Scuola di Dottorato in Fisica Applicata "G. Galilei" - a.a. 2004/05

Topics in Nanotechnology – part 2

Version 1, April 2005 Francesco Fuso, tel 0502214305, 0502214293 - fuso@df.unipi.it http://www.df.unipi.it/~fuso/dida

Deposition of thin films and heteroepitaxy

11/4/2005 - 16-18 - room T1

Outlook

- Thin films as a basic component of micro (and nano) technology
- Two-dimensional *quantum confinement* in thin heterostructures: excitons and optical properties
- Epitaxial growth: problems and limits in film thickness
- Nanotechnology by evaporation (Feynman's speech): *Molecular Beam Epitaxy*
- An overview of physical deposition methods (and a few words on chemical deposition methods)
- Examples of self-assembly in the organic world

Thin films of inorganic materials

Solid state materials: typically they have a *polycrystalline* nature:

- "grains" with a well defined structure (proper lattice structure);
- large scale organization (mutual arrangement of different grains);
- grain size strongly depending on the material (and on the deposition method)

Thin films:

- basic ingredients of solid state technology (micro- and nanotechnology);
- relevant also out of the electronics area (e.g., structural materials and coatings, tribological surfaces, ...).
- thickness varying through a few monolayers (below 1 nm) to hundreds nm;
- "geometry" can be considered 2D (e.g., columnar growth of the grains)

Very bad example: ceramic materials



AFM image (3D persepctive view) of YBCO film deposited onto metal subs. (scan size approx 2x2 µm², max. height approx 180 nm)



Semiconductor materials engineering





Recent semiconductors for the blue range (blue lasers)

See MRS Bull. 27 (July 2002)

Fig. 9.2. A plot of the low temperature energy bandgaps of a number of semiconductors with the diamond and zine-blende structure versus their lattice constants. The *shaded regions* highlight several families of semiconductors with similar lattice constants. Semiconductors joined by *solid lines* form stable alloys. [Chen A.B., Sher A.: *Semiconductor Alloys* (Plenum, New York 1995) Plate 1]

"Solid solutions" of alloys to tune band-gap

Da Yu and Cardona Fundamentals of Semicond. Springer (1996)

Semiconductor heterostructures



Schema di ua superreticolo formato con Al_xGa_{1-x} As/GaAs (c = na + mb è il parametro reticolare cella direzione z).

Multiple Quantum Wells (MQW): 2DEG quantum confinement



Fig. 9.3. Schematic diagrams of three arrangements of the confinement of electrons and holes in MOWs and superlattices formed by two semiconductors A and B with bandgaps E_{tA} and E_{gB} , respectively. In type I samples both the electrons and holes are confined in the same layer A. The energies of the confined particles are represented by *red lines*. In type IIA systems the electrons and holes are confined in different layers. Type IIB samples are a special case of type IIA behavior. They are either small gap semiconductors or semimetals

Es.: A=GaAs ($E_{gA} \sim 1.5 \text{ eV}$, lattice 5.653 Å) B=AlAs ($E_{gB} \sim 2.3 \text{ eV}$, lattice 5.62 Å) or B=Ga_{1-x}Al_xAs (con x typ. 0.3)

MQW: 1D potential wells

11.9.4 Nanostrutture a dimensionalità ridotta

Pozzi quantici (Q.W. dall'inglese Quantum Wells). Un caso interessante di naaostruttura si presenta quando le barriere sono così spesse che ogni strato tra esse racchiuso si può considerare totalmente isolato dagli altri. In tal caso la simmetria traslazionale è completamente interrotta nella direzione z, dove la differenza tra E_{gA} ed E_{gB} introduce un potenziale di confinamento V_0 . Il sistema presenta allora stati discreti nella direzione z, in corrispondenza ad ognuno dei quali si ha una banda bidimensionale in k_x , k_y (sottobanda).

Sviluppando la soluzione generale in funzioni di Bloch dei cristalli perfetti ed utilizzando l'approssimazione di considerare solo gli stati al massimo ed al minimo della banda, con un procedimento analogo a quello usato per i campi magnetici e le impurezze, si giunge alla seguente equazione per la funzione di inviluppo:

$$\left[-\frac{\hbar^2}{2}\left(\frac{1}{m_x^*}\frac{\partial^2}{\partial x^2} + \frac{1}{m_y^*}\frac{\partial^2}{\partial y^2} + \frac{1}{m_z^*}\frac{\partial^2}{\partial z^2}\right) - eV_0(z)\right]\psi(r) = E\psi(r).$$
(11.91)

Cerchiamo una soluzione del tipo:

$$\psi(r) = \varphi_n(z)e^{ik_x x + ik_y y} = \varphi_n(z)e^{i\vec{k}|\cdot\vec{r}}.$$
 plane waves along x and y (11.92)

Sostituendo la (11.92) nella (11.91) si possono separare due equazioni indipendenti:

$$\left[-\frac{\hbar^2}{2m_{\pi}^{\star}}\frac{\partial^2}{\partial z^2} - eV_0(z)\right]\varphi_n(z) = E_n(0)\varphi_n(z)$$
(11.93)

$$\left(-\frac{\hbar^2}{2m_x^4}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_y^4}\frac{\partial^2}{\partial y^2}\right)e^{i(k_xx+k_yy)} = E_{xy}e^{i(k_xx+k_yy)}.$$
(11.94)

La soluzione della (11.94) ha come autovalori quelli di una particella libera di muoversi nel piano xy:

$$E_{xy} = \frac{\hbar^2}{2m_x^*} k_x^2 + \frac{\hbar^2}{2m_y^*} k_y^2 = \frac{\hbar^2}{2m_{ij}^*} k_{ij}^2.$$
(11.95)

La soluzione della (11.93) dipende dalla forma di V(z). Nella ipotesi semplificatrice di una buca di larghezza L_w a pareti infinite, si ottiene:

$$E_n(0) = \frac{\hbar^2 \pi^2}{2m_x^*} \frac{n^2}{L_W^2}, \qquad \text{infinite potential well} \qquad (11.96)$$

ove n = 1, 2, ...

L'energia totale è dunque:

$$E_{n}(k_{|1}) = \frac{\hbar^{2}k_{||}^{2}}{2m_{||}^{*}} + E_{n}(0).$$



Schema di un pozzo quantico (Q.W.) con indicazione dei livelli da confinamento degli efestioni $(E_1, E_2, ...)$, o delle bucho (posani H_1 e H_2 , loggire L_1). Sono pure indicate le sottobarde $E_n(k_x, k_y)$ corrispondenti ad ogni livello, e la densità di stati (a gradino) in corrispondenza ad ogni soglia ti eccitazione.

Come si vede in fig. 11.33a, essa ha forma parabolica in dipendenza da $k_x e k_y$ e queste parabole sono separate fra loro della quantità $E_{n}(0)$. Le parabole E(k) in due dimensioni sono chiamate sottobande ed hanno densità di stati costante come indicato nel cap. 8 e mostrato in fig. 11.33b.

Considerando il potenziale finito, si ottiene una correzione alle espressioni precedenti dalle opportune condizioni al contorno. Il calcolo per gli stati di buca

è più complesso per la degenerazione della banda di valenza, che nomede un calcolo con l'operatore $E_{ij}(\vec{k})$ ottenuto dalla matrice di Luttinger. L'effetto principale è ottenibile dalla simmetria ridotta, che richiede la separazione degli stati di massa pesante da quelli di massa leggera E_{1hh} , E_{1hl} , E_{2hh} , ... deevy and light holes

In corrispondenza a tutti gli stati discreti si ottengono "sottobande" $E_n(k_x, k_y)$, di natura bidimensionale. A titolo di esempio riportiamo in fig. 11.34 sottobande calcolate di elettroni e buche per il caso più comune di pozzi quantici di GaAs, confinati da Ga_{1-x}Al_xAs (con x = 0.3).



into della banda di valenza del CaAs. (Da P. Banani, in Optical Properties of Servicenductors al. G. Martinez (Klover Academic Publisher, Dordrecht, NL, 1993) p. 27). Discrete energy level system (with partial degeneracy removal)

Excitons in MQW

Excitons: electron-hole pairs, produced, e.g., by photon absorption Electron-hole system is a bound system due to Coulomb force

Il calcolo dell'energia di legame degli eccitoni può essere effettuato in modo analogo a quello delle impurezze nei semiconduttori se le bande di valenza e di conduzione sono sferiche e non degeneri. Analogamente a quanto visto nel cap. 11, si ricava che i livelli idrogenoidi (riferiti alla cima della banda di valenza) hanno energie date da:

$$E_n = E_g - \frac{\mu e^4}{2\hbar^2 \epsilon^2} \frac{1}{n^2},$$
 hydrogen-like atom system (12.107)

ove n è il numero quantico principale, ε la costante dielettrica, e μ la massa ridotta del complesso elettrone-buca

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$
(12.108)

Nei semiconduttori abbiamo visto che $\varepsilon \simeq 10$ e $\mu \simeq 0.5m_e$, per cui l'energia di legame degli eccitoni sarà dell'ordine di qualche decina di meV. A causa della grande costante dielettrica l'eccitone è dunque debolmente legato e la distanza media elettrone-buca è dell'ordine di decine di distanze reticolari. Un eccitone con queste caratteristiche è chiamato eccitone di Wannier-Mott, e ne discuteremo in duratte dei distanze reticolari.

Exciton formation is favored in type I MQW thanks to space superposition of electron-hole wavefunctions (quantum confinement)



Figura 12.28

Fhorescenza eccitonica da un pozzo quantico (Q.W.) GaAs/Ga_{1-x}Al_xAs e dal substrato GaAs a 12 K. E_b indica la posizione dell'eccitone nel substrato, E_{1A} ed E_{1i} gli eccitoni di buca pesante e di buca leggera nel Q.W. Per confronto è riportata anche la nifiettività. Il picco di buca leggera compare soltanto ad alte temperature in fluorescenze, mentre è visibile in riflettività, (Da X. Chen, R. Cingolani, L.C. Andreani, F. Bassani e J. Massies, Il Nuovo Cimento D10, 847 (1988)).

Problems in heteroepitaxy

In principle, we aim at growing a thin layer of a (poly)crystalline material either over a substrate or another layer

Homo-epitaxy: no change in the lattice parameters (i.e., in the material!) **Hetero-epitaxy** (or pseudo-epitaxy): "slight" changes of the lattice parameters



Lattice matching is a crucial issue

Figure 7-1. Schematic illustration of lattice-matched, strained, and relaxed heter taxial structures. Homoepitaxy is structurally very similar to lattice-matched heter taxy.

Problems in the growth



Figure 7-10. Schematic composition of crystal defects in eptiaxial films: (1) threading edge dislocations; (2) interfacial misfit dislocations; (3) threading screw dislocation; (4) growth spiral; (5) stacking fault in film; (6) stacking fault in substrate; (7) oval defect; (8) hillock; (9) precipitate or void.

Large variety of defects can occur, often enhanced when nm-sized thickness is concerned

Some requirements for epitaxy

2.3 Film Growth Modes

Nucleation and growth of a film proceeds from energetically favourable places on a substrate surface and even the cleanest polished surface shows some structure. Figure 5 shows schematically the structure of a well-polished single-crystal surface. The characteristic features are the terraces of length, l_s , the steps and the kinks within the step line, which otherwise runs along well-defined crystallographic directions. If the surface diffusion is fast enough a randomly deposited adatom will diffuse to the energetically most favourable places like steps and especially kinks. If at lower temperatures the diffusion is slower, several mobile adatoms may encounter each other within a terrace and may form additional immobile adatom clusters within the terraces. Similarly, advacancies and their clusters might be formed at the end of the coverage of a terrace. By reducing the step distance and hence the diffusion length by vicinal surfaces, Figure 6, the step controlled growth may be extended to lower temperatures,.

The details of the growth modes for the simplest case of **homoepitaxy**, the growth of a film on a single-crystalline surface of the same material, is indicated in Figure 7. As discussed above, step propagation dominates at higher temperatures and/or small deposition rates and two-dimensional island growth will predominate if immobile clusters are formed by the encounters of mobile adatoms. This simple picture is, however, quite frequently modified: if the jump across the step is kinetically hindered multilayer growth will be observed. This enlarged activation energy for the jump across the step is called the Ehrlich-Schwoebel effect and can be understood in a simple model as the adatom is nearly dissociated from the surface in the saddle point of this jump.

Vicinal surface (engineering of the surface through substrate cutting)



Da R. Waser Ed., Nanoelectronics and information technology (Wiley-VCH, 2003)

Figure 6: Change of the step distance, *l*, by cotting a surface at a small angle to a major crystallographic direction, i.e., forming a vicinal surface.



(b) 2d-island growth, and

(c) multi-layer growth.

/ 2004/5 - ver. 1 - part 2 - pag. 10

Diffusion and Schwoebel barriers

Thin film formation implies *diffusion* of the impinging particle over the substrate (or the underlying layer)

Material diffusion at the atomistic level is a thermally-activated process involving a diffusion coefficient



Diffusion coefficientt: $D = D_0 \exp(-E/kT)$

Local change of the energy felt by the particle during diffusion close to the edge of a step D_0 turns out to depend on the site

In the initial stage, diffusion is affected by the substrate inhomogeneity at the atomistic level

Heteroepitaxy

(4)

If we want to grow an epitaxial film on a different substrate (so-called **heteroepitaxy**), two material parameters have to be considered in addition: the surface energy, γ , and the lattice parameter or lattice match of the two materials. For the case of good lattice match the difference in surface energy leads to two different growth modes as indicated in Figure 8a and b. As long as :

$$\gamma_{
m layer} + \gamma_{
m substrate/layer} \leq \gamma_{
m substrate}$$

we observe perfect wetting and pure layer by layer or *Frank-van-der-Merve growth*. For the opposite case, we observe island or *Volmer-Weber growth*. For this consideration the surface energies of the crystallographic orientations of actual interest must be applied, which are often not available in data reference tables. If there is a lattice mismatch between substrate and film, an additional growth mode may be observed as indicated in Figure & *Stranski-Krastanov growth*. A first layer may grow matched to the substrate, which yields additional strain energy. With growing thickness this strain energy increases in proportion to the strained volume and an island formation may become more favourable in spite of the larger surface area.

The contributions of strain and surface energy can quite generally be described in a simple model and the resulting difference in energy between island growth and layer growth is given by Eq. (5) and illustrated in Figure 9.

$$\Delta W = W_{\text{surf}} + W_{\text{relax}} = const_1 \gamma d^2 - const_2 k \xi^2 d^3 \tag{5}$$

k = bulk modulus, $\xi =$ strain

Considering films of the same volume content, the increased surface energy for the island growth Figure 8b, is proportional to the island area, d^2 , whereas the energy released by relaxation of the lattice is proportional to the sland volume, d^2 . A relaxation mode which is characteristic of isolated islands is shown in Figure 10 for a case where the film material has a larger bulk lattice parameter than the substrate. The model predicts a critical value, d_{crit} , where the island growth is finally more favourable and a fast decrease of the energy for larger sizes. However, the limits of the model are reached in this region as the simple relaxation mode is obviously no longer valid for large sizes.



Figure 11: Strain relaxation by misfit dislocations for the example of two initially cubic arystals. As the film has a larger lattice constant than the substrate the forced matching at the interface yields a tetragonal distortion of the film. By misfit dislocations this strain can be relaxed and the film can re-approach its cubic structure.



Frank-van der Merve



Volmer-Weber



Stranski-Krastanov

Figure 8: Growth modes of the hetero-epitaxy.



Figure 10: Strain relaxation in pseudomorphic (dislocation - free) islands.



island size

Figure 9: Energy contributions as a function of the island size [5].

Heteroepitaxy is strongly depending on the "surface energies"

Thin film deposition methods

In general: solid state material is converted into an elemental phase (e.g., atomic, molecular, ...) and let re-aggregate over a substrate (or another layer)



Deposition from a vapor

2.1 Gas Kinetics

The residual gas pressure in the system is one of the basic parameters to be controlled during film deposition as the residual gas atoms may collide with the depositing species or may hit the growing surfaces and may thus be incorporated in the film, Figure 1. For the simplest assumption that the gas atoms may be considered as not interacting masses with a Maxwell velocity distribution we obtain the mean free path length, λ , of the atoms or molecules

$$\lambda = \frac{1}{\sqrt{2\pi N d^2}} \tag{1}$$

d = molecular diameter, N = concentration of the gas. With the law of the ideal gas: $N = p/k_{\rm B}T$, $k_{\rm B} =$ Boltzmann constant, we obtain:

$$\lambda = \frac{k_{\rm B}T}{\sqrt{2}\pi p d^2} \tag{2}$$

For the example of air molecules we obtain a free path length which is of the order of a typical distance from source to substrate of about 20 cm at a pressure of $0.5 \cdot 10^{-3}$ mbar. This rather moderate vacuum level shows that the beam interaction is not a critical condition for the base vacuum. More critical is the number of residual gas atoms which hit the growing surface and limit the purity of the film if they are incorporated. This number can be expressed as

$$N_{\rm i} = p_{\rm i} \sqrt{\frac{1}{2\pi k_{\rm B} m_{\rm j} T}} \tag{3}$$

 m_i = atomic or molecular mass. Typical results are summarized in Tab. 2. Assuming a sticking coefficient of unity, the incorporation of residual gas atoms may be expressed in terms of monolayers and this growth rate may be rather high as compared to a typical growth rate of an epitaxial film i.e., one monolayer / s. Hence, for clean films **ultra-high** vacuum (UHV, better than 10⁻⁹ mbar) may be necessary.

	And in the second s	the local day has been been been been been been been bee	
10.2	6.7·10 ⁶	2.8-10 ²⁰	3.3.105
100	6.7·10 ³	2.8.1017	3.3·10 ²
10 ³	6.7.10 ⁰	2.8·10 ¹⁴	3.3 10-1
106	6.7.10-3	2.8·10 ¹¹	3.3 10 4
	10 ⁰ 10 ³ 10 ⁶	10 ⁰ 6.7·10 ³ 10 ³ 6.7·10 ⁰ 10 ⁶ 6.7·10 ⁻³	10^0 $6.7 \cdot 10^3$ $2.8 \cdot 10^{17}$ 10^3 $6.7 \cdot 10^0$ $2.8 \cdot 10^{14}$ 10^6 $6.7 \cdot 10^{-3}$ $2.8 \cdot 10^{11}$

Table 2: Some facts about residual air at 25 °C in a typical vacuum used for film deposition (after Chopra [2]).

2.2 Thermodynamics

Phase-diagrams are the starting point for considering the deposition of a new material in order to see the stability range of the envisaged phase and the existence of concurrent phases. Standard phase diagrams are given at ambient pressure, however, changes with pressure must be considered for vacuum deposition methods. Figure 3 shows as a simple example the phase diagram of the completely intermixing binary system Si-Ge and the change from ambient pressure down to the UHV region [3]. At 1 mbar there is not much change compared to atmospheric pressure and we observe a wide range of stability of the mixed homogeneous crystalline phase, c, of Si-Ge (the decomposition of this homogeneous phase at very low temperature is somewhat speculative). At higher temperatures the liquid, I, to solid (crystalline) phase transition is indicated and above 2000 K. the liquid to vapour, v, transition is shown. With decreasing pressure there is a strong decrease in temperature of the 1-v borderlines and even an overlap with the c-l lines. Finally, in the UHV region, 10⁻⁹ mbar, the liquid has disappeared and only direct sublimation, c, v is left at temperatures around 1100 K. Hence, re-evaporation of the material under UHV conditions and high temperatures must be considered. In addition, a comparison with the deposition rates and gas pressures discussed along with Table 2 shows that the deposition of the films usually proceeds under high supersaturation, i. e. conditions far from thermodynamic equilibrium.





Temperature in Degrees Centigrade

Molecular Beam Epitaxy: MBE, MOMBE



MBE sources

3.1.1 Sources

The schematic of the classical MBE source, the Knudsen cell, is Illustrated in Figure 13. The evaporation rate, N_a is described by the Hertz-Knudsen (or Langmuir) equation:

$$N_{\rm e} = \frac{p_{\rm e}A_{\rm e}}{\sqrt{2\pi m k_{\rm B}T}} \tag{6}$$

 p_e is the equilibrium vapour pressure and A_e the area of the aperture [7]. Therefore, the source can be precisely controlled by a single parameter, the temperature. However, the technical details are very complex and involve more parameters than shown in Eq. (6).

Figure 14 shows the principle of an electron beam evaporator. The electron beam is magnetically deflected by 270° and is centred on the source material. In this way a melt of the source material is produced on a block of the same material which can be held in a water-cooled cold crucible in order to avoid contamination of the melt.





Figure 14: Schematics of a electron beam evaporator for Si evaporation [7]; B: Si guard ring, C: catcher for backscattered electrons.

Figure 13: Schematics of a Knudsen cell and the distribution of the vapour beam intensity [7]. The distribution depends on the ratio L_0/d_0 and consequently on the filling level of the cell.

Da M. Ohring, The Materials Science of Thin Films, Academic (1992) Consider now a substrate positioned a distance / from a source aperture of area A, with $\phi = 0$. An expression for the number of evaporant species striking the substrate is

$$\dot{R} = \frac{3.51 \times 10^{22} PA}{\pi l^2 (MT)^{1/2}} \text{ molecules/cm}^2 \text{-sec.}$$
(7-13)

As an example, consider a Ga source in a system where $A = 5 \text{ cm}^2$ and l = 12 cm. At T = 900 °C the vapor pressure $P_{\text{Ga}} \approx 1 \times 10^{-4}$ torr, and substituting $M_{\text{Ga}} = 70$, the arrival rate of Ga at the substrate is calculated to be 1.35×10^{14} atoms/cm²-sec. The As arrival rate is usually much higher, and, therefore, film deposition is controlled by the Ga flux. An average monolayer of GaAs is 2.83 Å thick and contains $\sim 6.3 \times 10^{14}$ Ga atoms/cm². Hence, the growth rate is calculated to be $(1.35 \times 10^{14})/(6.3 \times 10^{14}) \times 2.83 \times 60 = 36$ Å/min, a rather low rate when compared with VPE.



Figure 4-3. Thickness uniformity across a 3" wafer represented as a mapping of quantum well photohuminescence. The MQW structure was grown using a SUMO Ga cell in a MOD GEN II system. Uniformity better than ± 1% was achieved. Data courtesy R. Sacks, Ohio State University and K. Stair, Northwestern University.

In-situ thickness control

Rutherford High Energy Electron Diffraction (RHEED) frequently used to diagnose film coverage and to measure film thickness



Figure 7-22. Real space representation of the formation of a single complete monolayer; $\bar{\theta}$ is the fractional layer coverage; corresponding RHEED oscillation signal is shown.



Figure 19: STM and RHEED results for the homo-epitaxial growth of Fe films on Fe(100) substrates. The growth was interrupted after 5 oscillations, as indicated by the arrow. The scale of the STM was changed between part a and b! The roughness of the films decreases strongly with temperature: rms (root mean square) amplitude 0.116 nm , 0.095 nm and finally at 250°C 0.06 nm [9].

An example of advanced capabilities of MBE

QC-laser crystal grown by Molecular Beam Epitaxy (MBE)



Cross-section of a few stages of QC-laser crystal crystal growth one atomic layer at a time

- Many (~ 500), few-atoms thick layers of alloy materials (AI, Ga, As, In);
- atomic control of layer thickness, 1 nanometer (nm) = 4 atomic layers
- atomically flat layer interfaces



Quantum cascade lasers (novel sources for the IR range)

Each semiconductor layer is the place where exciton recombination occur

Thickness must be carefully tuned in order to have operation at the desired wavelength

MBE is able to control thickness at the monolayer level while ensuring an ultra high level of purity

Limitations of MBE and alternative techniques

Main limitations of MBE (from the nanotechnological point of view):

- poor suitability with refractory materials (too high temperature);
- poor suitability wih complex materials (e.g., reactivity with oxygen);
- low kinetic energy of the particles and need for an annealing treatment

Alternative physical method: sputtering

Vaporization achieved through collisions with high energy particles (electrons, ions)







Sputtering vs vaporization

Da M. Ohring, The Materials Science of Thin Films, Academic (1992)

	сумрогацоп	Sputtering
	A. Production of	Vapor Species
1	Thermal evaporation mechanism	 Ion bombardment and collisional momentum transfer
2	Low kinetic energy of evaporant atoms (at 1200 K, $E = 0.1 \text{ eV}$)	2. High kinetic energy of sputtered atoms ($E = 2-30 \text{ eV}$)
3	Evaporation rate (Eq. 3-2) (for $M = 50, T = 1500$ K, and $P_e = 10^{-3}$) $\approx 1.3 \times 10^{17}$ atoms/cm ² -sec.	3. Sputter rate (at 1 mA/cm ² and S = 2) ~ 3 × 10 ¹⁶ atoms/cm ² -sec
4	Directional evaporation according to cosine law	4. Directional sputtering according to cosine law at high sputter rates
5	Fractionation of multicomponent alloys, decomposition, and dissociation of compounds	 Generally good maintenance of target stoichiometry, but some dissociation of compounds
6	Availability of high evaporation source purities	 6. Sputter targets of all materials are available; purity varies with material
	B. The Ga	Phase
1.	Evaporant atoms travel in high or ultrahigh vacuum ($\sim 10^{-6}-10^{-10}$ torr) ambient	 Sputtered atoms encounter high- pressure discharge region (~ 100 mters)
2	Thermal velocity of evaporant 10 ⁵ cm/sec	 Neutral atom velocity ~ 5 × 10⁴ < cm/sec
3.	Mean-free path is larger than evaporant-substrate spacing. Evaporant atoms undergo no collisions in vacuum	 Mean-free path is less than target- substrate spacing. Sputtered atoms undergo many collisions in the discharge
	C. The Conde	nsed Film
1.	Condensing atoms have relatively low energy	1. Condensing atoms have high energy ⁴
2.	Low gas incorporation	2. Some gas incorporation
3.	Grain size generally larger than for sputtered film	3. Good adhesion to substrate
> 4.	Few grain orientations (textured films)	4. Many grain orientations

Another physical method: pulsed laser deposition (PLD)



Some peculiarities of PLD

PLD is a *pulsed* process

- 1. UV laser energy is efficiently transferred to the target
- 2. A plasma is formed following interaction of the laser pulse with the vaporized material
- Vaporized material (plume) expands in a highly peaked beam
- 4. High energy elemental materials impinges onto the substrate favoring thin film formation even without postannealing.



Arrival of high energy particles onto the substrate

A few words on precursor-based (chemical) methods

4 Chemical Deposition Methods

Chemical deposition generally includes chemical solution deposition (CSD) as well as chemical vapour deposition (CVD). In both cases, chemical precursors are employed which undergo chemical reactions for the formation of the film. We will place special emphasis on CVD as this method finally allows the deposition of ultrathin films and the conformal deposition on complex-shaped structures which are essential for ULSI. CSD includes sol-gel techniques and metal-organic decomposition MOD and typically uses spin-on techniques for the distribution of a solute film which is subsequently processed and crystallized. Finally, we give a short introduction to a very different method for deposition from solutions, the Langmuir-Blodgett (LB) technique. LB techniques allow the deposition of monomolecular organic films on different substrates making use of the hydrophilic/hydrophobic orientation of the molecules.



Figure 30: Schematics of the gas flow and the atomic scale chemical environment in the region of the growing film surface during a MOCVD process.

4.1 Chemical Vapour Deposition

The general principles of CVD are well established and a number of reviews and tex books are available [20], [21], [22], which cover many generic issues common to an type of material. In CVD, film growth occurs through the chemical reaction of the conponent chemicals (i.e. precursors) which are transported to the vicinity of the substra via the vapour phase. The film-forming chemical reactions typically utilize therm energy from a heated substrate as depicted schematically in Figure 30. Other more spccial methods, which cannot be discussed here, couple non-thermal energy sources such as RF or microwave power or light into the reaction process in order to reduce the thermal reaction temperature required. In order to complete the system, a delivery system for the precursors and, finally, an exhaust system must be added. The most straightforward type of CVD involves chemical precursor compounds that are sufficiently stable gases and such processes are standard processes in CMOS technology for the deposition of insulators and interlayer dielectrics like poly-Si, SiO, SiN, and BPSG glasses. Figure 31 shows the schematics of a reactor for handling large batches of wafers simultancously. Examples of the reactions involved are the thermal decomposition of silane, SiH₄, for the deposition of:

•	Poly Si :	SiH4	与	$Si(s) + 2 H_2$	at 580-650 °C, and a pressure of ≈ 1 mbar;
•	Si-Nitride:	3 SiH ₄ +4 NH ₃	₽	${\rm Si_3N_4}{+}12{\rm H_2}$	at 700-900 °C, and atmospheric pressure;
•	Si-Dioxide:	$SiH_4 + O_2$	₽	$SiO_2 + 2 H_2$	at 450 °C;

These SiO_2 films are usually under high stress and are not conformal. Therefore alternative routes using organic precursors have been developed e.g., the TEOS (tetra-ethyl-ortho-silane) process:

 $Si(C_2H_5O)_4 + 12 O_2 \implies SiO_2 + 8 CO_2 + 10 H_2O at 700 °C.$

Similarly, for the processing of many metals and especially the group-II metals, special precursors in the form of organometallic compounds had to be developed and a special subgroup of CVD techniques, metal-organic-CVD. MOCVD, has therefore evolved. Efficient, reproducible MOCVD processes hinge critically upon precursors with high and stable vapour pressures and the chemistry is therefore the decisive step in the development of MOCVD.

Choice and operation of the precursor set the essential advantages/limitations

A few words on solution-based (chemical) methods

coating

multiple

4.2 Chemical Solution Deposition

The chemical solution deposition (CSD) method comprises a range of deposition techniques and of chemical routes which have been reviewed recently [23], [33]. A generalized flow chart of the CSD of oxide thin films is shown in Figure 42. The process starts with the preparation of a suitable coating solution from precursors according to the designated film composition and the chemical route to be used. Besides mixing, preparation may include the addition of stabilizers, partial hydrolysis, refluxing, or else. The coating solution is then deposited onto substrates by:

- spin-coating, where typically a photoresist spinner is employed and which is suitable for semiconductor wafers,
- *dip coating*, which is often used in the optics industry for large or non-planar substrates, and
- spray coating, which is based on a misting of the coating solution and deposition of the mist exploiting gravitation or an electrostatic force.

The wet film may undergo drying, hydrolysis and condensation reactions depending on the chemical route. The as-deposited film possibly represents a chemical or physical network. Upon subsequent heat treatment, a further hydrolysis and condensation and/or a pyrolysis of organic ligands may take place, again depending on the chemical route. The resulting film consists of amorphous or nanocrystalline oxides and/or carbonates. Upon further heat treatment, any carbonate will decompose and the film will crystallize through a homogeneous or a heterogeneous nucleation. Typically, the desired final film thickness is built up by multiple coating and annealing.

Depending on the type and reactivity of the precursors, the chemistry shows a wide spectrum of reaction types. On the one hand, there are the pure sol-gel reactions i.e. alkoxide precursor systems, which undergo hydrolysis and condensation reactions. The formation of SiO, coatings starting from Si alkoxides is the classical example of this type of reaction. The condensation leads to a chemical gelation in which - under appropriate reaction conditions - no pyrolysis reaction of any organic ligand occurs. At the other extreme, there is metal organic decomposition (MOD), which typically starts from carboxylates of the cations or, in special cases, from the nitrates. The carboxylates do not chemically react with water. Consequently, during heat treatment, first the solvents are evaporated, a process which is sometimes referred to as physical gelation. Upon further heating, the carboxylates pyrolytically decompose into amorphous or nanocrystalline oxides or carbonates. There is a wide spectrum of possible reaction routes between the pure sol-gel route and the MOD route. Depending on the type of alkoxides and a possible stabilization of the precursors, there may be a partial hydrolysis and condensation while some organic ligands remain in the gelated film and undergo pyrolysis upon further heat treatment. In the synthesis of multicomponent oxide films, often hybride routes are followed, i.e. there may be some precursors employed which tend to follow the sol-gel or partial sol-gel route while others undergo typical MOD reactions.

The microstructure formed during the CSD process strongly depends on the intermodynamics and kinetics of the solidstate reaction from the intermediate amorphous or nanocrystalline state after pyrolysis to the final equilibrium crystalline phase. This is controlled by the chemical composition of the film system (for details see e.g. ref. [23]).

Due to their low capital investment and simple processing, CSD techniques are widely used and are also applicable for micro- and nanoelectronics on a low level of integration, e.g. for present state FeRAMs.



An example of (nanotechnological) solution-based approach



Linear molecules with an head group (chemically reacting with the substrate) and an end group (with possibile specific functions)

Self-Assembling Monolayers (SAMs) I

Example: alkanethiolates

SAMs of alkanethiolates on gold[29,30] form by spontaneous adsorption of	MONOLAYERS		
alkanethiols $(X(CH_2))$ [27,30,36-42] and dialkyldisulfides $(X(CH_2))$ $S-S$	SURFACE	LIGAND	BINDING
$(CH_2)_m Y$ [41,43] (from the liquid or vapor phase) onto a clean gold surface	Au	RSH, ArSH (thiois)	RS-Au
according to:	Au	RSSR' (disufides)	RS-Au
	Au	RSR' (sulfides)	RS-Au
$\frac{X - R - SH + Au}{X - R - S - Au(I) \cdot Au(0)_n + \frac{1}{2}H_2} $ (1)	SiO ₂ , glass	RSICI3,RSIOR3	siloxane network
$\gamma_2(X-K-S)_2 + Au \rightarrow X-K-S Au(I) \cdot Au(0)_n.$	Si	[RCOO], (neat)	R-Si
	Si	RCH=CH ₂ , (RCOO) ₂	R-CH2CH2-Si
	GaAs	RSH	RS-GaAs
	Ag	RSH, ArSH	RS-Ag
	Cu	RSH, ArSH	RS-Cu
	metal oxides	RCOOH	₽CO ₂ MO _n
Linear molecules comprised of an alkyl	metal oxides	BCONHOH	BCONHOH ··· MO
chain and a thiol head make a	The on one	HOONINGIT	RCONHO MOn
spontaneous chemical bond with noble	Pt	RSH, ArSH	RSPt
motol (Au) ourfoodo	Pt	RNC	RNC-Pt

Monolayers (thickness < 1 nm) spontaneously formed by simple dipping the substrate into a SAM solution

Self-Assembling Monolayers (SAMs) II



Main role of SAMs in nanotechnology:

- molecular "templates" (i.e., a system to "hold" molecules/clusters on a surface)
- molecular resist in advanced lithography processes

SAM templates I



SAM "holds" small Gold clusters

SAM templates II

Au{111}

STM tip trajectory

STM tip Da J.M. Tour, Molecular Electronics (World Scientific, 2003)



We use self-assembly to control and STM to observe the switching of single molecules.

SAM "holds" intramolecular electronic components (e.g., "Tour wires") allowing their selective addressing through STM



Figure 12:

(a): Protruding molecular rod 16 out of a SAM layer of dodecylmercaptan.

(b) STM picture of the sample diplaying protruding rods 16 as brighter spots. Correlated maxima in the conductivity and the topology indicate the increased conductance through the molecular rods 16. [35]

Conclusions

 \checkmark A fundamental building block of technology (micro- and nano-) is represented by thin films

 \checkmark Thin films play a major role in a variety of fields (electronics, but also nanomaterials for structural or hard coating applications, ...)

✓ A "classical" example (especially for optoelectronics and photonics):
 MQW structures

 \checkmark Growth of thin films is a complex process involving different phenomena at the atomistic level

✓ Most relevant film deposition methods are based on vaporization (e.g., MBE)

 \checkmark An alternative route is represented by self-assembly with organic materials (linear molecules)

 \checkmark Use of SAMs in nanotechnology as templates and resists (to be discussed in the next lecture)