Appunti & trasparenze - Parte 9

Versione 2, Novembre 2003
Francesco Fuso, tel 0502214305, 0502214293 - fuso@df.unipi.it
http://www.df.unipi.it/~fuso/dida

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).

27/11/2003 - Fibo R1 16+2

Microscopia elettronica

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

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

Prime "peculiarità" microscopia 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)

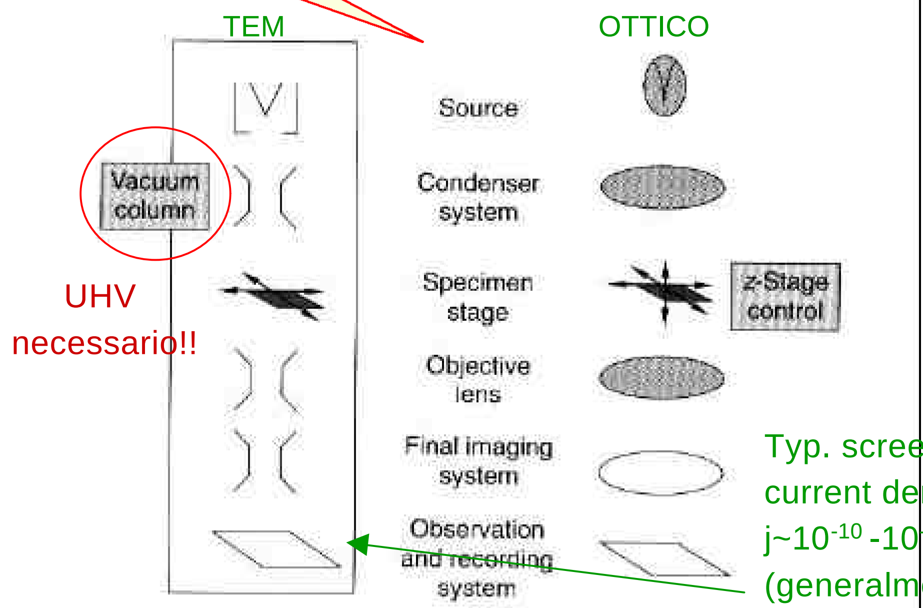


Figure 4.1 Similar to the transmission optical microscope, the transmission electro microscope has a source, a condenser system, a specimen stage, an objective lens and a imaging system, as well as a method for observing and recording the image

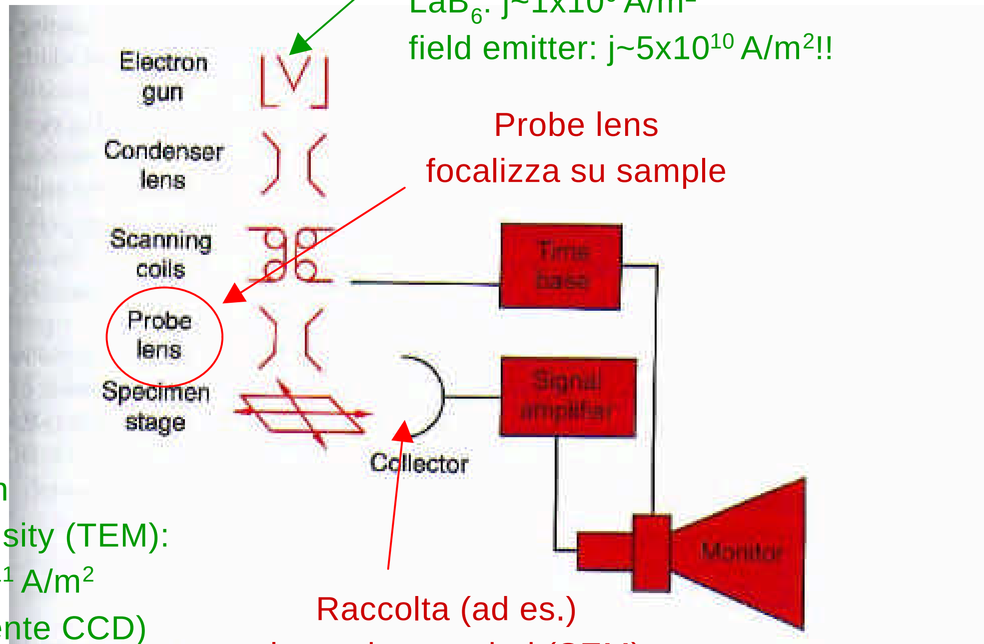


Figure 4.2 In the scanning electron microscope, a fine probe of high-energy electrons is focused on to the sample surface and then scanned across the surface in a television raster. A signal generated by the interaction of the probe with the sample is collected, amplified and displayed on a monitor with 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
Microstruct. Charact.
of Materials
Wiley (1999)

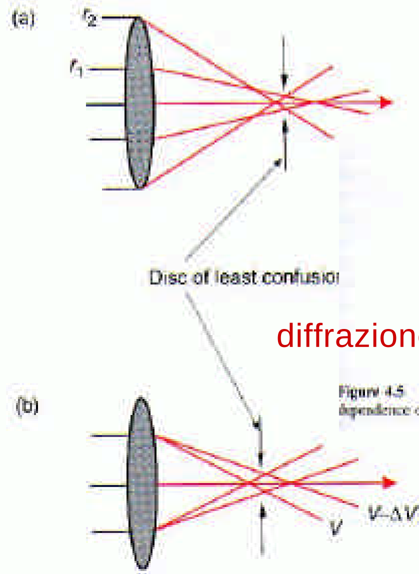


Figure 4.4 Spherical (a) and chromatic aberration (b) prevent a parallel beam from being brought to a point focus. Instead, a disc of least confusion is formed in the focal plane

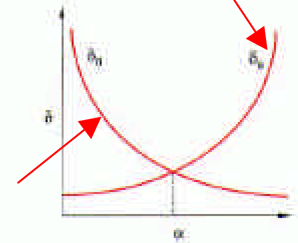


Figure 4.5 The diffraction and the spherical aberration limits on resolution have an opposite dependence on the angular aperture of the objective, so that an optimum value of α exists

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)

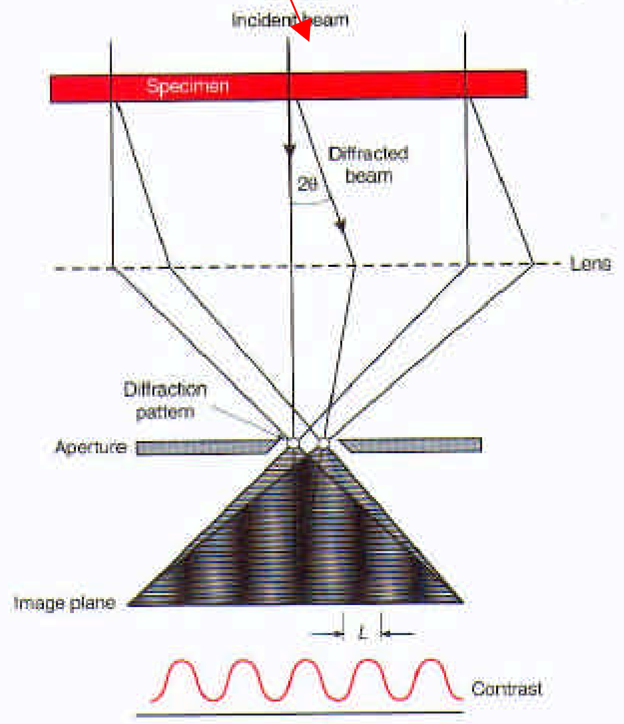
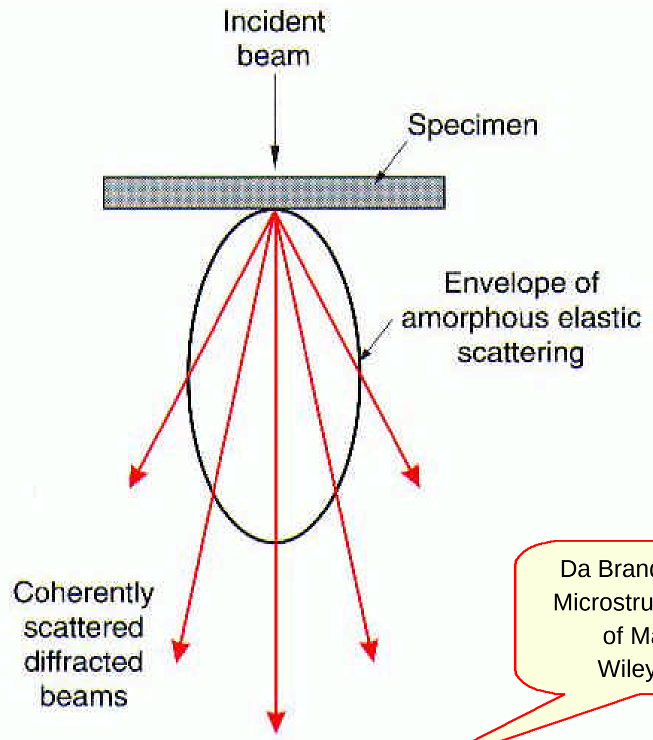


Figure 4.15 If the objective aperture accepts a Bragg-diffracted beam as well as the direct transmitted beam, $\alpha > 2\theta$, then an interference pattern will be formed in the image plane as a result of the difference in path lengths of the two beams



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

'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 :om 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

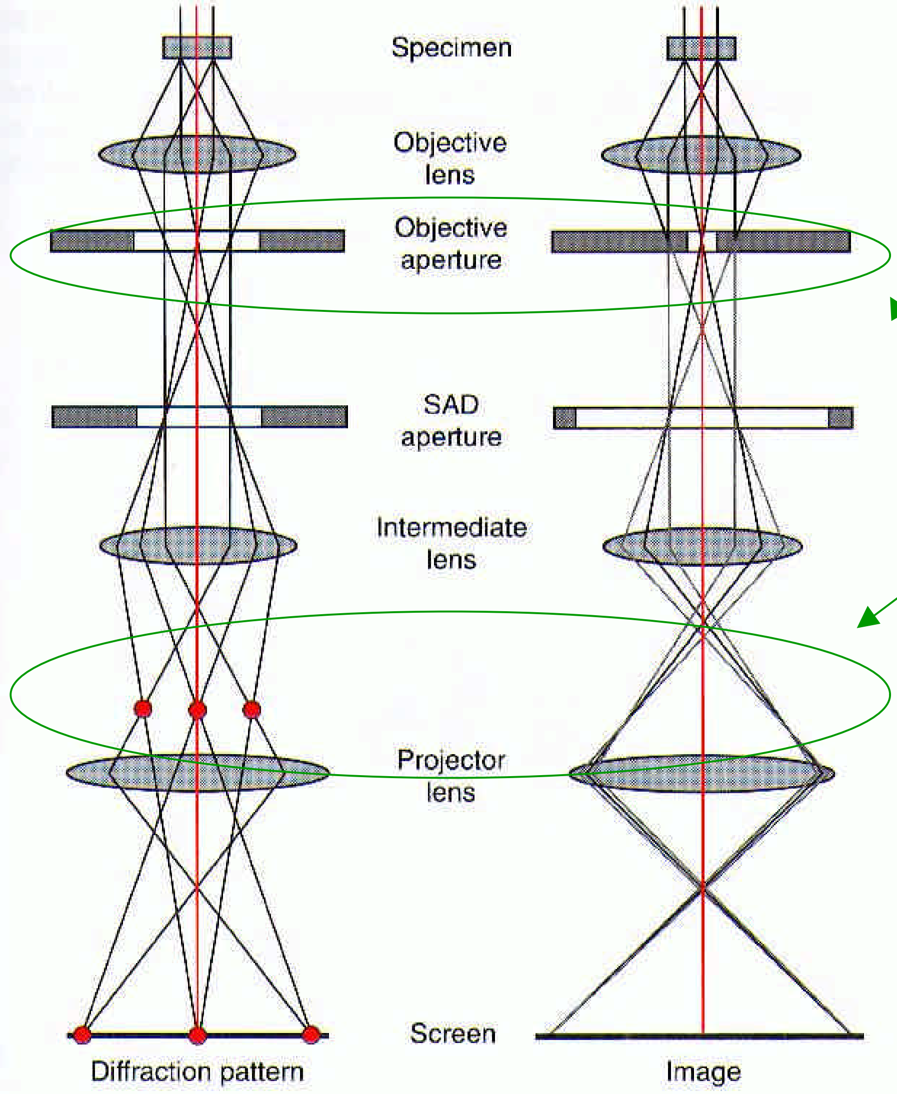


Figure 4.14 The transmission electron microscope can be used to image the specimen by focusing the final image in the plane of the fluorescent screen, or it can be used to image the diffraction pattern from the specimen. In the first case, to an excellent approximation, the image of the specimen is observed 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

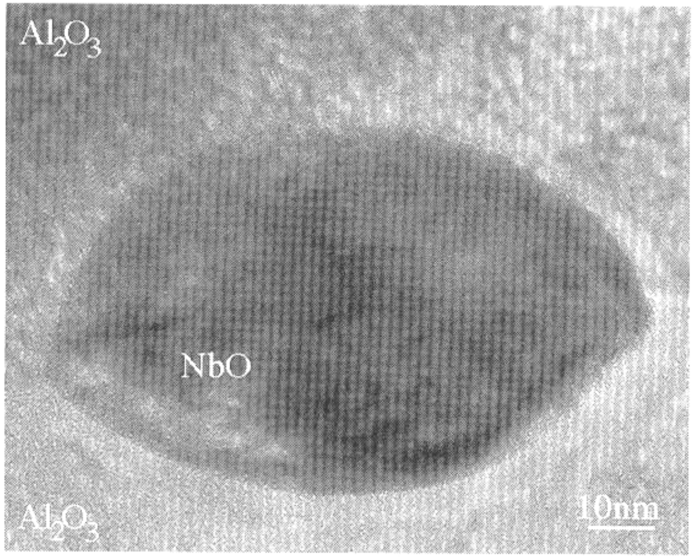


Figure 4.53 Transmission electron micrograph of a NbO particle located at a grain boundary in polycrystalline alumina. Phase contrast (lattice fringes) and mass–thickness contrast vary from the alumina grain to the NbO grain

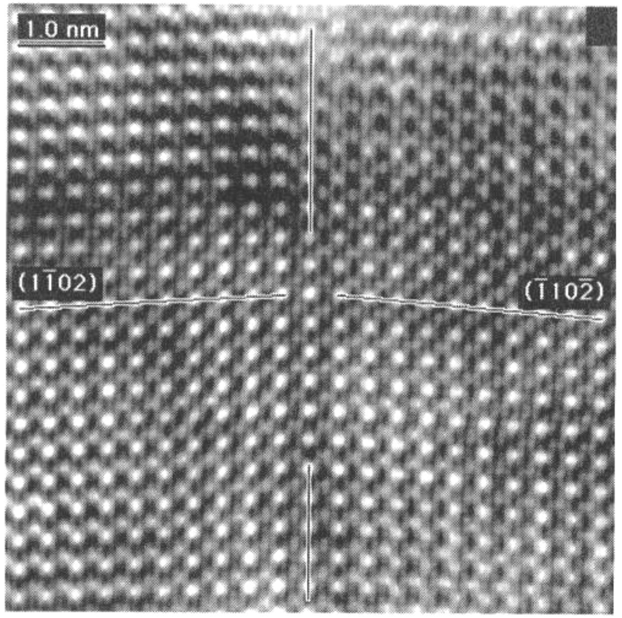


Figure 4.54 Lattice image of a rhombohedral twin in alumina

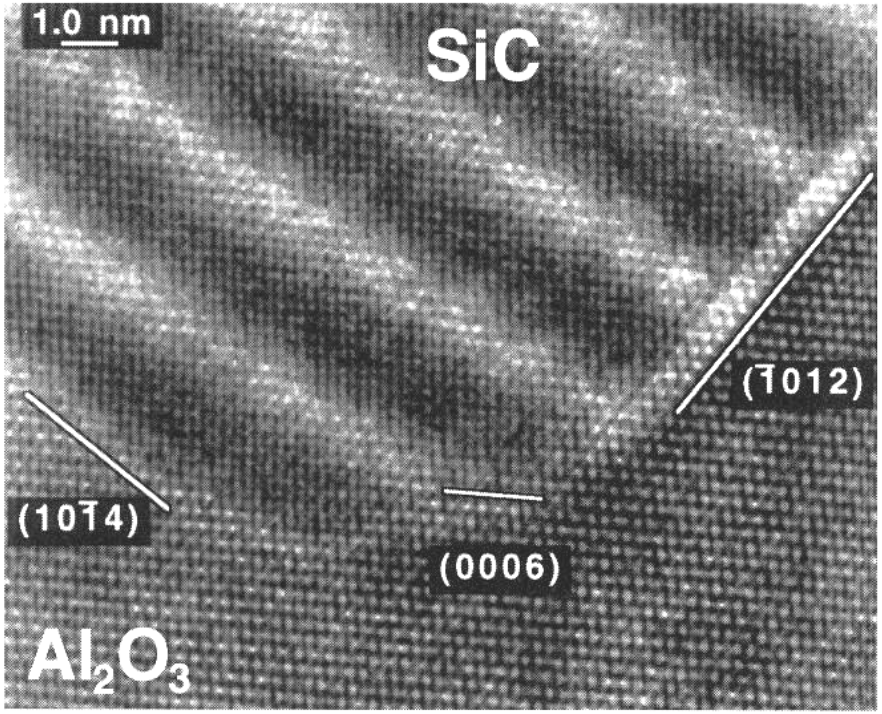


Figure 4.55 Lattice image of a SiC particle located within an alumina grain. The alumina lies along a low-index-zone axis, and is the source of the lattice image. A moiré pattern appears within the SiC particle due to overlap between the alumina and SiC (in the direction of the electron beam)

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

Generazione di elettroni secondari (SEM)

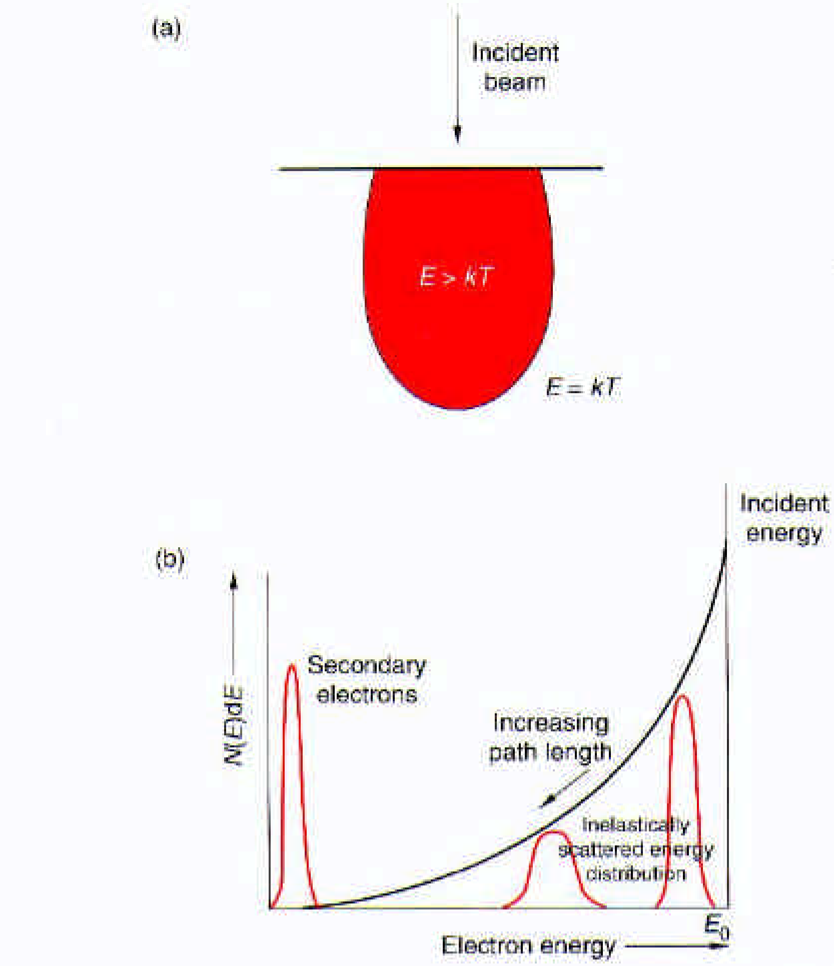


Figure 4.29 (a) The electron beam is inelastically scattered within an envelope bounded by the condition that the average energy has reached the thermal kinetic value kT. (b) The energy spread increases and the average energy of the electron falls as the path length within the solid increases (channelling 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

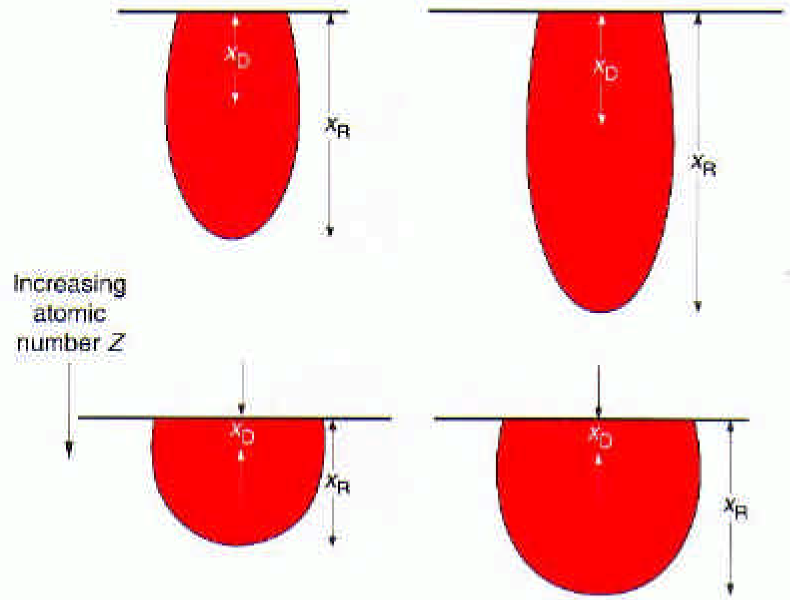
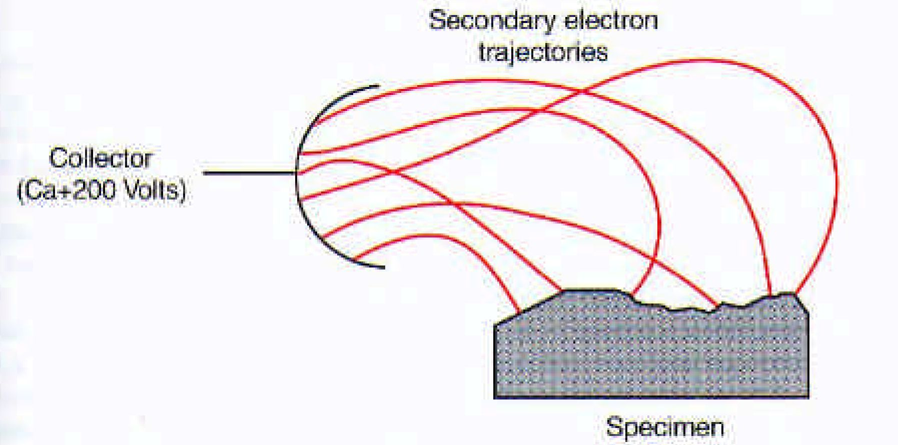


Figure 4.30 The inelastic scattering envelope for an incident beam of energetic electrons depends on both the incident energy and the atomic number of the target, and is qualitatively characterized by the two parameters, diffusion depth, and penetration depth (or range)



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

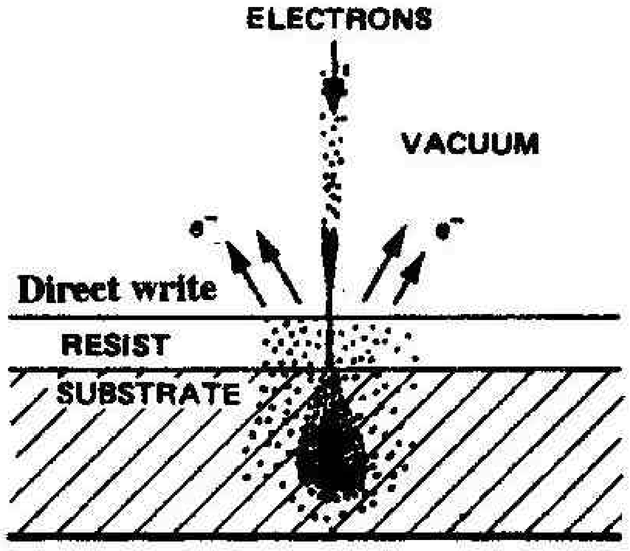
Energia elettroni secondari dipende da configurazione elettronica

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 elettroni (EBL)

Fascio focalizzato di cariche *accelerate* può essere usato per:
- scrittura diretta (soprattutto con ioni, Z maggiore, cfr. ion etching/milling)
- 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.

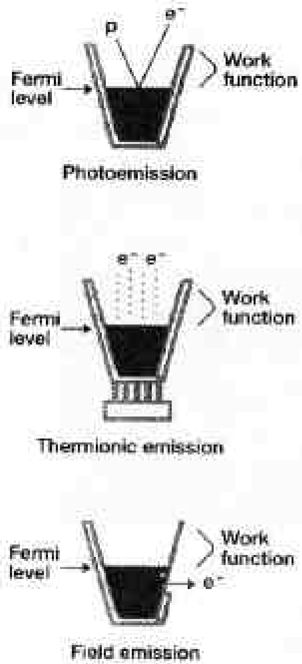
Understanding these mechanisms is where the water bucket comes in.

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)

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)

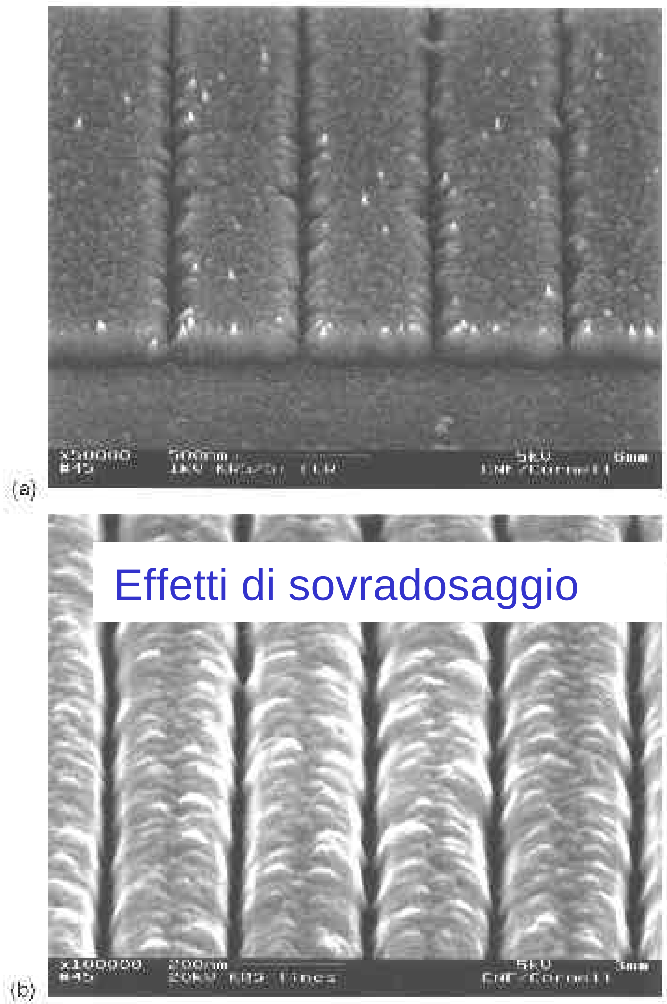
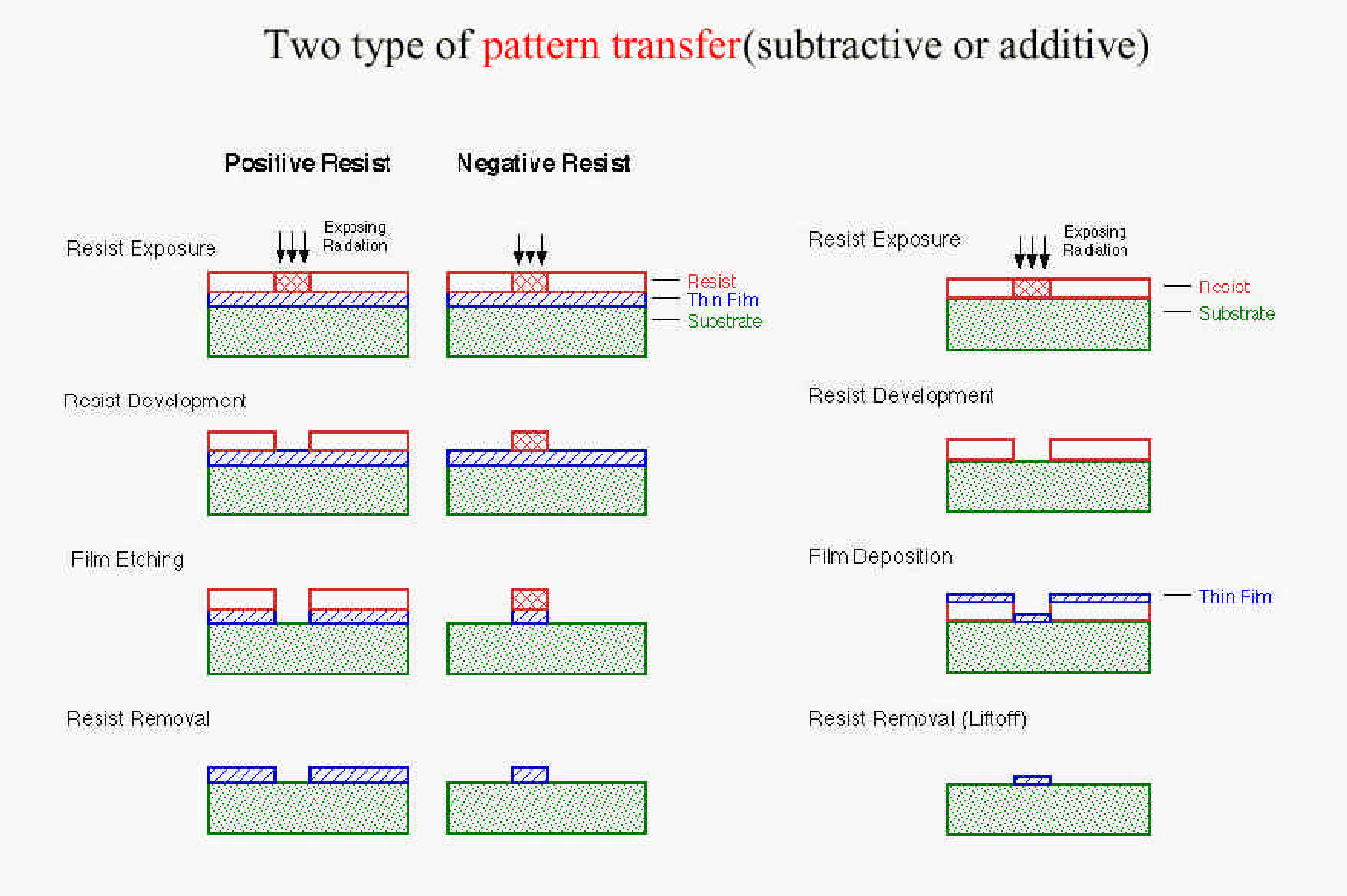


FIG. 3. Single pass lines etched into Si using the two step ECR etch, for KRS resist exposed at 1 keV (a) and a 20 keV (b) with line doses of 11 and 175 pC/cm, respectively.

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)

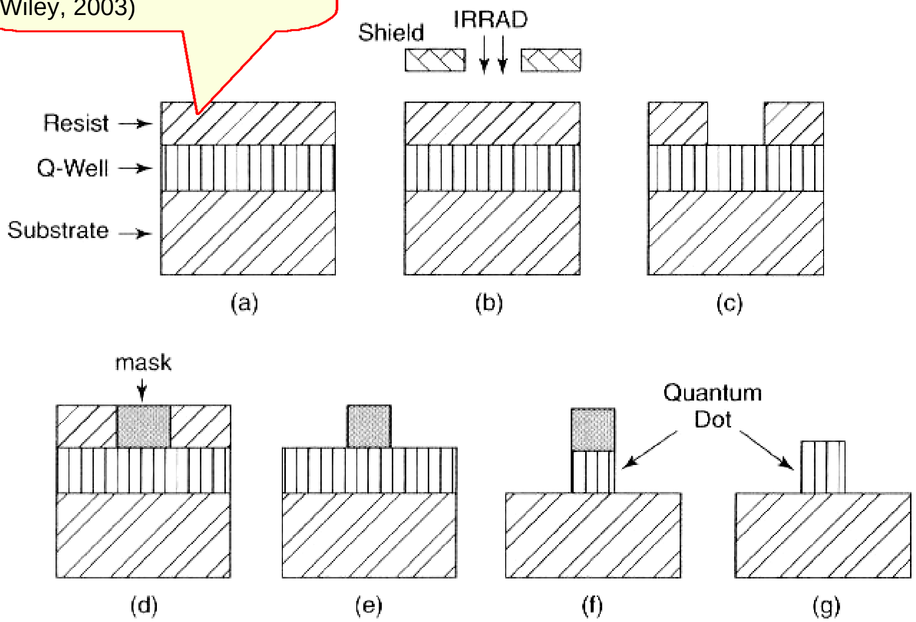


Figure 9.4. Steps in the formation of a quantum wire or quantum dot by electron-beam lithography: (a) initial quantum well on a substrate, and covered by a resist; (b) radiation with sample shielded by template; (c) configuration after dissolving irradiated portion of resist by developer; (d) disposition 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

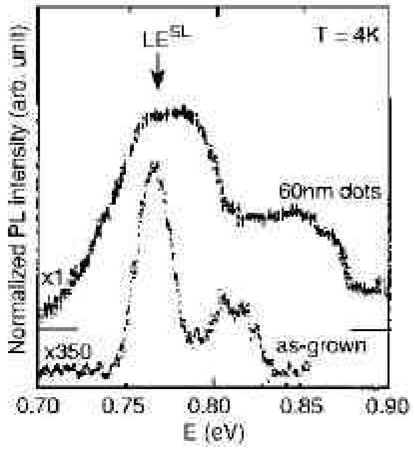


Figure 9.7. Photoluminescence spectrum of an array of 60-nm-diameter quantum dots formed by lithography, compared with the spectrum of the initial as-grown multiple quantum well. The intense peak at 0.7654 eV is attributed to localized excitons (LE) in the superlattice (SL). The spectra were taken at 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

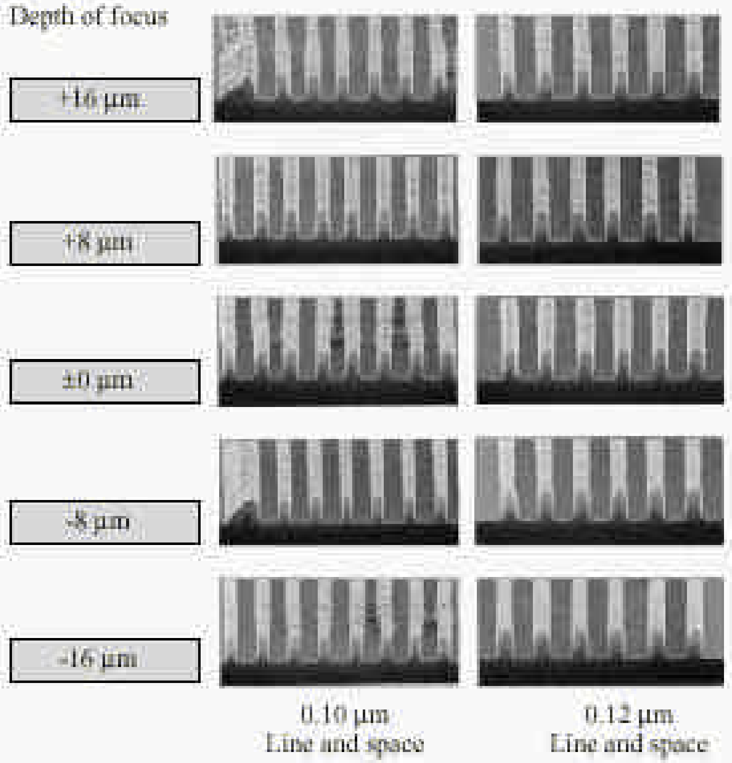


Fig. 3— Resolution and Depth of Focus.
Figure shows the resolution and depth of focus for 0.1μm and 0.12μm line-and-space patterns.

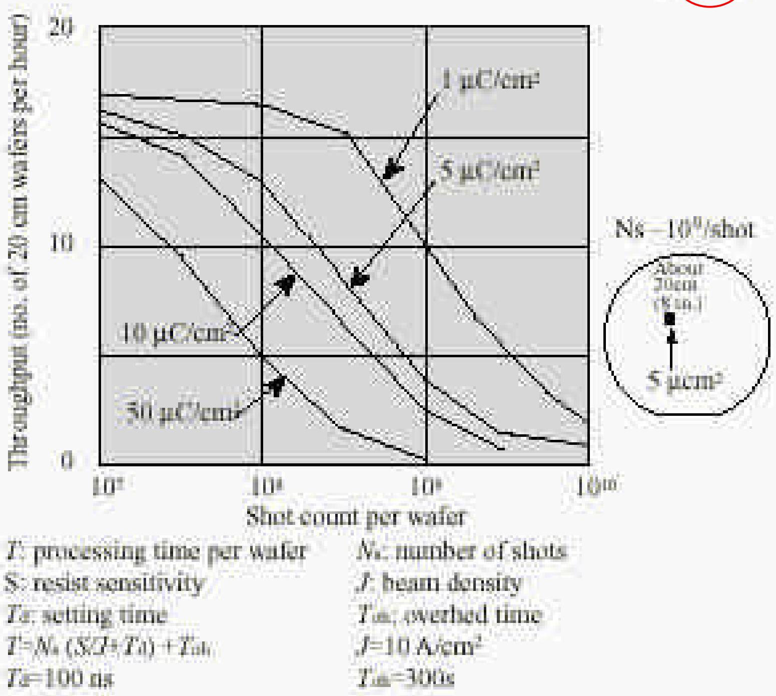


Fig. 4— Relationship Between Shot Count and Throughput.
Figure shows the relationship between shot count required to apply patterns to a wafer and throughput. The throughput diminishes as the shot count increases.

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