#### **Today's Workshop Topic**

• <u>Workshop on Nano Science and Catalysis</u> (NSC-2008)

#### The Theme

- To address various aspects of Nano- Science and Catalysis with respect their Synthesis Protocol and further leading to the processing
- <u>Characterization and evaluation</u> of such Nano materials for their industrial applications.

# Nano-Science/Technology

- THE Nano-Science could be termed as the basic discipline leading to the evolution of Nano-Technology
- Both may involve manipulation of materials at nanometer length scale to create Nano-structures having unique properties, the former at the R&D and the latter at commercial production level.

#### Nano-Technology/Nano Particles and Catalysis

- The Nanotechnology, as at presently defined, took start in the second half of the twentieth century
- However the Nanomaterials have been around for centuries.
- The very basis of the variety of natural materials around us and the evolution of the man kind itself speaks of the Nanotechnology
- Infect it was the recent realization of the nanoscale which lead scientists to imagine a new type of science where the atoms and molecules could be manipulated one by one with molecular machines

#### The Catalysis and Catalysts

#### What is Catalysis

**Catalysis** may be defined as action by an active reagent, referred to as **catalyst**, which takes part in a chemical reaction/process and can/should alter the rate of reactions favourably. (This may be one of many definitions)

Three key aspects of catalyst action involves:

- taking part in the reaction process by interacting with the reactants/product molecules
- altering the rates of reactions, in most cases the rates of reactions are increased and in certain cases the undesired reaction rates are also suppressed.
- Returning to its original form after reaction cycles.

### Catalysis/Catalysts (Continued)

- Looking at the situation it is evident that all catalytic processes must be taking place at microscopic level and with involvement of the Active Surfaces (in most of the cases) and their performance in future could be better rationalised profitable by involving the Nano Science.
- In fact the catalytic processes have always been on the Nanoscale and only our recent understanding of the Nano science/ technology enhanced our interests and understanding of the field and hence this workshop topic.

#### Catalysis/Catalysts (Continued)

Amongst many one may quote adsorption of gaseous products especially the lighter gases such as hydrogen in which case the finely divided Pd nano coated zeolites are being used for separation of the isotopic fractions and the separation process very much dependent on the morphology of the coated nanostructure with respect to the Pd present

#### Analytical Systems for Nano Materials Characterization

- While we discuss these systems some of the impotant property values of such Nano materials may be:
- <u>Physical and Chemical properties-</u> force, strength, length, particle size/form/ shape, <u>chemical</u> <u>composition</u>, surface area and topography/ <u>Morphology/Tomography</u>
- <u>Mechanical Properties</u>- elasticity, hardness, friction, adhesion, and durability
- <u>Electronic and Magnetic properties</u>- all aspects related to the photonic and magnetic properties
- Related to Manufactured Goods- structures, surface features, internal features etc.

## Nano-Characterization

- For <u>Nano-characterization</u> of materials we may include all the techniques used by the <u>MICROSCOPISTS/Microscopy techniques</u> and the <u>SPECTROSCOPISTS/</u> <u>Spectroscopic/Spectrometric techniques</u>.
- <u>These techniques</u> would be required to be developed further to meet the future challenges and vision to characterize complex heterogeneous samples( both organic and inorganic) in three dimensions over the relevant time and length scales say with 1.0 nm spatial resolution or better.

#### Techniques

#### What are the requirements

Depending upon the property values e.g.

- Bulk Techniques
- Compositional Analysis
- Impurity Analysis by Micro and nano techniques
- Impurity on Surfaces (Nano-Scale)
- Impurity in Bulk/ Depth Profiling (Nano-Scale)

## Analysis Techniques

- All Nano Materials would be analyzed/ characterized Mainly with the following point of view:
- Bulk Analysis to determine the Main Bulk of the materials
- Chemical composition, for each component of the material.
- Impurity Analysis for the total content of the impurity level present.
- Spatial distribution of the impurity levels following in depth profiling
- Surface finishing for contaminants and the nano Level which may effect the properties values.

# The Bulk Techniques

- The Normal Classical Techniques
- Electro-Analytical Techniques
- Spectrophotometric techniques rather complete range of Spectro-Chemical Techniques (UV/Vis/Ir-Ftir/).
- Atomic Absorption Spectrometric Analysis
- ICP-OES
- ICP-MS
- GD-OES/MS
- XRD/XRF

## Micro/Nano Techniques

- Atomic Absorption Spectrometry
- ICP-OES
- ICP-MS
- GD-OES
- GD-MS
- XRD/XRF
- FTIR/Raman

## Beam/Micro beam Techniques

- Electron beams/X-Rays, Wave Length /Energy Dispersive Spectroscopy
- Particle/ion beams, Mass Spectrometry
- Photons /Light absorption, Spectroscopy
- Metering, Microscopy

#### **Electromagnetic Radiation**



#### **Electromagnetic Radiation**

#### Electromagnetic radiation

X-ray, light, infra-red, microwave and radio waves are all e.m.r.'s, difference being their frequency thus the amount of energy they possess

• Spectral region of e.m.r.



#### **Destructive/Solution Techniques**

- AAS, ICP-OES, ICP-MS
- In all cases the sample has to be brought to a proper form for application/ presentation and all these and allied it has to be dissolved.
- Analysis to be accomplished following the procedural parameter well-known in each case

#### Destructive/Solution Techniques (Continued)

- The procedures to be followed keeping in view the precision and accuracy requirements and optimized for best detection limits.
- Impurities could be determined in ppm, ppb and ppt level
- While performing effect of interferences on the impurity values to be determined to be looked into very carefully.

# **ICP-OES**

- Inductively Coupled Plasma Spectroscopy techniques are the so-called "wet" sampling methods whereby samples are introduced in liquid form for analysis.
- In plasma emission spectroscopy (OES), a sample solution is introduced into the core of inductively coupled argon plasma (ICP), which generates temperature of approximately 8000°C. At this temperature all elements become thermally excited and emit light at their characteristic wavelengths.
- This light is collected by the spectrometer and passes through a diffraction grating that serves to resolve the light into a spectrum of its constituent wavelengths.
- Each wavelength correspond to individual element and its intensity to the concentration of that element

### **ICP-OES**

 Some of the instruments use the plasma flame in normal vertical position (Radial) and this is the case for most of the ICP-AES systems



# **ICP-MS**

 In Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), the inductively coupled argon plasma (ICP) used as an excitation source for the elements of interest. However in contrast to OES, the plasma in ICP-MS is used to generate ions that are then introduced to the mass analyzer. These ions are then separated and collected according to their mass to charge ratios. The constituents of an unknown sample can then be identified and quantitatively determined.

## Plasma in ICP-MS System

 The Endon (Axial) position is used with most of the ICP-MS Systems



## Ideal Uses for ICP-OES/MS Analysis

- Bulk quantitative survey analysis of major, minor or trace constituents
- High accuracy determinations of major and minor constituents in a wide range of materials
- Quality and process control.
- In ICP-MS the Detection limits are further decreased to the ppb/ppt and lower level.

## Strengths of ICP-OES/MS Analysis

- Many elements (up to 70 in theory) can be determined simultaneously in a single sample analysis.
- The useful working range is over several orders of magnitude.
- Instrumentation is suitable to automation, thus enhancing accuracy, precision and throughput.
- The combination of ICP OES and MS techniques is very powerful for determining an extremely wide range of elements from major components to very low detection limits (typically sub ppb) with high accuracy and precision.

## Limitations of ICP-OES/MS Analysis

- The emission spectra are complex and <u>inter-</u> <u>elemental interferences</u> are frequently there apart from the <u>Spectral</u> and <u>Matrix</u> <u>interferences</u>:
- In MS the common matrix elements and other molecular species may also interfere with the determination of some elemental species. Some doubly charged or molecular ionic species create difficulties in quantifications.
- Interference to be removed using <u>Matrix</u>
  <u>Matched Standards.</u>

## ICP-OES/MS

- ICP-OES/MS Technical Capabilities
- Signal Detected: Photons (OES) or lons (MS)
- Elements Detected: Up to 70 elements
- Detection Limits:
  ppm/ppb/ppt
- Depth Resolution: Bulk and impurity (ppm ,ppb ,ppt) technique
- Imaging/Mapping: No

## Relevant Industries for ICP-OES/MS Analysis

- Aerospace
- Sputter targets
- Chemicals
- Alloy producers
- Food/beverage
- Geological
- Pharmaceutical
- environmental water, wastewater, processing water

### GD-OES

- Like the ICP-OES the GD-OES could also be used for the Low level impurities.
- Glow discharge is used as the optical excitation source
- The energetic Ar<sup>+</sup> produced attacked the sample and through the sputter action ring the metallic atoms/ions in the plasma.
- The process leads to electronic excitation and emission of characteristic emission spectral line characteristic of the element present.
- The spectral data and the intensity determines the amount of the element present.
- The technique applicable to ppm/ppb level impurities.

#### **Destructive/Non-solution techniques**

- Such as GD-OES and GD-MS
- In such a case the sample is directly presented to the analysis after surface preparations cleaning etc.

#### **Glow-Discharge Mass Spectrometry (GDMS)**

Glow-Discharge Mass Spectrometry (GDMS), the sample to be analyzed forms the cathode in a low pressure (~ 100 Pa) gas discharge or plasma.

- Argon is typically used as the discharge gas.
- Argon positive ions are accelerated towards the cathode (sample) surface with energies from hundreds to thousands of eV resulting in erosion and atomization of the upper atom layers of the sample.
- Only the sputtered neutral species are capable of escaping the cathode surface and diffusing into the plasma where they are subsequently ionized. The atomization and ionization processes are thus separated in space and time, which appears to be a keystone for simplified calibration, quantification and the near matrix independence of this technique.
- Although the analysis can be more time consuming than in solution based analytical methods, the sensitivity, the ease of calibration, the flexibility and the capability to analyze wide variety of sample forms and matrices is impressive.
- Additionally, besides bulk element compositions, it is also possible to collect depth profiling information with very high sensitivity.

# Strengths of GDMS Analysis

- Full periodic table coverage (except H)
- Sub-ppb to ppt detection
- Minimal matrix effects
- Linear and simple calibration
- Capability to analyze insulators
- Depth profiling of coatings and oxide layers

# Ideal Uses for GDMS Analysis

- Trace and ultra-trace element determination in high purity metals, alloys, manufactured carbons and graphites, semiconductor materials, various oxides, carbides and ceramics.
- Depth profiling of flat surfaces for major, minor and trace elements.
- Identification of unknowns from minute amount of specimen
- Full element characterization of powders or particulate materials

# **GD-MS** Summary

- Signal Detected:
  lons
- Elements Detected: Full periodic table (except H)
- Detection Limits: Sub-ppb to ppt
- Depth Resolution: ~0.5 µm. Samples must be flat to be profile analyzed.
- Sampling Area Spot Size: Between 5 and 15 mm

# Limitations of GD-MS Analysis

- Sample inhomogeneity
- Volatile samples
- Not suited for organic materials/polymers

## Relevant Industries for GDMS Analysis

- Sputter targets
- Aerospace
- Refractory metals and alloys
- Rare earth metals and oxides
- Precious metals
- High purity materials production

#### Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

- In Laser Ablation Inductively Coupled Plasma Mass Spectrometry the sample is directly analyzed by ablating with a pulsed laser beam. The created aerosols are transported into the core of inductively coupled argon plasma (ICP), which generates temperature of approximately 8000°C. The plasma in ICP-MS is used to generate ions that are then introduced to the mass analyzer. These ions are then separated and collected according to their mass to charge ratios. The constituents of an unknown sample can then be identified and measured. ICP-MS offers extremely high sensitivity to a wide range of elements.
- For laser ablation, any type of solid sample can be ablated for analysis; there are no sample-size requirements and no sample preparation procedures. Chemical analysis using laser ablation requires a smaller amount of sample (micrograms) only. In addition, a focused laser beam permits spatial characterization of heterogeneity in solid samples, with typically micron resolution both in terms of lateral and depth conditions.

## Relevant Industries for LA-ICP-MS Analysis

- Glass and ceramics
- Forensics
- Semiconductor manufacturing
- Geological
- Failure Analysis
## Ideal Uses for LA-ICP-MS Analysis

- Major, minor and trace level compositional analysis of conductive, semi-conductive and nonconductive materials
- Contamination of plastics, pharmaceuticals organics or biological materials
- Failure, contamination and inclusion analysis
- Forensics analysis
- Environmental and mineral sample analysis
- Elemental distribution analysis

## Strengths of LA-ICP-MS Analysis

- Direct sampling multielement quantitative or semi-quantification at the surface and bulk for elemental composition of solids
- No chemical procedures for dissolution
- Reduced risks of analyte loss or crosscontaminations
- Independent of sample geometry
- Analysis of very small samples
- Determination of spatial distribution of elemental compositions

### Limitations of LA-ICP-MS Analysis

 The common matrix elements and other molecular species can interfere with the determination of some elements. Some doubly charged or molecular ionic species create difficulties in quantifications

# LA-ICP/MS Summary

- LA-ICP-MS
  Technical Capabilities
- Signal Detected:
  Ions
- Elements Detected: Up to 70 elements
- Detection Limits: ppb
- Depth Resolution:
  ~1 μm
- Lateral Resolution Spot Size: 4 - 100µm

## Fourier Transform Infrared Spectroscopy (FTIR)

- Fourier Transform Infrared Spectroscopy (FTIR) provides specific information about chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. Chemical bonds vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces a spectrum that can be used to identify functional groups and compounds.
- To be used for identifying and analyzing materials and/or the contaminants. For example, to determine if a device component is contaminated and what the contaminant is, so hat the source could be eliminate.
- Far infra red (4-400cm<sup>-1</sup>), Mid infrared (400-4000cm<sup>-1</sup>) and Near Infra red (4,000-14000cm<sup>-1</sup>)

### **FTIR Set-Up**



# FTIR (Continued)

- Ideally the FTIR could be used for:
- Identifying the molecular structure of organic compounds for <u>contamination</u> analysis
- Identification of organic particles, powders, films, and liquids (<u>material identification</u>)
- For example Quantification of O and H in Si, and H in SiN wafers.
- Contamination analysis (extracts, outgassed products, residues)

# **FTIR Summary**

#### Signal Detected:

Infrared absorption

- Elements Detected:
  Molecular groups
- Detection Limits: 0.1 - 1 wt%
- Depth Resolution:
  0.1 2.5 μm
- Imaging/Mapping: No
- Lateral Resolution/Probe Size: >=15 µm

# Strengths of FTIR Analysis

- Capable of identifying organic functional groups and often specific organic compounds
- Extensive spectral libraries for compound identifications available.
- Ambient conditions (not vacuum; good for volatile compounds)
- Typically non-destructive.
- Minimum analysis area: ~15 micron

# Limitations of FTIR Analysis

- Limited surface sensitivity (typical sampling volumes are ~0.8 µm)
- Minimum analysis area: ~15 micron
- Limited inorganic information
- Typically not quantitative and needs standards.

#### Gas Chromatography Mass Spectrometry (GC-MS)

- <u>Gas Chromatography- Mass Spectrometry (GC-MS)</u> identifies volatile and semi-volatile compounds and separates them into individual components using a temperature-controlled gas chromatographic program. During the analysis process, a sample is either injected into the chromatograph or it may come/be retrieved from another sampling device and carried through the chromatography column, under the set of conditions, specific for each application. This may lead to separated species are fed, quantitatively, component-wise, to a dedicated mass spectrometer for identification and final results.
- Often compounds cannot be analyzed by a particular method, if they are not in a form amenable to the analytical technique.
- Different general facilities generally available with this technique are given in the next paras.



# GC-MS (Continued)

- **Dynamic Headspace Analysis (HSA)** is used primarily for analyzing volatile compounds in matrices that cannot be directly injected into a gas chromatograph, including polymers, electronic components, wafers, biomedical devices, and environmental samples. In dynamic HAS mode, the sample is placed in a closed chamber and heated following a specified temperature/ time program. The out-gassed components are then collected and analyzed by GC/MS.
- **Pyrolysis** may be employed for nonvolatile organic compounds, such as wood, paper, or polymers. The sample is heated rapidly to 750°C or higher in order to thermally decompose it into smaller, more volatile fragments which are identified using the MS compopnent. It may be frequently used to examine materials for the presence of additives, such as plasticizers, antioxidants, flame-retardants, UV-stabilizers, or sizing treatments applied to cloth samples.

# GC-MS (Continued)

• Solids Probe is a volatilization technique that places a nonvolatile sample under vacuum near the mass spectrometer's ion source. As the molecules volatize during the heating time, they continuously enter the mass spectrometer's source and are ionized similar to the standard GC MS technique. The disadvantage of this technique is there is no separation step.

## Strength and Limitations

- The strength of the technique lies in :
- Identification of organic components by Separating the complex mixtures and following of the Mass spectrometry

# GC-MS (Uses)

- Ideal Uses for GC/MS Analysis
- Identifying and quantifying volatile organic compounds in mixtures
- Outgassing studies
- Testing for residual solvents
- Liquid or gas injections
- Evaluating extracts from plastics
- Evaluating contaminants on semiconductor wafers (thermal desorption)

# Strengths of GC/MS Analysis

- Identification of organic components by separating complex mixtures
- Quantitative analysis
- Trace-level determination of organic contamination (low to mid-ppb level for liquids and low nanogram level for solids (Dynamic Headspace Analy

# **GC/MS Technical Capabilities**

#### Signal Detected:

Molecular/characteristic fragment ions

- Elements Detected: Molecular ions to mass 800
- Detection Limits:
  400 ng (full scan)
  10 ng (outgassing)

# Limitations of GC/MS Analysis

- Sample must either be volatile or capable of derivitization
- If the sample is not volatile (as in headspace, pyrolysis, or direct probe), then this could not be followed.

## Auger Electron Spectroscopy (AES, Auger)

- Auger Electron Spectroscopy (AES, Auger)
- Auger Electron Spectroscopy (AES, Auger) is a surface-specific analytical technique that utilizes a high-energy electron beam(3-25kev) as an excitation source. Atoms that are excited by the electron beam can relax under the emission of "Auger" electrons. In AES we measure the kinetic energies of the emitted electrons, which are characteristic of elements present at the surface and "near-surface" of a sample.

## Auger Electrons



Initial Stage

**Final Stage** 

# Auger (Continued)

- The electron beam can be "focused" over a large or small surface area, or it can be directly focused on a small surface feature. This ability to focus the electron beam to a diameters of 10nm and less makes AES an extremely useful tool for elemental analysis of small surface features.
- Moreover, the ability to raster the electron beam over an adjustable surface area provides control over the size of the analytical area. When used in combination with ion sputter sources, AES can perform large- and small-area compositional depth profiling, and when used with Focused Ion Beam (FIB), it may be useful for analyzing cross sections. As well
- AES could be used for all kinds of industrial applications.
- This may be used at sub-micron particles size to determine contamination sources in wafer processing equipment or defects in electronic devices to investigate failure causes,
- or we may use Auger measurements to determine the oxide layer thickness of "electro-polished" medical devices.

# Auger Analysis

- Ideal Uses of Auger Analysis
- Defect analysis
- Particle analysis
- Surface analysis
- Relevant Industries for Auger Analysis
- Small-area depth profiling
- Process control
- Thin film analysis composition

#### **Auger Strength and Limitations**

- Strengths of Auger Analysis
- Small area analysis (as small as 30 nanometers or down to 6/8nm)
- Excellent surface sensitivity
- Good depth resolution
- Limitations of Auger Analysis
- Standards (SRMs)required for best quantification
- Insulators may be difficult
- Samples must be vacuum compatible
- Relatively poor detection sensitivity (0.1 at% at best)

#### Auger summary

- **Signal Detected** : Auger electrons from near the surfaces
- **Detection Limits**: 0.1-1.0 atom%
- Element detected: Li-U
- Depth Profiling: 20-200A°
- Imaging/Mapping : Yes
- Lateral resolution: >=0.2µM

>=100A°

 A focused ion beam can be scanned to create secondary electrons and Auger images

# Focused Ion Beam (FIB)

#### Focused Ion Beam (FIB)

- A Focused Ion Beam (FIB) instrument uses a finely focused ion beam to modify and image samples. FIB is chiefly used to create very precise cross sections of a sample for subsequent imaging via SEM, STEM or TEM or to perform <u>circuit modification</u>.
- Additionally FIB can be used to image a sample directly, detecting emitted electrons. The contrast mechanism for FIB is different than for SEM or S/TEM, so for some specific examples FIB can provide unique information. A dual beam FIB/SEM integrates these two techniques into one tool thus enabling sample prep. and SEM imaging without handling the sample.

# FIB (continued)

#### **Sample Preparation tool**

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- As a sample preparation tool, the FIB can accurately produce crosssections of a sample that are impossible to create otherwise:
- FIB has revolutionized sample preparation for TEM samples, making it possible to identify sub-micron features and precisely prepare cross sections.
- FIB-prepared sections are used extensively in SEM microscopy, where the FIB preparation, SEM imaging, and elemental analysis can happen on the same multi-technique tool.
- FIB-prepared sections are also used in Auger Electron Spectroscopy to provide elemental identification of subsurface features quickly and precisely.
- It is an ideal tool for examining products with small, difficult-to-access features, such those found in the semiconductor industry and for sub-surface particle identification.
- It is a good option for products that are hard to cross section, such as a soft polymer that is challenging to polish.

# FIB

- FIB Technical Capabilities
- Signal Detected:
  Electrons
- Depth Resolution:
  10 Angstroms
- Imaging/Mapping: Yes
- Lateral Resolution/Probe Size: 7 nm

#### Low Energy X-ray Emission Spectrometry (LEXES)

- Low Energy X-ray Emission Spectrometry (LEXES), is a near surface analytical technique that utilizes a high-energy electron beam as an excitation source. Atoms that are excited by the electron beam relax under the emission of characteristic x-rays. Similar to EDS, LEXES measures the energy of the emitted x-rays, which are characteristic of elements present in the near-surface region of a sample. The use of Wavelength Dispersive Spectrometers (WDS) increases the sensitivity of the technique as well is improves energy resolution, removing almost all interferences.
- The electron beam current can be very tightly controlled, allowing for very high precision measurements. Dopant concentrations, film composition, and/or film thickness can be mapped across wafers or compared between wafers with precisions of 1% or better.
- By using reference standards measurement accuracies of better than 5% can be obtained.
- Adjusting the energy of the incident electron beam allows layers as thin as 10 Angstroms or as thick as 1um to be analyzed. Finally, the LEXES electron beam can be focused into an area as small as 10um, allowing small areas to



# Ideal Uses for LEXES Analysis

- High precision ion implant dose measurement.
- Measuring ion implant uniformity across wafers
- Determining thin film composition
- Measuring film uniformity across wafers
- Measuring impurity levels in thin films

# Strengths of LEXES Analysis

- Non-destructive
- Whole wafer analysis (200 and 300 mm) as well as wafer pieces and small samples
- Mapping of full wafers
- Measurement precision typically <1%
- Measurement accuracy typically <5%
- No sample preparation requirements
- Can analyze areas as small as  $30 \mu m$  and layers as thin as  $1 \mu m$

# Limitations of LEXES Analysis

- Maximum analysis depth of ~1µm
- Maximum sample thickness of ~2mm
- Can have problems with insulating samples

# **LEXES Summary**

- LEXES Technical Capabilities
- Signal Detected: Characteristic x-rays
- Elements Detected: B-U
- Detection Limits: 5e13 atoms/cm2, 0.01 at-%
- Depth Resolution: N/A, no depth profile generated
- Imaging/Mapping: Yes
- Ultimate Lateral Resolution: ~10µm

## **Raman Spectroscopy**

- Monochromatic radiation incident on a sample, may interact with it by Reflection, Absorption and Scattering in some manner.
- In RAMAN Spectroscopy the Scattered light is analyzed and it is the change in the wavelength of the scattered photons which provided the Chemical and structural information about the sample.
- In Molecular systems these frequencies fall in the range associated with Rotational, Vibrational and Electronic level transitions.


### Raman Spectroscopy

- Raman Spectroscopy enables to determine the chemical structure of a sample and identify the compounds present by measuring molecular vibrations, similar to Fourier Transform Infrared Spectroscopy (FTIR). However, the method used with Raman yields better spatial resolution and enables the analysis of smaller samples.
- Raman is a good technique for the qualitative analysis of organic and/or inorganic mixed materials and can also be employed for semi-quantitative and quantitative analysis. It is often used to:

Identify organic molecules, polymers, biomolecules, and inorganic compounds both in the bulk and in individual particles

### Raman Spectroscopy

- Raman imaging and depth profiling is used to map the distribution of components in mixtures, such as drugs in excipients, tablets, and drug-eluting stent coatings
- Determine the presence of different carbon types (diamond, graphitic, amorphous carbon, diamond-like carbon, nanotubes, etc.) and their relative proportions, something for which it is particularly well suited
- Determine inorganic oxides and their valence state
- Measure the stress and crystalline structure in semiconductor and other materials
- small contamination areas, identify materials in small areas, and measure stress. The resulting data helps our clients resolve problems quickly, reduce cycle times, and improve production processes. We believe that no competing lab can match the skill set and experience of our staff. Plus, you can count on fast turnaround times, accurate data, and person-to-person service, ensuring you understand the information that you receive.

# Ideal Uses for Raman Analysis

- Identifying the molecular structure of organic and inorganic compounds for contamination analysis, material classification, and stress measurements
- Characterization of carbon Nano-materials (graphitic v. diamond), Semiconductors and thin films.
- Non-covalent bonding (complexes, metal bonding)
- Orientation (random v. organized structure)

### **Strengths of Raman Analysis**

- Capable of identifying organic functional groups and often specific organic compounds
- Spectral libraries for compound identification available
- Sample ambient conditions (no vacuum, good for semi-volatile compounds)
- Typically non-destructive
- Minimum analysis area: ~1 µm

### **Limitations of Raman Analysis**

- Limited surface sensitivity (typical sampling volumes are ~0.8 µm)
- Minimum analysis area: ~1 μm
- Limited inorganic information
- Typically not quantitative (needs standards)
- Fluorescence (much more intense than the Raman signal) can limit Raman usefulness

### **Raman Spectroscopy Summary**

- Raman Technical Capabilities
- Signal Detected:
  Raman scattering
- Elements Detected: Chemical and molecular bonding information
- Detection Limits: >=1 wt%
- Depth Resolution: Confocal mode 1 - 5 μm
- Imaging/Mapping: Yes
- Lateral Resolution/Probe Size: >=1 µm

### Particle Induced X-ray Emission (PIXE)

- Particle Induced X-ray Emission (PIXE) is performed simultaneously with <u>Rutherford Backscattering Spectroscopy (RBS</u>). During RBS analysis, characteristic x-rays are emitted from the sample, similar to those measured during EDS analysis. However, because the sample is bombarded with high energy He++ ions, there is little or no Bremstrahhlung background signal.
- The energy from the collected x-rays can be used to distinguish between two elements that are close in mass, and therefore emit a single signal using traditional RBS. Measuring the intensity of the signal allows for quantification of each element. While it is not possible to depth profile with PIXE, the technique is a useful complement to RBS, helping to resolve interferences and allow for more accurate quantification.

### PIXE



HARVARD PIXE SYSTEM

# PIXE

- Ideal Uses for PIXE Analysis
- Optimizing traditional RBS data for thin film analysis
- Identifying high-Z elements
- Quantifying ratios of elements that cannot be resolved by RBS

### Relevant Industries for PIXE Analysis

- Aerospace
- Defense

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- Semiconductor
- Telecommunications

# PIXE

#### Strengths of PIXE Analysis

- Non-destructive, quantitative analysis of elements heavier than Si
- Identification of elements that RBS cannot resolve

#### Limitations of PIXE A

No depth information

#### PIXE Technical Capabilities

- Signal Detected: Emitted x-rays
- Elements Detected: S-U
- Detection Limits: Z dependent

#### X-ray Photoelectron Spectroscopy/Electron Spectroscopy for Chemical Analysis (XPS/ESCA)

- X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is used to determine quantitative atomic composition and chemistry.
- It is a surface analysis technique with a sampling volume that extends from the surface to a depth of approximately 50-70 Angstroms.
- Alternatively, XPS can be utilized for sputter depth profiling to characterize thin films by quantifying matrix-level elements as a function of depth.
- XPS is an elemental analysis technique that is unique in providing chemical state information of the detected elements.
- The process works by irradiating a sample with monochromatic soft x-rays (~1.5 keV from AI or Mg), resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume.

# Plus points and limitations of XPS

#### Plus points

- Chemical state identification on surfaces
- Identification of all elements except for H and He
- Quantitative analysis, including chemical state differences between samples
- Applicable for a wide variety of materials, including insulating samples (paper, plastics, and glass)
- Depth profiling with matrix-level concentrations
- Oxide thickness measurements

#### Limitations of XPS Analysis

- Detection limits typically ~ 0.1 at%
- Smallest analytical area ~10 µm
- Limited specific organic information
- Sample compatibility with UHV environment

# **XPS-Summary**

- XPS/ESCA
  Technical Capabilities
- Signal Detected: Photoelectrons from near surface atoms
- Elements Detected:
  Li-U Chemical bonding information
- **Detection Limits:** 0.01 - 1 at% sub-monolayer
- Depth Resolution:
  20 200 Angstroms (Profiling Mode)
  10 100 Angstroms (Surface analysis)
- Imaging/Mapping: Yes
- Lateral Resolution/Probe Size: 10 µm - 2 mm

# SEM

- Scanning Electron Microscopy (SEM)
- Scanning Electron Microscopy (SEM) rasters a focused electron beam across a sample surface, providing high-resolution and longdepth-of-field images of the sample surface.
- SEM is one of the most widely used analytical tools in industry due to the extremely detailed images it can provide
- Coupled to an auxiliary <u>Energy Dispersive X-ray Spectroscopy (EDS)</u> detector, this technique also offers elemental identification of nearly the entire periodic table.

# SEM

### Uses for SEM Analysis

- High resolution images
- Elemental microanalysis and particle characterization
- Relevant Industries for SEM Analysis
- Aerospace,
- Biomedical,
- Compound Semiconductor
- Data Storage
- Electronics
- Lighting
- Pharmaceutical
- Semiconductor
- Solar Photovoltanics

- Automotive
- Biotechnology
- Defense, Displays
- Industrial Products
- Photonics
- Polymer
- Telecommunications

# SEM

- Strengths of SEM Analysis
- Rapid, high-resolution imaging
- Quick identification of elements present
- Good depth of field
- Versatile platform that supports many other tools
- Limitations of SEM Analysis
- Vacuum compatibility typically required
- May need to etch for contrast
- SEM may spoil sample for subsequent analyses
- Size restrictions may require cutting the sample
- Ultimate resolution is a strong function of the sample and preparation methodology

### **SEM-Summary**

- Signal Detected: Secondary & backscattered electrons and x-rays
- Elements Detected: B-U (EDS mode)

Detection Limits: 0.1 - 1 at%

• Depth Resolution: 0.5 - 3 µm (EDS)

Imaging/Mapping: Yes

Lateral Resolution/Probe Size: 15 - 45 Angstrom

### Secondary Ion Mass Spectrometry (SIMS)

- <u>SIMS</u>, is an analytical technique that detects very low concentrations of dopants and impurities.
- It can provide elemental depth profiles over a depth range from a few angstroms to tens of microns. SIMS works by sputtering the sample surface with a beam of primary ions. Secondary ions formed during the sputtering are extracted and analyzed using a mass spectrometer. These secondary ions can range from matrix levels down to sub-partsper-million trace levels.
- <u>The Primary</u> ion beam may have energy in the range of 1-10keV.
- In Static SIMS a low dose of the incident particles (5x10<sup>12</sup> atoms/cm<sup>2</sup>) is used to maintain the chemical integrity of the sample while
- In Dynamic mode the rapid profiling of the sample may destroy the Chemical Integrity of the sample.
- <u>Interpretation</u> of the Characteristic fragmentation patterns may result a chemical analysis of the few outer mono-layers of the material.

### SIMS

#### **Duoplasm atron**



### SIMS

#### **Cesium Surface Ionization Source**



# SIMS

- Ideal Uses for SIMS Analysis
- Dopant and impurity depth profiling
- Composition and impurity measurements of thin films (metal, dielectric, SiGe, III-V, and II-V)
- Ultra-high depth resolution profiling of shallow implants and ultra thin films (ULE implants and gate oxides)
- Bulk analysis, including B, C, O, and N in Si
- High-precision matching of process tools (ion implanters)
- Typical Industries for SIMS Analysis
- Semiconductor (primary), Aerospace, Automotive, Compound Semiconductor, Data Storage, Defense, Displays, Electronics, Lighting, Photonics, Solar Photovoltaics, Telecommunications

### SIMS, Applicability and Limitations

### <u>Applicability</u>

- Excellent detection sensitivity for dopants and impurities, with ppm or lower detection sensitivity
- Depth profiles with excellent detection limits and depth resolution
- Small-area analysis (10 µm or larger)
- Detection of all elements and isotopes, including H
- Excellent dynamic range (up to 6 orders of magnitude)
- Stoichiometry/composition possible, in some applications

### Limitations

- Destructive in Dynamic Mode of Application
- No chemical bonding information
- Element specific
- Sample must be solid and vacuum compatible required

### SIMS, Summary

- Signal Detected:
  Secondary lons
- Elements Detected: H-U including isotopes
- Detection Limits: >1010 - 1016 at/cm3
- Depth Resolution:
  >5 Angstrom
- Imaging/Mapping: Yes
- Lateral Resolution/Probe Size:
  >=10 µm (depth profiling)
  1 µm (imaging mode)

# SPM/AFM Spectroscopy

- Scanning Probe Microscopy/Atomic Force Microscopy (SPM/AFM)
- Scanning Probe Microscopy (SPM), more commonly known as Atomic Force Microscopy (AFM), provides atomic or near-atomic-resolution surface topography, which is ideal for determining angstrom-scale surface roughness on a sample. In addition to presenting a surface image, AFM can also provide quantitative measurements of feature sizes, such as step height, and other sample characteristics, such as capacitance measurements for identifying carrier and dopant distributions.
- Applications may incude assessing wafers (SiO2, GaAs, SiGe, etc.) before and after processing, determining processing effects (e.g. plasma treatment) on contact lenses, catheters, coated stents, and other biomedical surfaces, examining the impact of surface roughness on adhesion and other process challenges ,assessing trench shape/cleanliness on patterned wafers, determining whether morphology is the source of surface hazes etc.
- While working with the SPM and AFM analyst experience is very valuable.

# Working of AFM



## SPM & AFM

- Ideal Uses for SPM & AFM Analysis
- Three-dimensional surface topographic imaging, including surface roughness, grain size, step height, and pitch
- Imaging of other sample characteristics, including magnetic field, capacitance, friction, and
- <u>Relevant Industries for SPM & AFM Analysis</u>
- Aerospace, Automotive, Biomedical Biotechnology, Compound Semiconductor, Data Storage, Defense, Displays Electronics, Industrial Products, Lighting, Pharmaceutical, Photonics, Polymer, Semiconductor, Solar Photovoltaics and Telecommunications

# SPM & AFM

- Strengths of SPM & AFM Analysis
- Quantifying surface roughness
- Whole wafer analysis (150, 200, 300 mm)
- High spatial resolution
- Imaging of conducting and insulating samples
- Limitations of SPM & AFM Analysis
- Scan range limits: 100 microns laterally and 5 microns in z direction
- Potential problems with samples that are too rough and oddly shaped
- Tip-induced errors possible

# SPM & AFM

- SPM/AFM Technical Capabilities
- Signal Detected: Topography
- Depth Resolution:
  0.1 Angstrom
- Imaging/Mapping: Yes
- Lateral Resolution/Probe Size:
  15 50 Angstroms

### <u>STM</u>

The Scanning Tunneling Microscope can image the surfaces with unparalleled magnification upto the extent that individual atoms become visible.

However with this one could only image surfaces of materials that were conductors





### STM (Continued)

- The basic principle of ST-microscopy is based on the flow of tunneling current between its metallic tip (very sharp) and the conducting material.
- A small bias voltage is applied between the sample and the sharp tip. In case the distance between the tip and surface is large no current will flow. However as the tip is brought close to the surface without a physical contact a current will flow across the gap between the tip and the sample and this current referred as the tunneling current amount of which when is used for mapping sample surface.

## TEM/STEM

- Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) are related techniques that use an electron beam to image a sample. High energy electrons, incident on an ultra-thin samples allow for image resolutions that are on the order of 1 - 2 Angstroms. Compared to SEM, STEM has better spatial resolution, is capable of additional analytical measurements, and requires significantly more sample preparation.
- Although more time consuming than many other common analytical tools, the wealth of information available from these experiments is impressive. Not only can you obtain outstanding image resolution, it is also possible to characterize crystallographic phase, crystallographic orientation (both by diffraction mode experiments), produce elemental maps (using EDS), and images that highlight elemental contrast (dark field mode)—all from nm sized areas that can be precisely located. STEM and TEM can be the ultimate failure analysis tools for thin film and IC samples.

# SEM/STEM, Uses and Applications

- Uses of SEM/STEM Analysis
- Identification of nm sized defects on integrated circuits, including embedded particles and residues at the bottom of vias.
- Determination of crystallographic phases as a function of distance from an interface.
- Nanoparticle characterization: Core/shell investigations, agglomeration, effects of annealing...
- Catalyst support coverage.
- Ultra small area elemental maps.
- III-V super lattice characterization
- Relevant Industries for SEM/STEM
- AnalysisCompound Semiconductors
- Intergrated circuit
- Magnetic media
- Nanomaterials
- MEMS
- Opto-electronics
- Semiconductors

# Plus points and limitations

- Strengths Points of SEM/STEM Analysis
- The ultimate elemental mapping resolution of any analytical technique.
- Sub 0.5 nm image resolution.
- Small area crystallographic information

- Limitations of S/TEM Analysis
- Significant sample preparation time
- Samples are often prepared that are <100nm</li>
- Some materials not stable to electron beam

### **SEM/STEM Summary**

- Signal Detected: Transmitted electrons, scattered electrons, x-rays
- Elements Detected: B-U (EDS)
- **Detection Limits:** 0.1 1%
- Imaging/Mapping: Yes (EDS)
- Ultimate Lateral Resolution: <0.2 nm

# **TOF-SIMS**

- Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is a surface analytical technique that focuses a pulsed beam of primary ions onto a sample surface, producing secondary ions in a sputtering process.
- Analyzing these secondary ions provides information about the molecular and elemental species present on the surface. For example, if there were organic contaminants, such as oils adsorbed on the surface, TOF-SIMS would reveal this information, whereas other techniques may not. Since TOF-SIMS is a survey technique, all the elements in the periodic table, including H, are detected.
- Moreover, TOF-SIMS can provide mass spectral information; image information in the XY dimension across a sample; and also depth profile information on the Z dimension into a sample.
- The surface sensitivity of TOF-SIMS makes it a good first pass at problem solving. Once you have an idea of what you are dealing with, you can then use other techniques to obtain additional information.

# **TOF-SIMS**

#### Ideal Uses ofr TOF-SIMS

- Surface microanalysis of organic and inorganic materials
- Mass spectra direct from surfaces
- Ion imaging of surfaces
- <u>Relevant Industries to use TOF-SIMS Analysis:</u>
- Aerospace, Biomedical/biotechnology, Compound Semiconductor, Data Storage, Defence, Displays, Electronics, Industrial Products, Pharmaceutical, Photonics, Polymer, Semiconductor Solar, Photovoltaics, Telecommunications
### **TOF-SIMS**

#### Strengths of TOF-SIMS Analysis

- Specific molecular information on thin (sub-monolayer) organic films/contaminants
- Surface analysis that allows more complete characterization of a surface
- Excellent detection limits (ppm) for most elements
- Quantitative element analysis of Si and GaAs
- Probe size ~0.2 µm for imaging
- Insulator and conductor analysis
- Non-destructive
- Depth profiling is possible
- Whole wafers up to 200 mm
- Limitations of TOF-SIMS Analysis
- <u>USUAlly</u> not quantitative without standards
- Samples must be vacuum compatible
- It can be too surface sensitive:
  - Sample packaging and prior handling may influence quality of results
  - May lead to surface-damaging
- Very surface specific—only examines top couple of monolayers

### **TOF-SIMS** Sumary

- TOF-SIMS Technical Capabilities
- Signal Detected: Molecular and elemental species
- Elements Detected: Full periodic table coverage, plus molecular species
- Detection Limits:
   107 1010 at/cm2 sub-monolayer
- **Depth Resolution:** 1 - 3 monolayers (Static mode)
- Imaging/Mapping: Yes
- Lateral Resolution/Probe Size: ~0.20 μm

### Total Reflection X-ray Fluorescence (TXRF)

 Total Reflection X-ray Fluorescence (TXRF) utilizes extremely low-angle x-ray excitation of a polished sample surface. The incident angle of the x-ray beam (typically 0.05°) is below the critical angle for the substrate and limits excitation to the outer most surface layers of the sample. The fluorescence photons emitted from the surface atoms are characteristic of the elements present. A highly surface-sensitive technique, TXRF is optimized for analyzing surface metal contamination on semiconductor wafers.

### TXRF

- Ideal Uses for TXRF Analysis
- Metallic surface contaminations
- Semiconductor wafers

#### <u>Relevant Industrial applications</u>

- Semiconductor
- Telecommunication
- Compound Semiconductors
- Solar and Photonics

#### **TXRF Plus points and limitations**

- Plus points of TXRF Analysis
- Trace element analysis
- Survey analysis
- Quantitative
- Non-destructive
- Automated analysis
- Whole wafer analysis (up to 300 mm)

- Limitations of TXRF Analysis
- Cannot detect low-Z elements (Li, Na, Al)
- Polished surface required for best detection limits

### **TXRF** Summary

- 1. Signal Detected: Fluorescent x-rays from from surface
- Elements Detected: S-U
- Detection Limits: 109 - 1012 at/cm2
- **Depth Resolution:** 30 - 80 Angstrom (Sampling Depth)
- Imaging/Mapping: Optional
- Lateral Resolution/Probe Size: ~10 mm

### Applications

- Identifying stains and discolorations
- Characterizing cleaning processes
- Analyzing the composition of powders and debris
- Determining contaminant sources
- Examining polymer functionality before and after processing to identify and quantify surface changes
- Measuring lube thickness on hard disks
- Obtaining depth profiles of thin film stacks (both conducting and non-conducting) for matrix level constituents
- Assessing the differences in oxide thickness between samples
- These insights into a product's chemical makeup allow you to make product and process improvements more quickly, enabling you to reduce cycle time and save money.

#### **Typical Industrial uses**

- Automotive, Biomedical/biotechnology, Compound Semiconductor
- Data Storage, Defence, Displays, Electronics, Lighting
- Different other Industrial Products
- Pharmaceuticals, Polymer
- Semiconductor, Solar, Photovoltaics and Photonics,
- Telecommunications

#### X-ray Diffraction (XRD)

 X-ray Diffraction (XRD) is a powerful nondestructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of x-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the atomic decoration within the lattice planes. Consequently, the x-ray diffraction pattern is the fingerprint of periodic atomic arrangements in a given material. An online search of a standard database for xray powder diffraction patterns enables quick phase identification for a large variety of crystalline samples.

### XRD

- Ideal Uses for XRD Analysis Phase identification for a large variety of bulk and thin-film samples
- Detecting crystalline minority phases (at concentrations greater than ~1%)
- Determining crystallite size for polycrystalline films and materials
- Determining percentage of material in crystalline form versus amorphous
- Relevant Industries for XRD Analysis
- Measuring sub-milligram loose powder or dried solution samples for phase identification
- Analyzing films as thin as 50 angstroms for texture and phase behaviors
- Measuring residual stress in bulk metals and ceramics

#### **XRD Analysis plus points and limitations**

- Nondestructive analysis
- Quantitative measurement of phase contents and texture orientation
- Minimal or no sample preparation requirements
- Ambient conditions for all analysis
- Limitations of XRD Analysis
- Cannot identify amorphous materials
- No depth profile information
- Minimum spot size of ~50um

#### **XRD Technical Capabilities**

- Signal Detected: Diffracted x-rays
- <u>Elements Detected:</u> All elements, assuming they are present in a crystalline matrix
- <u>Detection Limits:</u> Quantitative multiphase analysis: ~1%
- External standard quantitative analysis: ~0.1%
- Special quantitative analysis (quartz, polymorphs): ~0.02%
- Minimum film thickness for phase identification: ~20 Angstroms

#### Depth Resolution:

Adjustable sampling depth between ~20 Angstroms to ~30 microns, depending on material properties and x-ray incidence angles

- Imaging/Mapping: None
- Lateral Resolution/Probe Size: Point focus: 0.1mm to 0.5mm Line focus 2mm to 12 mm

### X-ray Fluorescence (XRF)

X-ray Fluorescence (XRF) is a non-destructive technique that is used to quantify the elemental composition of solid and liquid samples. X-rays are used excite atoms in the sample, causing them to emit x-rays with energies characteristic of each element present. The intensity and energy of these x-rays are then measured. XRF is capable of detecting elements from Na-U in concentrations from PPM range to 100%. Because Xrays are used to excite the sample depths as great as 10µm can be analyzed. Through the use of appropriate reference standards, XRF can accurately quantify the elemental composition of both solid and liquid samples.

### **XRF/Ideal Uses and application**

- Ideal Uses of XRF Analysis may include:
- Measuring metal film thickness up to several microns
- Full wafer mapping (up to 300mm wafers) of film thickness with high precision and accuracy
- Elemental identification in unknown solids, liquids, and powders of all types
- Identification of metal and alloys
- <u>Relevant applications may include:</u>
- Aerospace, Automotive, Data Storage, Defense, Electronics, Industrial Products
- Lighting Polymers Semiconductors

### The Techniques\*\*\*\*

- AEM
- EELS
- EDS
- AEM-PEELS
- SEM/EPMA
- SEM-AES
- EDS/WDS
- SIMS/LMMS
- XRF
- XPS
- RBS

### The Techniques\*\*\*\*

- AP-FIM
- AEM-EELS
- AEM-Xray
- NSOM
- SEM/EPMA
- EDS/WDS/xray
- UV/V-FM/Micro Raman
- FTIR
- PIXE
- XRF/XRD
- NDP/PGNP
- RBS
- TXRF
- SIMS/LMMS
- ISS/XPS

### The Techniques\*\*\*\*

- Electron Microscopy
- SPM
- Ion Microscopy
- X-Rays
- Evanescent Probe Microscopy
- Micro-Raman
- Micro-IR
- NMR
- Dielectic Analysis

#### **Techniques with Detection Ranges**



Analytical Spot Size

#### Limit of detection with Lateral Spatial Resolution for different Techniques



## Depth Resolution Vrs. Lateral spatial resolution for different techniques



#### Chemical Specificity with Spatial Resolution for Different Techniques



#### **Mass Spectrometry**

- Quadruple Mass Spectrometer
- Magnetic Sector mass spectrometer
- TOF Mass Spectrometer.

#### **Optimum use/Piece of advice**

- All techniques have good points and deficiencies and cosmetics.
- All have matrix effects
- All need Standards SRMs.
- All to be followed in Clean Atmosphere
- All need trained technicians
- And Some one Who know the basis and could manage maintenance.

# Relevant Industries to employ the characterization techniques

Aerospace **Biomedical/biotechnology Compound Semiconductor Data Storage Electronics** Industrial Products Pharmaceutical Solar Photovoltaics **Telecommunications** Semiconductor and

**Automotive** Defense Displays Polymer Lighting **Photonics** Semiconductor Environment Many More

### Thanking you for kind Attention