COVALENT
METROLOGY

Welcome

ADVENTURES IN WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE (WDXRF): FLEXIBLE ELEMENT ANALYSIS FOR THIN FILMS AND MORE

SPEAKER:

Meredith Beebe
Semiconductor X-ray
Metrology Specialist,
Rigaku

January 27, 2022 | 11am PT

Rigaku

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Advancements in
Instrumentation Series

Episode 29

COVALENT METROLOGY

Silicon Valley-based analytical labs and platform delivering quality data and expert analysis for advanced materials and device innovation

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Who We Are, Who We Serve

500+ Clients, 40-60 Added / Quarter

50+ People, 14 PhDs

Cutting-edge Analytical Capabilities

Lab Location: Sunnyvale, CA

Covalent Technical Groups and Organization

PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis

- DPA / Mechanical Cross-section
- Dye & Pry Test
- EBIC / OBIC failure analysis
- Hot Spot Detection
- IR Imaging / Emission Microscopy
- NIR Imaging
- Root-Cause Failure Analysis

Electron Microscopy and Scanning Probe Microscopy

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM)
- Scanning Acoustic Microscopy (SAM)
- SEM (+ EDS)
- FIB-SEM (+ EDS)
- S/TEM (+ EDS / + EELS)
- Nano-indent / Nano-scratch

Optical Microscopy & Spectroscopy

- Chromatic Aberration
- Digital Optical Microscopy
- FTIR and ATR-FTIR
- Laser Scanning Confocal Microscopy
- Spectral Ellipsometry
- UV-Vis-NIR Spectroscopy
- White Light Interferometry

X-Ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micron-spot ED-XRF
- WDXRF
- Micro-computed X-ray Tomography (Micro-CT)
- 2D X-ray Inspection & X-ray Radiography

Elemental / Chemical Composition Analysis

- EPMA
- GD-OES
- GC-MS
- ICP-MS and LA-ICP-MS
- Raman Microscopy & Spectroscopy
- NMR (1D or 2D; solid / liquid)

Particle Analysis

- Dynamic Light Scattering (DLS)
- Laser Diffraction Particle Size Analysis (PSA)
- Particle Zeta Potential

Material Property Characterization

- DSC
- DMA & TMA
- Rheometry
- TGA
- Surface Zeta Potential
- Porometry / Porosity
- Gas Adsorption
- Gas Pycnometry
- Foam Density
- Tap Density

Surface Spectroscopy Analysis

- Dynamic-SIMS
- ToF-SIMS (Static-SIMS)
- Ion Scattering Spectroscopy (ISS)
- Ultraviolet Photoelectron Spectroscopy (UPS)
- X-ray Photoelectron Spectroscopy (XPS)

Covalent Partners

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- Partnership announced Fall, 2018
- Covalent is home to Rigaku's
  Silicon Valley Semiconductor Division Metrology Lab:
  - SmartLab XRD / XRR with full set of optics + heated stage
  - CT Lab HX 130 X-ray Micro-CT
  - AZX 400 WDXRF with 200 mm and 300 mm cassettes / FOUP (in clean booth)

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Introducing

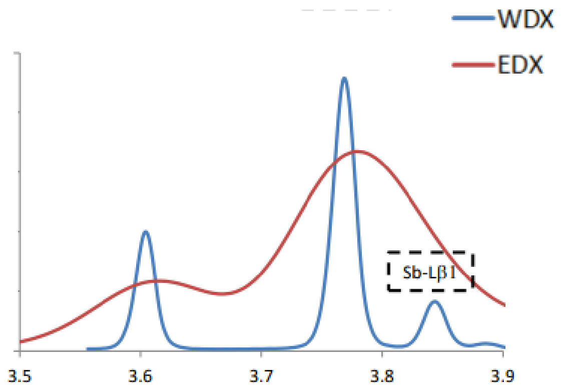
Meredith Beebe

Semiconductor X-ray Metrology Specialist,
Rigaku

- Over 20 years in semiconductor industry spanning roles both as an end user in the fab (as a process characterization engineer) and as an applications expert for multiple vendors
- Subject matter expert known across the industry for trace metal and contamination analyses employing X-rays, VPD-ICP-MS, SIMS, AFM, and Auger
- Provides a platform to address ever-changing metrology demands for yield improvement and advanced device development
- Helps Rigaku customers to understand and develop improved strategies for contamination monitoring, metrology optimization, and she provides key insights from direct customer experience to contribute to Rigaku's leadership in X-ray metrology

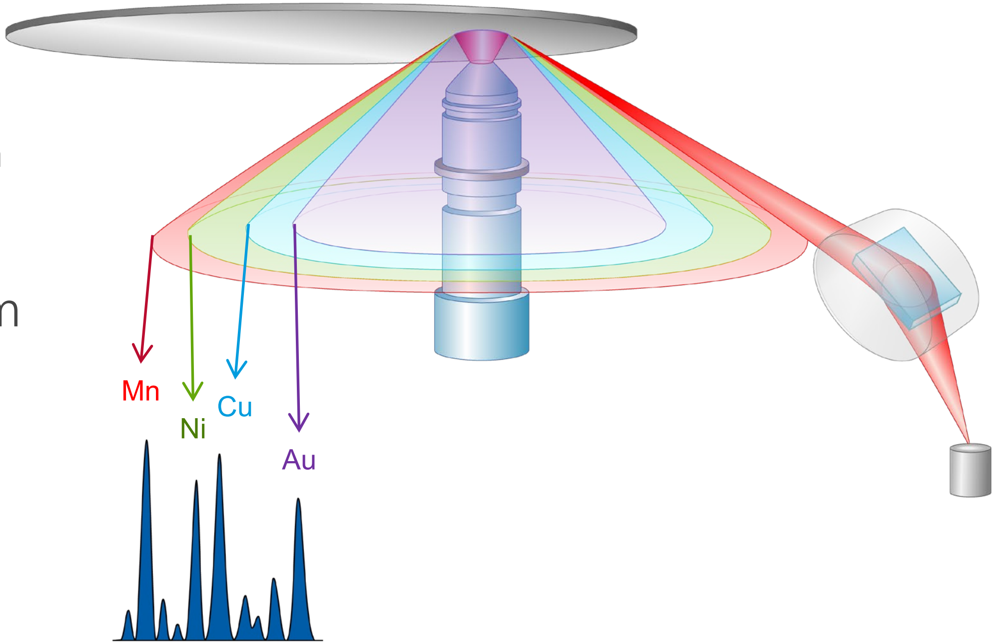
OUTLINE

- WDXRF technique overview
  - Principles of X-ray fluorescence
  - Sequential and simultaneous spectrometers
  - Qualitative and quantitative methods
  - Comparison of WDXRF to EDXRF
- Rigaku AZX 400 spectrometer overview
- Application studies
  - PZT
  - Sputtering target
  - MRAM
- Summary/Q&A

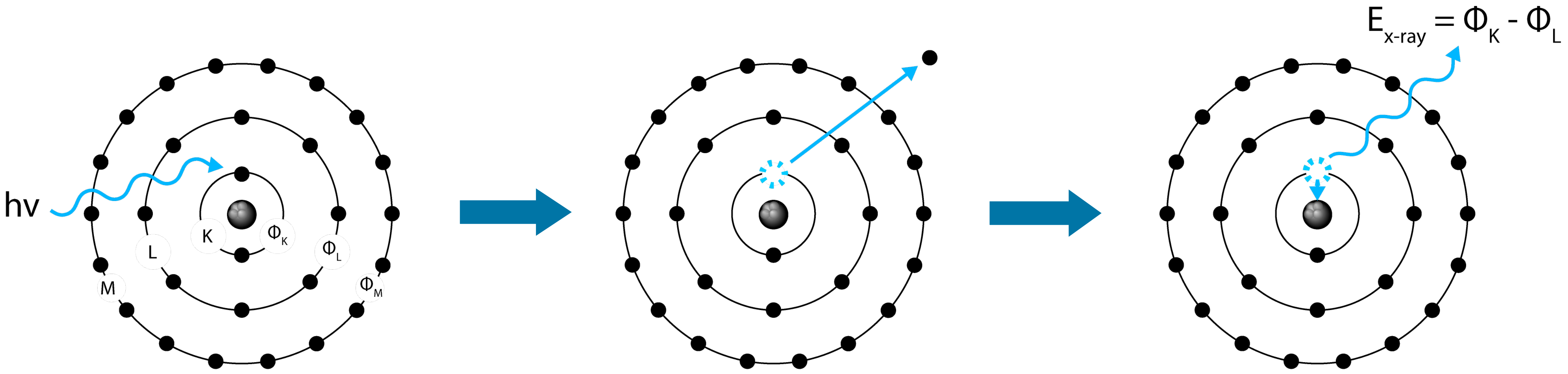


FLEXIBILITY OF RIGAKU’S AZX 400 WDXRF

- Non-destructive detection of a wide range of elements from Be-U
  - Example application– MRAM
  - Particularly suited to light elements such as boron through aluminum
  - Ultra-thin MgO film @ 1 nm
- Flexible sample handling supporting enterprise needs from process R&D to manufacturing
  - Example application– Sputtering target
  - Multiple sample adaptors allow for various shapes and sizes of coupons, targets, and wafer samples
  - Sample size range up to 380 mm
- Film thickness measurements from angstroms to microns
  - Example application– PZT
  - High-precision measurements



BASIC PRINCIPLES OF X-RAY FLUORESCENCE



$$E_{x\text{-ray}} = \Phi_K - \Phi_L$$

X-ray (high-energy photon) is directed at the sample.

Incident X-ray with sufficient energy ejects an electron from an atom leaving a vacancy.

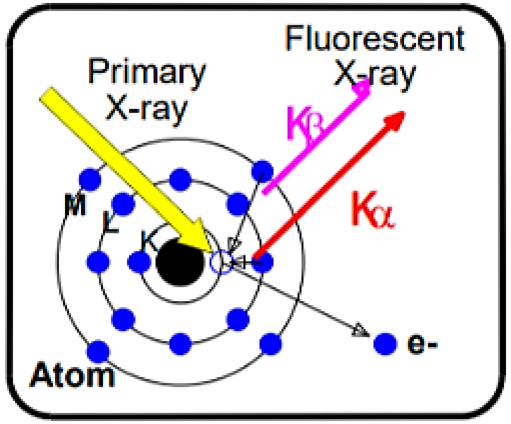
This vacancy puts the atom in an unstable excited state with a higher energy.

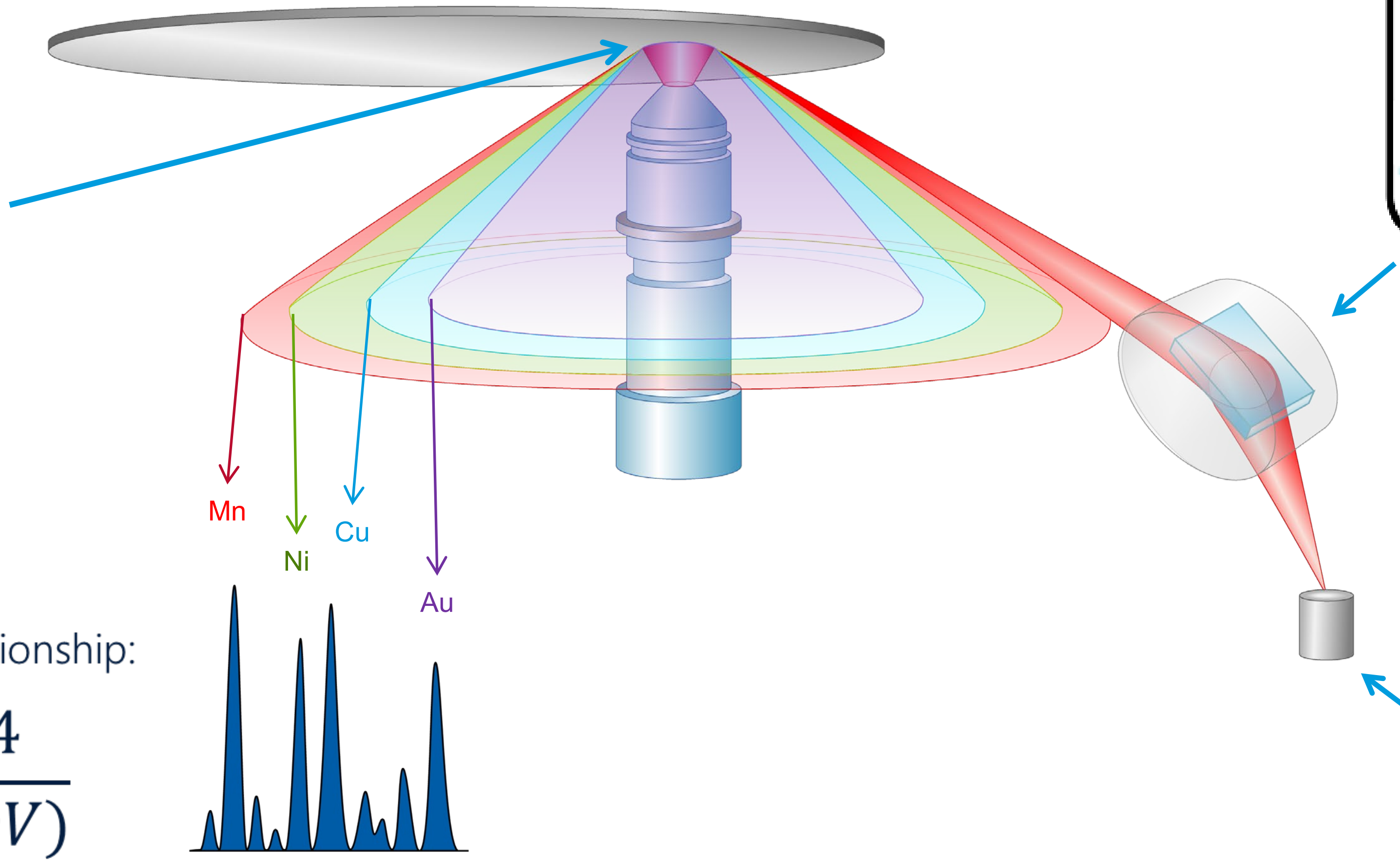
Atom relaxes to restore to its original configuration. It transfers an electron from an outer shell to the lower energy level to fill vacancy.

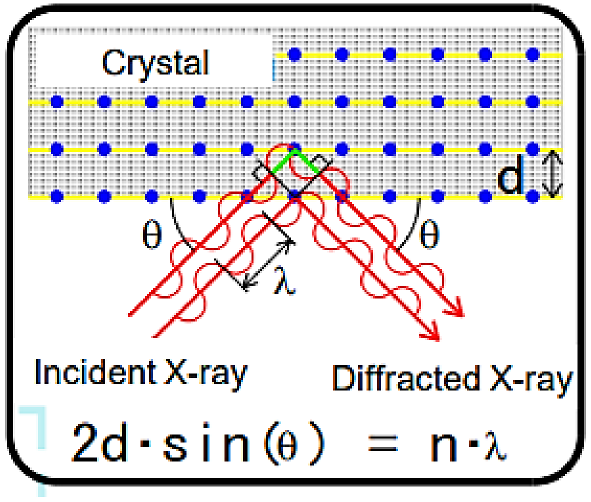
The replacing electron loses energy, which is radiated as X-rays of a characteristic energy.

The intensity of fluorescent X-ray photons is proportional to a given element.

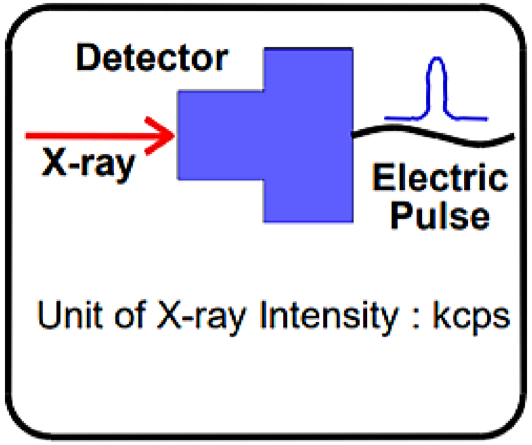
FUNDAMENTALS OF WDXRF







$$2d \cdot \sin(\theta) = n \cdot \lambda$$

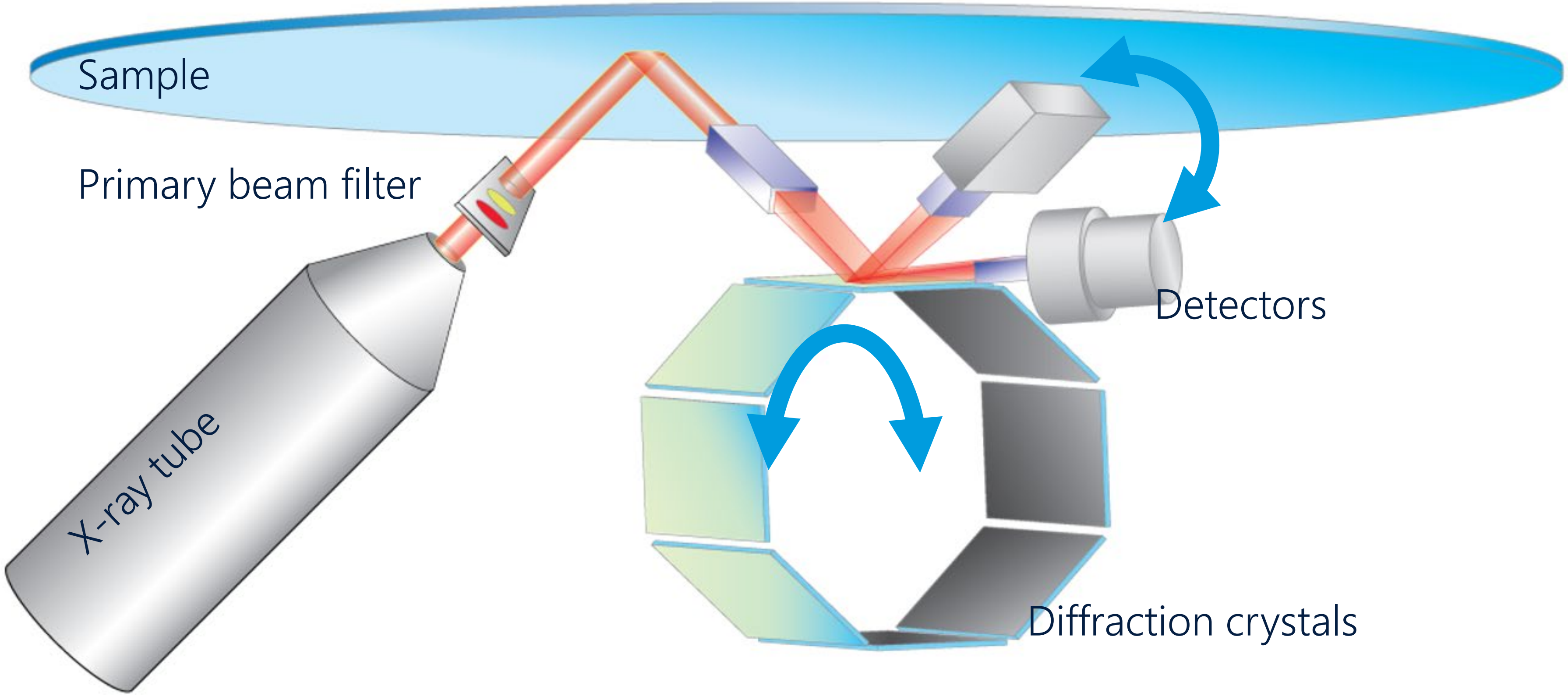


Unit of X-ray Intensity : kcps

Wavelength-energy relationship:

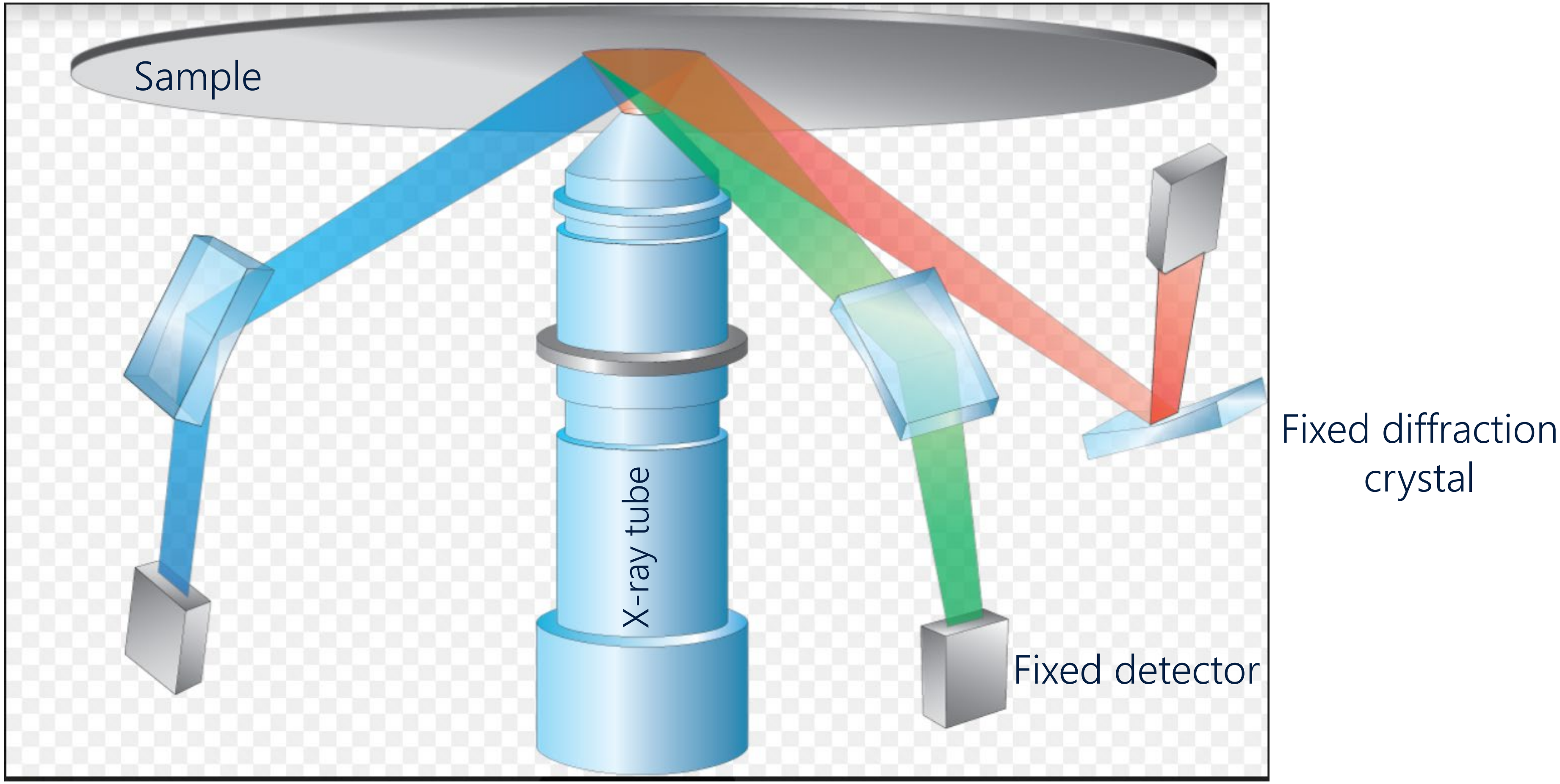
$$\lambda\ (\text{Å}) = \frac{12.4}{E\ (keV)}$$

SEQUENTIAL WDXRF



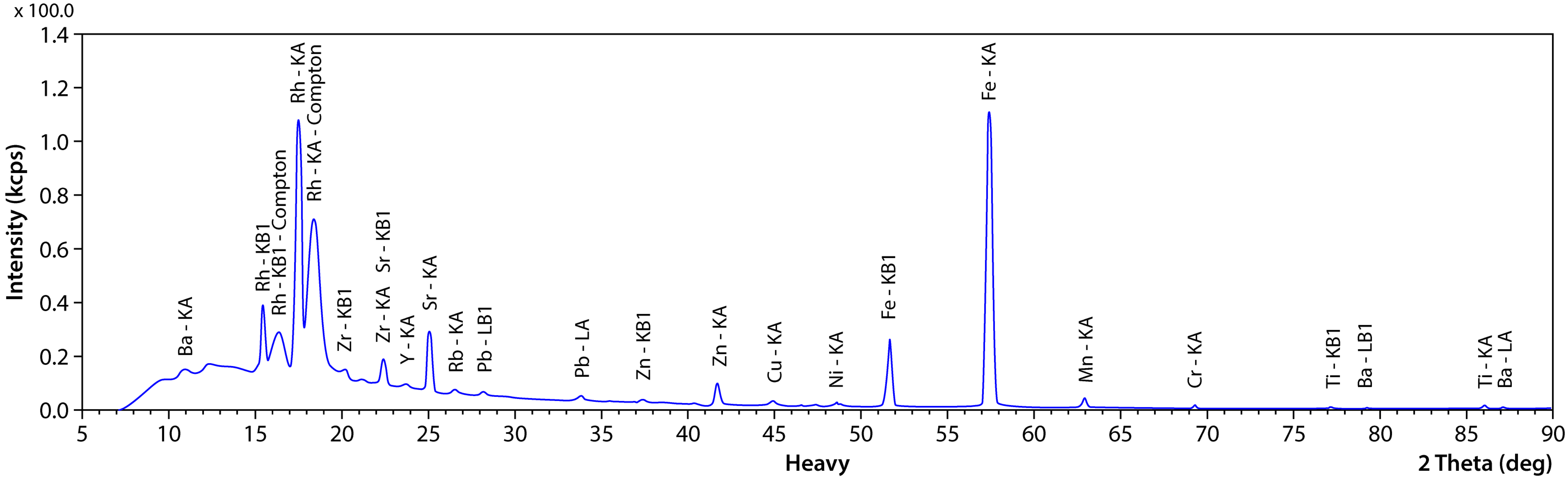
Sequential spectrometers use a moving detector on a goniometer to move through an angular range to measure the intensities of many different wavelengths.

SIMULTANEOUS WDXRF



Simultaneous spectrometers are equipped with a set of fixed detection systems, where each system measures the radiation of a specific element.

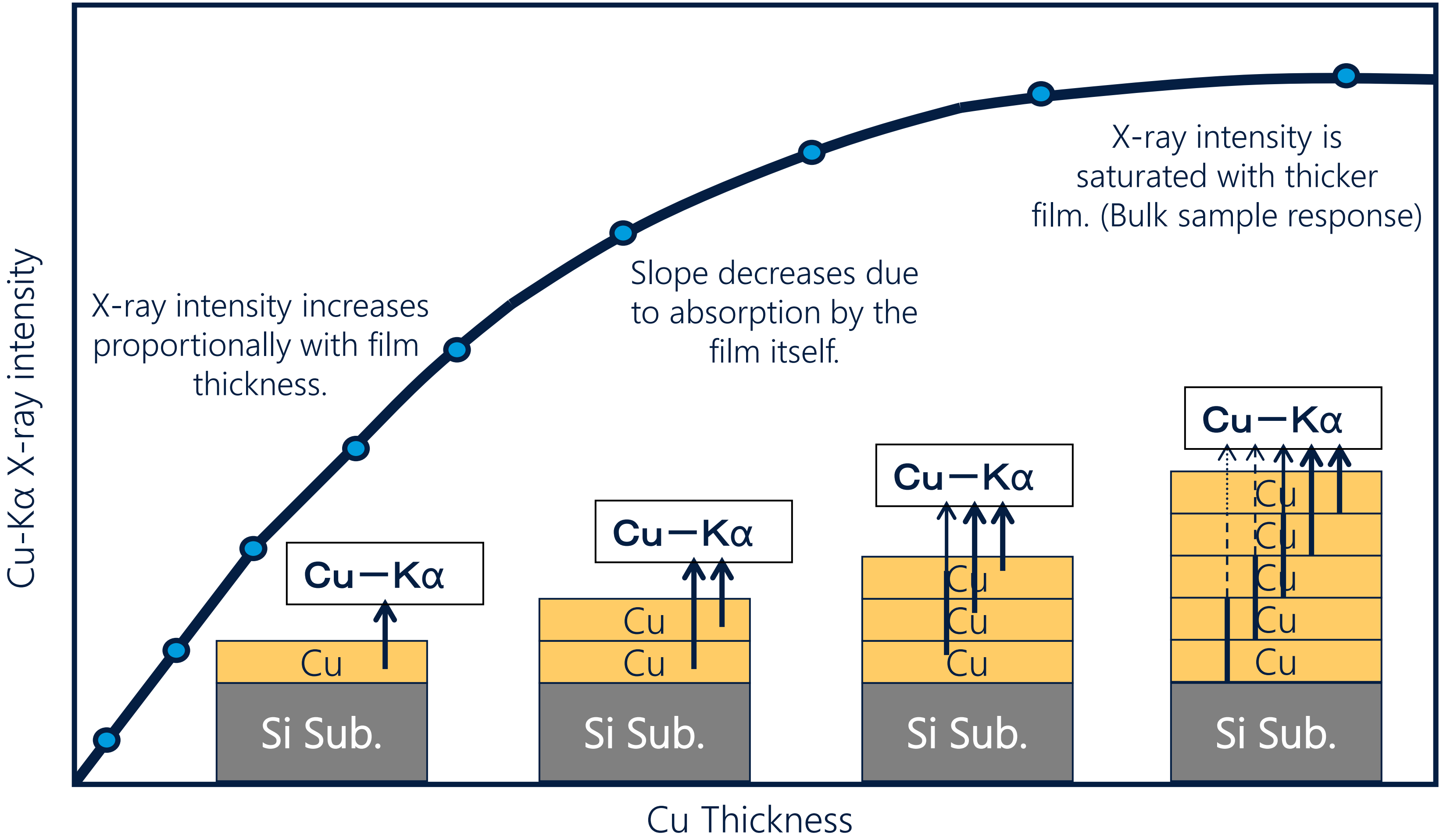
QUALITATIVE SCANS



Non-quantitative scans of elements across the periodic table can be set up to identify elements present in the sample

FILM THICKNESS AND X-RAY INTENSITY

Film thickness is obtained by calibration based on the relationship between thickness and X-ray intensity.

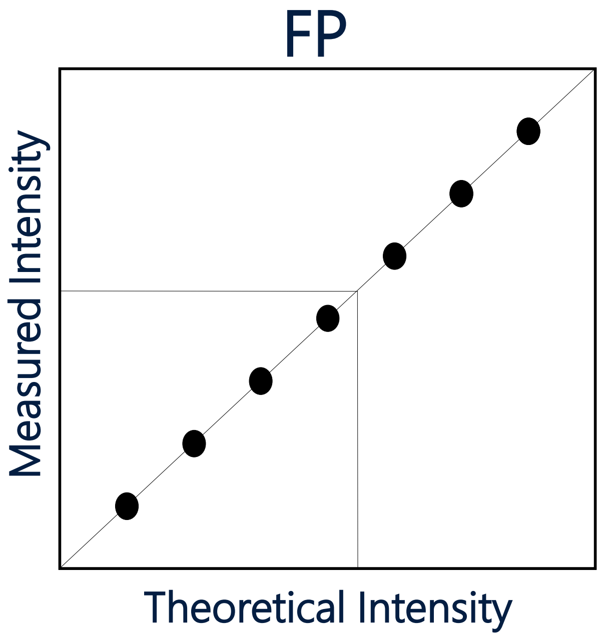


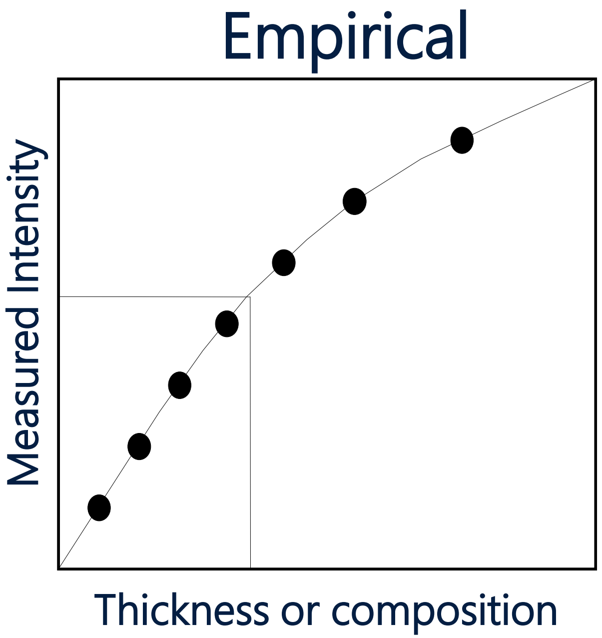
QUANTITATIVE METHODS

Standardization models to address thin film and bulk samples

- Fundamental parameter (FP)
  - Pure element or “type standards”– quantitative
    - Type standards are similar in composition to “unknowns” to be measured
    - Improves accuracy of FP calibration
  - Library standards– semi-quantitative
    - Computer-stored calibration parameters
    - Helpful when calibration standards are not available
  - Density is important for determining linear thickness
- Empirical models
  - Relies on a suite of calibration standards covering the range and thickness values expected of “unknown” product

FP AND EMPIRICAL CALIBRATIONS

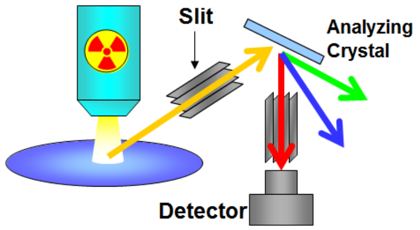
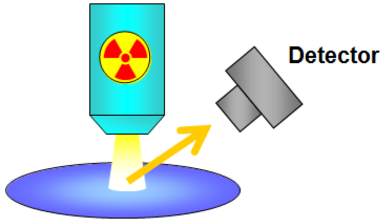




- Theoretical vs measured intensity
- Theoretically linear
- Thickness and composition analysis can be done simultaneously with multiple layers
- Few standards are enough, pure metals can be used

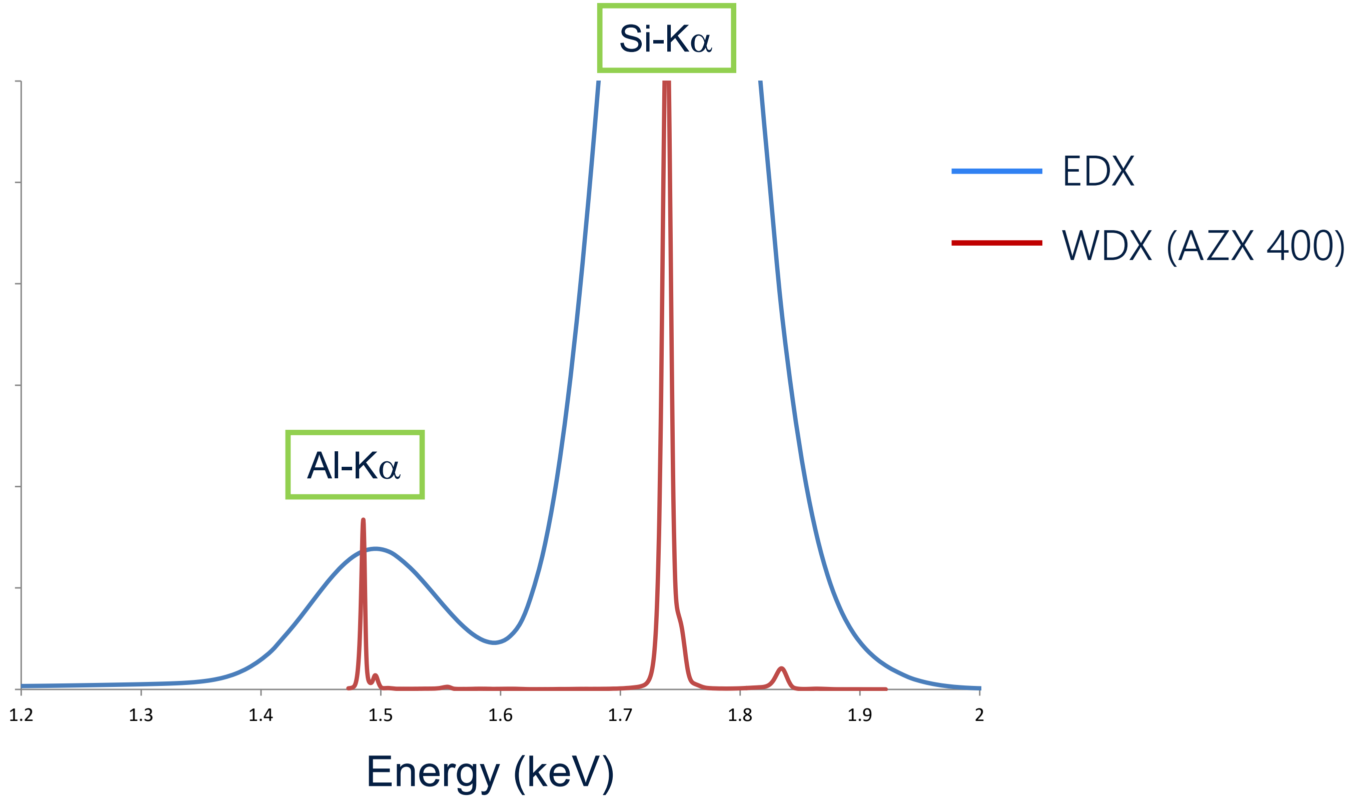
- Measured intensity vs standard value
- Not usually linear
- Analyzes only thickness or composition
- Range of standards necessary for each element, thickness, and composition

WDXRF AND EDXRF COMPARISON

	WDXRF	EDXRF
System Set-up		
Measurable Elements	Be - U	Al - U
Quantitative Method	**Advanced FP Method is available** FP method enables thickness and composition analysis with one recipe.	**Usually Empirical Method** Empirical method cannot analyze thickness and composition simultaneously and requires a range of standards for thickness and composition calibration.
Analyzable Structure	**Multiple stacked layers can be analyzed** FP method considers absorption effects of other layers and can analyze complex compounds and multi-layered samples.	Single layer or A few layers of simple structure
Analyzable Thickness	< 1 nm or more	10 nm or more

RESOLUTION COMPARISON OF WDXRF AND EDXRF

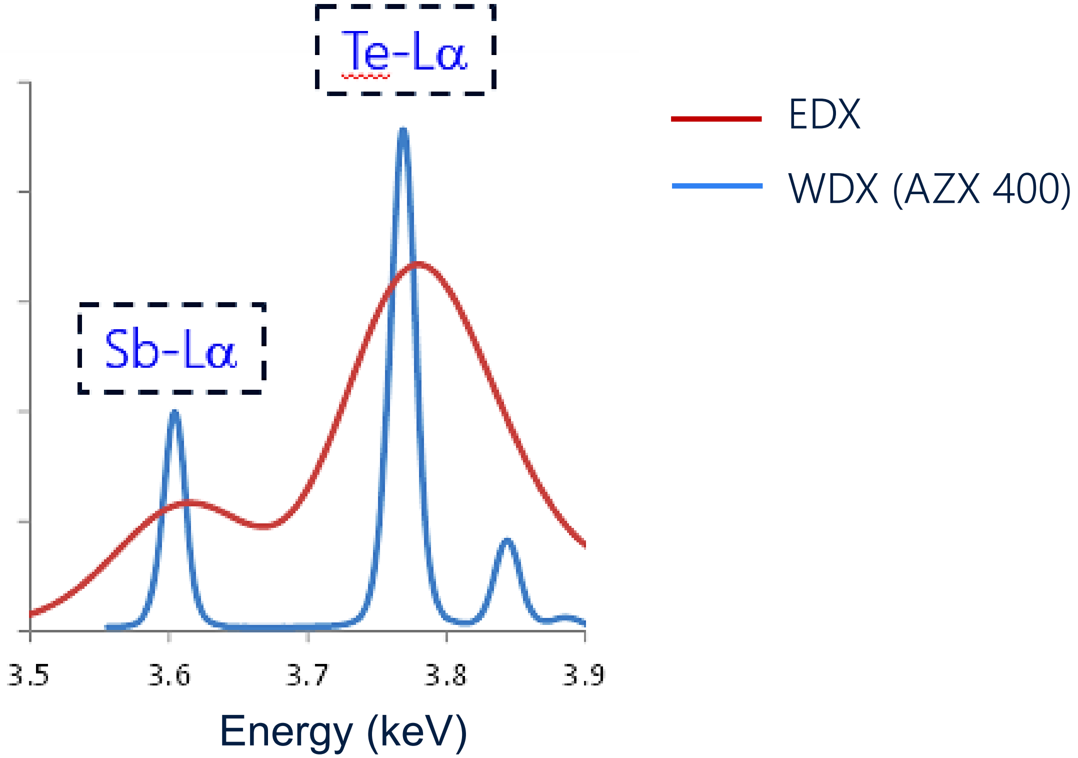
1 µm Al film



WDXRF can clearly resolve the Al-Ka peak (1.487 keV) without influence from the substrate Si-Ka peak (1.740 keV).

RESOLUTION COMPARISON OF WDXRF AND EDXRF

GST film with Ge, Sb, and Te



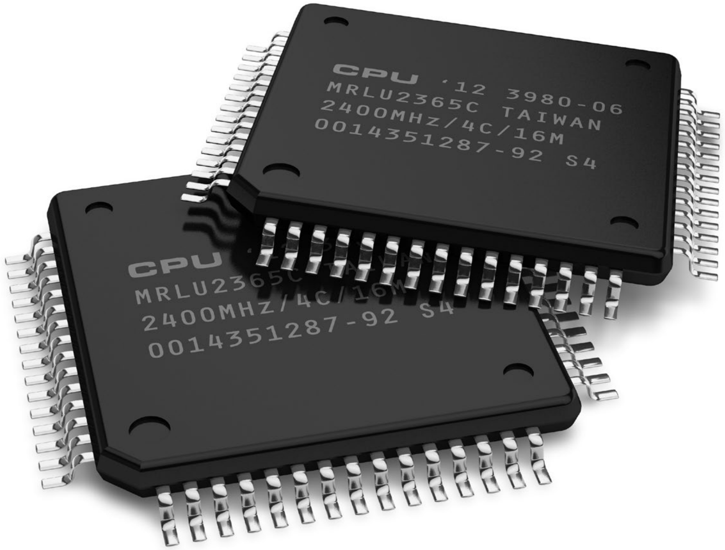
Clear separation of Sb-La (3.606 keV) and Te-La (3.770 keV) peaks in GST film with WDXRF.

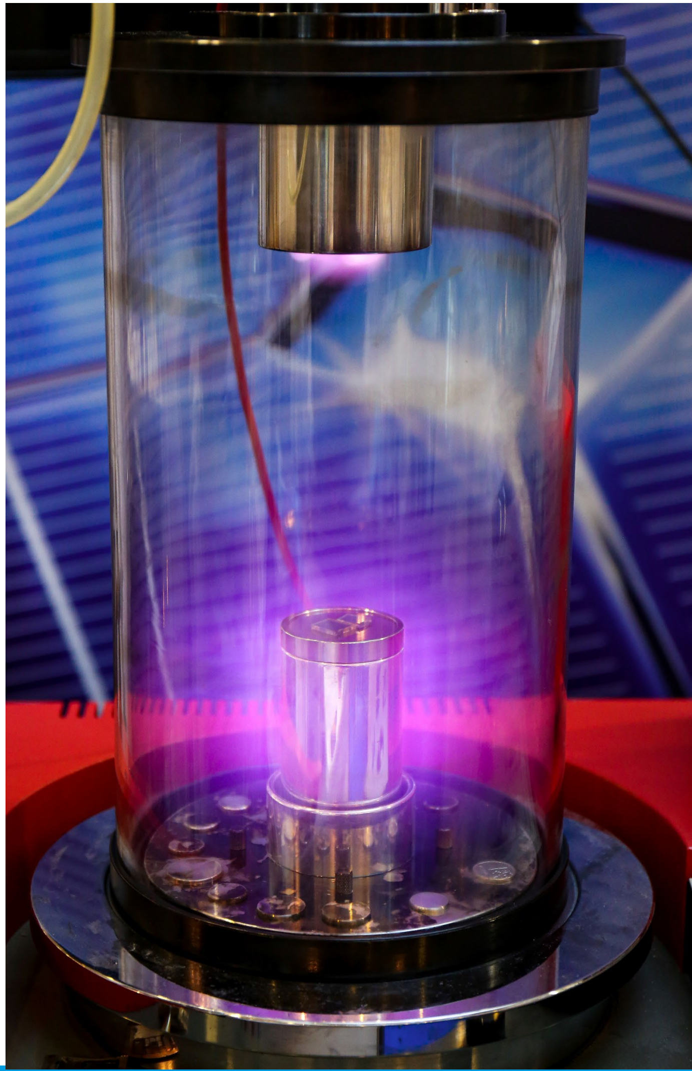
SEQUENTIAL WAVELENGTH DISPERSIVE XRF RIGAKU AZX 400

- 4 kW sealed X-ray tube, sequential type goniometer, primary beam filter; Measurement spot sizes 30, 20, 10, 1, and 0.5 mm in diameter
- Flexibility to measure a variety of sample types, including 50 - 300 mm wafers, coupons, and sputtering targets. Auto wafer loader option available.
- Analyzes elements from Be to U with a range from ppm to % or thickness range of Å to μm
- Well-suited for process R&D and low-volume, high product mix environments
- SEMI and CE compliant with a small footprint, 1376 (W) x 1710 (H) x 890 (D) mm

3 DIFFERENT APPLICATIONS OF WDXRF

- MRAM
- Sputtering target
- PZT

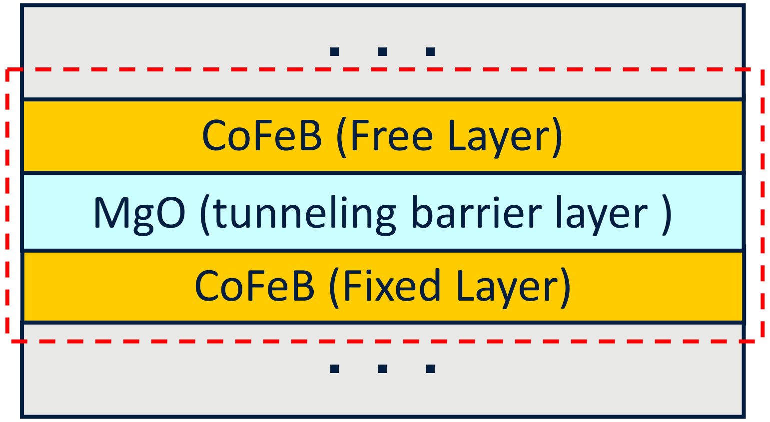




APPLICATION 1: MRAM

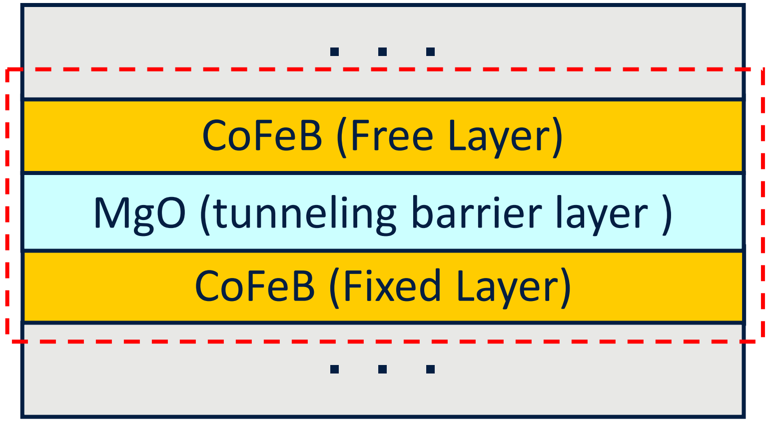
Magnetoresistive random access memory

- MRAM is a non-volatile random-access memory which stores data in magnetic domains.
- Faster writing speeds and re-writing times than flash memory.
- MRAM basic structure is a magnetic tunnel junction (MTJ).



MTJ structure consists of two ferromagnetic (FM) layers separated by an insulating tunnel barrier.

APPLICATION 1: MRAM



Good adventure for WDXRF	
✓	MTJ structure has light elements of Mg and B.
✓	High elemental resolution necessary to separate overlapping peaks.
✓	High precision required for thickness and composition repeatability measurements

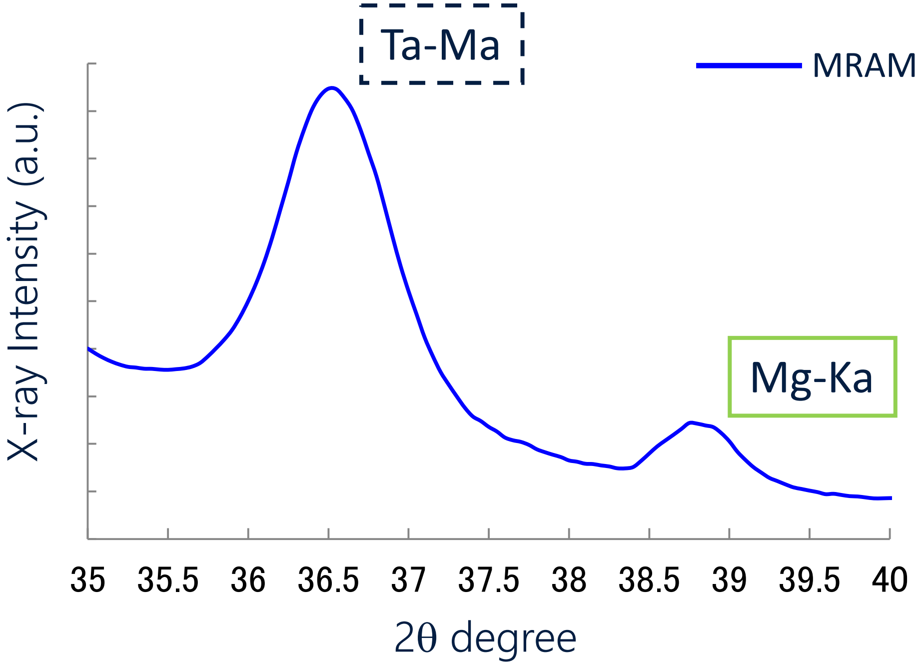
- Thickness and composition monitoring of each layer are necessary quality controls for manufacturing.

ANALYSIS OF MgO LAYER

Ta layer is often used as a cap and/or barrier around the MTJ structure.

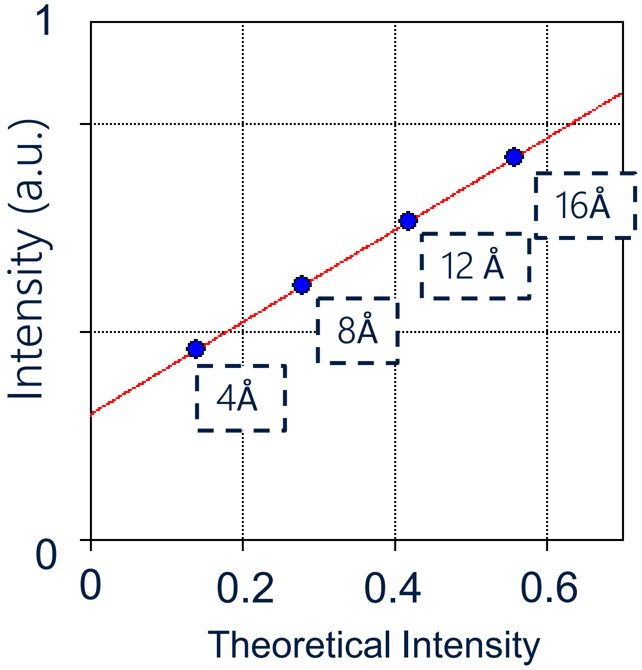
In this case, the Ta-Ma peak that is near Mg-Ka (1.254 keV) is fully resolved.

With EDXRF, the Mg-Ka peak can overlap with the high background of Si-Ka (1.74 keV) and Ta-Ma (1.77 keV).



ANALYSIS RESULTS OF MgO LAYER

FP calibration of Mg



10 times measurement of each sample

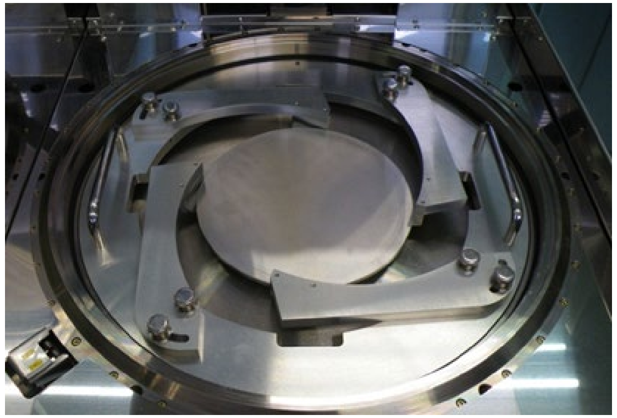
	MgO Thickness			
Target Thickness	0.4	0.8	1.2	1.6
Unit	Nm			
Data No.	10	10	10	10
AVERAGE	0.40	0.80	1.20	1.60
MAX	0.40	0.81	1.21	1.61
MIN	0.39	0.80	1.20	1.60
RANGE	0.01	0.01	0.01	0.01
Std. Dev.	0.0035	0.0042	0.0046	0.0052
R.S.D. (%)	0.88	0.52	0.39	0.32

WDXRF FP calibration of ultra-thin Mg thickness range from 4-16 Å.

This technique can see 1 Å steps and ultra-thin thicknesses of 5 Å, which can be difficult for other methods.

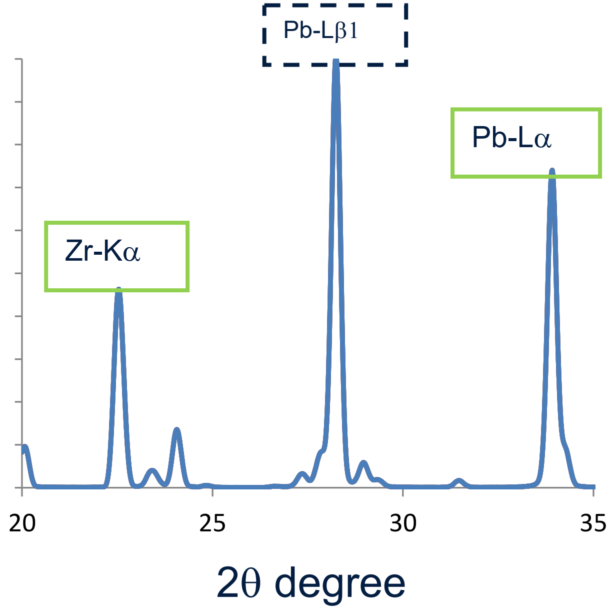
APPLICATION 2: SPUTTERING TARGET ANALYSIS

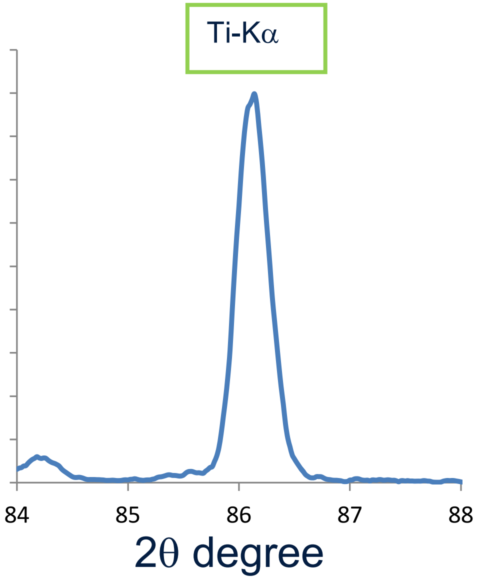
- Sputtering targets are used to create thin films in sputter deposition tools.
- Composition and trace element detection is important to manufacturers.
- Stoichiometry of target composition can change with use

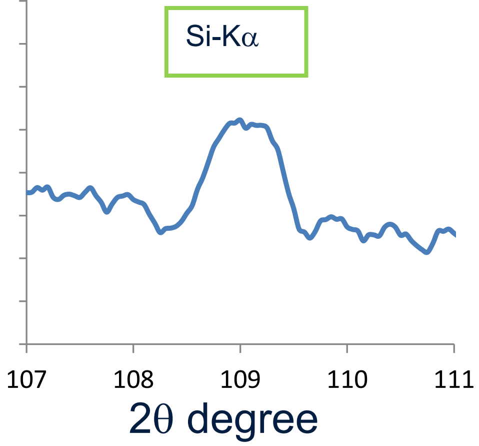


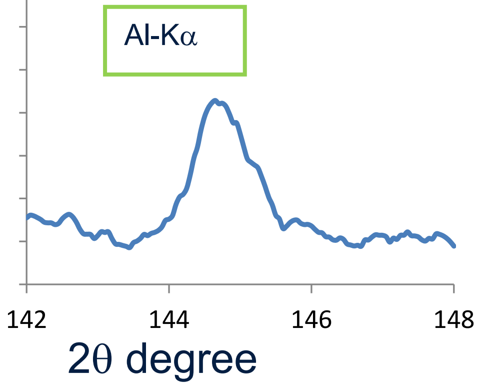
Good adventure for WDXRF	
✓	Non-destructive and no sample prep needed for analysis
✓	Wide elemental range (Be-U) for various sputtering target materials
✓	Library standards can be used if standards are not readily available
✓	AZX 400 can accommodate large target samples or wafer samples from sputter target deposition

TARGET QUALITATIVE SCAN









Huge peaks are observed for Pb, Zr, and Ti dominant elements.

AZX 400 primary filters are used in analysis to suppress the background and high X-ray intensity for these elements and avoid counting loss errors for Pb and Zr.

This target also had trace amounts of Si and Al.

TARGET REPEATABILITY MEASUREMENT

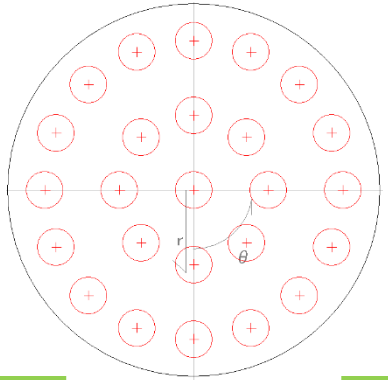
Component	PbO Comp.	ZrO2 Comp.	TiO2 Comp.	SiO2 Comp.	Al2O3 Comp.
Unit	mol%	mol%	mol%	mol%	mol%
Data No.	10	10	10	10	10
AVERAGE	54.798	23.407	21.659	0.087	0.050
MAX.	54.849	23.438	21.722	0.089	0.053
MIN.	54.758	23.373	21.575	0.082	0.048
RANGE	0.091	0.065	0.147	0.007	0.005
Std. Dev.	0.025	0.023	0.041	0.002	0.002
R.S.D.(%)	0.05	0.10	0.19	2.65	3.05

Table: 10 times measurement of center point

Element Spectrum	Pb La	Zr Ka	Ti Ka	Al Ka	Si Ka
kV-mA	50kV – 60mA			30kV – 100mA	
Primary Filter	*F-Cu	*F-Cu	*F-Sn	OUT	OUT
Diameter	20 mm				
Slit	S2	S2	S2	S4	S4
Analyzing Crystal	LiF1	LiF1	LiF1	PET	PET
Detector	SC	SC	SC	F-PC	F-PC
Counting Time (s) Peak	10	10	10	20	20
Background	5	5	5	10	10

*Usually, primary filters are used to reduce the diffraction interference, but for this measurement they were used to reduce background and high intensity.

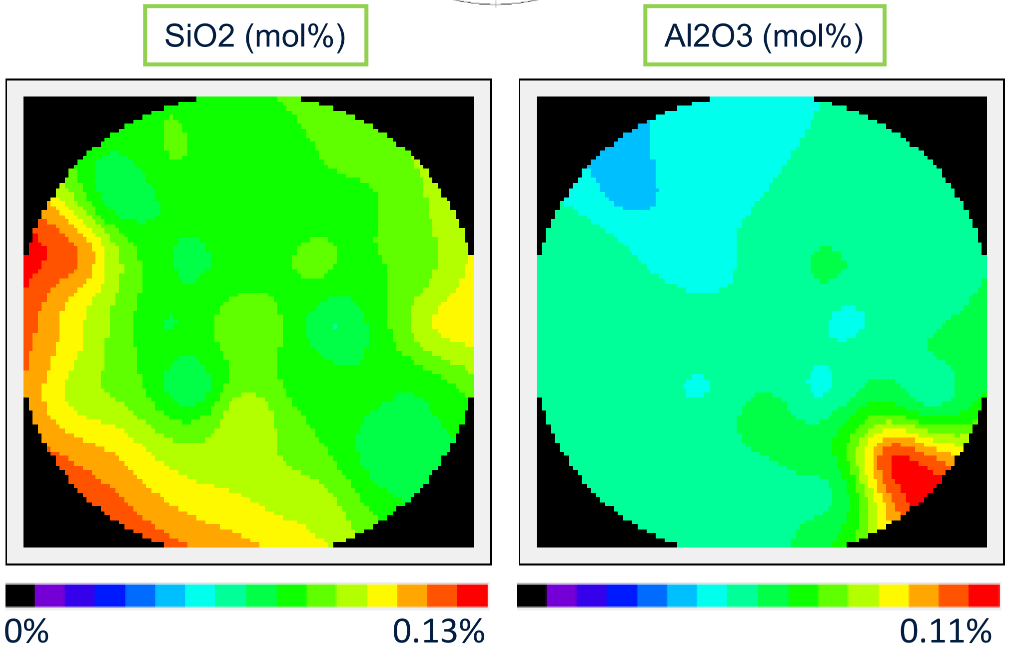
25 PT MAPPING ANALYSIS



25 pt map

Component	PbO Comp.	ZrO2 Comp.	TiO2 Comp.	SiO2 Comp.	Al2O3 Comp.
Unit	mol%	mol%	mol%	mol%	mol%
Data No.	25	25	25	25	25
AVERAGE	54.782	23.427	21.654	0.085	0.053
MAX.	54.888	23.480	21.860	0.112	0.099
MIN.	54.620	23.353	21.501	0.065	0.040
RANGE	0.268	0.127	0.359	0.047	0.059
Std. Dev.	0.064	0.034	0.090	0.013	0.011
R.S.D.(**%**)	0.12	0.14	0.41	15.49	19.96

Table: 25-point mapping test

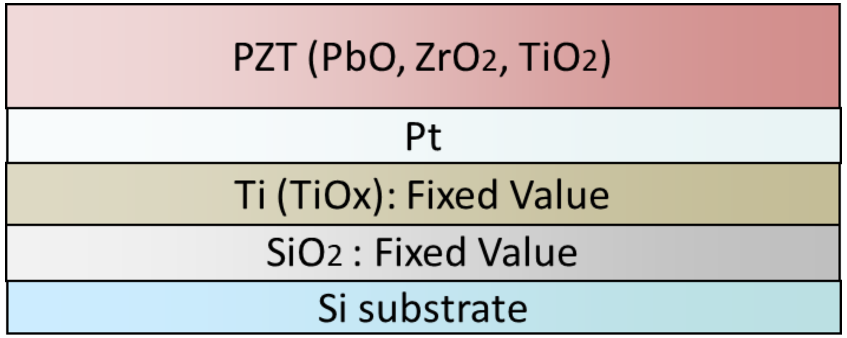


Maps of the trace SiO2 (mol%) and Al2O3 (mol%) detected

APPLICATION 3: PZT, LEAD ZIRCONATE TITANATE

(Pb[Zr(x)Ti(1-x)]O3)

- Piezo-electric material is in various sensors and MEMS devices in ink-jet printers, gyroscopes, mirrors for wearable devices, and more.
- Both the PZT thickness and composition are critical to device performance.



PZT (PbO, ZrO_2, TiO_2)

Pt

Ti (TiOx): Fixed Value

SiO_2 : Fixed Value

Si substrate

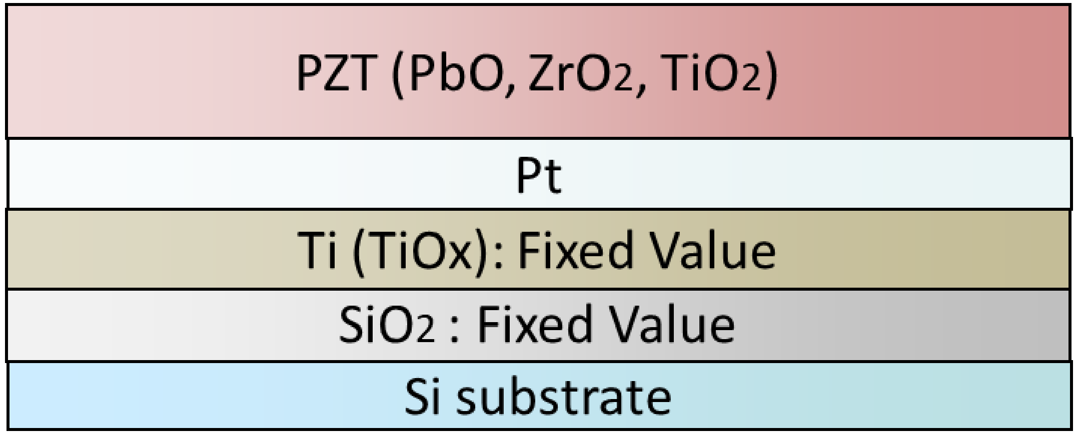
Good adventure for WDXRF	
✓	High spectral resolution needed to separate Pb, Pt, Ti overlapping peaks
✓	FP analysis can analyze complicated multilayer stacks for film thickness and composition
✓	AZX 400 can accommodate PZT wafer samples, coupons, and pure metal disc standards

PZT ANALYSIS WITH WDXRF

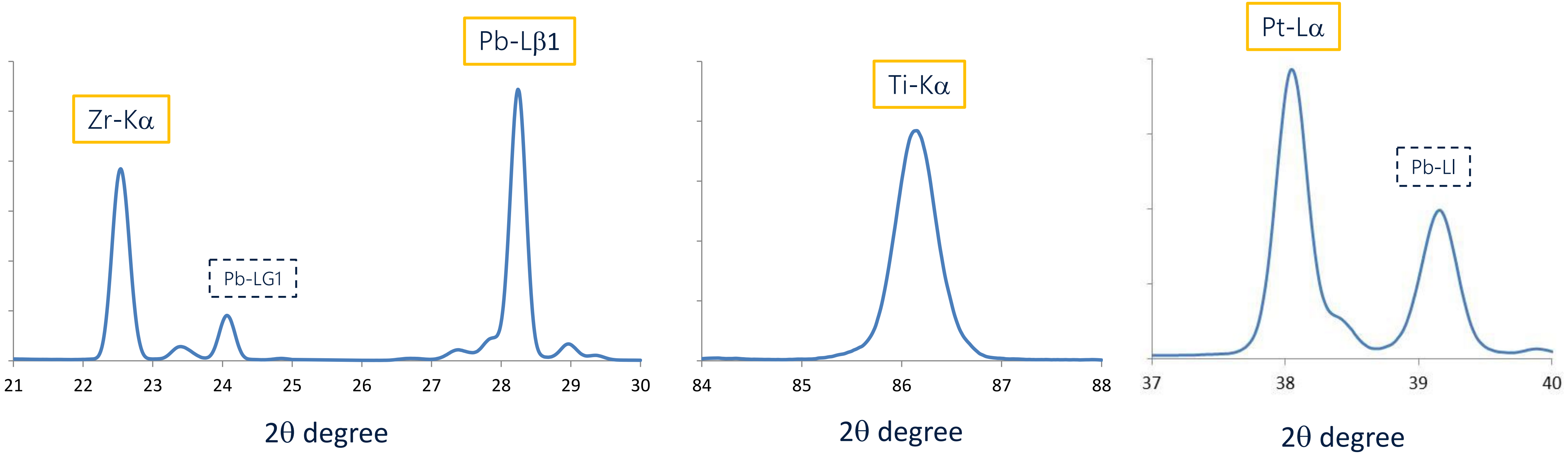
- FP analysis allows for TiOx layer thickness to be a fixed value.

  This enables Ti to be measured and accounted for from the PZT layer.

- Pure metal standards of Pb, Zr, and Ti can also be used.



QUALITATIVE CHART OF PZT SAMPLE



1 µm PZT and 100 nm Pt spectra.

WDXRF high spectral resolution resolves the Pb-L line, Pt-L line, and Zr-K line that overlap each other in EDXRF.

PZT ANALYSIS RESULTS

Layer	PZT						Pt
Component	Thk.	PbO Conc.	ZrO2 Conc.	TiO2 Conc.	Pb / (Zr+Ti)	Zr / (Zr+Ti)	Thk.
Unit	nm	mol%	mol%	mol%	-	-	nm
AVERAGE	3282.1	49.42	26.27	24.31	0.977	0.519	100.0
MAX.	3288.7	49.48	26.35	24.38	0.979	0.521	100.2
MIN.	3272.3	49.37	26.19	24.23	0.975	0.518	99.7
RANGE	16.4	0.11	0.15	0.15	0.004	0.003	0.5
Std. Dev.	4.7	0.034	0.041	0.052	0.0013	0.0009	0.15
R.S.D.(%)	0.14	0.07	0.16	0.21	0.14	0.17	0.15

Table: 10 times repeatability measurement of PZT/Pt multilayer

Thickness and composition of the PZT and Pt layer are calculated.

10x repeat thickness measurements <.2% RSDs.

Composition of PbO, ZrO2, TiO2 are calculated.

Pb/(Zr+Ti) and Zr/(Zr+Ti) composition ratios are also determined from measured mol%.

*Measurement from fixed channel WDXRF system

AZX 400 MEASUREMENT FLEXIBILITY

- **Different sample adaptors** to accommodate a range of sample sizes
- **Vacuum option**
- Library standards are available for semi-quantitative analysis if standards are not readily available.
- **FP method** and **high peak resolution** enable resolution of complicated spectra and overlapping peaks.
- Primary beam filters – **diffraction elimination**

WDXRF THIN FILM APPLICATIONS

- Semiconductor films

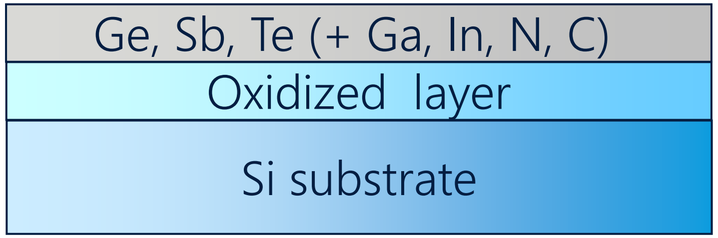
  Doped poly-Si (B, P, C, N, As), SiGe

- Insulative films

  Insulator film: PSG, BPSG
  Low-k film: AsSG, FSG SiOC
  Nitride film: Si_3N_4, SiON
  High-k film: La_2O_3, HfO_2, Ta_2O_5, Al_2O_3

- Metal, conductive films

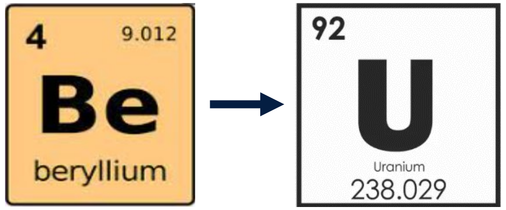
  Metal alloy film: AlSiCu, AlCu, TiW, TaAl
  Metal film: W, Mo, Ti, Co, Al, Cu, Ir, Pt, Ru
  Silicide film: WSix, MoSix, TiSix, CoSix, NiSix
  Nitride film (Barrier): TiN, TaN, WN



- Other

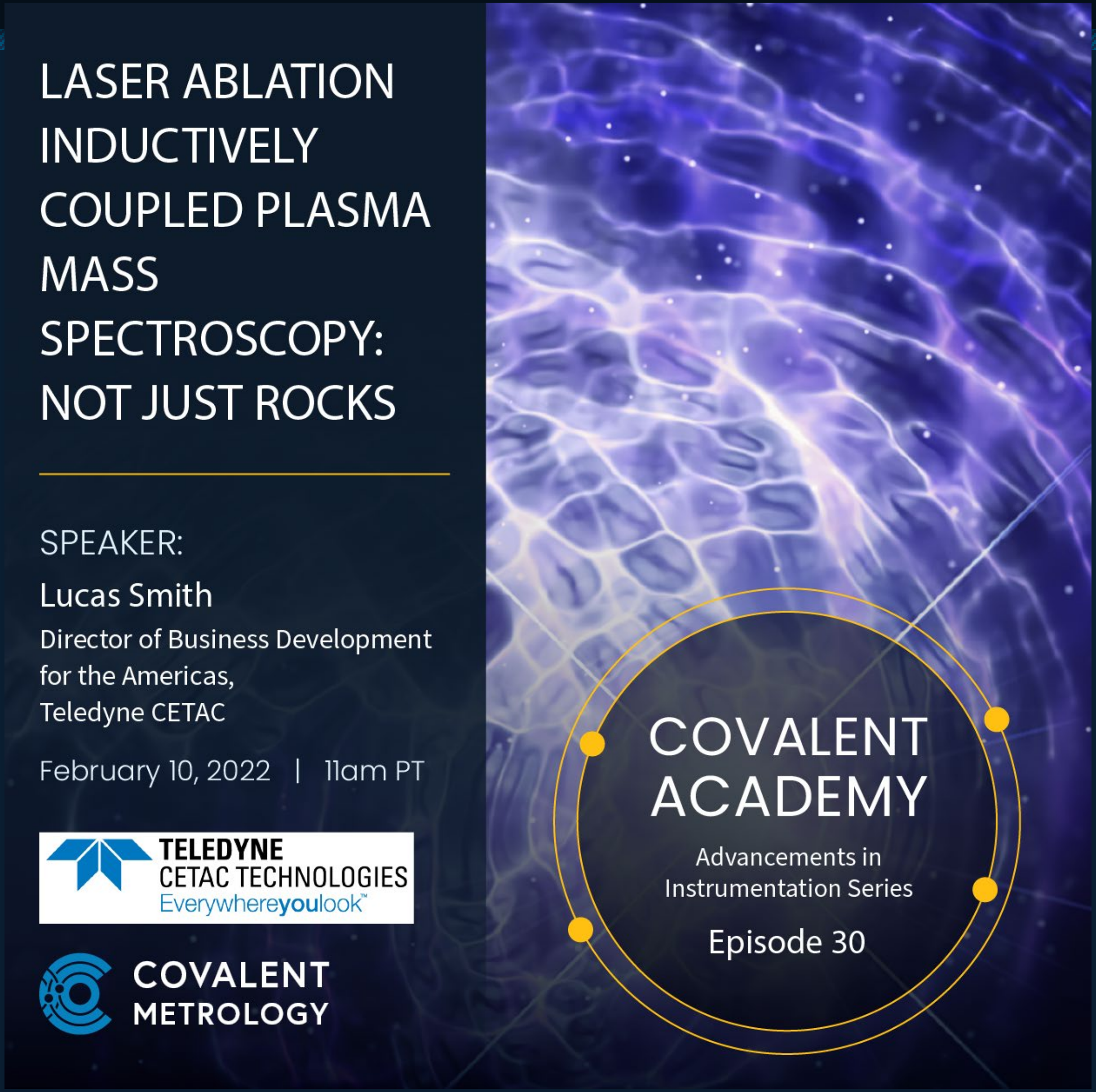
  Power Device: Au(Ag)/Ni/Ti/Al (backside electrode)
  Universal Memory: MRAM (MgO, CoFeB), GST, PZT
  MEMS (piezo, mobile): PZT, (Sc,Ta)AlN, SAW, F-BAR
  Other Purposes: LED, sputtering target, photomask, F, Cl residue, C film

KEY FEATURES OF WDXRF



- **Non-destructive detection** for wide range elements from
- **Ultra thin film thickness measurements** from 0.1 nm
- **High peak resolution** and fundamental parameter (FP) analysis can analyze multilayer stacks with complicated compounds
- Multiple sample adaptors allow for **various shapes, coupons, and wafer samples from 50 mm- 380 mm**
- Library standards in software provides **semi-quantitative measurement analysis without standards**
- **Qualitative measurements scan for smaller element groups or from Be-U**

Coming Up…



LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROSCOPY: NOT JUST ROCKS

SPEAKER:

Lucas Smith

Director of Business Development for the Americas,
Teledyne CETAC

February 10, 2022 | 11am PT

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- link is in the chat -

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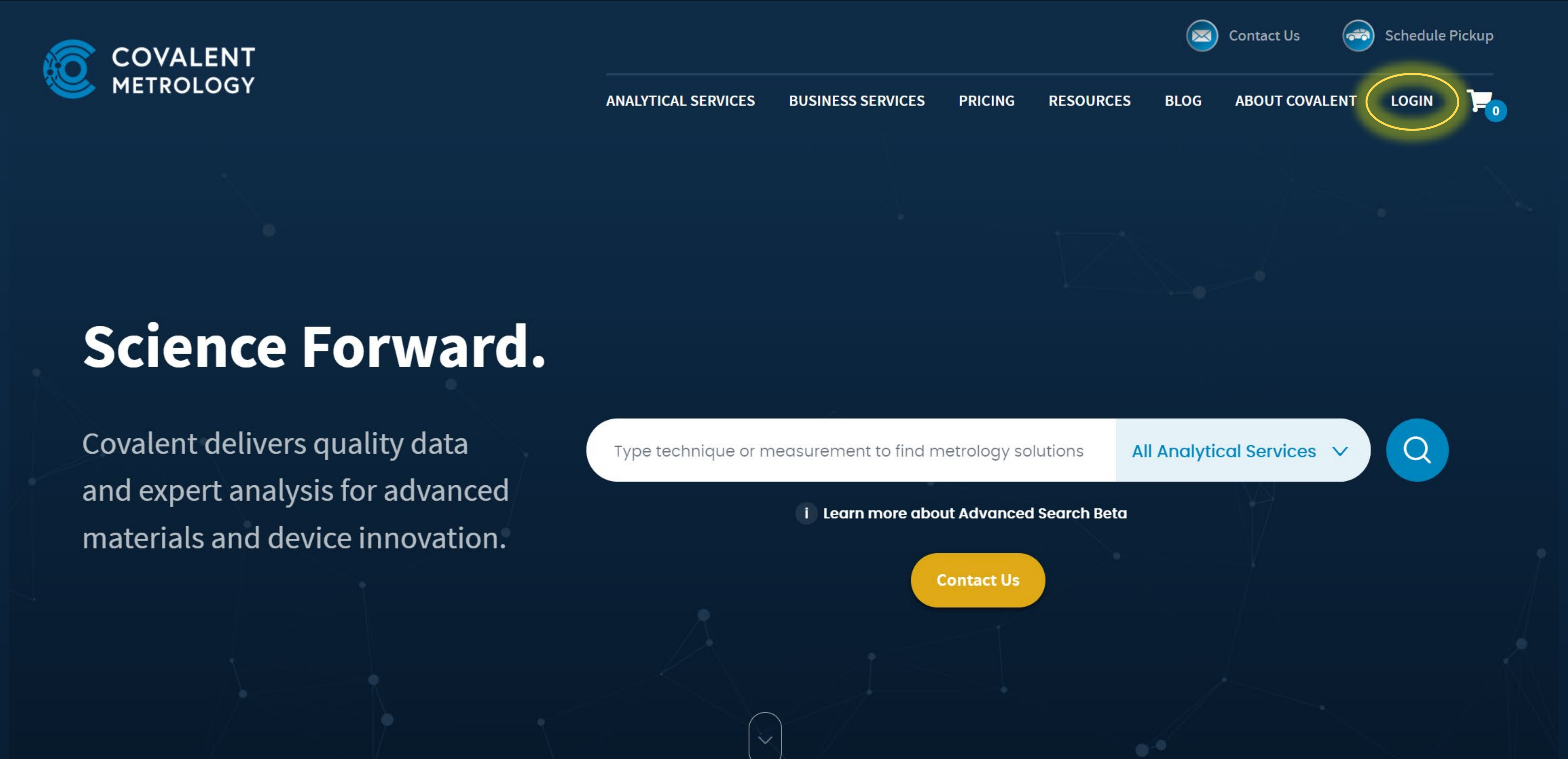

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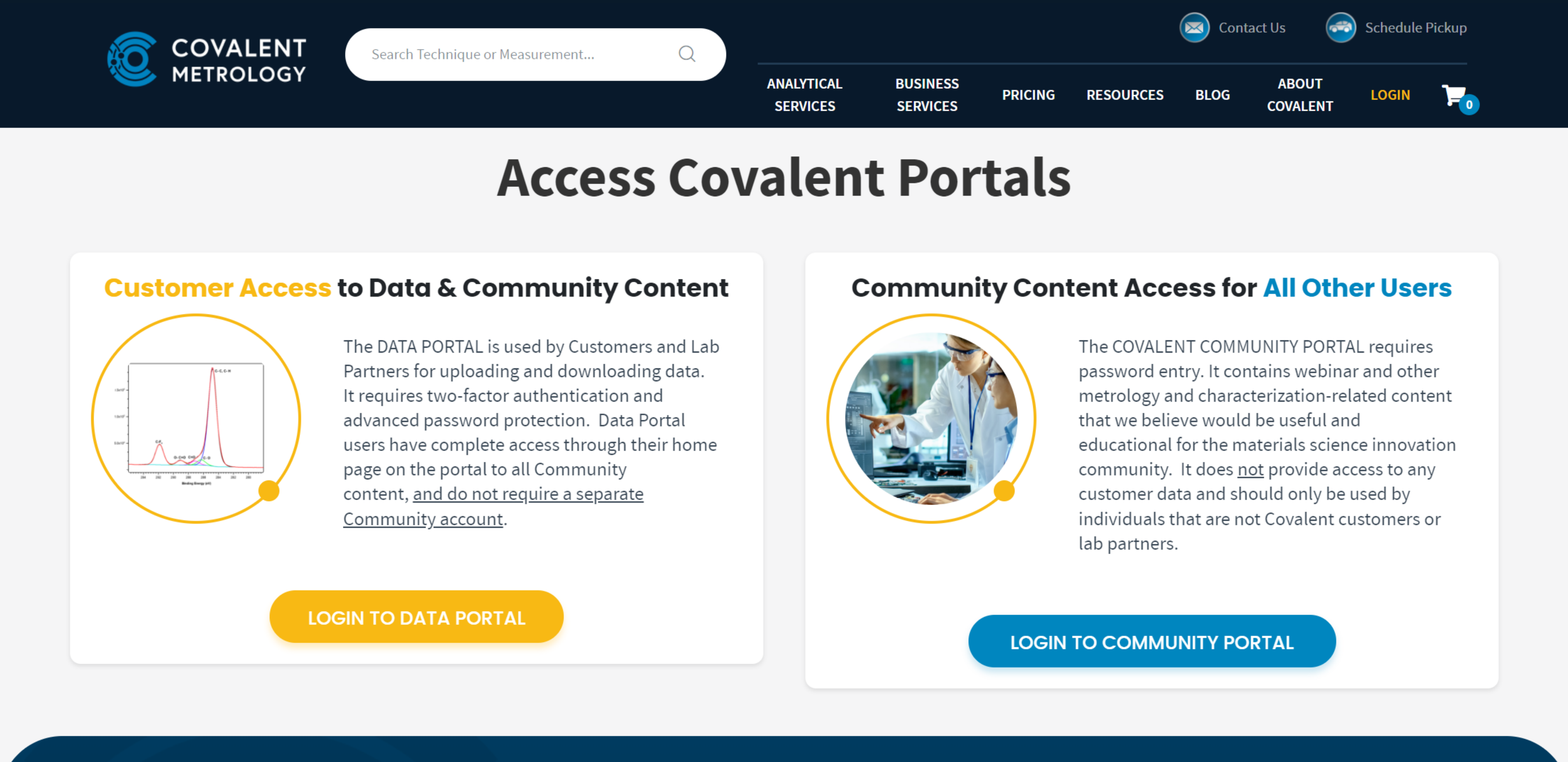

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Q & A
Session

COVALENT METROLOGY

Thank you