Appunti & trasparenze - Parte 9

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Metodi di osservazione e fabbricazione di nanostrutture con fasci di cariche: microscopia elettronica SEM, TEM per analisi morfologiche e strutturali; litografia a fascio elettronico (EBL, SCALPEL) e a fascio di ioni focalizzati (FIB).

25/11/2004 - ITI M 9.30+1

Introduzione

Idea fondamentale dell'ottica elettronica (e ionica):

- ✓ sostituire radiazione elettromagnetica con onde di materia con lunghezza d'onda di de Broglie (molto bassa per particelle veloci);
- ✓ impiego di cariche permette manipolazione accurata con campi elettrici e magnetici (statici)

$$\lambda = h/mv \qquad mv^2/2 = eV$$

Elevata risoluzione, sia per analisi (**microscopia elettronica**) che per fabbricazione (**litografia con fasci di cariche**)

ma

tecniche tipicamente “seriali” (a scansione)

apparati complessi

necessità sistemi UHV

difficoltà di collimare cariche (per repulsione Coulombiana)

Lunghezza d'onda di de Broglie

Aspetto fondamentale:
λ di de Broglie per fascio di
elettroni accelerati

Componenti importanti:
lenti elettromagnetiche per realizzare fasci intensi (collimati o focalizzati)

Prime "peculiarità" ottica elettronica:

- elevata energia cinetica delle cariche
  --> possibile danneggiamento campioni

- superficie campioni a potenziale definito
  --> necessità preparazione (se isolanti)

- complessità preparazione fascio elettronico
  e necessità UHV

4.1.1 Wave Properties of Electrons

The focusing of an electron beam is possible because of the dual, *wave–particle* character of electrons. This wave–particle duality is expressed in the *de Broglie relationship* for the wavelength of a particle:

$$\lambda = h/mv \tag{4.1}$$

where m is the mass of the particle, v is its velocity and h is the Planck constant. Assuming that the accelerating voltage in the electron gun is V, then the electron energy is given by:

$$mv^2/2 = eV \tag{4.2}$$

where e is the charge on the electron. It follows that $\lambda = h/(2meV)^{0.5}$, or $\lambda = (1.5/V)^{0.5}$ nm when V is in volts. This numerical value is approximate, since at the accelerating voltages commonly used in the electron microscope, the *rest mass* of the electron, m_0, is appreciably less than the *relativistic mass*, m, and a correction term should be included, in the equation:

$$\lambda = \frac{h}{\sqrt{\left[2m_0eV\left(1+\frac{eV}{2m_0c^2}\right)\right]}} \tag{4.3}$$

where c is the velocity of light. The relativistic correction amounts to *ca* 5 % at 100 kV, rising to 30 % at 1 MV. The electron wavelength at 100 kV is 0.00370 nm, which is nearly two orders of magnitude less than the interatomic spacings typical of the solid state. At 10 keV, which is typical of many applications of scanning electron microscopy, the wavelength is only 0.012 nm, still appreciably less than the interatomic distances in solids.

SEM e TEM

Da Brandon Kaplan
Microstruct. Charact.
of Materials
Wiley (1999)

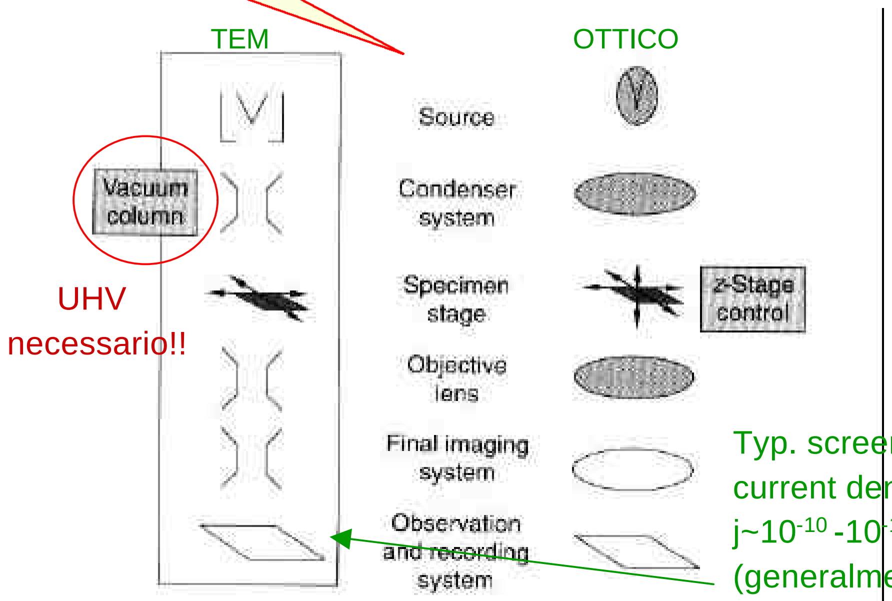

Figure 4.1 Similar to the transmission optical microscope, the transmission electro microscope has a source, a condenser system, a specimen stage, an objective lens and a imaging system, as well as a method for observing and recording the image

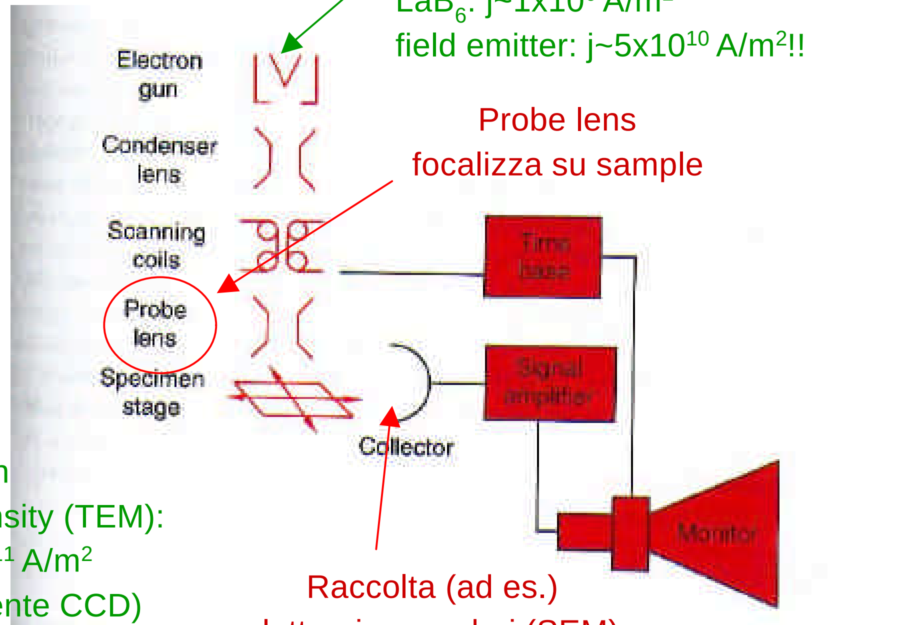

Figure 4.2 In the scanning electron microscope, a fine probe of high-energy electrons is focused on to the sample surface and then scanned across the surface in a television raster. A signal generated by the interaction of the probe with the sample is collected, amplified and displayed on a monitor with the same time base as the raster used to scan the sample

Transmission Electron Microscope (TEM)
("analogo" a microscopio ott. a trasm.)

Scanning Electron Microscope (SEM)
("analogo" a microscopio ott. a rifl.)

Processi di scattering e^-/materiale: elastici ed inelastici (più importanti in SEM)
Immagine ricostruita da scansione (SEM: processo "seriale")
Necessità assottigliare campione (TEM: preparazione difficile con "mole" e ion-milling)
Accelerazione typ. e^-: decine di keV (TEM), keV (SEM, anche <1keV e in basso vuoto)

Cenni di ottica elettronica

Lenti costituite da configurazioni di campi elettromagnetici statici
--> possibilità controllo focalizzazione!!

Risoluzione “teorica” sub-nm e
profondità di campo ampia (TEM)

4.1.1.3 RESOLUTION AND FOCUSING

Given that the maximum beam divergence in the electron microscope is less than 1°, the Raleigh criterion for the image of a point source can be reduced to the following, $\delta = 0.61\lambda/\mu \sin\alpha \approx 0.61\lambda/\alpha < 60\lambda$. By inserting the value for the wavelength at 100 kV, 0.0037 nm, the potential resolution of the electron microscope should be of the order of 0.2 nm. At higher operating voltages, an even better resolution should be possible (see below).

As a gross approximation, we can use the light-optical expression for depth of field, $d \approx \delta/\alpha$, so that the thin-film specimens used in transmission electron microscopy should be of the order of 20–200 nm in thickness if both the top and bottom of the film are to be in focus simultaneously. A similar evaluation can be used for the depth of focus, $D = M^2 d$, so that at a magnification M of 10000 the expected depth of focus is of the order of metres! There is no problem whatsoever in focusing an image on a fluorescent screen and subsequently recording the same image on a photographic emulsion placed some distance *beneath* the focusing screen.

Da Brandon Kaplan
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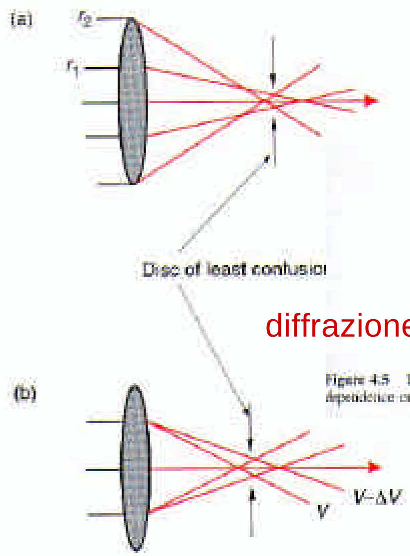
aberrazione sferica



diffrazione

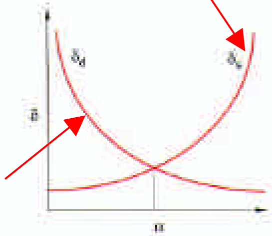


Figure 4.5 The diffraction and the spherical aberration limits on resolution have an opposite dependence on the angular aperture of the objective, so that an optimum value of α exists

aberrazione cromatica

Figure 4.4 Spherical (a) and chromatic aberration (b) prevent a parallel beam from being brought to a point focus. Instead, a disc of least confusion is formed in the focal plane

Analoghi elettronici dell’ottica
convenzionale

Ottica elettronica “sensibile” a fenomeni di aberrazione, astigmatismo,…
Difficoltà controllo repulsione Coulombiana fra elettroni
Possibilità effetti di carica spaziale (in campioni non buoni conduttori)

Meccanismi di contrasto (*soprattutto* TEM)

Interazione elastica elettroni/materiale (*nel TEM*)

1. mass thickness (materiali amorfi, intensità dipende da quantità materiale attraversata)
2. diffraction (materiali cristallini --> diffrazione Bragg, sensibilità a difetti cristallini)
3. phase contrast (per alta apertura numerica, legata a interferenza di *vari* fasci diffratti)

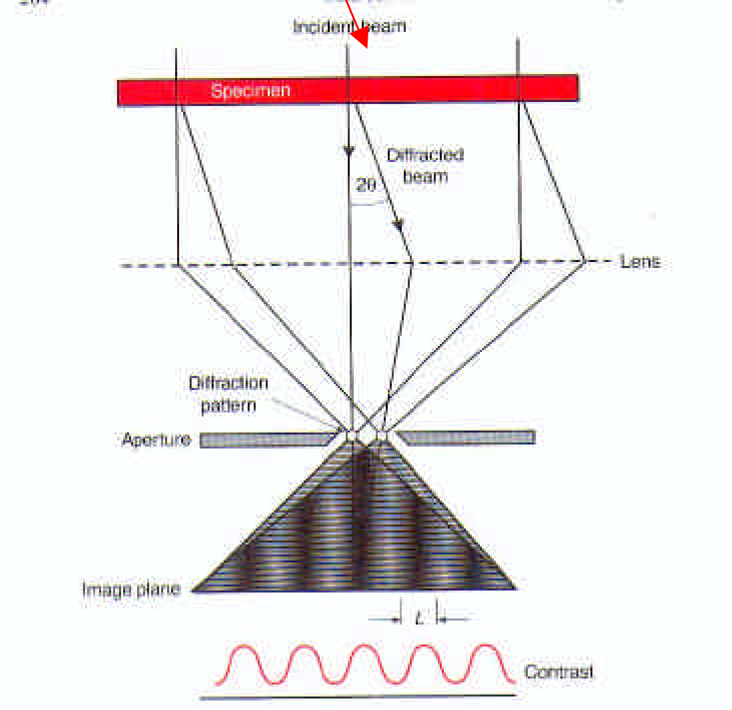
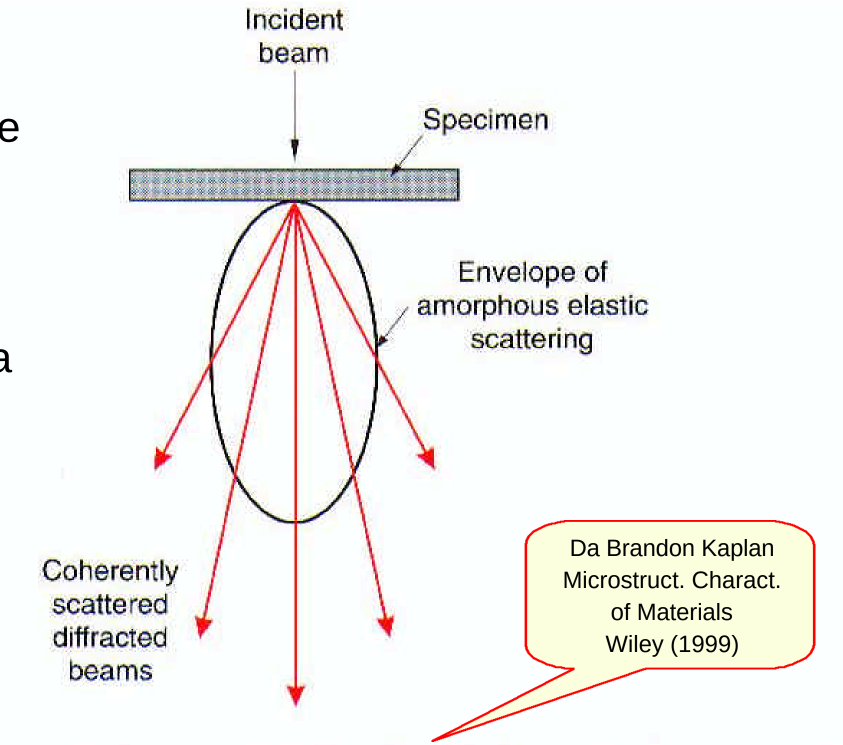


Figure 4.15 If the objective aperture accepts a Bragg-diffracted beam as well as the direct transmitted beam, $\alpha > 2\theta$, then an interference pattern will be formed in the image plane as a result of the difference in path lengths of the two beams



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igure 4.12 The incident beam is elastically scattered by the sample, either randomly (a lassy or amorphous specimen), or coherently (a crystalline phase). The image may be formed rom the direct transmitted beam, by a diffracted beam, or by the interference of the diffracted eams with each other and/or the direct transmitted beam (see text for details)

Informazioni morfologiche e strutturali (*spesso "convolute"*) ottenibili con elevata risoluzione spaziale

Bright/dark field TEM

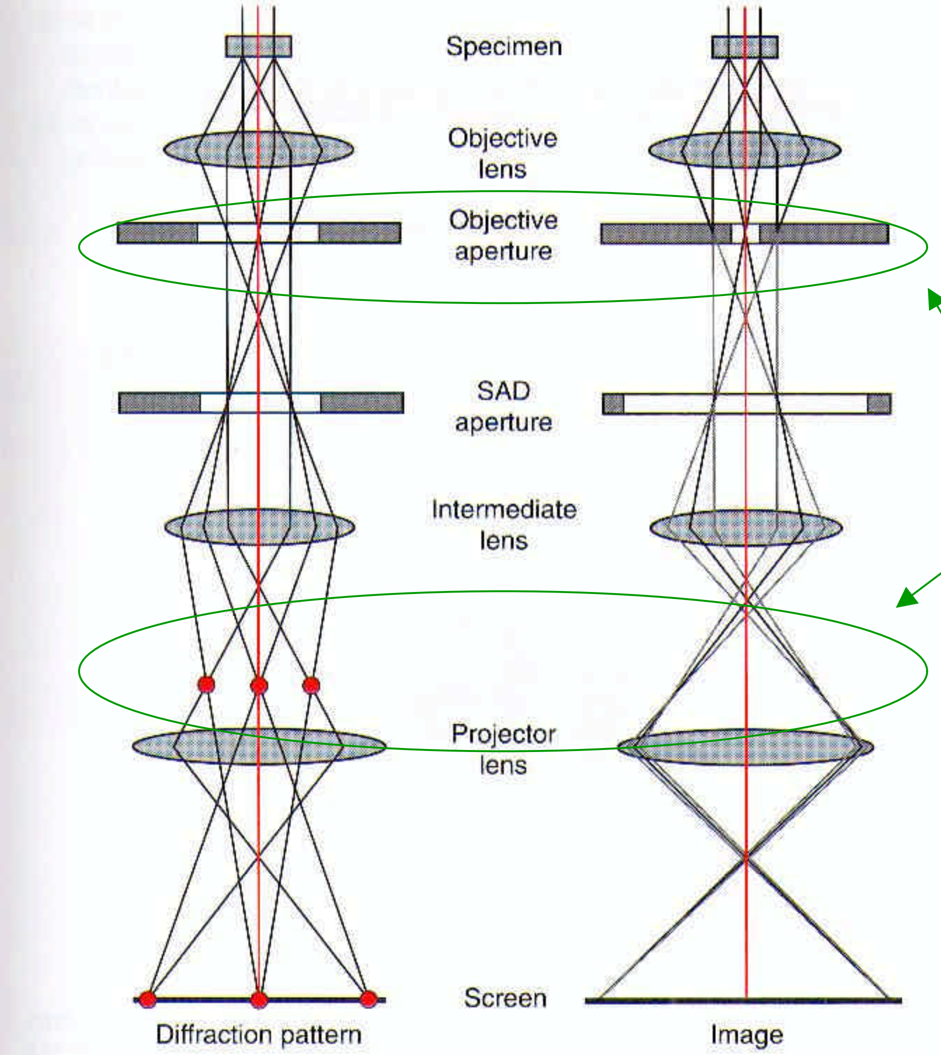


Figure 4.14 The transmission electron microscope can be used to image the specimen by focusing the final image in the plane of the fluorescent screen, or it can be used to image the diffraction pattern from the specimen. In the first case, to an excellent approximation, the image of the specimen is observed when the imaging system is focused on the front focal plane of the objective (the position of the specimen), while the diffraction pattern is observed when the imaging system is focused on the back focal plane of the objective (which corresponds to the first image plane for the diffracted and transmitted beams)

In materiali cristallini (anche *nano*crist.!!): possibilità di ricostruire il reticolo (concettualmente simile a XRD)

Operativamente: modifica apertura numerica (accettanza) obiettivo e condizioni di focalizzazione

Contrasto esaltato da difetti reticolari, stacking faults (irregolarità di crescita), anti-phase boundaries (difetti ai bordi grano in policristalli), coherency strains (deformazioni reticolari su media scala),...

Da Brandon Kaplan Microstruct. Charact. of Materials Wiley (1999)

Esempi di TEM images ad alta risoluzione

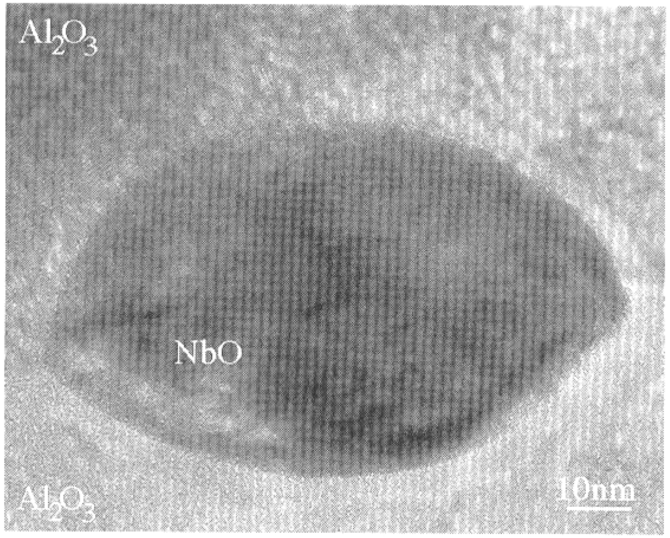


Figure 4.53 Transmission electron micrograph of a NbO particle located at a grain boundary in polycrystalline alumina. Phase contrast (lattice fringes) and mass–thickness contrast vary from the alumina grain to the NbO grain

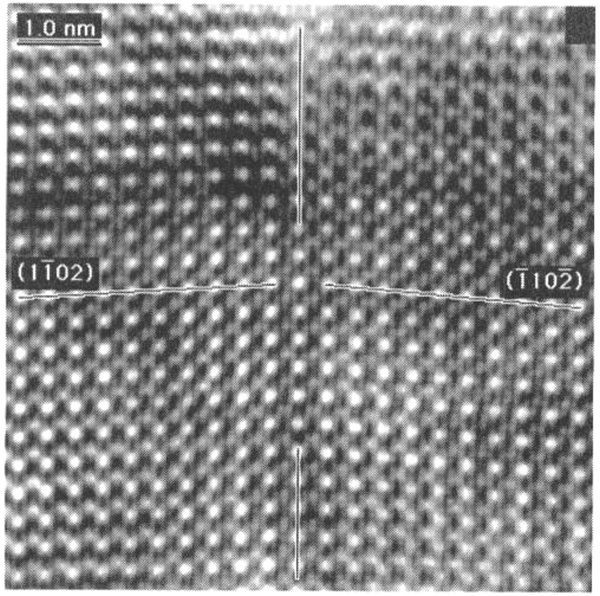


Figure 4.54 Lattice image of a rhombohedral twin in alumina

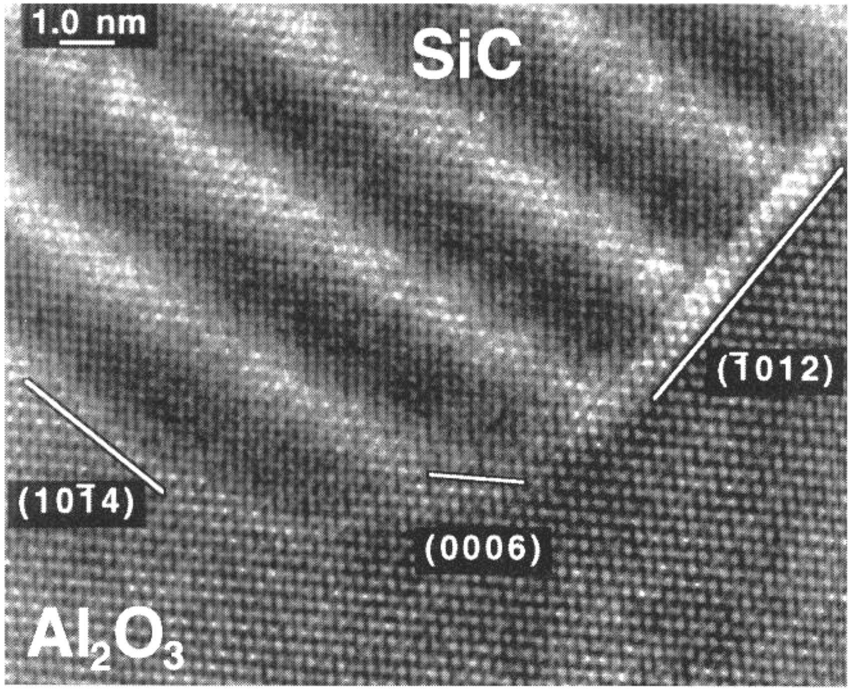


Figure 4.55 Lattice image of a SiC particle located within an alumina grain. The alumina lies along a low-index-zone axis, and is the source of the lattice image. A moiré pattern appears within the SiC particle due to overlap between the alumina and SiC (in the direction of the electron beam)

Informazioni estremamente dettagliate su campioni cristallini sottili (previa interpretazione e per morfologia “piatta”)

Generazione di elettroni secondari (SEM)

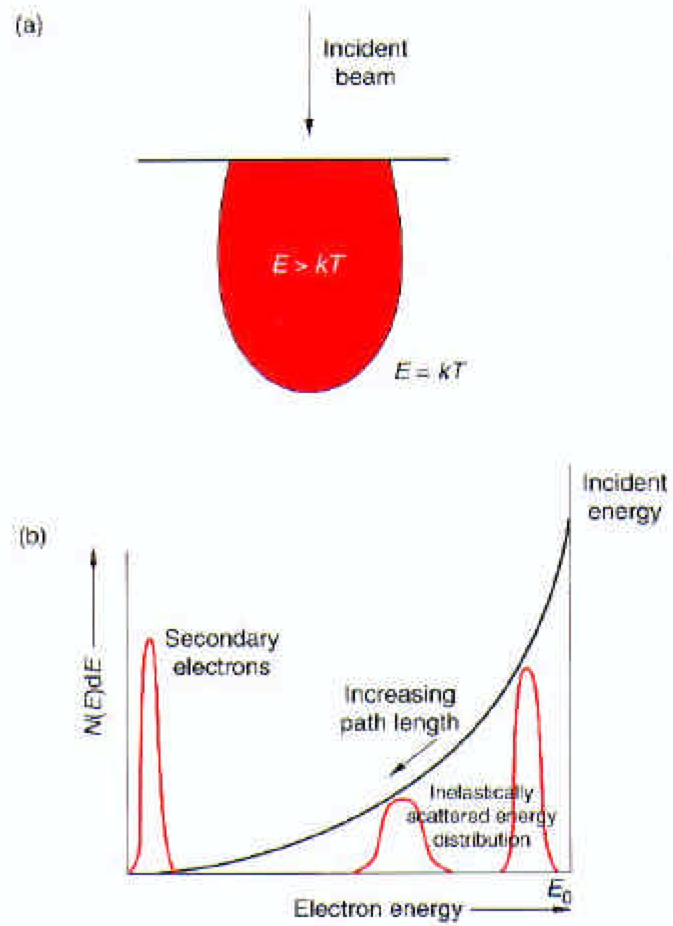


Figure 4.29 (a) The electron beam is inelastically scattered within an envelope bounded by the condition that the average energy has reached the thermal kinetic value *kT*. (b) The energy spread increases and the average energy of the electron falls as the path length within the solid increases (channelling effects and lattice anisotropy being ignored). (c) Random scattering models for individual electrons (Monte Carlo simulation) provide a vivid image of both the energy distribution and the spatial distribution of the electrons in the volume of the material beneath the beam, as well as the origin of the back-scattered electron signal

Da Brandon Kaplan
Microstruct. Charact.
of Materials
Wiley (1999)

Nel SEM gli elettroni *non* attraversano il campione:

--> analisi anche di campioni spessi
--> conducibilità campione cruciale (metallizzazione campioni isolanti)
--> contrasto legato *prevalentemente* a generazione di **elettroni secondari**
--> risoluzione inferiore a TEM (contrasto per processi meno “diretti”, minore influenza del reticolo cristallino, possibili effetti di campo locale per l’energia relativamente bassa degli elettroni secondari,…)

SEM: interazione anelastica elettroni/materiale

Meccanismi di contrasto nel SEM

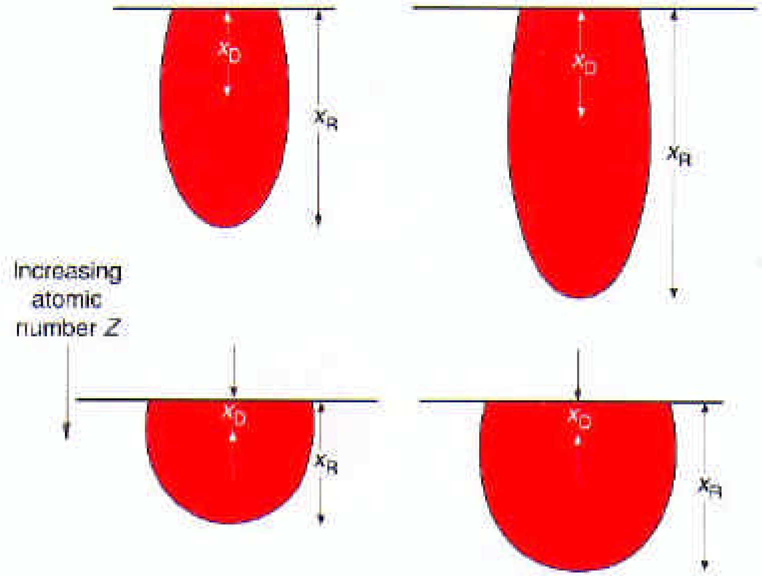
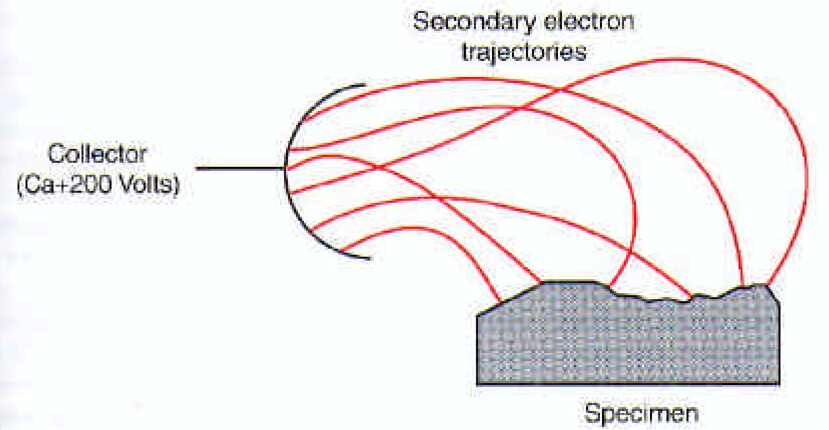


Figure 4.30 The inelastic scattering envelope for an incident beam of energetic electrons depends on both the incident energy and the atomic number of the target, and is qualitatively characterized by the two parameters, diffusion depth, and penetration depth (or range)



igure 4.37 Secondary electrons can be collected from regions of the surface which are not the 'line of sight' of the collector

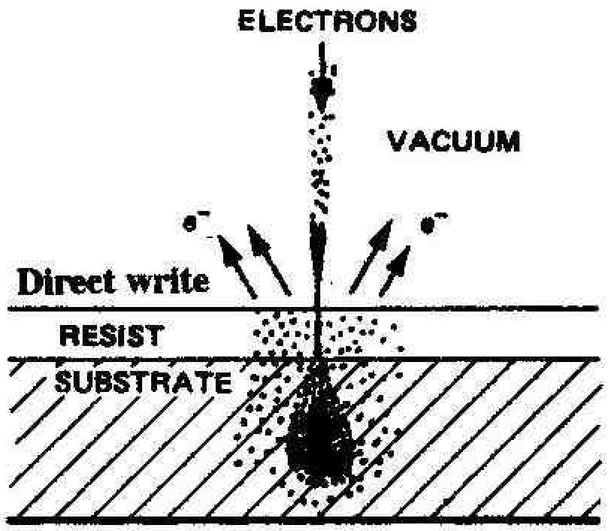
Risoluzione spaziale dovuta a focalizzazione fascio elettronico, non a meccanismi di raccolta degli elettroni secondari

Sezione d'urto scattering inelastico dipende da numero atomico Z
Energia elettroni secondari dipende da configurazione elettronica
Intenità fascio elettroni secondari dipende da lunghezze di penetrazione e diffusione, cioè da densità materiale, Z, carattere metallico, ...

Ulteriori informazioni *locali* di **microanalisi** da scattering inelastico (es.: X-ray Photoelectron Spectr. - XPS, Rutherford BackScattering - RBS, Secondary Ioniz. Mass Spectr. - SIMS, …)

Litografia da fascio di cariche

Fascio focalizzato di cariche *accelerate* può essere usato per:
- etching, milling etc. (funziona meglio con masse ioniche)
- scrittura (impressione) di un resist e successivo trasferimento pattern



(b) ELECTRON-BEAM LITHOGRAPHY

TABLE 1.6 Electron- and Ion-Beam Applications

Electron-Beam Applications	Ion-Beam Applications
Nanoscale lithography	Micromachining and ion milling
Low-voltage scanning electron microscopy	Microdeposition of metals
Critical dimension measurements	Maskless ion implantation
Electron-beam-induced metal deposition	Microstructure failure analysis
Reflection high-energy electron diffraction (RHEED)	Secondary ion mass spectroscopy
Scanning auger microscopy	

Da Madou, Fundamentals of microfabr. CRC (1997)

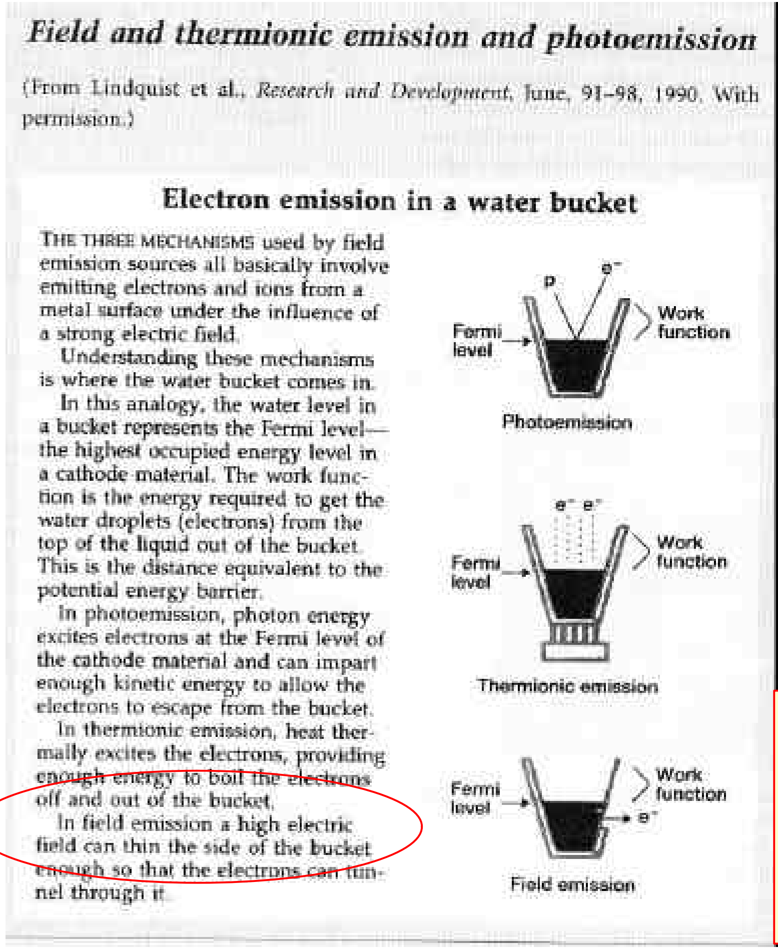
Tecnica di scrittura "seriale" (pattern generato in sequenza) --> alti tempi di processo
(in linea di principio è possibile anche litografia con maschera su area estesa, ma maschera è critica)
Sviluppi recenti: array di emettitori ad effetto di campo (es. nanowires, nanotubes)

Requisiti fascio elettronico per litografia

Risoluzione spaziale legata a **focalizzazione** del fascio (come in SEM)

Necessità fasci intensi (per velocità processo, efficienza scrittura, ...), ma a basse differenze di potenziale (alcuni kV)

--> field emitters (eventualmente in array per EBL parallela)



Field and thermionic emission and photoemission

(From Lindquist et al., *Research and Development*, June, 91–98, 1990. With permission.)

Electron emission in a water bucket

THE THREE MECHANISMS used by field emission sources all basically involve emitting electrons and ions from a metal surface under the influence of a strong electric field.

Understanding these mechanisms is where the water bucket comes in.

In this analogy, the water level in a bucket represents the Fermi level—the highest occupied energy level in a cathode material. The work function is the energy required to get the water droplets (electrons) from the top of the liquid out of the bucket. This is the distance equivalent to the potential energy barrier.

In photoemission, photon energy excites electrons at the Fermi level of the cathode material and can impart enough kinetic energy to allow the electrons to escape from the bucket.

In thermionic emission, heat thermally excites the electrons, providing enough energy to boil the electrons off and out of the bucket.

In field emission a high electric field can thin the side of the bucket enough so that the electrons can tunnel through it.

Micro- e nano-fabbricazione necessaria per field emitters

This carbide crystalline tip, with a radius of 100 angstroms, or 10 nanometers at the top and 0.5 micron at the base, emits electrons in a tiny beam.

Difficoltà in manipolazione fasci di cariche: repulsione Coulombiana
(ma vantaggi nella flessibilità di focalizz. e dose impartitaal resist)

Scrittura diretta con fascio di elettroni

5.1 Electron Beam Direct Write

In electron beam direct write electrons are formed to a beam and are accelerated to a determined position on the wafer surface, where the resist has to be exposed to form the pattern. An electron beam system consists of the electron source or electron gun, the electron-optical system (the electron column), a mechanical wafer stage and a controller system. A schematic view of an electron beam lithography tool is given in Figure 18.

The two types of electron guns which are commonly used are thermionic sources, on the one hand, and field emission sources, on the other hand. In thermionic sources the electrons are emitted by heating the source material, such as tungsten (W) or lantanum hexaboride (LaB_6). While LaB_6 offers a higher brightness (10^5(A/cm^2)/steradian)) and a longer lifetime (~1000 h) than W (10^4(A/cm^2)/steradian; ~100 h), W has the advantage that vacuum requirements are not as high as for LaB_6. Nevertheless, LaB_6 has become the standard source for thermionic e-beam sources.

In field emission sources the electrons are extracted from a sharp tip by a high electric field. Though these sources have a high brightness (10^7(A/cm^2)/steradian)), they are unstable and require a ultrahigh vacuum. Therefore they have not been widely adopted in electron beam lithography systems.

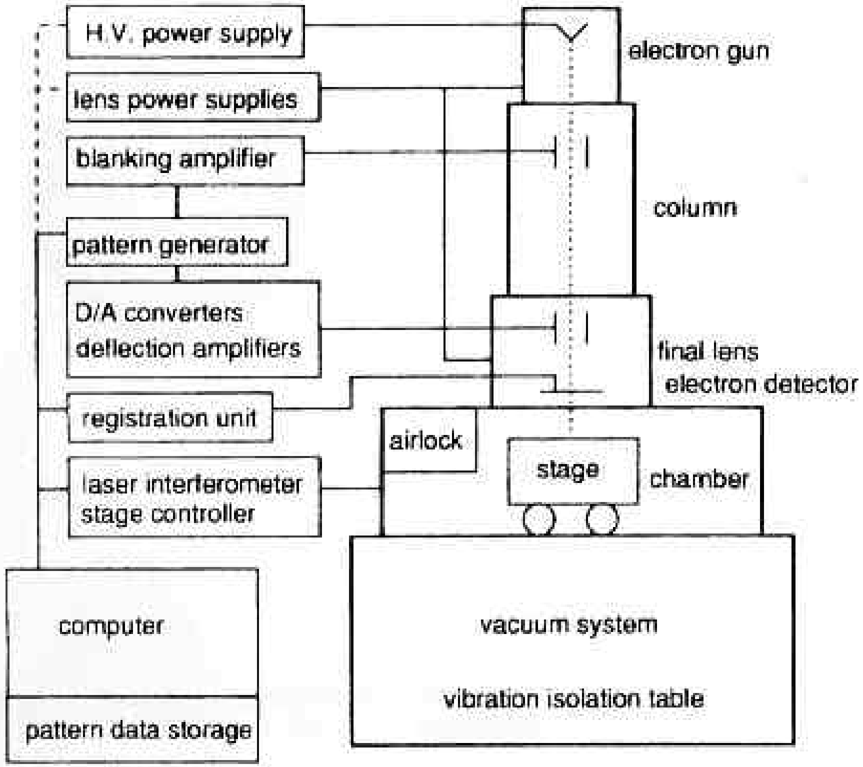
In the electron column the extracted electrons are formed to a beam with a definite diameter or shape. Therefore different electron-optical elements as focusing and defocusing lenses and apertures are employed. Further parts of the column are a beam blank to switch the beam on and off and a beam deflection system, with which the beam is positioned on the wafer.

Since the deflection system can only address a field of 400 – 800 µm (depending on spot size and tool), it is necessary to move the sample under the beam from one exposure field to the next by a mechanical wafer stage. The position of the stage is measured by an interferometer, so it is possible to adjust the beam with an accuracy of ~5 nm.

The whole system has to be under vacuum to enable the electron beam to be formed and has to be isolated from vibrations. Further requirements are low electromagnetic stray field, because this would hamper the positioning of the beam.

The pattern, which is given as a CAD file, is translated into movements of the electron beam/wafer stage by a computer. During an illumination, the tilt of the sample is measured continuously and the focus is adjusted. There are two exposure schemes: In the first one, the raster scan scheme, the deflection system and the wafer stage address every point of the sample, but the beam is switched on and off according to the structure. In the second scheme, the vector scan scheme, only the points which have to be illuminated are addressed. Hence the vector scan scheme is less time-consuming than the raster scan scheme.

The time needed for the illumination of a whole wafer depends on the pattern, but because the electron beam direct write is a serial method, it is time-consuming and not suitable for the industrial mass production of microelectronic circuits. Nevertheless, because the resolution is pushed to a few nanometers, it has a high impact on research activities and is the method of choice for defining the pattern on the masks used for optical lithography.



Resists in EBL e risoluzione spaziale

Resists organici (es. PMMA, stessi meccanismi di fotoresist!!) oppure inorganici (es. film sottili di fluoruri, calcogenuri amorfi, AsS, AsSe,…)

Problemi EBL:
scattering inelastico elettroni da resist (o substrato)
--> elettroni secondari, raggi-X, etc.
--> riduzione risoluzione spaziale (cfr. anche XRL)

- Uso di resist "robusti" (typ. Inorganici) e compatti (film sottili policristallini o amorfi)
- Spessori resist ridotti (per evitare fenomeni secondari), typ.< 100 nm
- Uso di basse differenze di potenziale e controllo accurato della dose

Risoluzione spaziale ultima fortemente influenzata da processo di interazione con resist (e substrato)

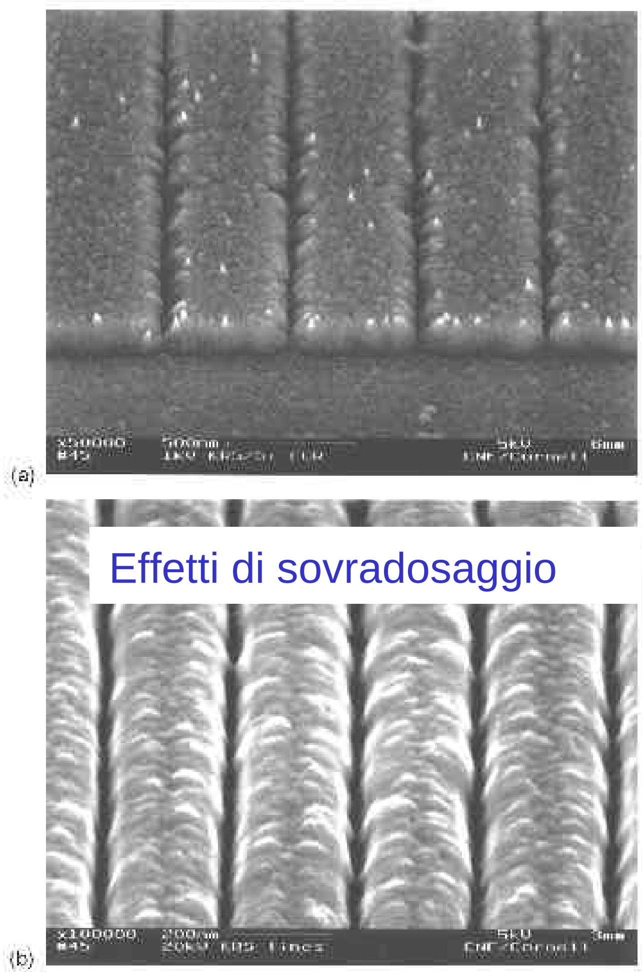
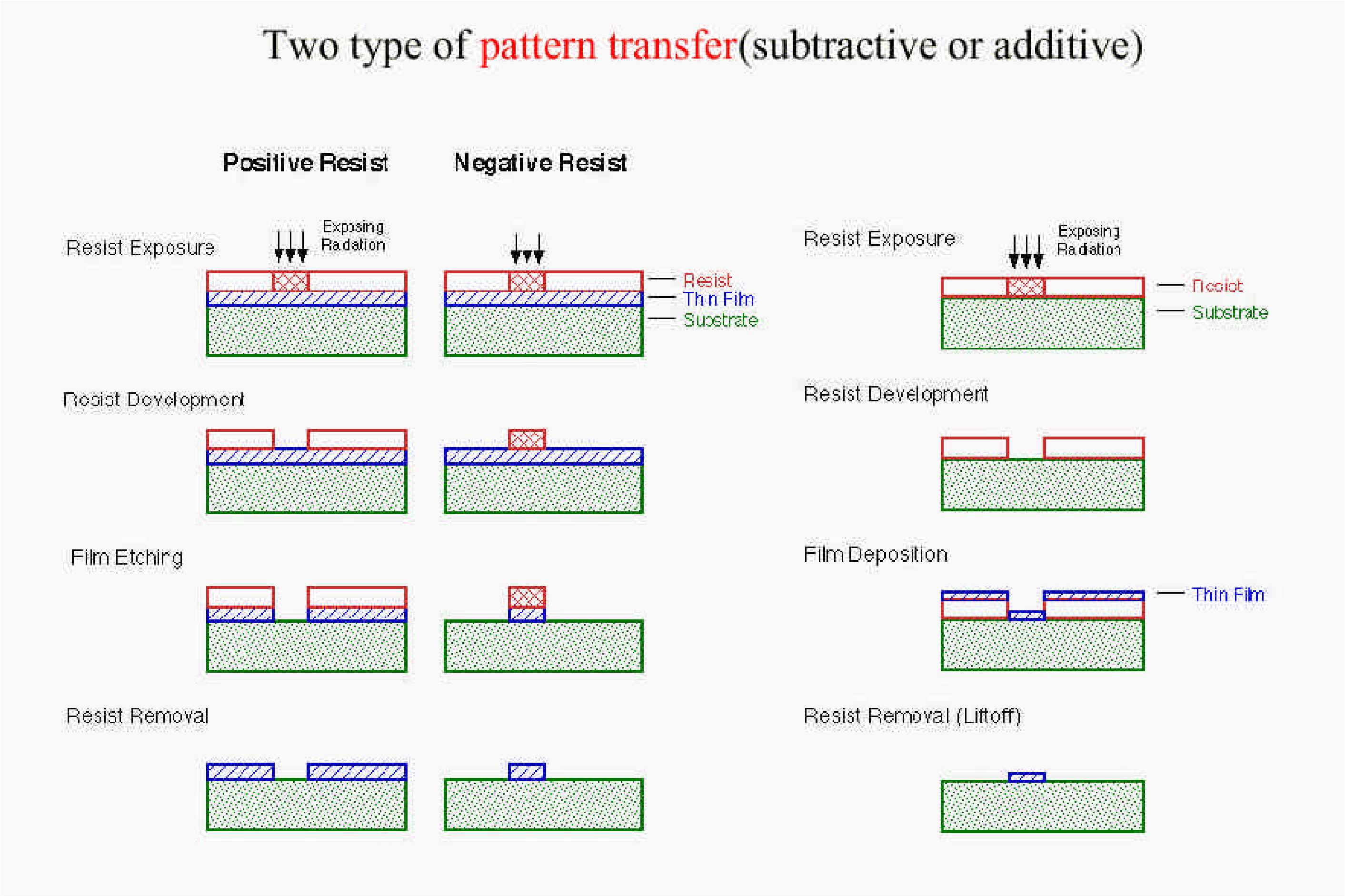


FIG. 3. Single pass lines etched into Si using the two step ECR etch, for KRS resist exposed at 1 keV (a) and a 20 keV (b) with line doses of 11 and 175 pC/cm, respectively.

Possibilità di patterning sottrattivo o additivo



Alta flessibilità di processo (purchè EBL sia integrata con fabbricazione)

Esempio di fabbricazione EBL di QD "nanostrutturati"

C.P.Poole F.J.Owens
Introd. to Nanotechnology
(Wiley, 2003)

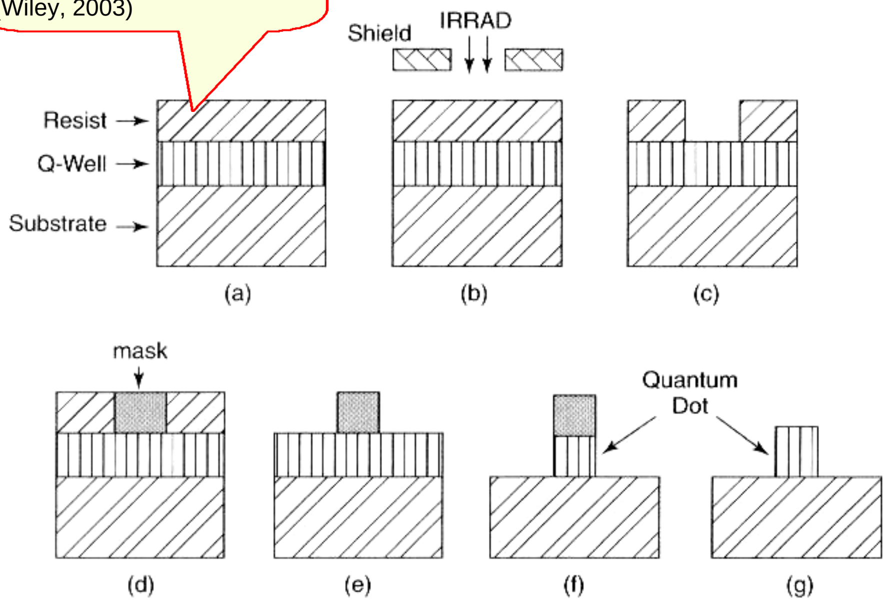


Figure 9.4. Steps in the formation of a quantum wire or quantum dot by electron-beam lithography: (a) initial quantum well on a substrate, and covered by a resist; (b) radiation with sample shielded by template; (c) configuration after dissolving irradiated portion of resist by developer; (d) disposition after addition of etching mask; (e) arrangement after removal of remainder of resist; (f) configuration after etching away the unwanted quantum-well material; (g) final nanostructure on substrate after removal of etching mask. [See also T. P. Sidiki and C. M. S. Torres, in Nalwa (2000), Vol. 3, Chapter 5, p. 250.]

Fotoluminescenza eccitonica
esaltata in QDs

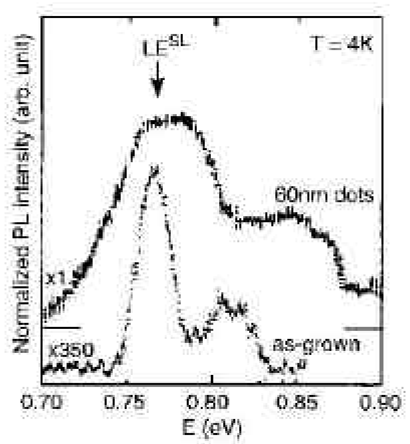


Figure 9.7. Photoluminescence spectrum of an array of 60-nm-diameter quantum dots formed by lithography, compared with the spectrum of the initial as-grown multiple quantum well. The intense peak at 0.7654 eV is attributed to localized excitons (LE) in the superlattice (SL). The spectra were taken at temperature 4 K. [From T. P. Sidiki and C. M. S. Torres, in Nalwa (2000), Vol. 3, Chapter 5, p. 251.]

Tecniche litografiche (EBL)
+
crescita film sottili

Diffusione industriale EBL

Brochure di sistema EBL commerciale Hitachi (1999!!)

Hitachi Review Vol. 48 (1999), No. 6

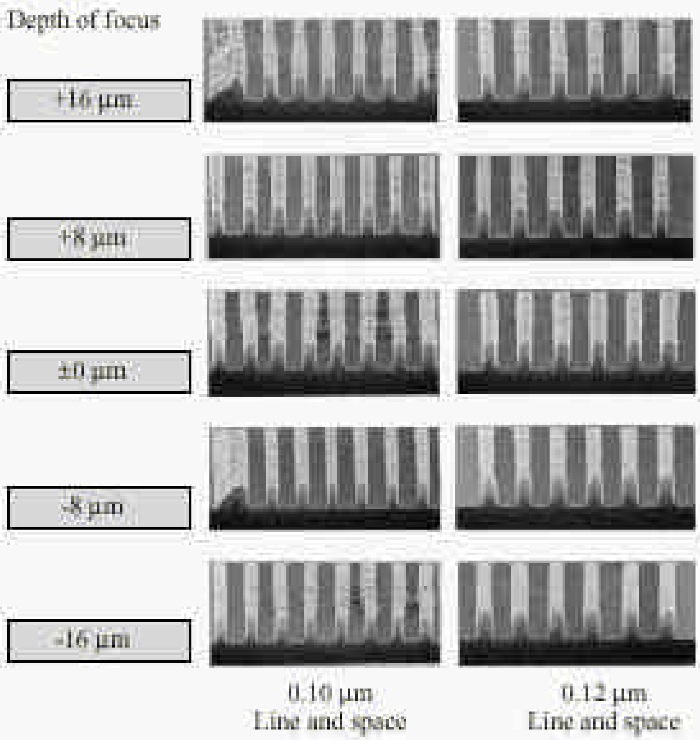


Fig. 3—Resolution and Depth of Focus.
Figure shows the resolution and depth of focus for 0.1µm and 0.12µm line-and-space patterns.

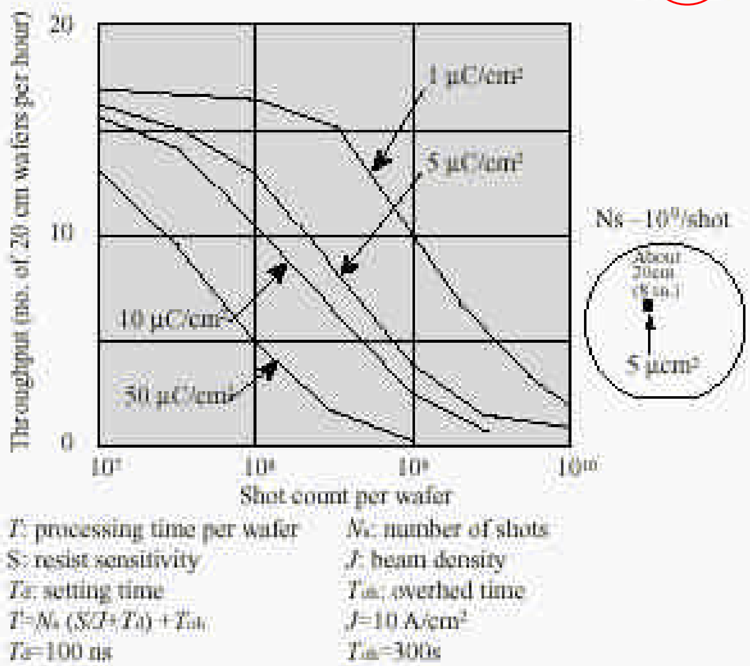


Fig. 4—Relationship Between Shot Count and Throughput.
Figure shows the relationship between shot count required to apply patterns to a wafer and throughput. The throughput diminishes as the shot count increases.

Possibilità diffusione industriale (*per dispositivi non di massa*)
e sviluppi oltre la "barriera" dei 10 nm

SCALPEL

5.2 SCALPEL

The drawback of electron beam direct write is the serial character of the method. In mass production, where throughput is concerned, exposure times of several hours are not acceptable. Though there are electron optics which could enable projection lithography analogously to optical projection lithography, this method suffers from the huge penetration depth of electrons. The masking layers have to be thick to stop a significant part of the electrons.

One method of circumventing this problem is the SCALPEL method (scattering with angular limitation in projection electron beam lithography). In SCALPEL a broad beam of electrons, 2 to 3 mm in diameter, is scanned across a mask consisting of a silicon-nitride membrane layer (~100 – 150 nm), on which a patterned scattering layer (25 to 50 nm of gold or tungsten) is situated (Figure 20a). The electrons, which only strike the membrane layer, will pass this layer mostly unscattered, while the electrons, which strike the scattering layer, will be distracted strongly from their path. The unscattered electrons are focused through an aperture and projected onto the wafer, while the scattered electrons will be blocked. So a high contrast image can be achieved.

As a projection lithography method, SCALPEL offers the advantage of image reduction thus making mask fabrication easier. The mask itself consists of silicon struts, between which the membrane layer is clamped (Figure 20b). The width of the membrane corresponds to the diameter of the electron beam, while it is a few cm in length. By means of the projection optics behind the aperture the electrons coming from two different membrane areas separated by a silicon strut can be stitched together at the wafer, so circuits of 2 cm times 3 cm can be exposed.

Possibilità di superare i limiti dovuti al carattere seriale con tecniche di “proiezione”

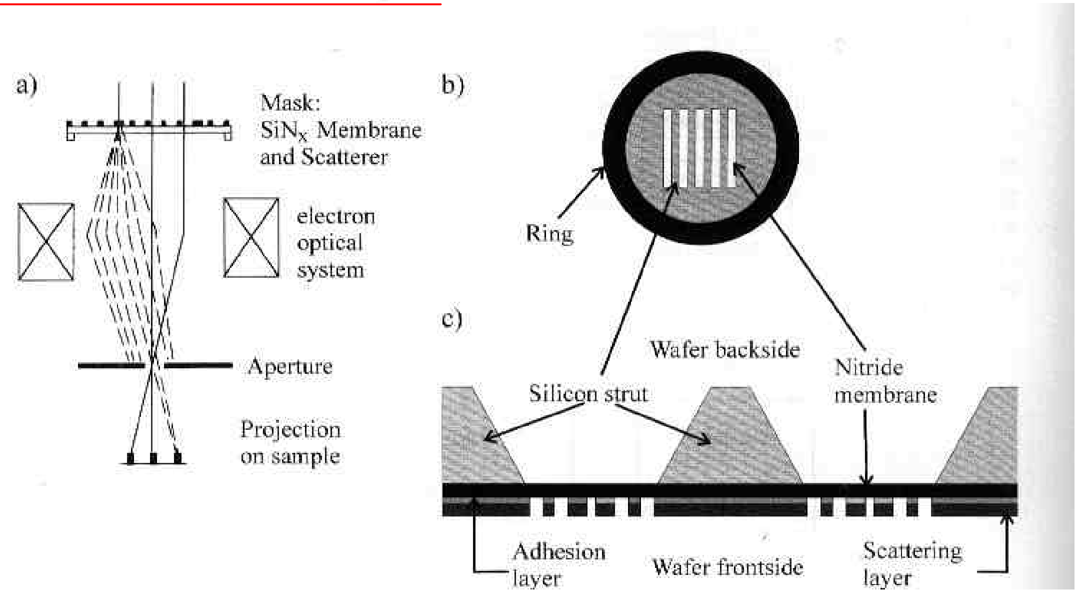


Figure 20:
(a) Electron path through a SCALPEL tool. A parallel beam of electrons passes through the mask; a scattering layer in which the pattern is inscribed scatters the electrons, so that they are not focused through an aperture by the electron optical system; only the unscattered electrons will pass the aperture. These electrons are projected onto the sample [16], [43].
(b) Top view of a mask and
(c) cross-sectional view of the mask. The masks are strips and separated by silicon struts. The masks are illuminated in series and the pictures of the masks are projected onto the adjacent sample .

Focused Ion Beam (FIB)

6.1 Focused Ion Beam

The setup of a focused ion beam (FIB) tool is similar to an electron beam lithography tool, but instead of an electron beam a focused ion beam is used either to expose a resist locally, as in electron beam lithography, or to modify the substrate directly. The heavy ions impinging on the surface will sputter the material or, depending on energy, will intermix the layers at the surface of the sample. By means of this so-called ion milling the properties of the material at the surface will be altered. Another possibility is the local deposition of an additional layer. The impinging ions can induce the decomposition of a gas. As in a Chemical Vapor Deposition (CVD) process, where the decomposition of the process gasses is induced globally by thermal activation (Low Pressure CVD) or by a plasma (Plasma Enhanced CVD), this local decomposition leads to a local deposition of the material.

Besides a certain impact on the structure definition in the research environment, the direct modification of the surface, the sputtering as well as the deposition, enables the method to be used in the most important application of FIB in industry, namely mask repair. Mask production is very expensive and due to some failure in the processing (e.g. dirt sticking on the mask or a mistake in the electron beam pattern generator) a mask can be faulty. Either some parts of the masking layer, which should have been removed, are still present, or some parts of the masking layer are removed in excess. These faults can be cured by FIB.

Impiego di ioni (alta energia cinetica) introduce ulteriori possibilità

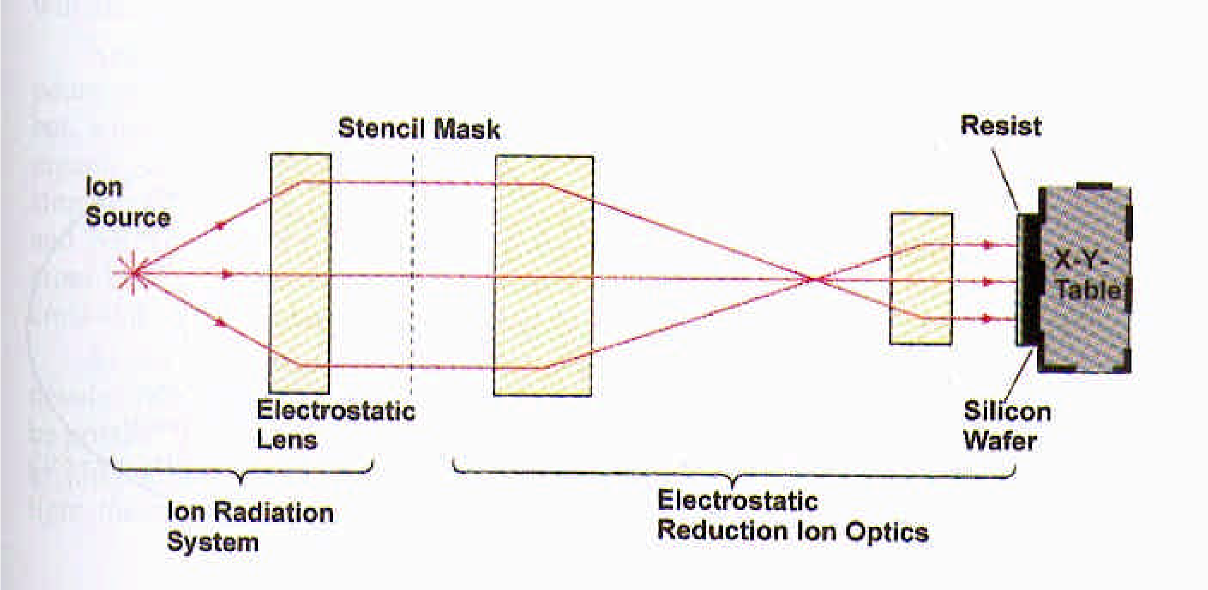


Figure 21: Schematic view of an ion projection lithography tool.