CdL Scienza dei Materiali - Fisica delle Nanotecnologie - a.a. 2003/4

Appunti & trasparenze - Parte 3

Versione 2b, Ottobre 2003

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

- Materiali, dispositivi e nanotecnologie per immagazzinamento dati (RAM, ferroelettrici, supporti magnetici, supporti ottici,...)

20/10/03 9.30+3 ITI L, I

Principali metodi di immagazzinamento informazioni

Metodo	Fondamento	Esempi	Problematiche
elettrico	cariche contenute in condensatore	RAM, ROM, EEPROM,...	Tunneling, singolo elettrone, Coulomb blockade,...
magnetico	magnetizzazione domini ferrom.	Hard-disk	Modalità lettura,"meccanica" superparamagnetismo
ottico	Modifica riflettività/ assorbimento locali	CD, CD-RW, DVD, ...	Potenza per la lettura/scrittura, diffrazione ottica, campo ottico prossimo

Forti aspettative per la miniaturizzazione (es. DRAM)

ITRS Technology Nodes and Chip Capabilities[2]

	2001	2005	2010	2016
DRAM Half-Pitch (nanometers)	130	80	45	22
DRAM Memory Size (mega or gigabits)	512M	2G	8G	64G
DRAM Cost/Bit (micro-cents)	7.7	1.9	0.34	0.042
Microprocessor Physical Gate Length (nanometers)	65	32	18	9
Microprocessor Speeds (MHz)	1,684	5,173	11,511	28,751

Limiti “teorici” nella miniaturizzazione

2.1.1 Theoretical Limits

In order to understand the theoretical limits of information storage, it is useful to place CMOS in the context of a general purpose computation system. There are three important limits, which determine the ultimate performance of such systems. These limits are the thermal limit, the quantum limit, and the power dissipation limit (see figure 2.1). The energy necessary to write a bit determines the thermal limit. This energy must be bigger than the average energy of the thermal fluctuations, kT, otherwise bit errors will occur. For CMOS, the energy necessary to write a bit is about 10^{-13} J (10^{6} eV) which corresponds to a temperature of 10^{10} K. The trend in CMOS is to decrease this energy and thereby decrease the power dissipated. The optimum value for the energy to write a bit for room temperature operation is about 4×10^{-19} J (2 eV), which is one hundred times greater than kT.

The energy needed to read or write a bit and the frequency of the circuits are limited by the uncertainty principle, $\Delta E\ \Delta t \geq h$. To prevent bit errors, the circuit cannot operate too close to the minimum uncertainty product. The quantum limit is then approximately given by $E/f = 100\ h$ where E is the energy needed to write a bit and f is the clock frequency. CMOS circuits operate far above the quantum limit but as scaling continues below 100 nm, the limit will eventually be approached as E decreases and f increases (See Table 1).

The next important limit is the power dissipation limit, determined by the power density $p = EfnP$, where n is the device density, and P the probability that the device switches in a clock cycle, typically $P \sim 0.1$. The maximum tolerable power density is about 100 W/cm^2. This means that the energy, the frequency, and the packing density are limited by $Efn \sim 100$ W/cm^2. At high frequency, a high device density is desirable, and therefore a low energy per bit is desirable. CMOS circuits operate near the power dissipation limit. These three limits can be summarised in an energy - delay diagram as shown in figure 2.1.

See R. Compaño et al.
MEL-ARI EC Project
Technol. Rodmap 1999

Limite “termico”
Limite “quantistico”
Limite “dissipativo”

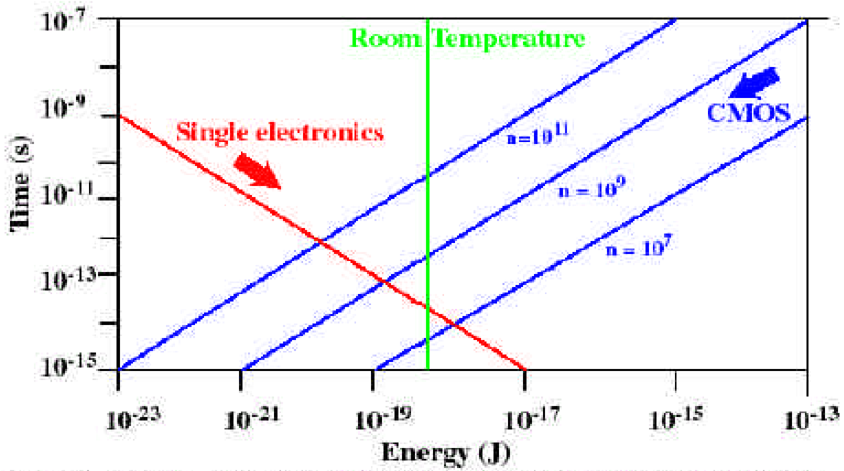


Figure 2.1:- An energy - delay diagram for single electronics. Room temperature operation can only be achieved to the right of the line labelled room temperature. The lower left-hand corner of the diagram is inaccessible due to quantum fluctuations and the lower right-hand corner of the diagram is inaccessible due to dissipation. The dissipation limit is represented by three lines, each corresponding to a different device density, n. The current trends in CMOS and single electronics are indicated in the diagram [Hadley 1996].

Esistono condizioni “teoriche” che impongono compromessi operativi nella miniaturizzazione

Data storage: memorie RAM

Immagazzinamento attraverso “intrappolamento” di cariche in dielettrici

See R. Compaño et al.
MEL-ARI EC Project
Technol. Rodmap 1999

	Conventional Memory		Quantum Dot Memory			
	DRAM	Flash	SET	Nano-flash		Yano-type
				Multidot	Single dot	
device structure						
read time	~10 ns	~10 ns	1 ns	~10 ns	~10ns	~20 µs
write time	~10 ns	~1 ms	1 ns	~100 ns	~1 µs	~10 µs
erase time	~ 1ms	~1ms	~ 1ns	~1 ms	<1 ms	~10 µs
retention time	~1 s	~10 years	~1s	~1 week	~5 s	~1 day
endurance cycles	infinite	10^6	infinite	10^9	10^9	10^7
operating voltage	3 V	15 V	1 V	5 V	10 V	15 V
voltage for state inversion	0.2 V	~5 V	~ 0.1 V	0.55 V	0.1 V	0.5 V
electron number in write bit	10^5	10^5	1 (excluding ne to change gate potential)	10^3	1 (excluding ne to change gate potential)	2 (excluding ne to change gate potential)
cell size	~12 F²/bit	~9F²/bit	9-12 F²/bit	9F²/bit	9F²/bit	2F²/bit

Table 2.1:- Performance comparison among conventional and proposed memories (modified after data from Hitachi Cambridge Laboratory). For complete overview see table I.1 in Annex I

Dispositivi “convenzionali”: DRAM e Flash Memories

Baarth et al.,
IBM J Res Dev (2002)

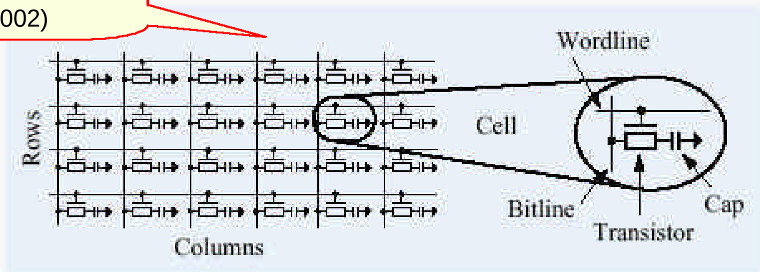


Figure 1

DRAM cell array.

Fundamental DRAM operation

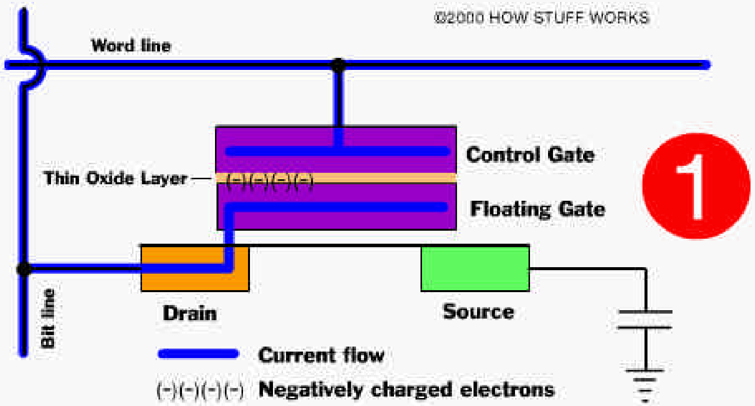
DRAM memory arrays are composed of wordlines (or rows) and bitlines (columns); see **Figure 1**. At the cross-point of every row and column is a storage cell consisting of a transistor and capacitor [6]. The data state of the cell is stored as charge on the capacitor, with the transistor acting as a switch controlling access to the capacitor. With the switch on (wordline activated), charge can be read from or written to the storage cell. The rest of the DRAM support circuits are dedicated to controlling the wordlines and bitlines to read and write the memory array.

www.howstuffworks.com

Flash memory is a type of **EEPROM** chip. It has a grid of columns and rows with a cell that has two transistors at each intersection (see image below). The two transistors are separated from each other by a thin oxide layer. One of the transistors is known as a **floating gate**, and the other one is the **control gate**. The floating gate's only link to the row, or **wordline**, is through the control gate. As long as this link is in place, the cell has a value of 1. To change the value to a 0 requires a curious process called **Fowler-Nordheim tunneling**.

Tunneling is used to alter the placement of electrons in the floating gate. An electrical charge, usually 10 to 13 volts, is applied to the floating gate. The charge comes from the column, or **bitline**, enters the floating gate and drains to a ground.

This charge causes the floating-gate transistor to act like an electron gun. The excited electrons are pushed through and trapped on other side of the thin oxide layer, giving it a negative charge. These negatively charged electrons act as a barrier between the control gate and the floating gate. A special device called a **cell sensor** monitors the level of the charge passing through the floating gate. If the flow through the gate is greater than 50 percent of the charge, it has a value of 1. When the charge passing through drops below the 50-percent threshold, the value changes to 0. A blank EEPROM has all of the gates fully open, giving each cell a value of 1.



The electrons in the cells of a Flash-memory chip can be returned to normal ("1") by the application of an electric field, a higher-voltage charge. Flash memory uses **in-circuit wiring** to apply the electric field either to the entire chip or to predetermined sections known as **blocks**. This erases the targeted area of the chip, which can then be rewritten. Flash memory works much faster than traditional EEPROMs because instead of erasing one byte at a time, it erases a block or the entire chip, and then rewrites it.

Intrappolamento di carica (*quanta??*) necessario per funzionamento memorie

See R. Compaño et al.
MEL-ARI EC Project
Technol. Rodmap 1999

Esempi di memorie "alternative" (miniiaturizzate e con poca carica)

2.2.1.2 Nano-flash device

Nano-flash devices are basically three terminal devices where a floating gate is charged and the charge produces a large change in the threshold voltage of the transistor channel. The design allows an intermediate between DRAM and Coulomb blockade potentially allowing higher density than DRAM at lower power and higher operating temperatures.

In addition, nonvolatile Dram-like memories based on the Coulomb blockade effect are intensively investigated. Both Hitachi's PLED [Nakazato 1997] and Likharev's NOVORAM being [Likharev 1998] are prominent examples. The key issue is the creation of extremely flexible tunnel barriers, for instance by multiple barriers or sandwiched barriers.

2.2.1.3 Yano memory

The Yano type memory is a 2 terminal device where information is stored in deep traps in poly-Si. The devices are created on a 3 nm thick Si film using 0.25 µm technology where one or more dots are formed naturally in the vicinity of a FET in which trapped charge modulates the threshold voltage of the FET [Yano 1998]. The device can be operated at room temperature and has been integrated in very large-scale memories (128 Mb in 8k x 8k x 2 units of which half was operational) although it is not certain if Coulomb blockade is of any relevance for device operation. One of the major problems of this type of memory is relying on the natural formation of dots and the resulting poor control of device characteristics. This may be a major hurdle to manufacturability [Yano 1998]. The advantage is a small cell size of 2F2, one quarter of a folded-data line DRAM cell size.

Effetto di Coulomb-blockade sfruttato per intrappolare *pochi* elettroni

Memorie non-volatili con materiali “alternativi”

Ferroelectric properties

Ferroelectrics are a class of material with polarisation dipoles that can be re-orientational by a sufficiently strong external electric field. Polarisation is defined as the charge per unit area on a plane orthogonal to the direction of the polarisation vector and has units of Cm^{-2}. The magnitude and orientation of the polarisation vector, P, is dependant on the magnitude and orientation of the electric field E and the crystal structure of the sample being poled. Hysteresis arises from the energy required to reverse the dipole, as positive and negatively polarised dipoles have the same energy. Energy dissipated during polarisation reversal is equivalent to the area of the loop. Figure 1 shows the relationship of P against E.

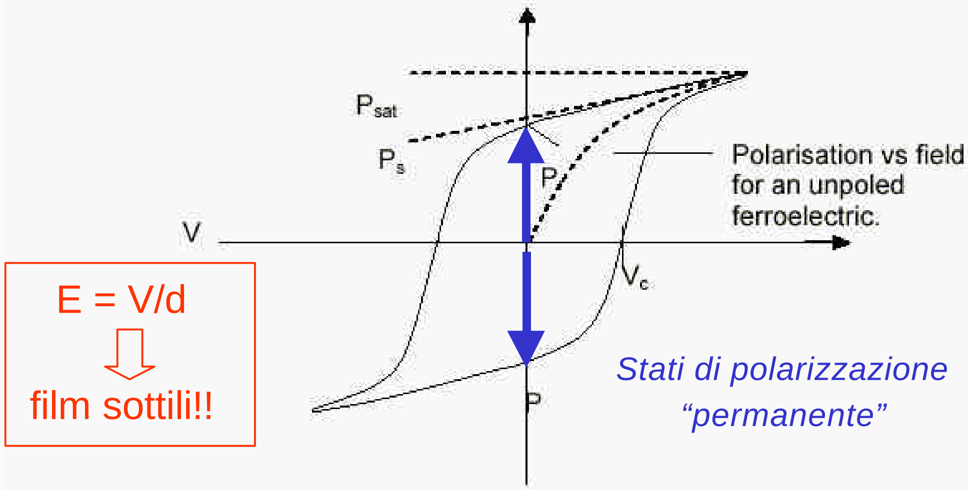


Figure 1 Ferroelectric polarisation loop

La ferroelettricità può essere sfruttata per immagazzinare info *anche* in assenza di campo applicato

⇓

- Sviluppo materiali ferroel.
- Sviluppo tecnologie di preparazione strati sottili

Ferroelettrici ceramici (es. PZT,…)

Il più semplice tipo di prototipo ferroelettrico è la struttura centrosimmetrica perovskitica, caratteristica, per esempio, del $PbTiO_3$. Esso presenta una transizione alla fase ferroelettrica (che avviene in modo discontinuo) alla temperatura di 493 °C, con una deformazione della struttura da perovskitica a tetragonale. La fase polare è stata ricondotta allo spostamento dello ione Ti^{4+} verso uno degli atomi di ossigeno, disposti ottaedricamente attorno ad esso (Fig. 1.8).

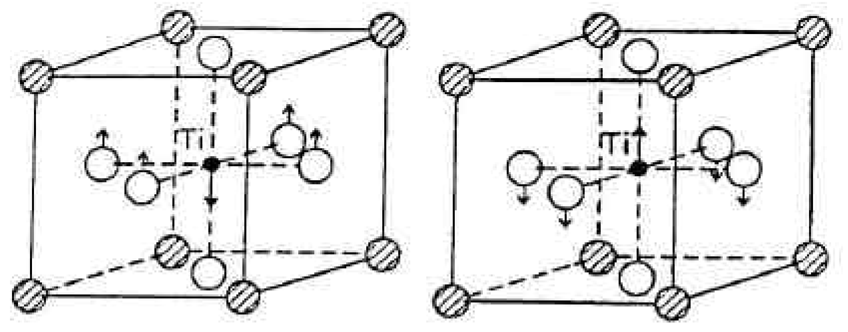
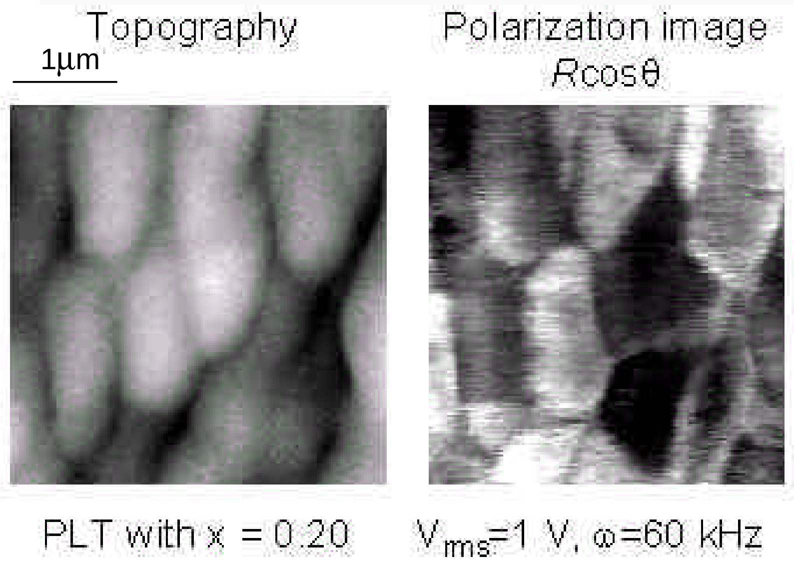


Figura 1.8: Deformazione della struttura del titanato di piombo da perovskitica a tetragonale. Da [18].

Ossidi (o miscele di ossidi) ceramici con struttura perovskitica



Polarizzazione dovuta a spostamento delle cariche (legami quasi-ionici)

Analisi AFM/EFM (Voltage modulation scanning probe microscopy) di domini ferroelettrici in film di PLT (lead lanthanum titanate) cresciuto per PLAD

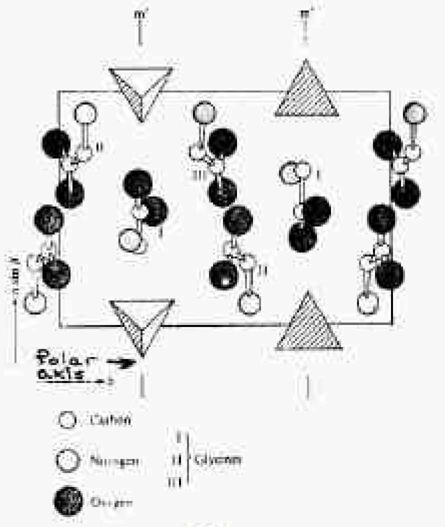
See http://www.df.unipi.it/gruppi/struttura/ma/page.htm

Ferroelettrici "molecolari" (es. TGS,…)

TriGlycine Sulfate (TGS)

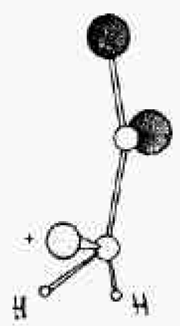
The crystals of TGS you are given have been grown from an aqueous solution by slow evaporation. The solubility curve that makes this possible is shown in Figure 1. The morphology of the crystals is shown in Figure 2. The crystal structure is complex and of fairly low symmetry (monoclinic). The mechanism by which the spontaneous dipole moment is created is also complex and is not yet fully understood. However, crudely speaking, the glycine molecule I in Figure 3 on average lies on a plane of mirror symmetry in the structure at $T \geq T_c$ and there is no net dipole moment. We say the structure is "centrosymmetric" in its high-temperature phase. For $T < T_c$ on the other hand, the nitrogen atoms in the glycine molecules are found to be displaced to the left (or right) of the mirror plane, along the polar axis b. Thus a dipole moment is set up in each unit cell. The co-operative displacement of all such nitrogen ions in the sample thus produces a macroscopic dipole moment in much the same way that unpaired spins co-operatively align to create a magnetic moment in e.g. iron.

Struttura monoclina



(a)

Glicina

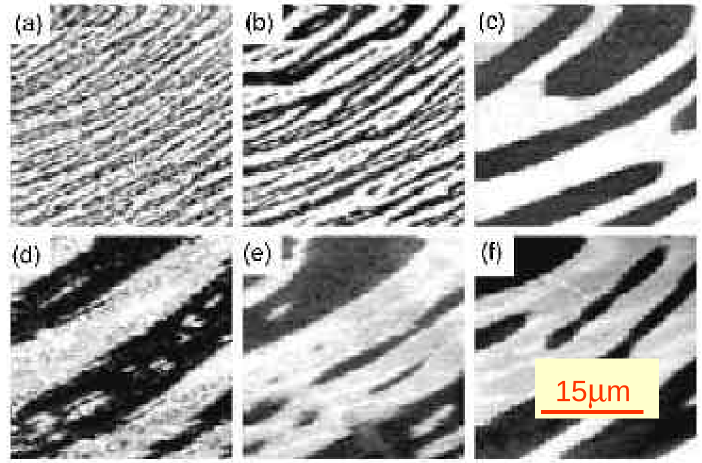


$H_2 NCH_2CO_2H$

(b)

Figure 3. View along the c-axis of the structure of TGS (after Hoshino, Okaya and Pepinsky, 1959; Itoh and Mitsui 1973) showing the three glycine groups I, II, and III. The suphate ions are shown as tetrahedral. m and m' are mirror planes in the high temperature phase.

See Adv Phys Lab, Univ Michigan (2002)



Domini ferroelettrici in film di TGS in funzione della temp. (immagini EFM)

See http://www.df.unipi.it/gruppi/struttura/ma/page.htm

Polarizzazione legata a transizione di fase dipendente dalla temperatura

⇩

Possibilità scrittura opto-termica

Data storage con ferromagneti (hard disks)

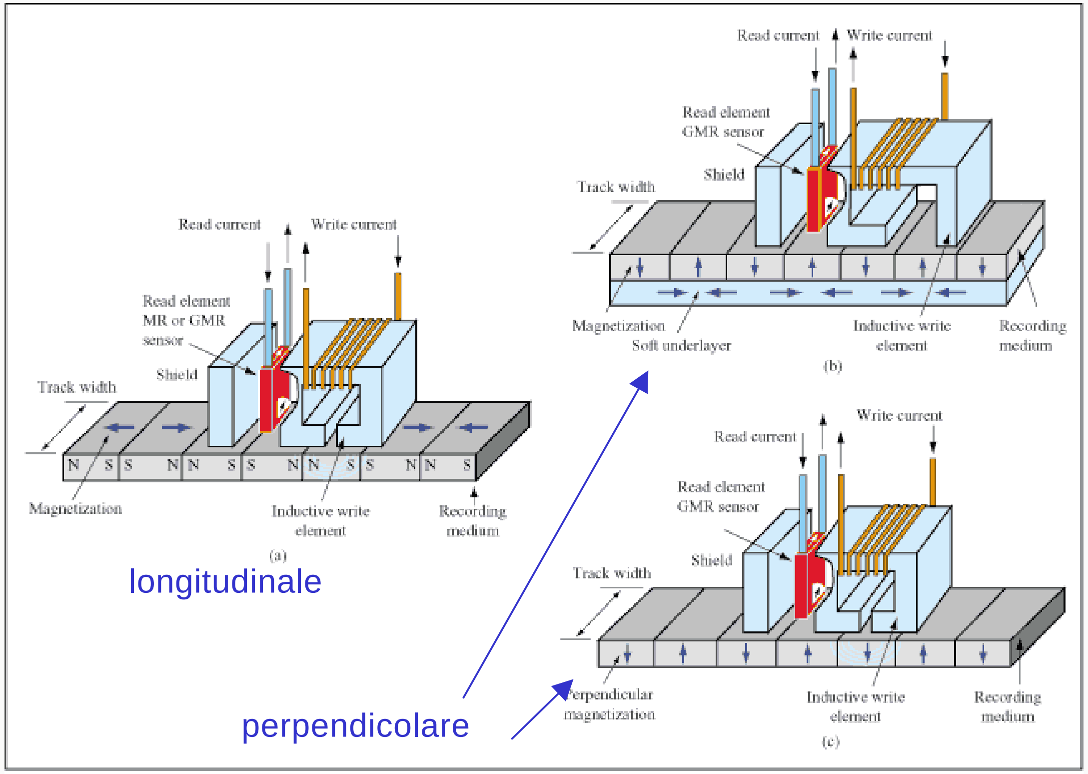


Figure 9

(a) Longitudinal magnetic recording. (b) Type 1 perpendicular recording, using a probe head and a soft underlayer in the medium. (c) Type 2 perpendicular recording, using a ring head and no soft underlayer.

Thompson, Best, IBM J Res Dev (2000)

Informazione immagazzinata nella magnetizzazione di domini isolati
(grani magnetici - leghe ferrose, oppure con NiCr, Co - isolati in matrice amagnetica)

Miniaturizzazione = aumento densità superficiale dei domini
⇩
nanodomini magnetici

Problemi “meccanici” nell’aumento di densità

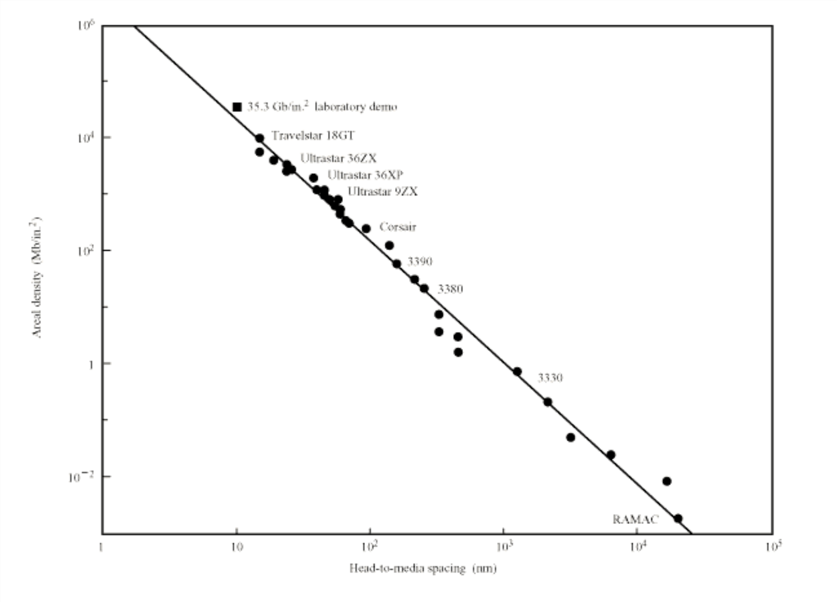
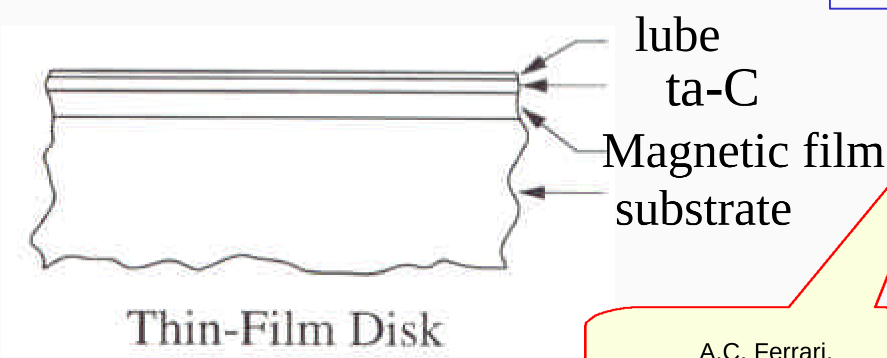


Figure 6

Head-to-media spacing in IBM magnetic hard disk drives vs. product areal density.

Ottenere un rapporto S/N accettabile richiede distanze nanometriche tra superficie e testine (rugosità, coating!!)

Overcoat requirements	Material requirements
• Reduce corrosion • Reduce friction • Reduce stiction • Reduce wear • Magnetically inert • Thermal management • Electrical isolation	• Dense pinhole free film • High hardness and E modulus • Eliminate surface roughness • Enhance surface chemistry



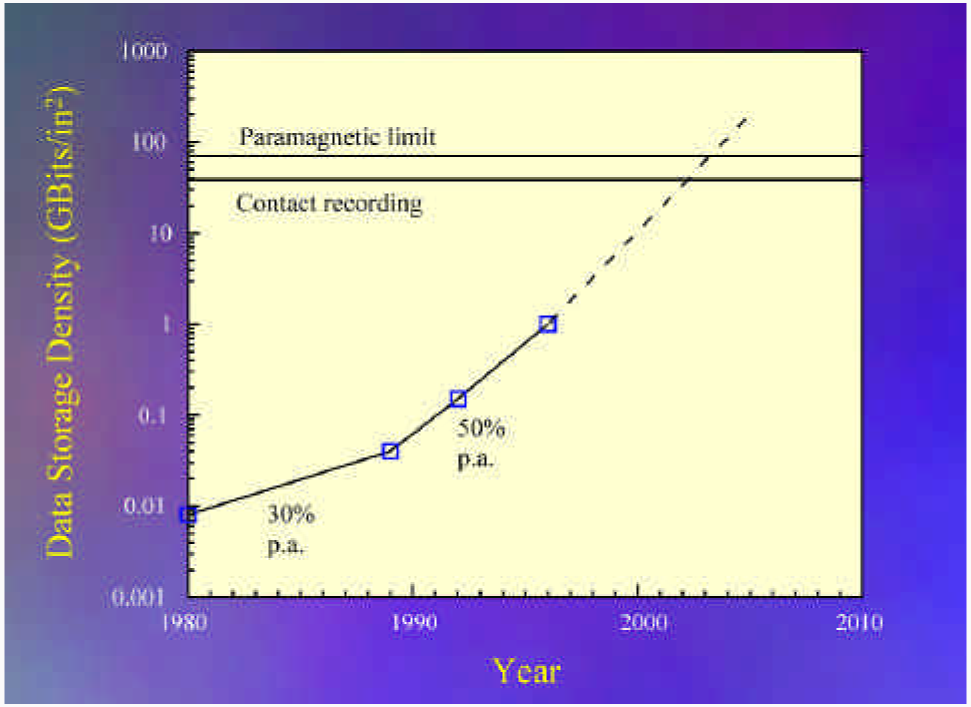
A.C. Ferrari,
Cambridge University

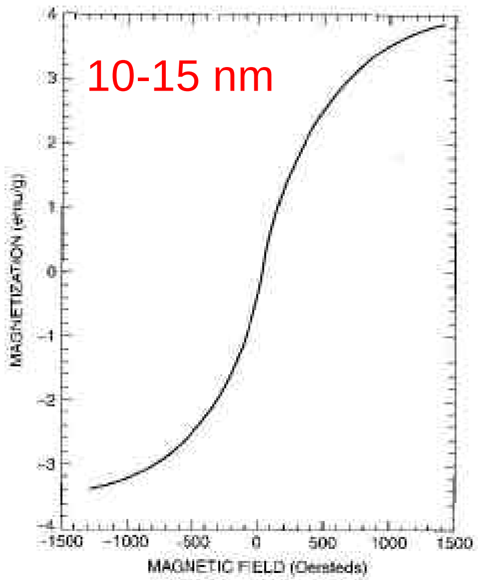
Scelta materiali e tecnologia
del coating (es., film sottili
di Carbonio amorfo) essenziale
per sviluppo dispositivi

Materiali *superparamagnetici*

I primi hard-disk (1950) erano simili ai nastri magnetici, cioè spray coatings con particelle di ossidi ferrosi

Attualmente sviluppo materiali superparamagnetici (nanoparticelle di materiali *senza isteresi* e con grande magnetizzazione residua





igure 7.4. Reversible magnetization curve for nanosized powders of a Ni–Fe–Co alloy that ibits no hysteresis. An oersted corresponds to 10^{-4} T (tesla). [Adapted from K. Shafi et al., Mater. Res. 15, 332 (2000).]

y powders of $Fe_{69}Ni_9CO_2$ having grain sizes of 10–15 nm prepared by decom-ition of solutions of $Fe(CO)_5$, $Ni(CO)_4$, and $Co(NO)(CoO)_3$ in the hydrocarbon vent decalin ($C_{10}H_{18}$) under an inert-gas atmosphere showed almost no hysteresis

Poole, Owens, Introd. to nanotechnology (wiley, 2003)

“Limite” superparamagnetico

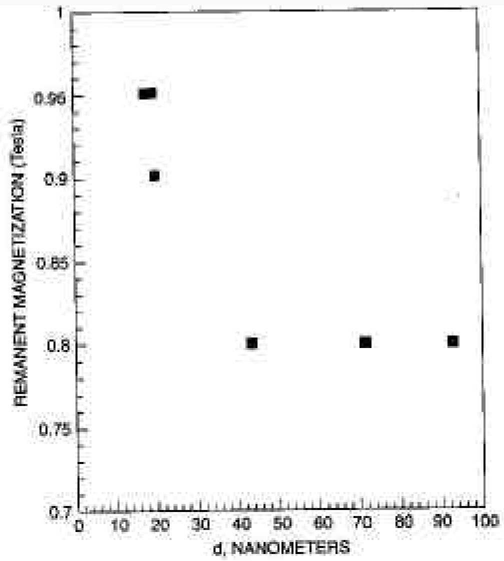


Figure 7.5. Dependence of the remnant magnetization M_r on the particle size d of th… that form the structure of a Nd–B–Fe permanent magnet normalized to the value M_r(9… 90-nm grain size. [Adapted from A. Manaf et al., *J. Magn. Magn. Mater.*, 101, 360 (19…

Consider the simplest sort of permanent magnet particle. It is uniformly magnetized and has an anisotropy that forces the magnetization to lie in either direction along a preferred axis. The energy of the particle is proportional to $\sin^2$, where is the angle that the magnetization makes to the preferred axis of orientation. At absolute zero, the magnetization lies at one of two energy minima (equals 0 or 180°, logical zero or one). If the direction of the magnetization is disturbed, it vibrates at a resonant frequency of a few tens of gigahertz, but settles back to one of the energy minima as the oscillation dies out. If the temperature is raised above absolute zero, the magnetization direction fluctuates randomly at its resonant frequency with an average energy of kT. The energy at any time varies according to well-known statistics, and with each fluctuation will have a finite probability of exceeding the energy barrier that exists at = ±90°. Thus, given the ratio of the energy barrier to kT, and knowing the resonant frequency and the damping factor (due to coupling with the physical environment), one can compute the average time between random reversals. This is an extremely strong function of particle size. A factor of 2 change in particle diameter can change the reversal time from 100 years to 100 nanoseconds. For the former case, we consider the particle to be stable. For the latter, it is a permanent magnet in only a philosophic sense; macroscopically, we observe the assembly of particles to have no magnetic remanence and a small permeability, even though at any instant each particle is fully magnetized in some direction.

Polarizzazione residua aumenta con miniaturizzazione grano, ma l’interazione cooperativa tra domini diventa minore

“limite” superparamagnetico

Densità “teorica” attuale
~ 25 Gb/cm^2
Densità max effettiva
~ 5 Gb/cm^2

Materiali nanostrutturati con magnetoresistenza colossale

Aumento S/N richiede uso di testine di lettura più sensibili
Materiali magnetoresistivi sensibili a stato della magnetizzazione locale

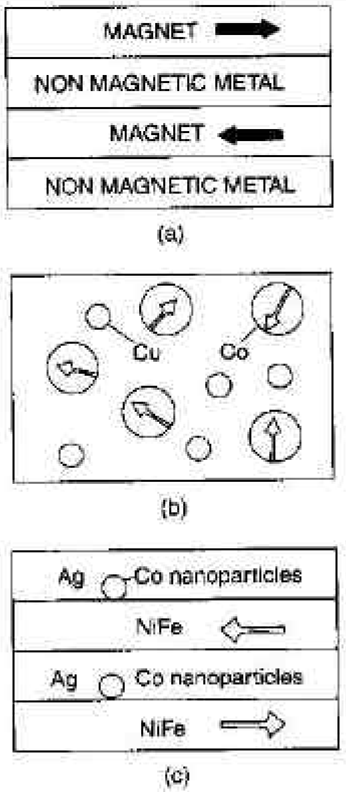


Figure 7.15. Three arrangements for producing colossal magnetoresistance: (a) layers o nonmagnetic material alternating with oppositely magnetized (arrows) ferromagnetic layer (b) randomly oriented ferromagnetic cobalt nanoparticles (large circles) in a nonmagnetic coppe matrix (small circles); (c) hybrid system consisting of cobalt nanoparticles in a silver (Ag) matri sandwiched between nickel–iron (NiFe) magnetic layers, with alternating magnetizatior indicated by arrows.

Layered structures con alternanza di strati magnetici e non-magnetici, oppure dispersioni di singoli domini magnetici, oppure sistemi misti

Magnetoresistenza dovuta a dipendenza dello scattering elettronico (conduzione diffusiva, alla Drude) da polarizzazione magnetica delle nanoparticelle

Dispersioni di domini magnetici nanometrici (dimensioni ~ λ_{dB} elettroni di conduzione) esaltano magnetoresistenza

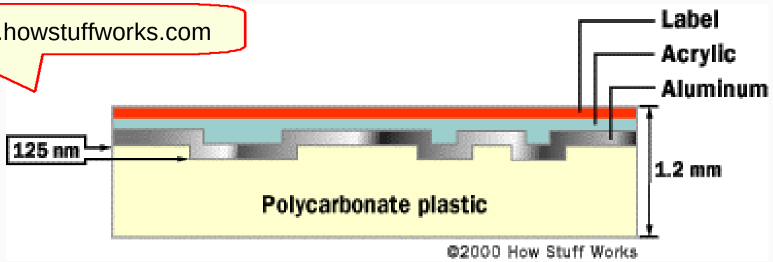
Poole, Owens, Introd. to nanotechnology (wiley, 2003)

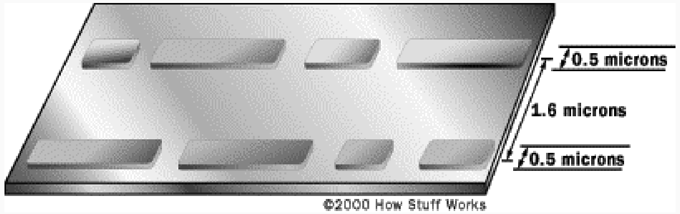
Data storage ottico (CD, CDRW, DVD,...)

Idea di base: superare limiti e difficoltà dei supporti magnetici (con economia!!)

Soprattutto: miniaturizzare testina di lettura (e, possibilmente, allontanarla dal supporto

www.howstuffworks.com

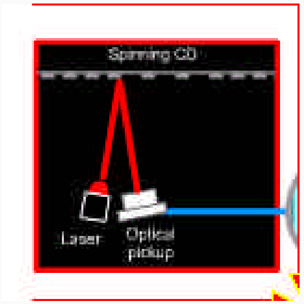




CD-ROM originario: bit costituiti da "buchi" su film riflettente di Al evaporato su strato di policarbonato (morbido)

Impressione: stampa superficiale sul policarbonato (no riscrivibile!)

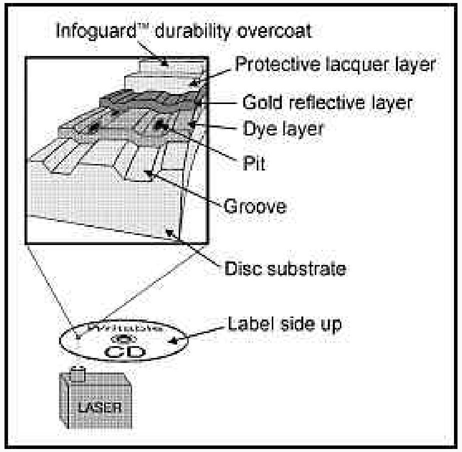
Lettura: deflessione di un fascio laser



Scrittura ottica (CD riscrivibili)

The physical structure of a writable CD differs from that of a CD-ROM. A writable CD is molded from polycarbonate too, but without pits. Like a long-playing phonograph record, a writable CD has a smooth spiral groove running over most of its surface. This groove, molded into the top side of the polycarbonate substrate, serves to guide the powerful laser beam that does the writing

When you write data to a CD-R, the writing laser (which is much more powerful than the reading laser) **heats up** the dye layer and changes its transparency. The change in the dye creates the equivalent of a non-reflective bump. This is a permanent change, and both CD and CD-R drives can read the modified dye as a bump later on.



Uso di un photoresist (un colorante) per impressionare la superficie e modificare *localmente* la riflettività

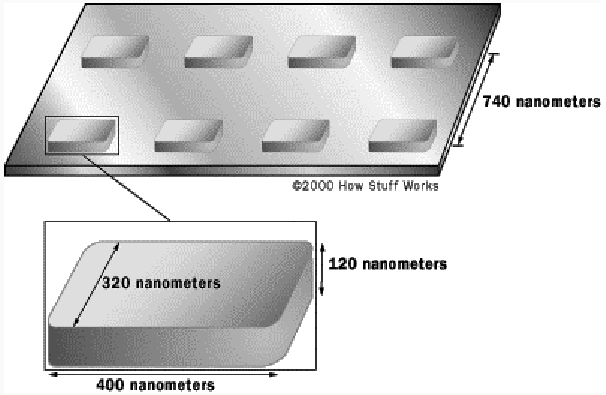
Organic dye-in-polymer (DIP) medium for write-once-read-many (WORM) optical discs

Abstract

A dye containing solution composition for use in forming optical recording media comprises about 0.1 to about 5 parts cyanine dye; about 0.1 to about 5 parts polyvinyl acetate resin and about 100 to about 90 parts co-solvents. The dye containing solution is applied to a substrate of an optical recording medium by a spin coating process to form a recording layer having a uniform thickness. The resultant optical recording medium is suitable for reading and writing with a laser beam.

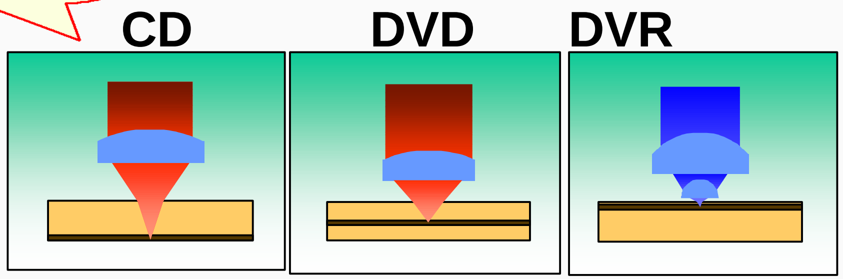
www.kodak.com

DVD e DVD-R: maggiore densità

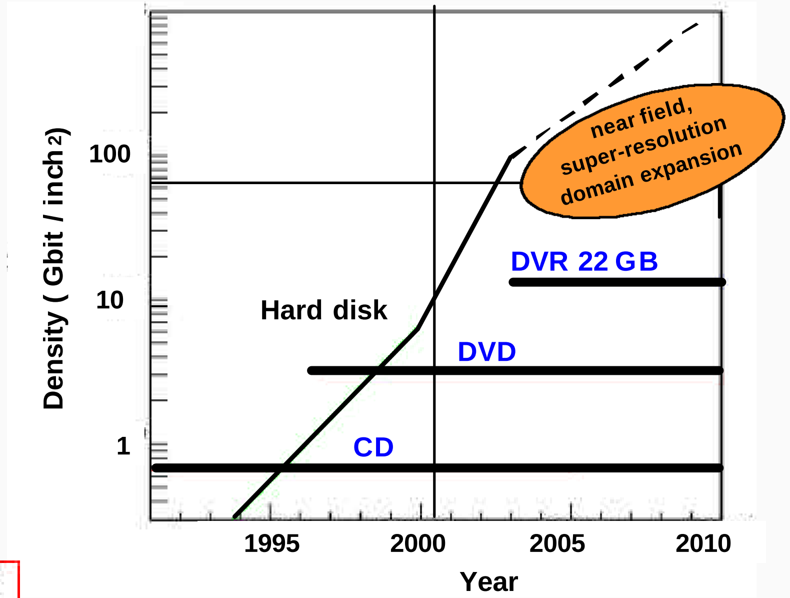


A.C. Ferrari,
Cambridge University

Potenzialità attuali dell'optical storage e limiti



	CD	DVD	DVR
λ (nm)	780	650	400
NA	0.45	0.6	0.85
Capacity (GB)	0.65	4.7	22



Parameter	CD	DVD	4th Generation
λ (nm)	780	650	400
NA	0.45	0.60	0.85-1.5
Track pitch (μm)	1.6	0.74	0.3-0.15
Velocity (m s⁻¹)	1.2	4.0	3-25
Substrate thickness (mm)	1.2	0.6	1.2-2
Spot size λ/2NA (μm)	0.9	0.55	0.25-0.13
Capacity (GB)	0.65	4.7	100

Limiti principali:
- omogeneità dye layer (spin coating, materiali defect-free)
- **diffrazione ottica**

⇩

campo ottico prossimo??