiency. Because of these issues, EBSD-specific sample preparation may be required [13]. For plan-view analysis, broad beam ion etching can be used to smooth the film surface. This can be done in conjunction with careful abrasive polishing as well. For cross-sectional analysis, mechanical polishing is typically required prior to ion milling. In either case, low energy (0.5-2.5 keV) ions typically produce the highest quality EBSD patterns. Cross-sections allow visualization of the microstructure relative to the direction of current flow. This may be important depending on the geometry of the grain boundaries. Plan-views typically allow for better collection statistics with more grains and grain boundaries observed.

As CdTe and CIGS films are semiconductors, some care must be exercised to avoid charging and drift problems during OIM mapping. Appropriate selection of electron beam current and OIM acquisitions speeds are needed to avoid these problems. Typically, faster acquisition speeds are a good method as, in addition to avoiding localized charge effects, they also help counter stage drift and beam stability issues. Additionally a thin carbon coating applied to the film surface may improve conductivity without adversely effecting EBSD pattern quality.

CIGS films can present a challenge to EBSD as well. These materials have a tetragonal chalcopyrite structure, which exhibits cubic pseudo-symmetry. Careful analysis of the EBSD patterns is required in order to accurately determine the correct crystallographic orientation variant [14].

Summary

- The demand for alternative sources of energy is expected to continue to grow
- Photovoltaic thin film solar cells provide a commercially viable technology that can capture increased power generation market share
- Polycrystalline CdTe and CIGS thin films have higher efficiencies than single crystal devices
- The performance of these thin films is influenced by the crystallographic structure, grain boundary character, and grain size
- EDAX's Orientation Imaging Microscopy (OIM™) is a market-leading analytical technique capable of measuring all of these factors simultaneously with sub-micron resolution
- OIM™ also has unique capabilities of characterizing Twin Boundaries



This image shows an orientation map from a CdTe photovoltaic thin film. The white lines indicate twin boundaries, which exhibit superior electrical properties than random high-angle grain boundaries. 45% of the boundaries are twin boundaries.

NOTE: To review the complete applications note on our website, use the link below.

http://www.edax.com/search-application/thin-film-photovoltaics.cfm

TIPS & TRICKS

Quantification in Wavelength Dispersive Spectrometry (WDS)

In samples where peak overlaps are not resolved and/or concentrations of elements are below the detection limits for Energy Dispersive Spectrometry (EDS), WDS should be used. Also, for elements with concentrations < 5 wt%, WDS is preferred due to the higher accuracy and precision. WDS should, however, not be seen as a separate technique, but rather as complementary to EDS.

For WDS quantification, scanning is done using the so-called reduced scan mode (see Figure 1). In this mode, the peak is scanned over the peak width at half height (FWHM) multiplied by the reduced scan fraction. This parameter is typically set to 1.5.

By default, 3 background points are measured both before (bkgL) and after the peak (bkgH). Changing the start and/or end eV of a scan will change the position of the background points.

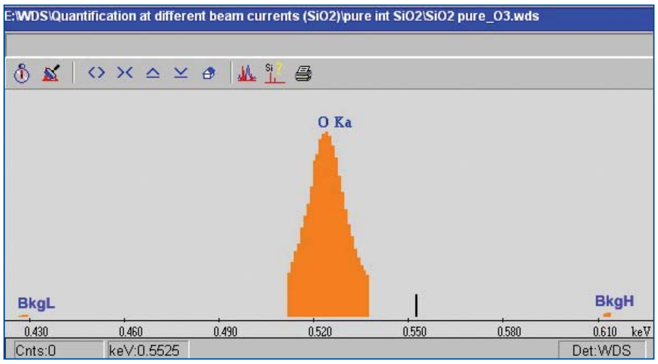


Figure 1: Reduced scan mode for O Ka.

For quantification, pure intensity values for elements have to be determined. First, the optimal Z-height (where max counts are found) is set using the Z-stage shell program. Then either pure element standards or compound (i.e. multi-element) standards are run for typically 5-10s dwell time in reduced scan mode.

Pure intensity values are calculated by the software by typing in the known concentration of elements in the standard and could be stored as pure intensity Tables (.std files). As an EDS spectrum is run at the same time with WDS, pure intensities for EDS can also be determined and stored as a Table.

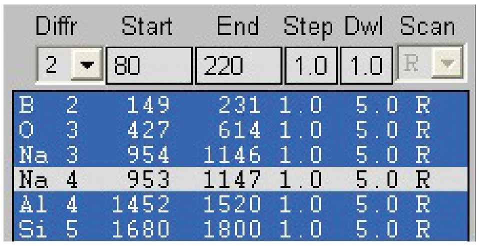
Since pure intensity values are expressed in cps/nA, dwell times and beam current conditions can be different for standards and unknown samples. Important is that SEM accelerating voltage and the reduced scan fraction is the same in both cases.

The beam current for quantification is measured in a Faraday cup (FC). Beam current is the current without any losses due to secondary and/or back-scattered electrons.

In quantification, normalization is typically turned off. When the total amount is in between 98-102 wt%, the analysis was done correctly.

Removing element labels from the WDS spectrum will automatically quantify these elements by EDS, using the EDS/WDS quant routine.

When running similar samples each time, the list with elements including all settings (like start eV, end eV, dwell time and more) can be stored as a scan list. Just opening this .cfg file is enough to have the same parameters back. See Figure 2, showing an example of a saved scan list for a Borosilicate glass analysis.



	Diffr	Start	End	Step	Dwl	Scan
	2	80	220	1.0	1.0	R
B	2	149	231	1.0	5.0	R
O	3	427	614	1.0	5.0	R
Na	3	954	1146	1.0	5.0	R
Na	4	953	1147	1.0	5.0	R
Al	4	1452	1520	1.0	5.0	R
Si	5	1680	1800	1.0	5.0	R

Figure 2: Scan list for Borosilicate glass

For running analysis on different positions, WDS multi-point (see Figure 3) could be used. Many stage positions can be put into the Table. WDS spectra will be measured automatically for all the elements and points selected in the set-up. In between each analysis location, the beam current in the Faraday cup can be measured automatically.

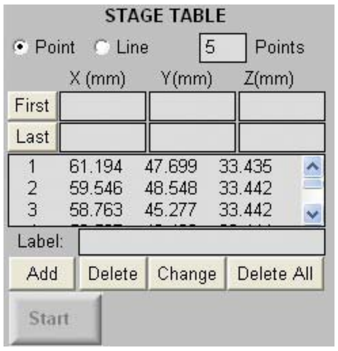


Figure 3: Multi-point for WDS analysis.

After the run, all spectra from the different stage positions can be read in and quantified in only 1 step, using the MultiQ button (see figure 4).

Figure 4: : Multi Quant button.

TSL 10th Year Anniversary

This year marks the 10th anniversary of EDAX's acquisition of TSL. TSL was founded in 1993 to commercialize a new microscopy technique called Orientation Imaging Microscopy (OIM™). OIM™ is based on the automated collection and orientation determination of Electron Backscatter Diffraction (EBSD) patterns for the analysis of texture, grain boundaries, and microstructure of crystalline materials within a Scanning Electron Microscope (SEM). Prior to this, texture information was typically collected with X-ray diffraction while grain boundary information was obtained using a TEM, although on a limited statistical basis. This new characterization capability in fact lead to the naming of TSL, which stands for TexSEM Labs, or Texture in the SEM Labs.

OIM™ is based on the thesis work of Dr. Stuart Wright, who is currently Director of Applications Science at EDAX. Stuart was a member of Dr. Brent Adams' research group at both Brigham Young University and Yale University. This group's work led to a Henry Marion Howe Medal award winning publication for the best paper in Metallurgical Transactions in 1993. Figure 1 shows the 1st OIM™ image ever collected from a deformed aluminum sample.

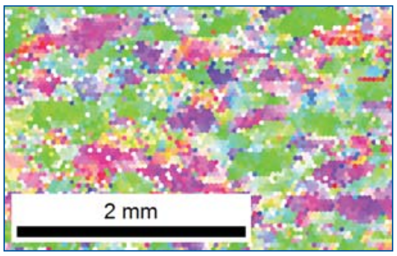


Figure 1 – First OIM™ image collected from a deformed aluminum sample.

Prior to acquiring TSL, EDAX had established a distribution relationship to offer TSL's PC based products in 1997. This collaboration helped to accelerate the transition away from the initial UNIX-based product offerings. The acquisition was formally completed in 1999. One of the priorities after the merger was to develop integrated EDS and EBSD products. This resulted in the 2000 introduction of EDAX's Pegasus product and in 2002, EDAX's patented ChiScan technology, which enables faster and more accurate analysis of multiphase materials. This advanced functionality is unmatched in the marketplace to the present day, a theme that is echoed in Figure 2.

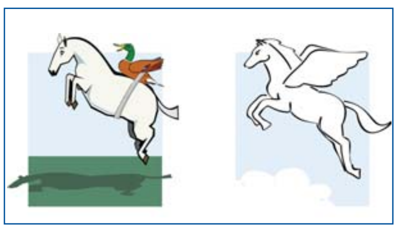
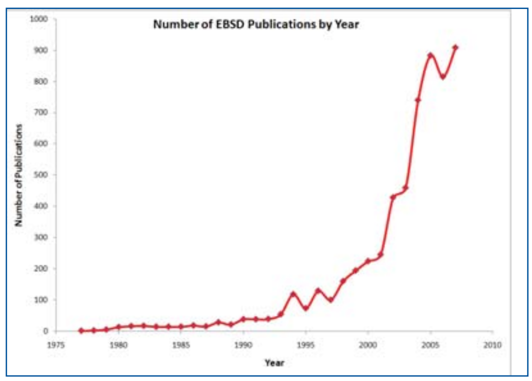


Figure 2 – Their Integration on the left, our integration on the right.

EDAX has also pioneered the development of high-speed EBSD detectors. With the introduction of the DigiView series of detectors in 2001, OIM™ was no longer limited by analog video frame rates. The debut of the Hikari camera in 2006 more than doubled the previous possible acquisition rate. Today the Hikari camera can collect and index more than 450 patterns per second. To put this in perspective, the 1st OIM™ shown in Figure 1 was collected at approximately 4 seconds per point, for a total collection time of 34 hours. Equivalent data could now be collected in just over a minute. Clearly this increase in data output has helped lead to the increased number of EBSD related publications over time, as shown in Figure 3.

Figure 3 – EBSD publication by year.



EBSD applications continue to grow, with applications to a wide range of materials: from meteorites to trilobites, solar cells to batteries, and nanometer scale pillars for deformation experiments to centimeter scale single crystals for turbine blades. As these applications continue to grow and develop, EDAX is committed to providing the best characterization tools available.

TRAINING AND EVENTS

World-Wide Events

October 18-22	Southern Association of Forensic Scientist (SAFS Fall)	Orlando, FL
October 25-29	MS&T (The Materials Science & Technology Exhibition) Formerly called ASM	Pittsburgh, PA
October 28-29	Fall 2009 California Associations of Criminalist (CAC Meeting)	San Jose, CA
December 1-3	MRS (Materials Research Society)	Boston, MA

***Please see our website, www.edax.com for a complete list of our tradeshows

World-Wide Training

To help our present and potential customers obtain the most from their equipment and to increase their expertise in EDS microanalysis, WDS microanalysis, EBSD/OIM and Micro-XRF, we organize a number of Operator Courses at the EDAX facilities in North America; Tilburg, NL; Wiesbaden, Germany; and Japan.

Europe

Tilburg = (T) (in English)
Wiesbaden = (W) (in German unless stated otherwise):

Microanalysis Courses: 3-4 Day

- ◆ November 17-26 (W)
- ◆ November 23-26 (T)

Microanalysis Courses: 2 Day

- ◆ November 12-13 (T)

LEX Course: 3 Day

- ◆ October 13-15 (T)

Pegasus Courses:

- ◆ October 19-23 (W)

Japan

Microanalysis Courses:

- ◆ October 7-9 Tokyo
- ◆ November 11-13 Osaka

For more information on our training classes, please visit our website at: **www.edax.com/service/user.cfm**

North America

Microanalysis Courses:

- ◆ October 19-23 Mahwah, NJ
- ◆ December 7-11 Mahwah, NJ

Particle Course:

- ◆ November 10-12 Mahwah, NJ

EBSD OIM™ Academy Course:

- ◆ October 13-15 Draper, UT

Micro-XRF Course:

- ◆ October 6-8 (Orbis only)

Paul Pomykala joined North American Philips Lighting Corporation (Lustra Lighting) in November, 1974 working in the Mail Room/ Print Shop. In the mid 1980's the company moved from East Rutherford, NJ to Hightstown, NJ. An opportunity opened in Philips Electronic Instruments (PEI), Mahwah for a Printing Press Operator and Paul transferred to the new position. After gaining experience he eventually advanced to Print Shop Supervisor. Years later, EDAX moved their clean room from Prarie View, IL. to Mahwah, NJ and the print shop was closed in order to build a clean room. At that time an opening developed in the Engineering Department for a blueprint operator. Paul took the position, which has evolved into his current position as Engineering Services Administrator.

Paul's responsibilities include engineering document control, which encompasses processing Technical Non-Standard Requests, Production Releases, Engineering Change Notices and Part Substitutions. Other responsibilities are entering new part numbers and Bills of Materials into the database. Paul also maintains the Engineering Scans database to insure that all the latest electronic scanned drawings are available to users. During his career at EDAX he has received Instant Quality Recognition Awards as well as the Presidents Award for Excellence.

Paul has been married to his wife Elfi for 30 years and they have two sons, Paul Jr. (23) and Michael (21). Paul Jr. is currently a senior at Montclair State University, studying education, while Michael is attending The University of Sciences in Philadelphia pursuing a career as a PhD in physical therapy.

Some interests Paul pursues include traveling with his wife Elfi, and fishing on the St. Lawrence River in upstate NY, where he has a small boat and trailer. He also enjoys walking, biking, and following the sports world.

Harrie van der Putten is based in the office of EDAX in Tilburg, the Netherlands. As a Sales Manager for EDAX B.V., he is responsible for the sales of all EDAX products in the Benelux region and since the beginning of this year he is now also responsible for the Micro XRF product range all over Europe. Harrie was born and raised in Helmond near Eindhoven in the Netherlands and holds a degree in analytical chemistry.

Harrie began his career with EDAX in March 2000 after he had worked for Philips Research and also for several years in technical sales with ASM Lithography, Promosol and Metron Technology in particular in the semiconductor industry. His early focus at EDAX was concentrated on the sale of the EDAX EDS Microanalysis products in the Benelux, along with the products of Gatan that EDAX Europe was selling as a distributor in those days. Harrie has seen the EDAX product range expand rapidly over the years with new products in EDS, WDS, EBSD and EDXRF. He enjoys meeting with customers to listen to their requirements and works hard to fulfill their needs.

Harrie lives with his wife Marjolein and son Niek in the town of Deurne, which is close to the city of Eindhoven in the Netherlands. In his spare time, he enjoys playing tennis with friends and listening to music.

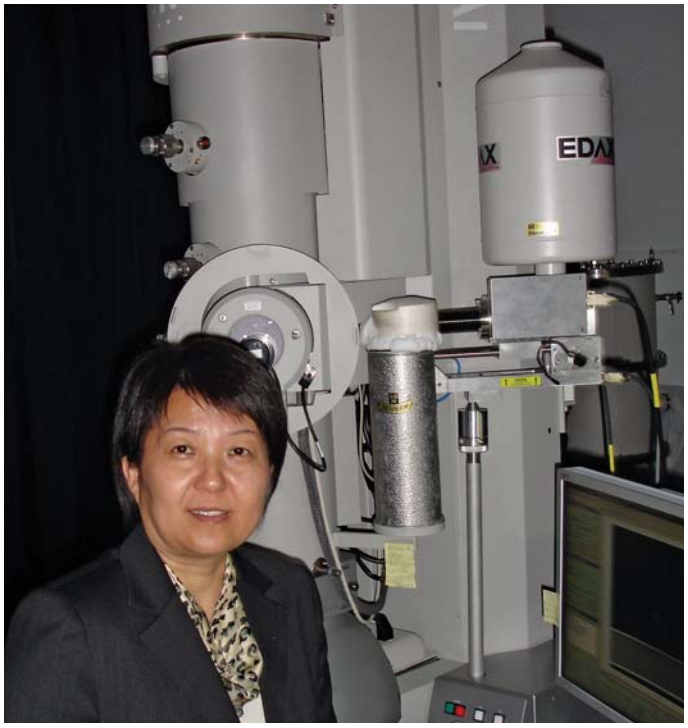
Materials Analysis Technology Inc. (MA-tek), Taiwan

The company MA-tek, head quartered in Hsinchu, Taiwan, was established in 2002 to provide analytical services to many semiconductor and storage media manufacturers in the area, including IC, TFT-LCD, LED, MEMS, solar cell, nano devices/materials, and advanced research in academic fields. .

The CEO of MA-tek, Dr. Hsieh, explains, "Many of the bigger semi and disk drive companies around here have their own analytical capabilities, like SEM and EDS, however, very few have TEM or Dual Beams, FIB, SIMS and XPS. We have invested in all of these expensive tools and also in well experienced people to use the tools to their fullest capabilities".

Since their start in 2002, MA-tek has grown and now has 140 employees in four locations in Taiwain. In the past year, MA-tek has also added a service laboratory in Shanghai. They currently see an increased amount of samples being sent to them from the USA and Europe. Dr. Hsieh continues, "We have noticed that our business model of offering the best of tools as well as operators and extremely fast turn-around makes us competitive with service labs that are more local to customers far away from Taiwan. The fact that we can keep very reasonable pricing and excellent services also helps".

Besides growing internationally, MA-tek is also growing the services they offer. This means investing in new tools and getting trained operators to run them. To handle the guaranteed turn-around-time of 24 hours for complete sample analysis, MA-tek run three shifts. This also helps to maximize the utilization of the advanced analysis tools as well as being able to communicate live with customers around the globe.



The five MA-tek locations have in total nine EDAX EDS systems, three of which are on TEMs and six on SEMs. Dr. Hsieh adds, "Our business model requires us to have the very best tools. This means that we simply can not tolerate down time. Performance, at the same time, must be at the highest level available. EDAX is our choice for EDS and has lived up to the high expectations we must have to be successful".

For more information on MA-tek, please visit their website at www.ma-tek.com.

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