Tecnología de Materiales

VICENTE MUÑOZ SANJOSÉ

Técnicas de caracterización

Table 1.1. Experimental Methods in use for analysis of epitaxial semiconductor layers

Method	*ex-situ*	*in-situ*	References
Reflection High Energy Electron Diffraction (RHEED)		×	B. A. Joyce [1.1], P. K. Larsen and P. J. Dobson [1.10]
Low Energy Electron Diffraction (LEED)		×	M. Henzler [1.21] M. P. Seah [1.22]
Auger Electron Spectrocopy (AES)	×	×	M. Grasserbauer and H. W. Werner [1.23]
Secondary Ion Mass Spectroscopy (SIMS)	× destructive		A. Benninghoven et al. [1.24]
Rutherford Back-scattering (RBS)	×		S. T. Picraux et al. [1.25]
Nuclear Reaction Analysis (NRA)	×		W. F. van der Weg and F. H. P. M. Habraken [1.26]
Transmission Electron Microscopy (TEM)	× destructive		H. Cerva, H. Oppholzer [1.27], H. Cerva [1.28], F. A. Ponce et al. [1.29], L. Reimer [1.30]
Scanning Electron Microscopy (SEM)	×	×	D. E. Newbury et al. [1.31]
Scanning Tunneling Microscopy (STM)	×	×	H.-J. Güntherodt and R. Wiesendanger [1.32]

Table 1.1. (continued)

Method	*ex-situ*	*in-situ*	References
Electron Paramagnetic Resonance (EPR)	×		R. C. Newman [1.33]
Electrical Characterisation (Hall effect,DLTS)	× destructive	×	R. A. Stradling and P. C. Klipstein [1.34]
Photo Electron Spectroscopy (PES) (XPS, SXPS, UPS)		×	M. Cardona and L. Ley [1.36], G. V. Marr [1.37]
Extended X-Ray Absorption Fine Structure (EXAFS)	×	×	C. C. Koningsberger and R. Prius [1.38]
Near-Field Optical Microscopy	×		E. Betzig et al. [1.19]
Photoluminescence	×		E. C. Lightowlers [1.39] M. A. Herman et al. [1.40] M. Illegems [1.9]
Electro-Photo-reflectance	×		D. E. Aspnes [1.11] F. H. Pollak [1.41]
Raman spectroscopy	×	×	M. Cardona [1.42]
Ellipsometry	×	×	D. E. Aspnes [1.12] J. B. Theeten [1.43]
Far Infrared Spectroscopy (FIR)	×	×	R. A. Stradling, P. C. Klipstein [1.34] T. Dumelow et al. [1.35]
Reflection Anisotropy Spectroscopy (RAS)	×	×	D. E. Aspnes [1.12]
X-Ray diffraction		×	A. Segmüller et al. [1.16], A. Segmüller [1.18] S. T. Picraux et al. [1.25] P. F. Fewster [1.15] B. K. Tanner [1.17] HRXRD-Conference [1.44]
X-Ray topography	×		Z. J. Radzimski et al. [1.45] R. Köhler [1.46]

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Energia en función de parametro de red

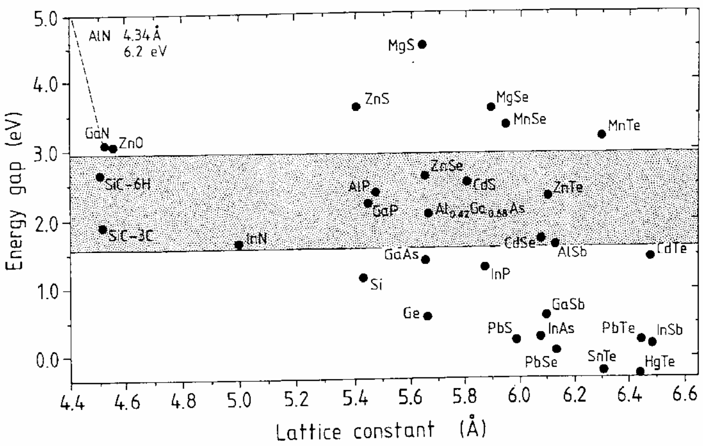

Fig. 1.1. Energy gap vs. cubic lattice constant of elemental group IV semiconduc tors and of III-V, II-VI and IV-VI compound semiconductors

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Analisis superficial y de la fase gaseosa

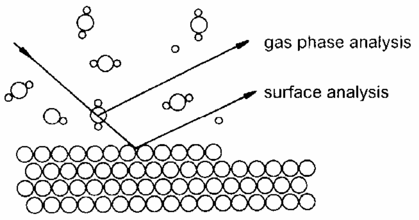

Fig. 1.2. Schematic setup of gasphase analysis and surface analysis in gasphase epitaxial growth. *Information needed*: (i) Gasphase: Gas velocity, gas temperature, identification of molecules, concentration. (ii) Surface: structure, composition. *Methods for analysis*: Elastic light scattering, absorption, Raman scattering, Coherent Anti-Stokes Raman Scattering (CARS), Spectroscopic Ellipsometry (SE), Reflectance Anisotropy Spectroscopy (RAS), Second Harmonic Generation (SHG)

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Reflectometría

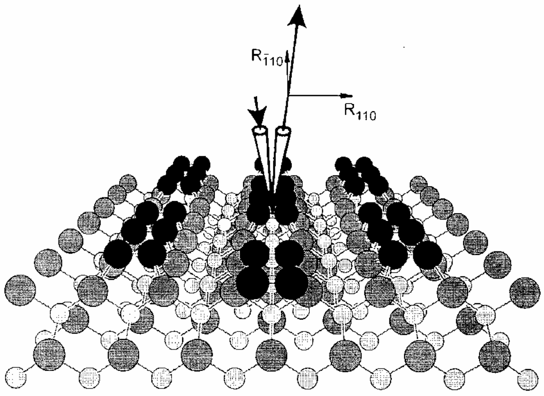

Fig. 1.3. Schematic setup of reflectance anisotropy spectroscopy (RAS) experiment. *Interaction with*: Anisotropic electronic surface states. *Information on*: Surface reconstructions, oxidation/deoxidation, exchange reactions, growth rate, morphology

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Elipsometría

1. Introduction 5

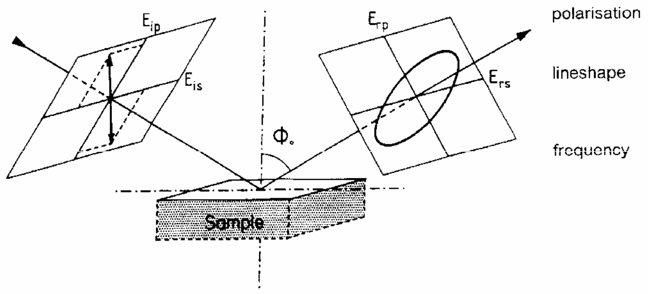

Fig. 1.4. Schematic setup of ellipsometry experiments on epitaxial layers. *Interaction with*: Electronic interband transitions (surface and bulk). *Information on*: Energy gaps versus temperature, strain and chemical composition, layer thickness with submonolayer sensitivity, layer dielectric functions

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Raman

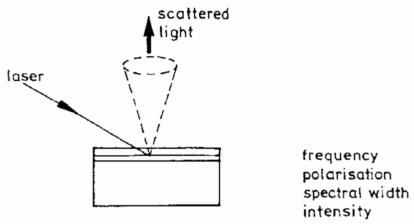

Fig. 1.5. Schematic setup of Raman scattering experiments on epitaxial layers. *Interaction with*: (i) Lattice vibrations: optical and acoustical phonons, local vibrations. (ii) Electronic excitations: plasmons, single particle excitations, impurity states. *Information on*: (i) Structural properties: crystalline quality, orientation, strain. (ii) Chemical properties: composition, reacted phases at interfaces. (iii) Electronic properties: impurities, free carriers, potential barriers

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Espectroscopia del infrarrojo lejano

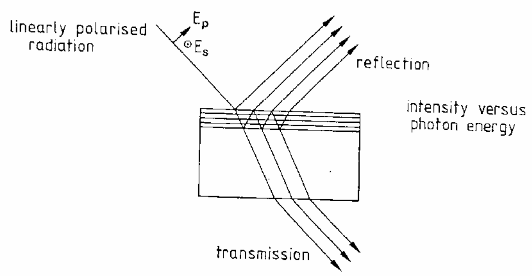

Fig. 1.6. Schematic setup of far infrared spectroscopy experiments on epitaxial layer systems. *Interaction with*: (i) Lattice vibrations: optical phonons, local vibrations. (ii) Electronic excitations: free carriers, impurity states. *Information on*: (i) Structural properties: crystalline quality, layer thickness. (ii) Vibronic properties: frequency and damping of TO phonons and of local modes. (iii) Electronic properties: binding energy and concentration of impurities, free carriers concentration and damping, low dimensional effects like subband energies, minibands, impurities in quantum wells.

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Rayos X

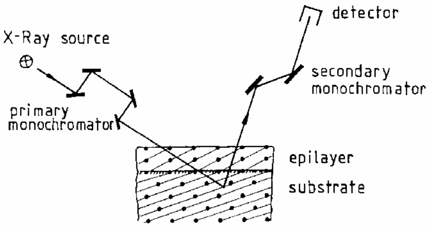

Fig. 1.7. Schematic setup of High Resolution X-Ray Diffraction (HRXRD) of epitaxial layers with primary and secondary monochromators indicated. *Experimental observation*: Bragg intensity for different scans through reciprocal space. *Information on*: (i) Geometry: crystal structure, film thickness, superlattice periods, tilt and terracing. (ii) Strain: elastic strain and relief, distortions, interfacial strain, inhomogenity. (iii) Crystalline perfection: mosaic spread, interface roughness, interdiffusion

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Rayos X

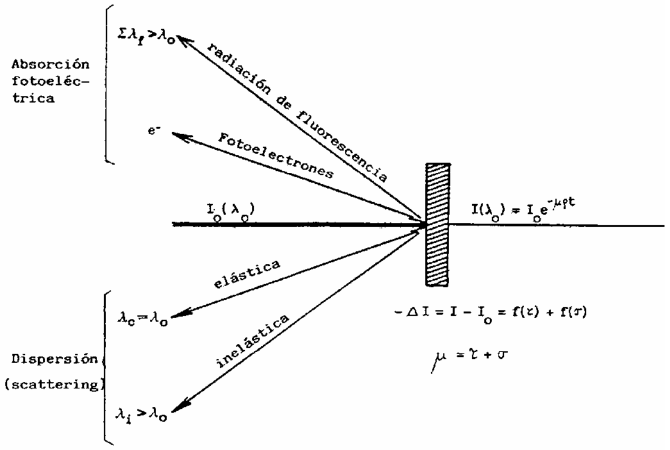

Figura 13.14. *Fenómenos de interacción de los rayos X con la materia.*

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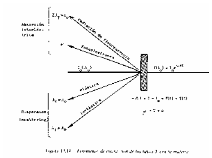
Rayos X



- Tecnicas de rayos X
  - Espectroscopicas
    - Absorcion
    - Emision
      - fluorescencia fotoelectrones
  - Difractométricas

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Técnicas de absorción de Rayos X

* Radiografía (Microrradiografía).
  — Microrradiografía de contacto.
  — Microscopía de rayos X de proyección.

* Absorciometría de rayos X.
  — Absorción de rayos X policromáticos.
  — Absorción de rayos X monocromáticos.
  — Absorciometría de rayos X en la discontinuidad de absorción.

* EXAFS (Espectroscopía de la estructura fina de absorción de rayos X).
  — XANES (Espectroscopía de la estructura fina de absorción de rayos X en la zona más próxima a la discontinuidad).

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Técnicas de emisión de Rayos X

(a). **Técnicas basadas en el Efecto Fotoeléctrico. (Excitación con rayos X).**

(a1). *Estudian el espectro de fluorescencia de rayos X emitido:*
* Espectrometría de fluorescencia de rayos X (XRFS).
  — de dispersión de longitudes de onda.
  — de dispersión de energías.
* Espectroscopía de rayos X (X-Ray Spectroscopy).
  — Espectroscopía de rayos X blandos (Soft X-Ray Spectroscopy).

(a2). *Estudian los electrones (fotoelectrones) emitidos:*
* Espectroscopía de electrones para el análisis químico (ESCA).
  [Espectroscopía de fotoelectrones de rayos X (XPS)].
* Espectroscopía de electrones Auger (AES).

(b). **Técnicas basadas en la emisión de rayos X primarios.**

* Excitación con iones (protones y partículas alfa principalmente):
  — Espectroscopía de emisión de rayos X producidos por partículas (PIXE o PIXEA).
* Excitación con electrones:
  — Microsonda de electrones.
  — Microscopía electrónica (de transmisión y barrido).

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Métodos generales de difracción de Rayos X

Clase de radiación (λ)	Características de la muestra Estacionaria/móvil	Nombre de la Técnica
Policromática	Monocristal estacionario	Laue.
Monocromática	Monocristal móvil. (Con movimiento de rotación total o parcial, o de precesión, alrededor de ejes convenientemente elegidos. Película fotográfica, o contador, estacionaria o móvil).	Cristal giratorio Cristal oscilatorio Weissenberg Buerger-precesión Difractómetro de monocristales
Monocromática	Polvo policristalino (existen simultáneamente todas las posibles orientaciones en los cristalitos).	Cámaras de polvo de: — película plana — película cilíndrica — focalización Difractómetro de polvo

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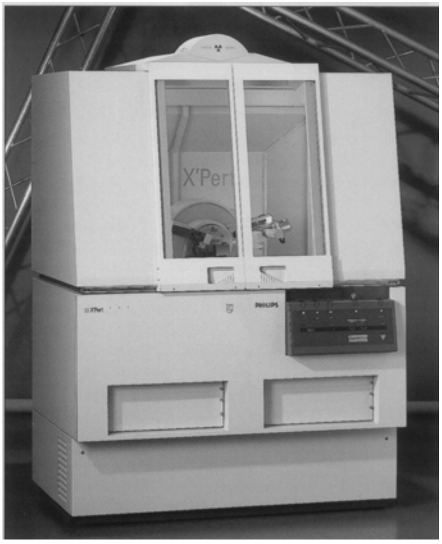
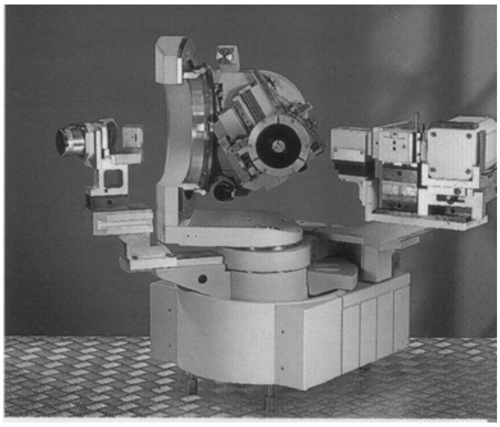
Rayos X

Capas delgadas





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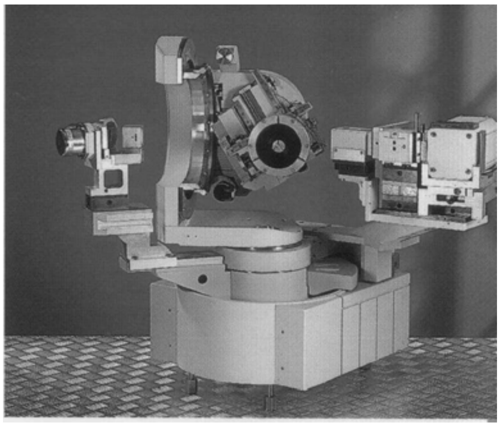
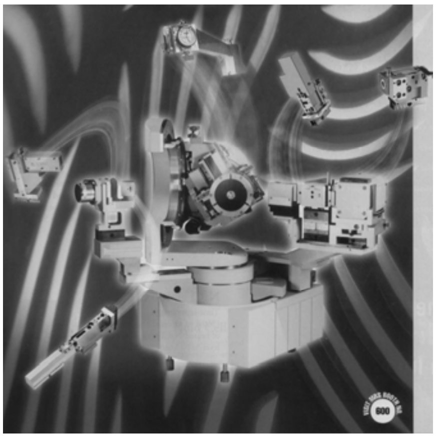
Rayos X

Capas delgadas





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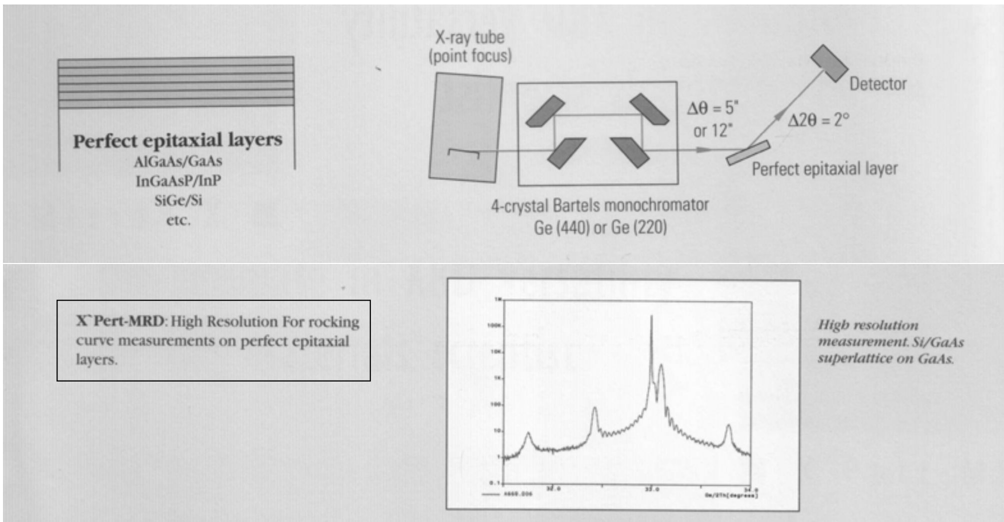
Rayos X

Capas delgadas



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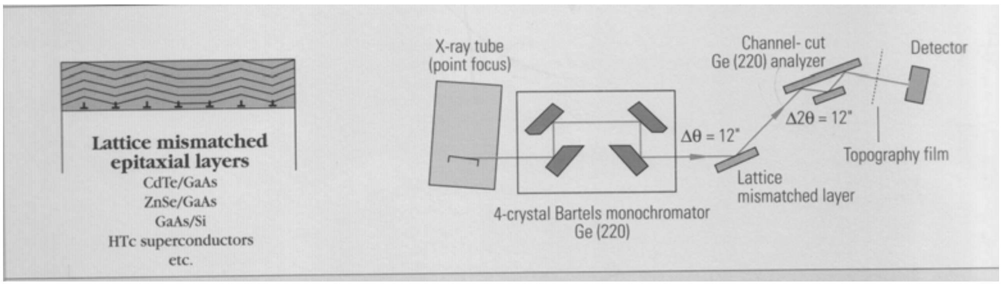
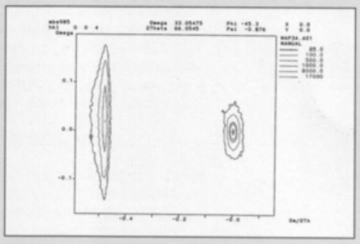
Rayos X

Capas delgadas



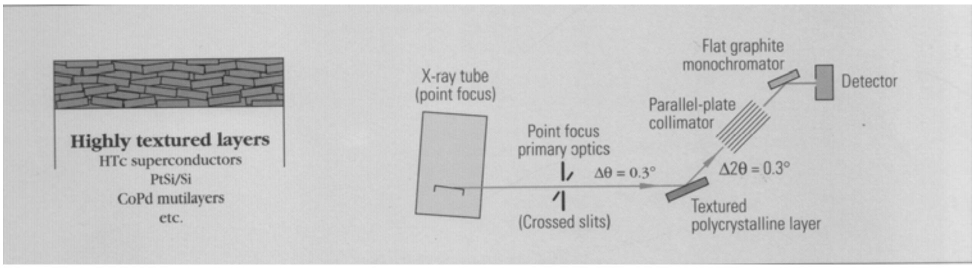
X`Pert-MRD: **Triple Axis** Adding the triple-bounce channel-cut Ge(220) analyzer crystal turns the X'Pert-MRD into a triple-axis diffractometer. The acceptance angle of the detector (2θ resolution) is limited to 12 arc-seconds. This makes it possible to separate lattice strain effects — ie. differences in 'd' spacing — from lattice orientation effects.

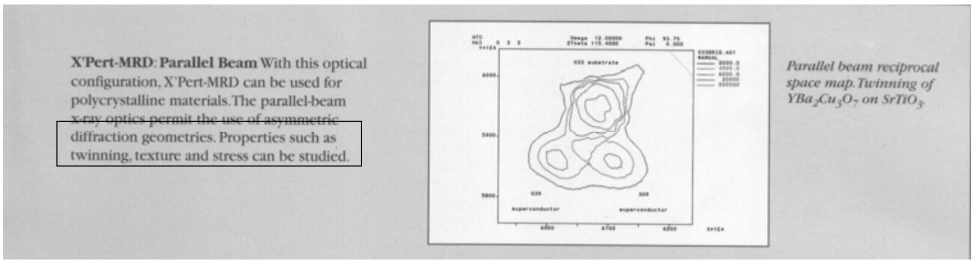


High resolution triple-axis diffraction space map. Partially relaxed $Ga_{1-x}In_xAs$ on GaAs.

Rayos X

Capas delgadas





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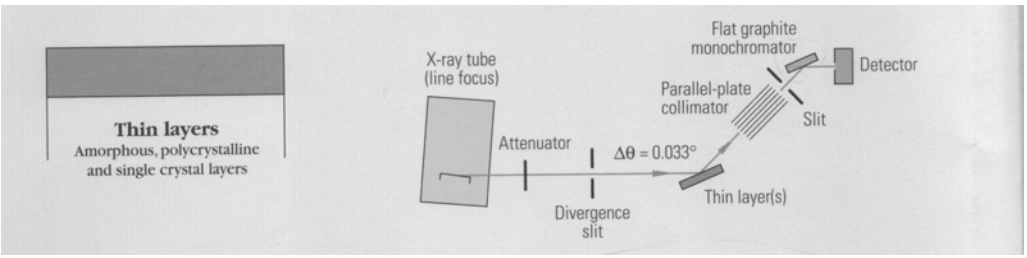
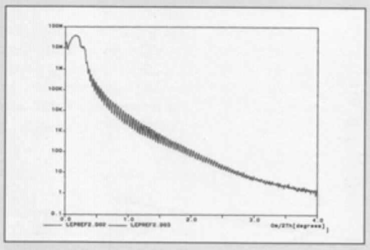
Rayos X

Capas delgadas



X'Pert-MRD: Glancing incidence diffraction and reflectometry The line focus optics allow measurement of the phase composition of thin films. With the incident beam attenuator, ultra-high dynamic range reflectometry measurements can be performed to study layer thickness, interface quality and density.



Reflectivity measurement of a 300 nm Si_3N_4 layer on GaAs, showing more than seven orders of magnitude in the dynamic range.

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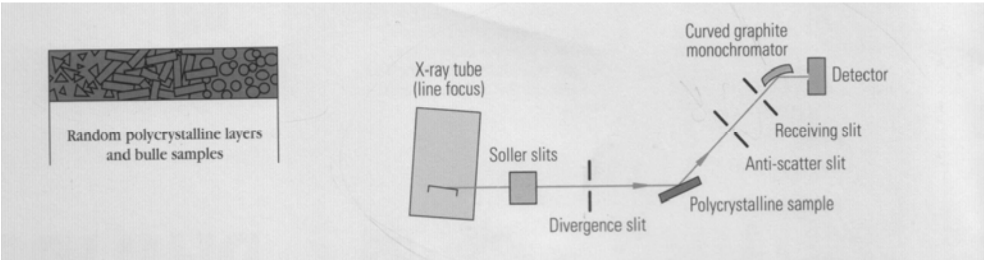
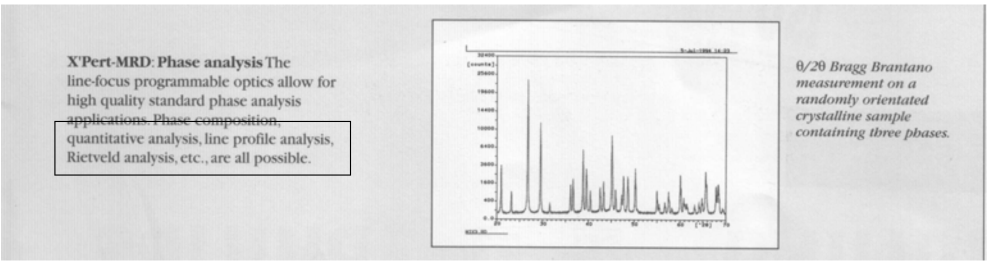
Rayos X

Capas delgadas





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Microscopia Electrónica

Transmisión

Barrido

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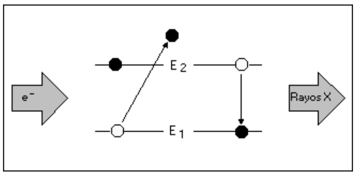
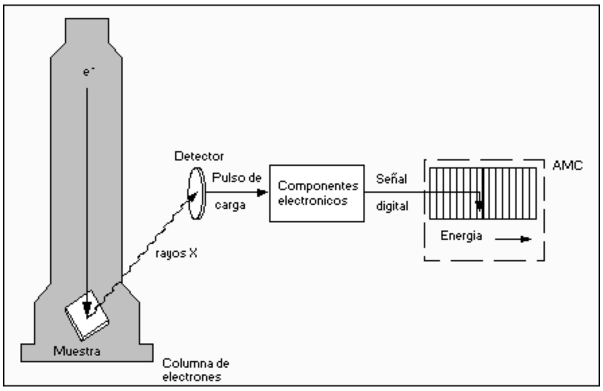
SEM





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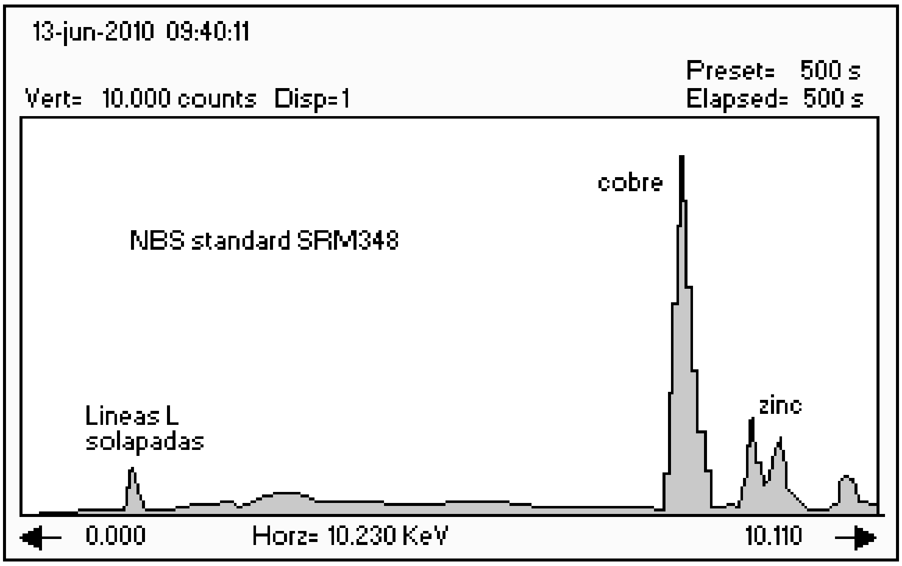

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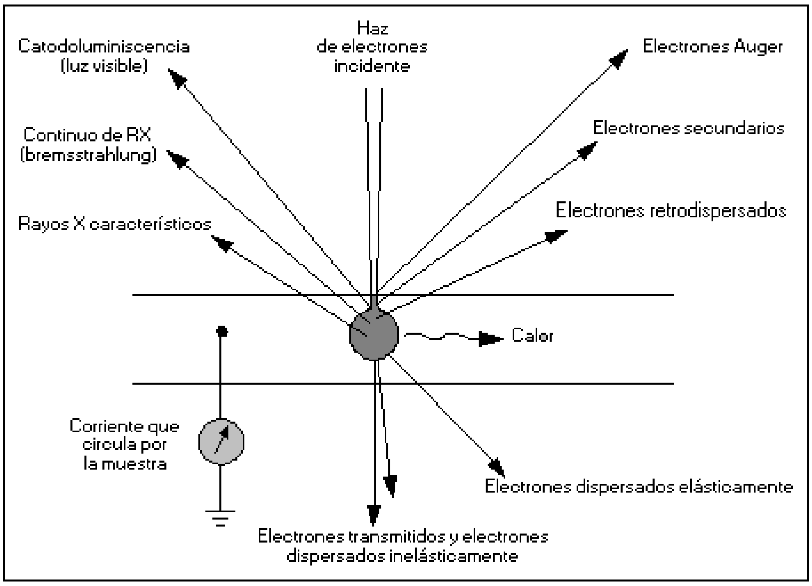

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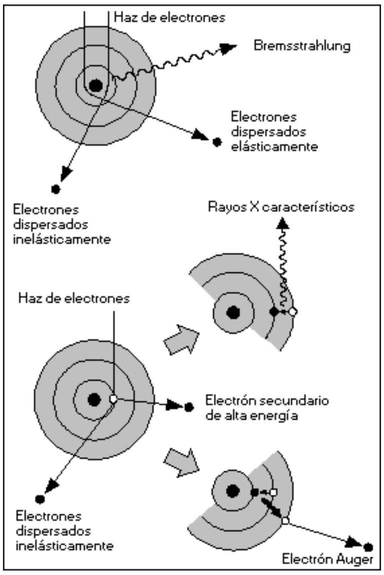

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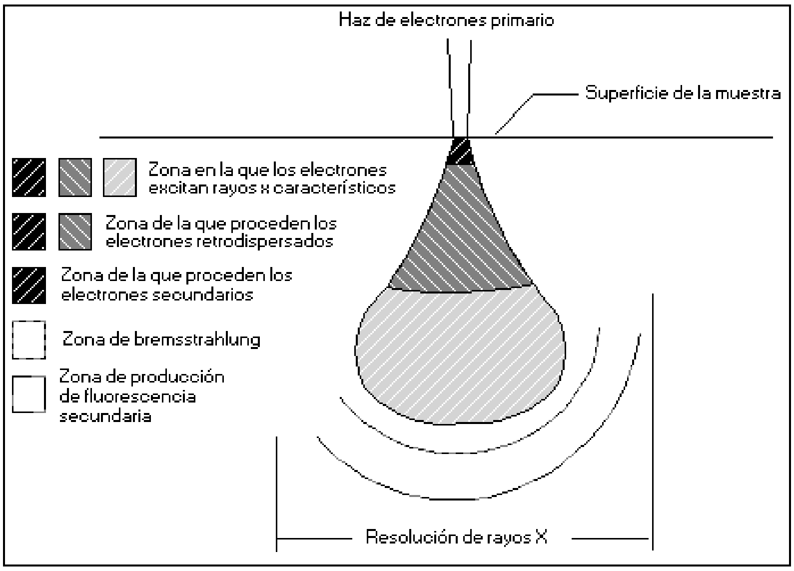

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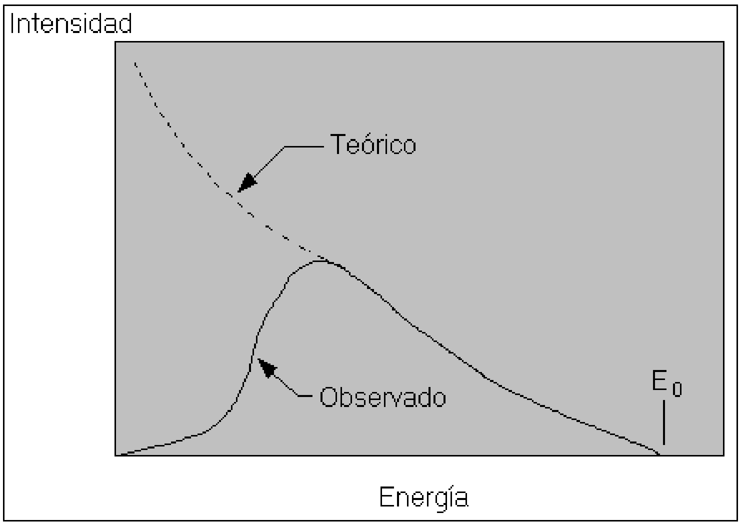

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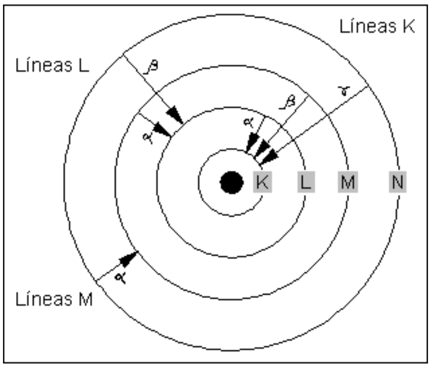

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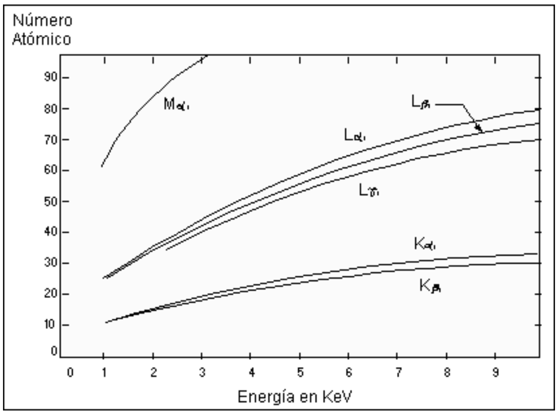

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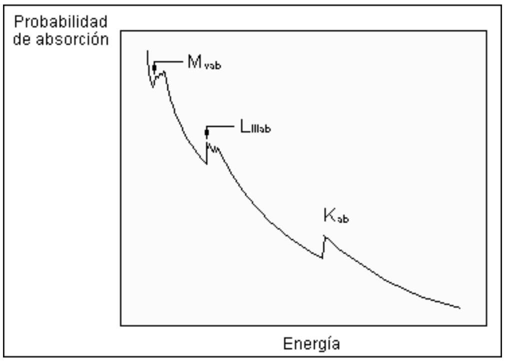

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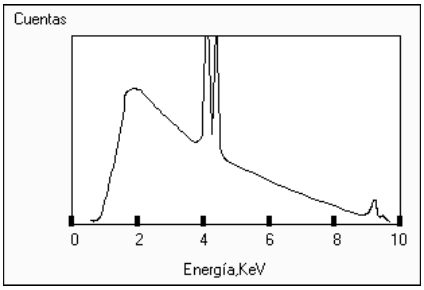

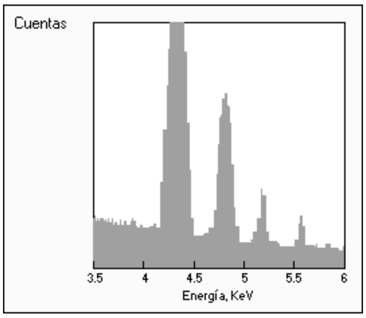

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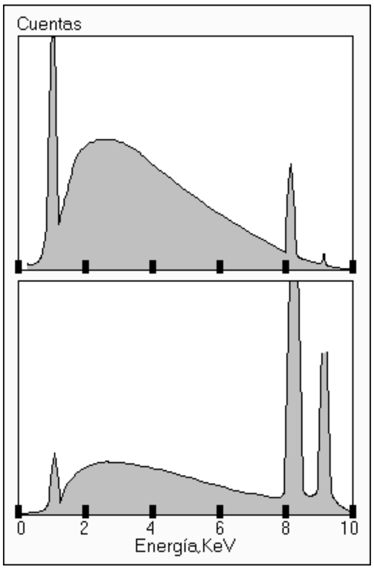

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SEM

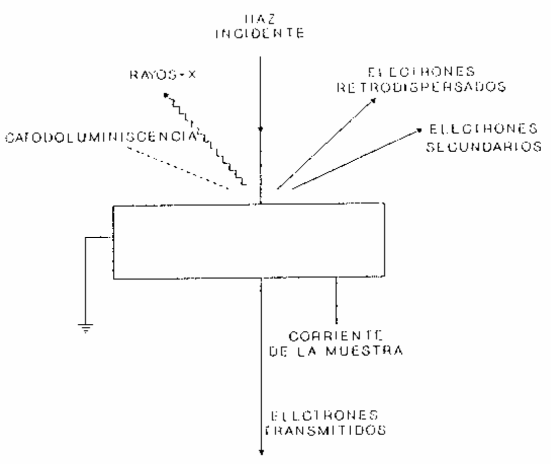

Figura 22. *Algunas de las señales que pueden ser utilizadas en un microscopio electrónico de barrido.*

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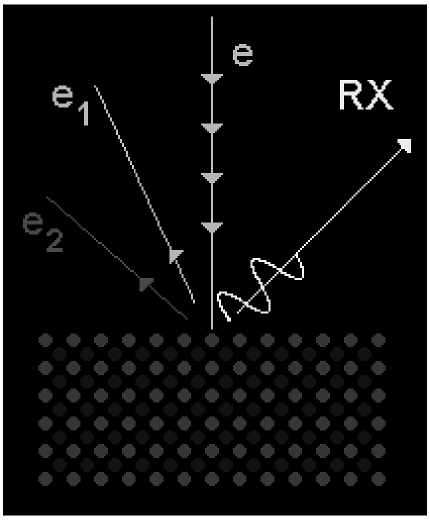
Interacción de electrones con la materia



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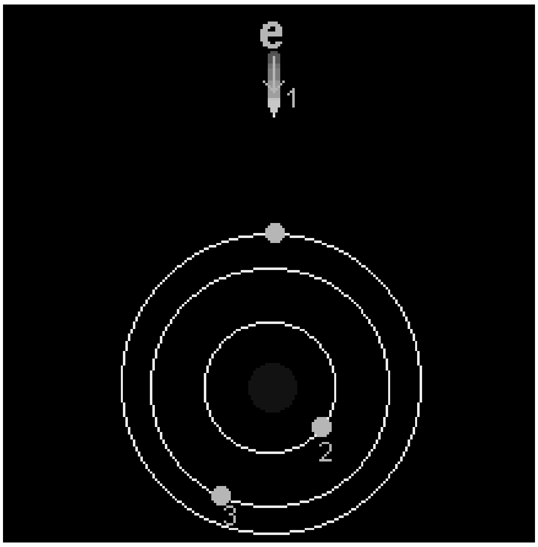
Electrón 1 ----- Electrón retrodispersado
Electrón 2 ----- Electrón secundario



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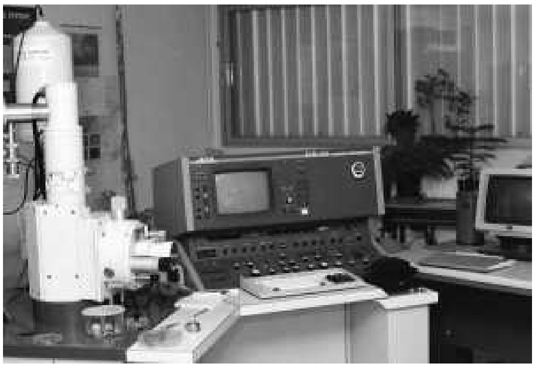
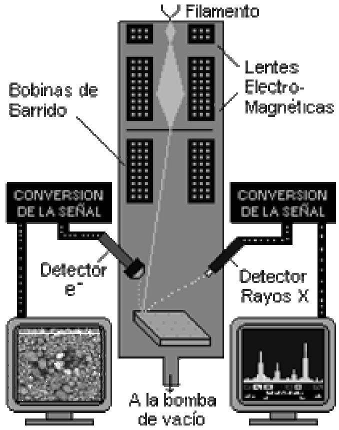
Microscopio electrónico de barrido





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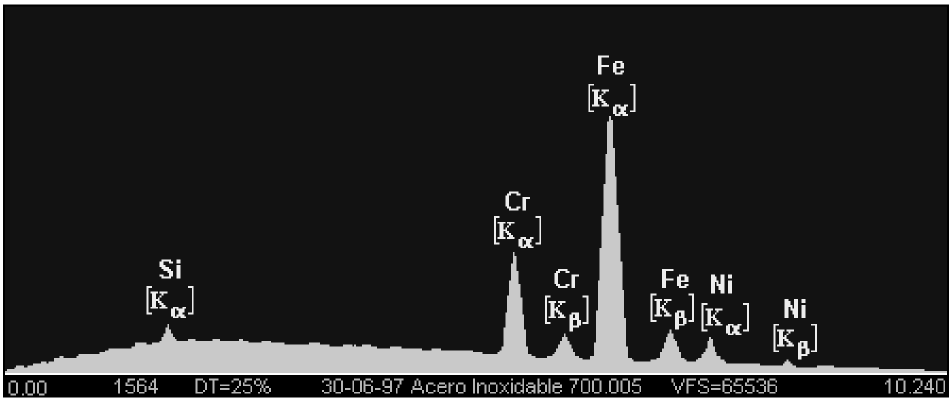
EDAX



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Perfiles de concentración

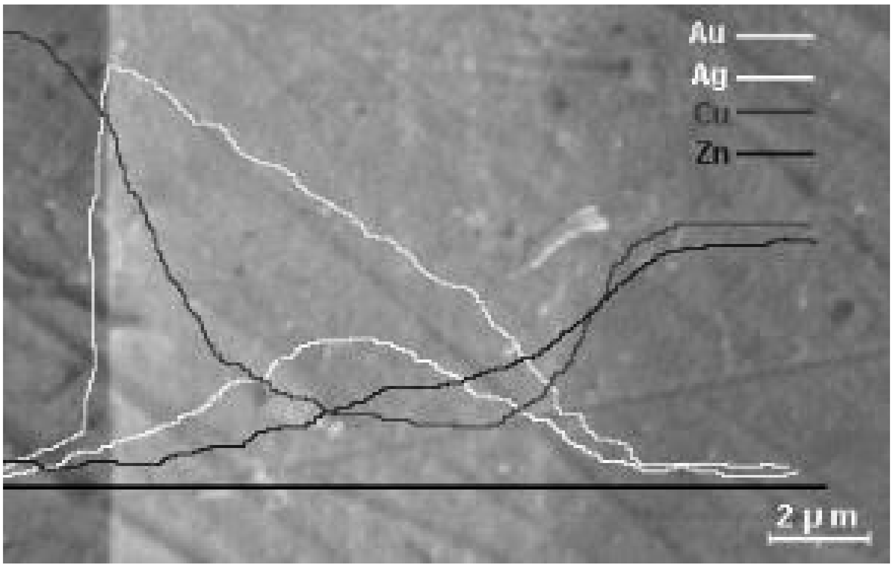

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Imagen de electrones retrodispersados

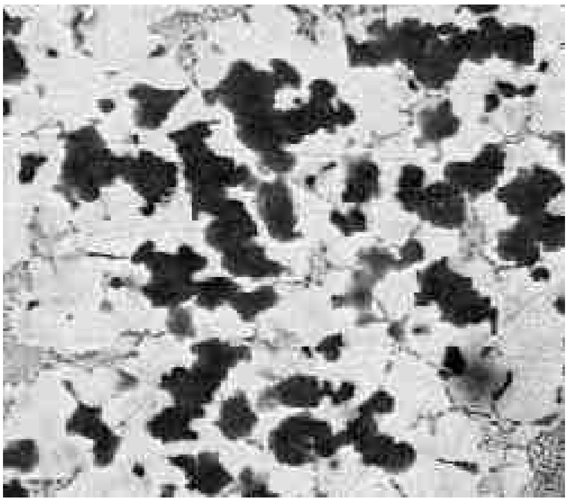

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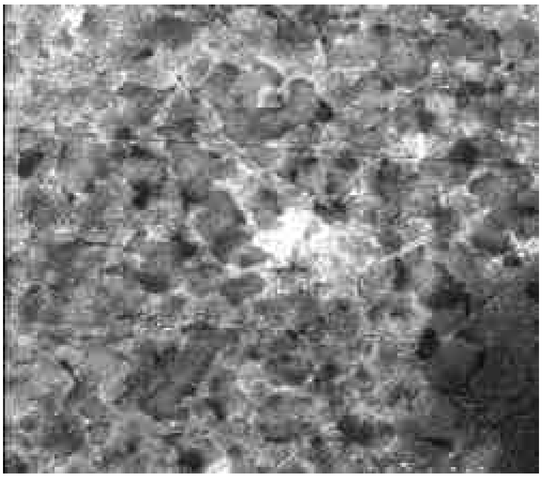
Imagen de electrones secundarios



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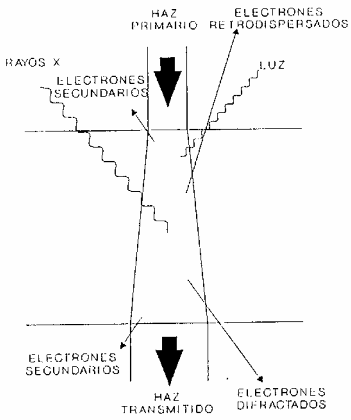
TEM



ıra 14. *Efectos que se pueden detectar cuando un haz de electrones primarios de alta energía incide sobre una muestra de espesor* m.

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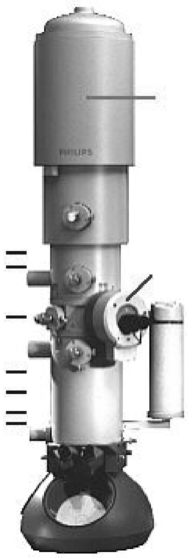
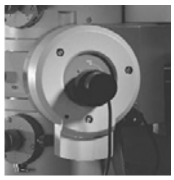
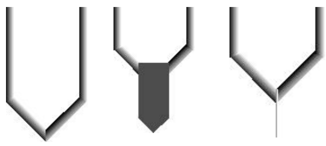
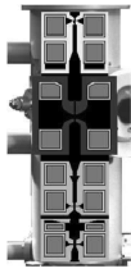
Column of a TEM

The cylindrical vessel at the top contains the electron gun (indicated by the green line). The specimen stage or goniometer is found halfway down the column (the red line). The location of the electron lenses is indicated by the blue lines on the left (we'll look at lenses in more detail further on). The vacuum system is found throughout the column





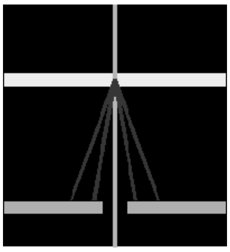


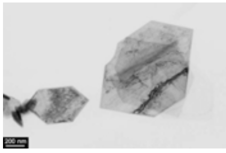


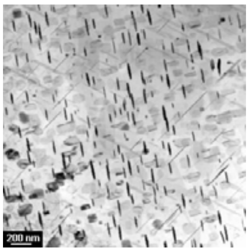
Methods in TEM

•Bright field : the standard method of recording TEM images.
•Diffraction : a difficult to understand but very useful method for getting information about crystals.
•Dark field : a second often-used imaging method.
•High-resolution TEM imaging : (too) simply stated, a way of 'seeing atoms'.
•Analysis : providing the chemical composition of the material we are looking at.

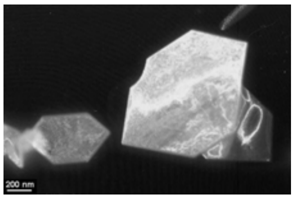
Bright field

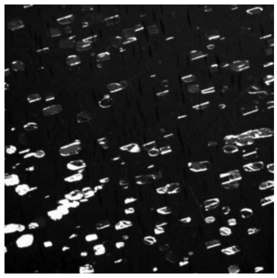






Dark field





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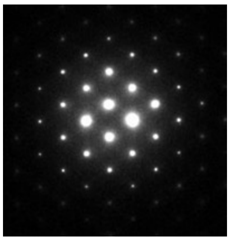
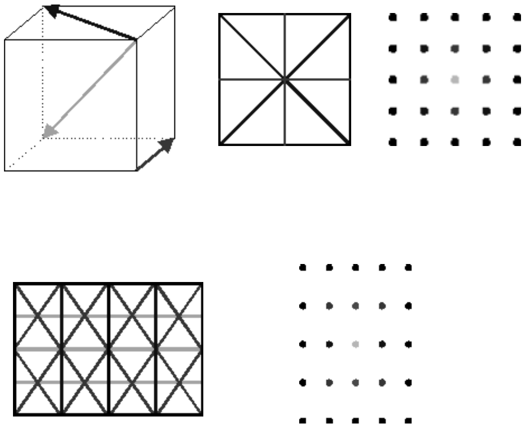
Diffraction





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Ejemplo de microscopia TEM

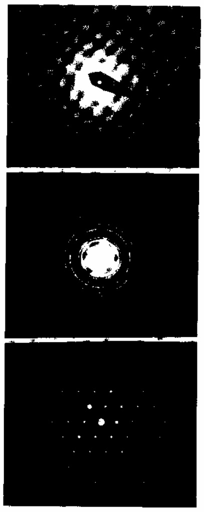

Figura 19. *Diagramas de difracción de electrones dependiendo de la cristalinidad del material. (a) TeO_2 poco cristalizado. (b) óxido mixto de uranio y lantano policristalino. (c) Monocristal de óxido mixto de uranio y lantano.*

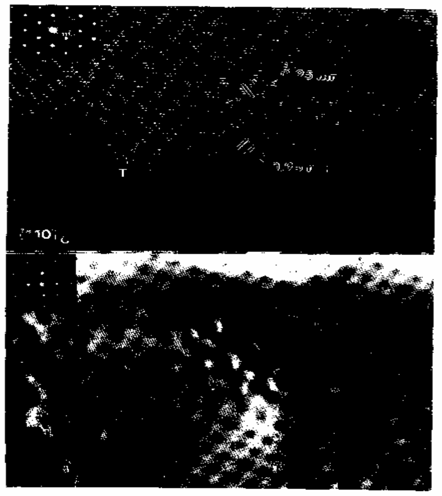

Figura 17. *Imágenes de alta resolución de un óxido mixto de uranio y lantano con sus correspondientes diagramas de difracción. (De P. García Chain, Tesis Doctoral, U. A. M. 1992).*

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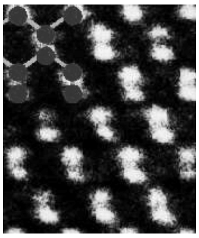
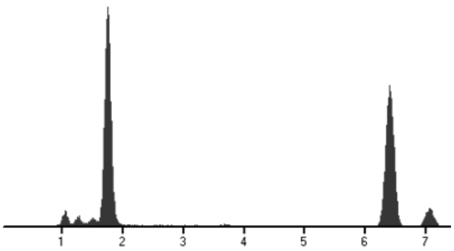
High-resolution TEM imaging



High-resolution image of silicon displaying dumbbells (pairs of silicon atom columns). The distance between the atom columns in a dumbbell is 0.14 nanometres. The real structure is drawn in colour (the green lines are used to highlight the arrangement and have no direct meaning).

Analysis



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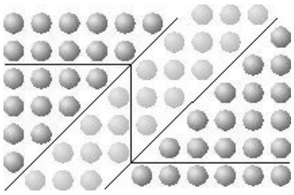
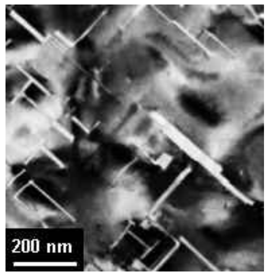
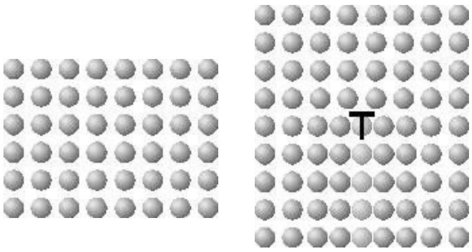
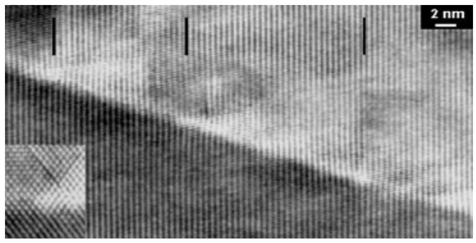
Twins and dislocations









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Microscopía de efecto tunel

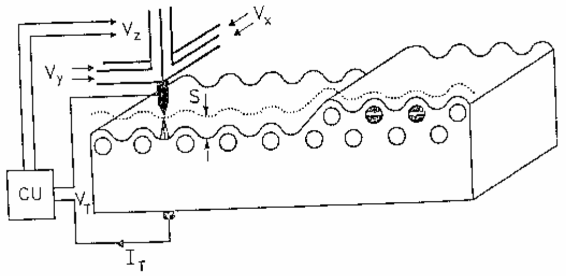

Figura 23. *Esquema de la operación de un microscopio de efecto túnel. La unidad de control CU, envía una señal V_z al elemento piezoeléctrico vertical de manera a mantener la corriente I_t constante, mientras la punta se desplaza a lo largo de la muestra por medio de las señales V_x, V_y aplicadas a los elementos piezoeléctricos horizontales. En la figura se observa la traza dibujada por la punta durante un rastreo sobre la muestra (s, distancia punta-muestra) a lo largo de la dirección Y. En la traza se puede observar el efecto de un escalón (información topográfica), y el efecto espectroscópico debido a dos átomos de impureza con un exceso de carga negativa (De G. Binning y H. Rohrer, IBM J. Res. Dev. 30 (1986) 355).*

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STM

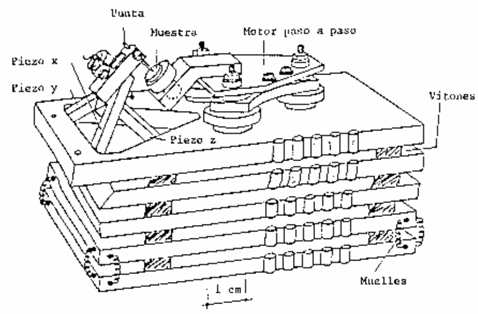

*Figura 24. Modelo de bolsillo de STM desarrollado por Ch. Gerber. Para
minar el efecto de las vibraciones mecánicas, [illegible]
cas separadas entre ellas por vitones, excepto las dos primeras que están
paradas por un conjunto de muelles. El microscopio propiamente dicho va
ntado en la última placa y contiene un trípode de tres piezoeléctricos a lo
go de tres direcciones X, Y, Z mutuamente perpendiculares. El trípode de
zoeléctricos mueve la punta con gran precisión. La muestra va unida a un
tor paso a paso que utiliza un disco piezoeléctrico y que efectúa una secuencia
vimiento-anclaje. (De Ch. Gerber, G. Binning, H. Fuchs, O. Marti y H.
Rohrer, Rev. Sci. Instrum. 57 (1986) 221).*

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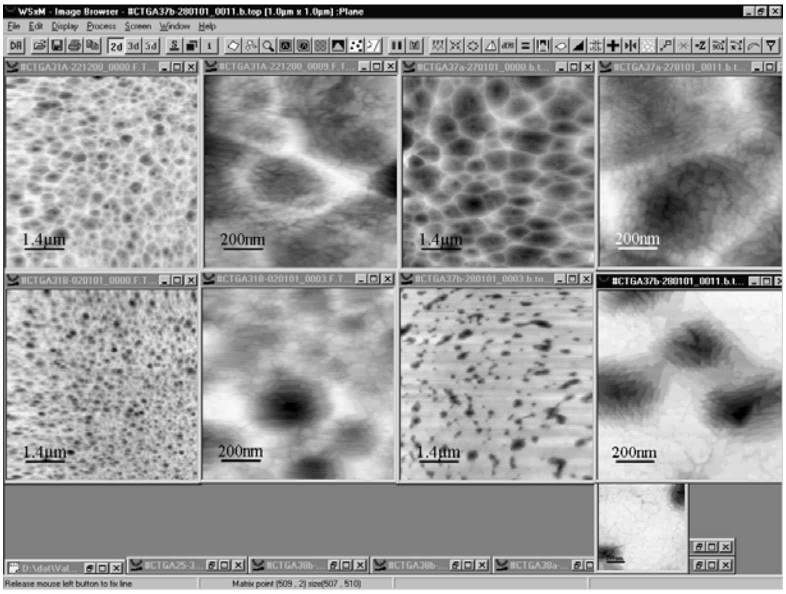
Microscopía de fuerzas atómica



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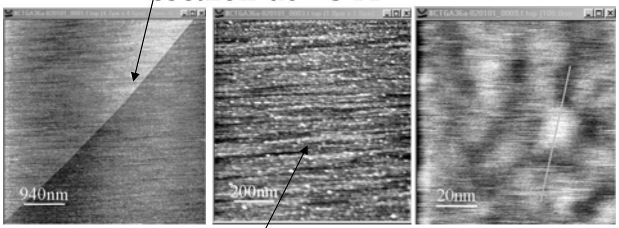
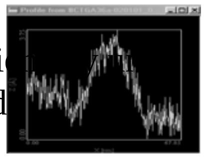
Microscopía de fuerzas atómica

escalón de ~5 Å



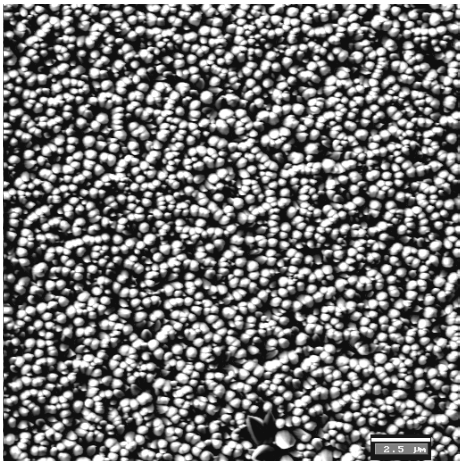
rug = 0.35 nm

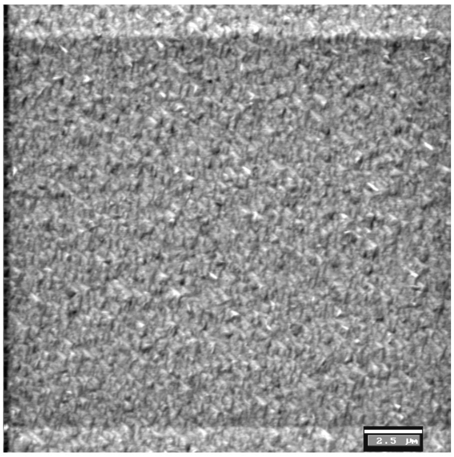
parece que tambi
dirección marcad



los clusters son mucho más pequeños que en la muestra CTGA30a-b

ZnO





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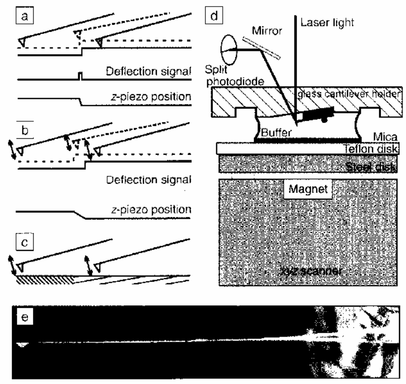

Figure. Atomic force microscopy (AFM) operation modes and instrumentation. (a) Contact mode, using the cantilever deflection as feedback signal. (b) Oscillation mode, using the oscillation amplitude as a feedback signal. (c) Oscillation mode, monitoring the phase difference between the driving force and cantilever oscillation. (d) Experimental setup for an atomic force microscope. A computer is used to control the movements of the sample and cantilever and store data on the surface contours measured. The instrument is operated with the sample adsorbed on a solid support (e.g., mica) in a buffer solution under ambient conditions. (e) Scanning electron microscopy image of an AFM cantilever and pyramidal tip. The contact-mode cantilever used for biological applications is a rectangular or triangular blade, typically ~0.4–0.8 μm thick, 100–200 μm long, and 20–40 μm wide. The pyramidal tip has a spherical end with a radius as small as 10 nm.

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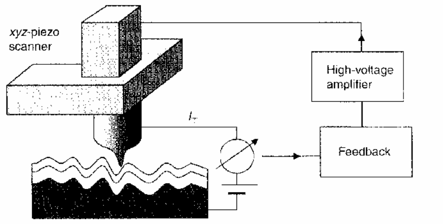

Figure 1. The basic components of scanning probe microscopy (SPM) are shown for the case of scanning tunneling microscopy (STM): xyz-piezo scanners move the probing tip across the sample surface. The tunneling current, I_T, is used, in the case of STM, as the input signal to the feedback loop. The output signal of the feedback is amplified and then fed to the z-piezo to control the distance between the probe tip and the sample. Other scanning probe microscopes send different signals to the feedback loop, derived from interactions such as force (scanning force microscopy, magnetic force microscopy) or light (scanning near-field optical microscopy).

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Scanning Probe Microscopy in Materials Science

Table I: Various Scanning Probe Microscopy (SPM) Techniques.

Name(s) of Technique	Acronym(s)	Mode of Operation	What is Measured?
Scanning tunneling microscopy	STM	Tunneling current controls *z*-regulating feedback loop.	Atomic-scale imaging of morphology (indirectly), or location of orbitals at particular energy levels. When tunneling voltage is varied, the measured current yields a spectrum. This variation of the technique is called scanning tunneling spectroscopy (STS) and yields information on both filled and empty states of the sample's band structure.
Atomic force microscopy *or* Scanning force microscopy	AFM, SFM	Cantilever-spring deflection controls *z*-regulating feedback loop.	Nanoscale measurements of surface morphology, materials properties, and forces between tip (which may be functionalized) and surface.
Friction force microscopy *or* Lateral force microscopy	FFM, LFM	Cantilever-spring deflection controls *z*-regulating feedback loop while torsional deflection of spring is displayed.	Friction can be measured and differentiated on a nanometer scale. When this is related to the surface chemistry, this is often referred to as chemical force microscopy (CFM), and tips are often surface-treated in order to enhance contrast.
Magnetic force microscopy	MFM	Deflection of cantilever spring caused by magnetic forces between magnetized tip and surface controls *z*-regulating feedback loop.	Magnetic field gradient above a sample.
Electric force microscopy	EFM	Deflection of cantilever spring caused by electrostatic forces between tip and surface controls *z*-regulating feedback loop.	Electric field gradient or surface potential above a sample.
Scanning Kelvin probe microscopy	SKPM	Capacitive force is measured between oscillating tip and surfaces while the sample voltage is varied until the electrostatic field is compensated.	Map of surface contact potential difference.
Scanning capacitance microscopy	SCM	Capacitance is measured between oscillating tip and surfaces while scanning a biased tip above the sample surface.	Map of surface capacitance.
Near-field scanning optical microscopy *or* Scanning near-field optical microscopy	NSOM, SNOM	An optical fiber with a small aperture is scanned in very close proximity to the sample, and the transmitted or reflected light is detected and/or analyzed spectroscopically.	Optical images of a surface with resolution of ~100 nm; optical images of smaller emitting species, such as single fluorescent molecules.

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