Thin Films Deposition (deposição de filmes finos)

Objectivos

1. Perceber porque são necessários os vários materiais
2. Saber quando a deposição de um filme fino é necessária no processo de fabrico.
3. Perceber a diferença entre CVD e PVD
4. Descrever os processos PVD (evaporação térmica, canhão de electrões-ebeam, sputtering)
5. Descrever o processo CVD
6. Descrever o processo de deposição electroquímica
7. Conhecer o processo de medição da taxa de deposição e espessura, durante a deposição.
8. Descrever um processo de spin-coating, e saber quando pode ser utilizado.
9. Descrever o processo de oxidação térmica.
10. Saber como é fabricado o silício monocristalino ou policristalino

Insulators and Conductors

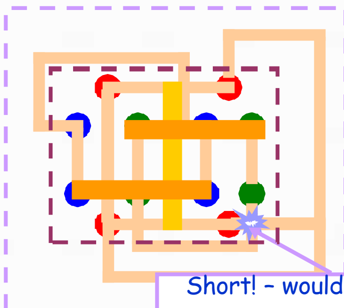
- In the process of making integrated circuits individual transistors are created on the silicon (~25million in the die of each Celeron !!).
- To be of any use these transistors have to be connected to power supplies and input and output signals etc. so that they can switch on and off and in doing so, relay information.
- As the number of transistors in a die had increased so too has the number of layers required to connect up all the transistors in a meaningful manner.
- Currently on the 859 process 6 layers of metal are needed to route all the signals. Therefore 6 insulating layers are also needed to prevent shorts between all these metals lines.

Why so many layers ?

- All 25 million transistors on a die need to be connected in a meaningful manner.
- While it would be possible to make all these connections using one metal layer only, this layer would need to be very complex and would take up a huge amount of silicon space.

Cell size with 1 layer metal

Cell size with 3 layer metal



Imagine top down view of contacts.

Need to connect contacts of same colour to each other.

Use Metal 1.

Instead, add M1

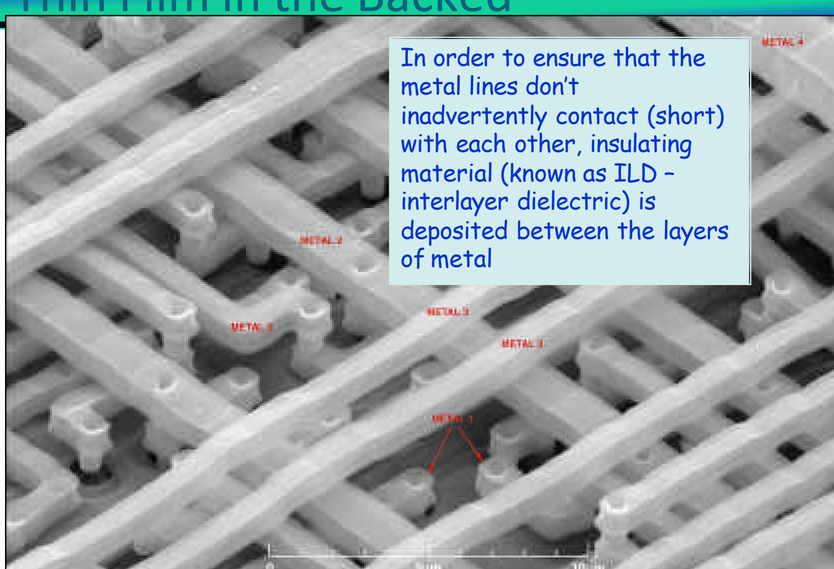
Then M2, running over M1

Then M3, running over M2

Short! – would have to redesign transistor to spread contacts out further → even bigger

Die size = $$$

Thin Film in the Backed



In order to ensure that the metal lines don't inadvertently contact (short) with each other, insulating material (known as ILD – interlayer dielectric) is deposited between the layers of metal

Materiais usados nas microtecnologias

- Materiais compatíveis com Si
- Si, puro
- p-Si, n-Si, dopagem com Boro ou Fósforo
- Si Wafer com os cristais orientados nas direcções [100], [110], [111]
- Polisilício puro, cristais sem orientação
- Poly-p, Poly-n, dopagem com Boro ou Fósforo respectivamente
- SiO_2, isolante, quase transparente à luz visível (n=1.4-1.5), ideal para membranas finas, exibe stress residual compressivo
- Si_3N_4, isolante, quase transparente à luz visível (n=2.2-2.5), ideal para membranas finas, exibe stress residual em tensão.
- Al, metal utilizado para as ligações, bom grau de dureza para evaporação térmica ou sputtering.

E ainda...

Materiais com propriedades específicas

- Termoeléctricas: Bi_2Te_3 / Sb_2Te_3
- Piezoeléctricas: AlN, PolySi
- Ópticas: ITO, Ag, Au
- Magnéticas: Co, Ni ?
- Estruturais: Ti, W
- Térmicas: Coef. Expansão, isolante, condutor
- Bio-compativies:
- Quimicas: LiPON, LiCoO
- Mecânicas

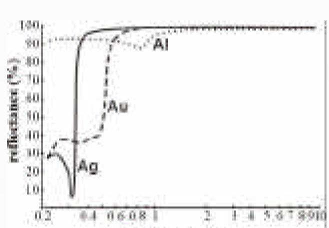
Alguns exemplos !!!

Filmes finos

- Formação de filmes finos (na ordem dos micrómetros ou menor) de diferentes materiais sobre um wafer de silício
- Estes filmes podem ser formatados e padronizados por técnicas litográficas e técnicas de corrosão dos materiais em causa
- Metais nobres como o Au e a Ag, contaminam os circuitos de microelecrónica causando falhas, portanto wafers de silício com metais nobres têm que ser processados usando equipamento dedicado apenas a esta tarefa.
- Os metais nobres geralmente são padronizados recorrendo à técnica de *lift-off*.

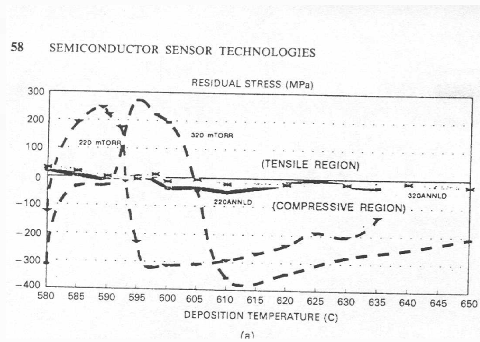
Materiais usados nas microtecnologias

- Materiais não compatíveis com Si
- Ag e Au, muito macios para evaporação, mas com boas propriedades ópticas para a zona do visível e infra-vermelho respectivamente.
- Cu, material de baixa resistividade comparado com o Al. Requer processo especial para fazer o seu crescimento em wafers de silício.
- TiO_2, filmes finos para filtros ópticos



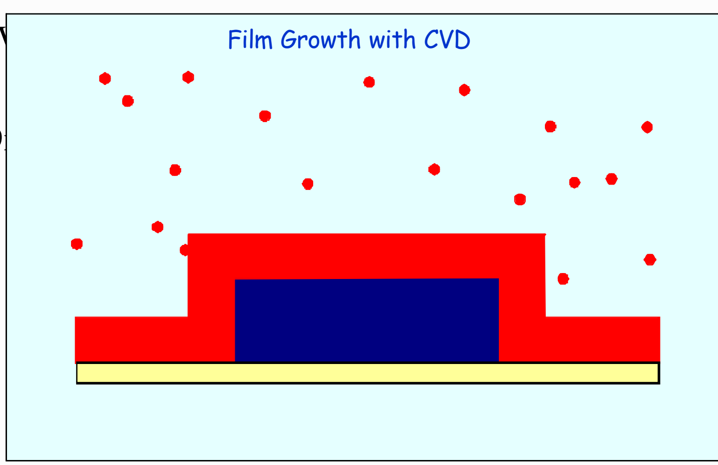
Stress residual em filmes finos

- Condições de deposição (temperatura, pressão) dos filmes fazem variar o stress residual. O *LPCVD* Si_3N_4 apresenta stress residual de 0.125-1 GPa conforme a variação de tempeatura e o *annealing*. Em baixo está representado o stress residual do *LPCVD Poly* quando depositado a diferentes pressões e sem *annealing*.



CVD Vs PVD

- CVD – Chemical Vapour Deposition
- PV
- D



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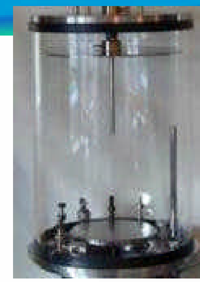
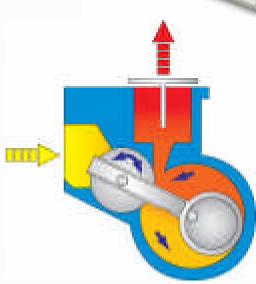
Intel Ireland

Uma câmara de vácuo …



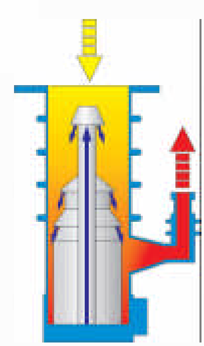
Uma câmara de vácuo …

Precisa de bomba de vácuo



Bomba rotativa

Bomba turbo-molecular



Bomba difusora

PVD – Physical Vapour Deposition

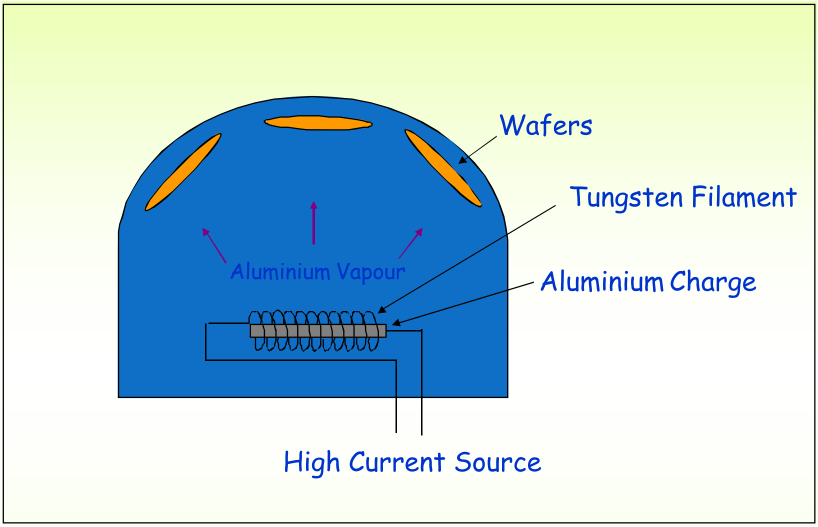
1. Thermal evaporation
2. E-beam
3. Sputtering

Physical Vapour Deposition

- This method of thin film deposition refers to several different deposition techniques.

  1. Evaporation systems
     - Thermal evaporation

Physical Vapour Deposition



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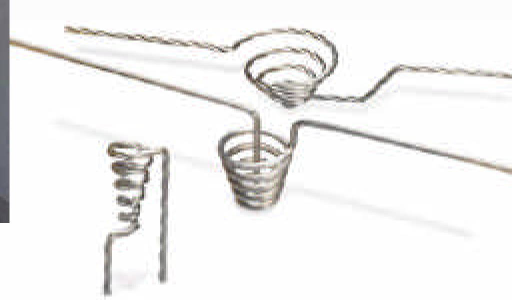
Evaporação térmica



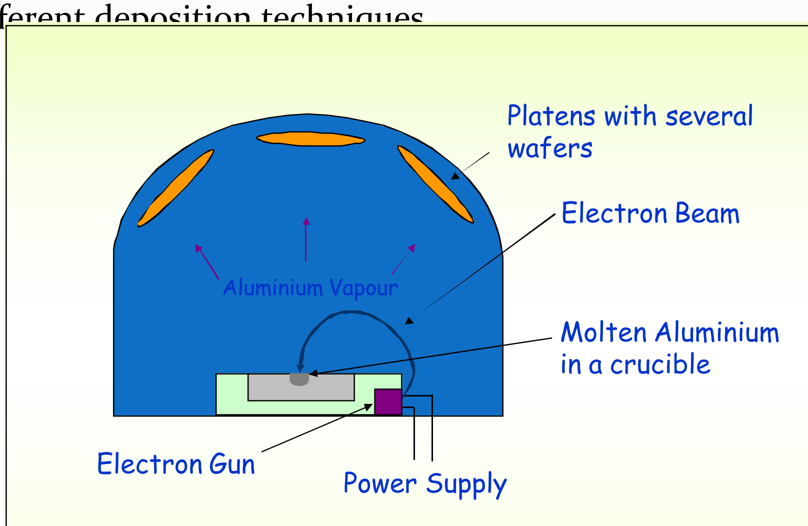
Physical Vapour Deposition

- This method of thin film deposition refers to several different deposition techniques.

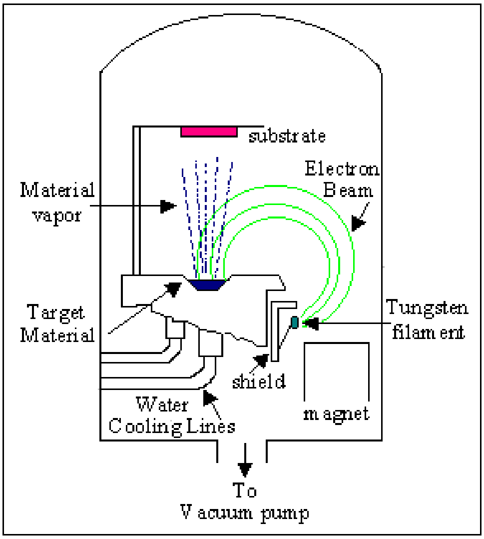
1. Evaporation systems
   - Thermal evaporation
   - Electron beam evaporation

Physical Vapour Deposition

- This method of thin film deposition refers to several different deposition techniques.



E-beam

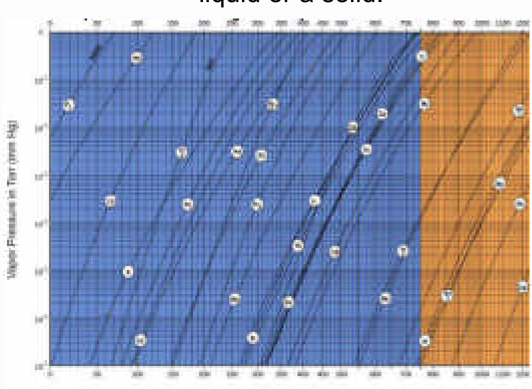


Pressão de vapor

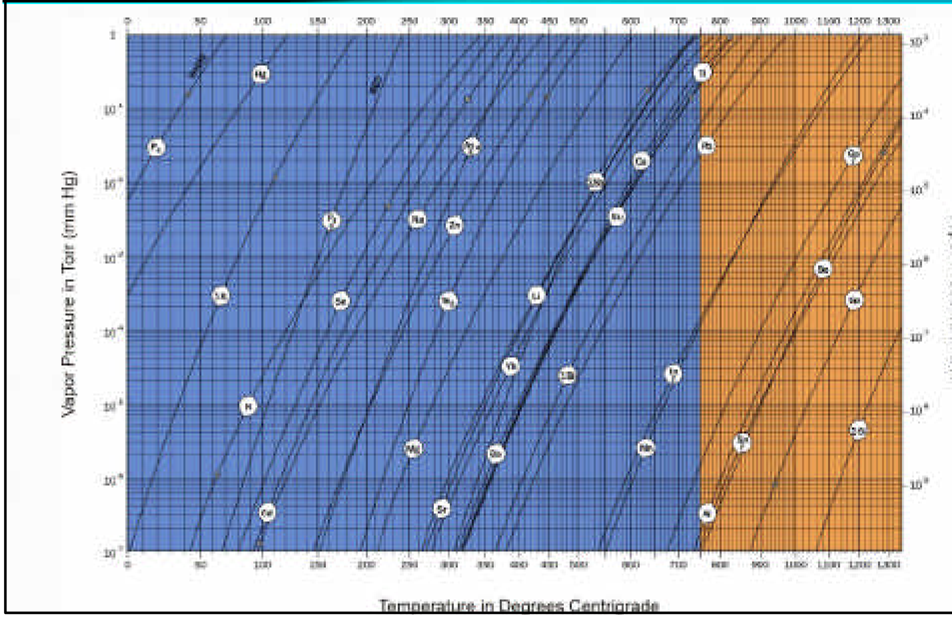
Vapor pressure is the pressure of a vapor in equilibrium with its non-vapor phases (i.e., liquid or solid).

Most often the term is used to describe a liquid's (solid's) tendency to evaporate.

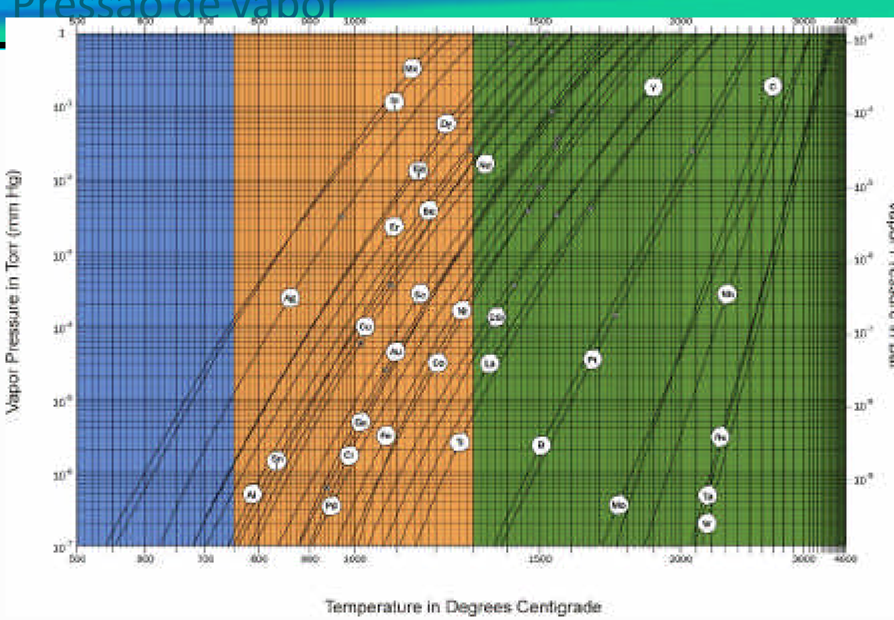
It is a measure of the tendency of molecules and atoms to escape from a liquid or a solid.

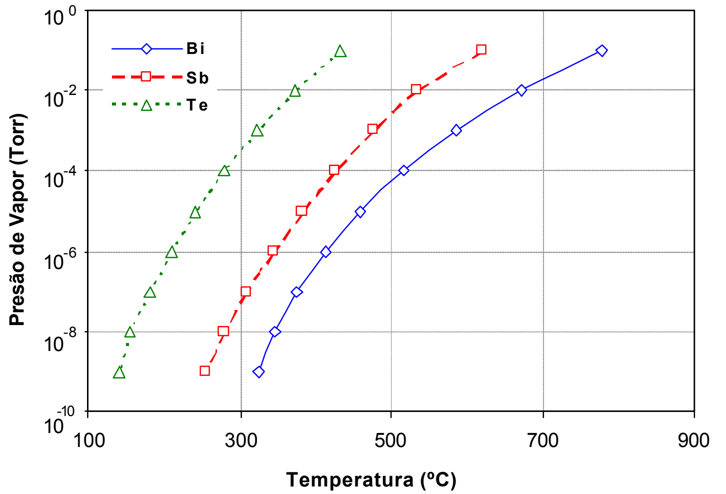


Pressão de vapor



Pressão de vapor





Pressão de vapor em função da temperatura do telúrio, antimónio e bismuto [[i]].

[i] Helin Zou, "Preparation and Characterization of bismuth Telluride and antimony telluride thermoelectric thin films", Phd Thesis, Cardiff UK.

Evaporação de composto

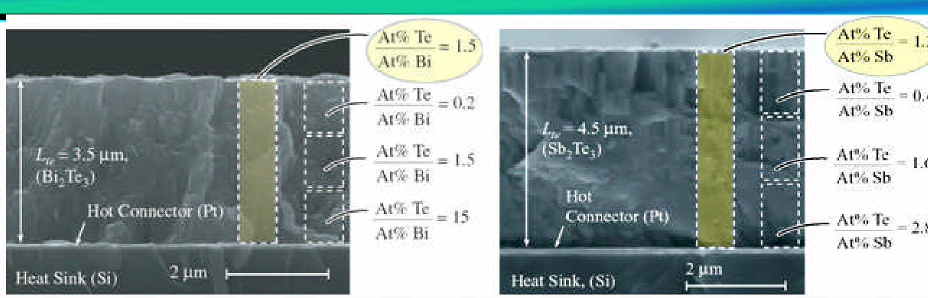


Imagem SEM da secção de um filme de Bi_2Te_3 (esquerda) e Sb_2Te_3 (direita) depositados por evaporação térmica e respectiva análise de composição média em três regiões da secção [[i]].

[i] Luciana W. Silva and Massoud Kaviany, "Miniaturized Thermoelectric Cooler",Proc. of IMECE'02, New Orleans, USA, Nov, (2002) 17-22.

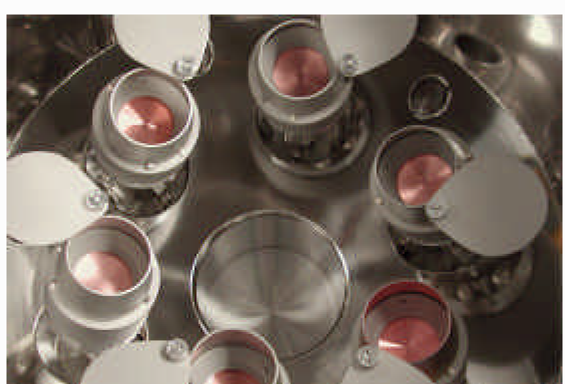
Pressão de Vapor vs Temperatura de Fusão ?

Element	Symbol	Melting Point °C	Density (, g/cm^3)	Z-ratio	Temperature°C @ Vapor Pressure (Torr) 10^{-8}	10^{-6}	10^{-4}	Evaporation Method	Crucible	Boat	Remarks
Aluminum	Al	660	2,7	1,08	677	821	1010	eBeam (xlnt), Thermal	TB, BN, ZB	BN,TB CG,W	Alloys and wets. Fill Boat 2/3.
Chromium	Cr	1890	7,2	0,305	837	977	1157	eBeam (good),	G	CG, Cr rod	Adheres well. High rates possible. Sublimes.
					........sublimes.......						
Gold	Au	1062	19,3	0,381	807	947	1132	eBeam (xlnt), Thermal	CG, BN, Al_2O_3	W, Mo, Al_2O_3	May not adhere well. Films soft.
Platinum	Pt	1769	21,45	0,245	1292	1492	1747	eBeam (xlnt), Thermal	CG, ThO_2	W	Alloys with metals; poor adhesion; films soft
Silicon	Si	1410	2,42	0,712	992	1147	1337	eBeam (fair), sputter	BeO, Ta, CG	W, Ta	Alloys with W; SiO produced above 4x10^{-6}; n = 1.6
Silicon Dioxide	SiO_2	1610-1710	2.2-2.7	1	--	--	~1025	eBeam (xlnt), sputter	Al_2O_3	--	n = 1.47
Silicon Nitride	Si_3N_4		3,44	--	--	--	~800	eBeam, sputter	--	--	n ˜ 2.1
Silver	Ag	961	10,49	0,529	847	958	1105	eBeam (xlnt), Thermal (Mo	Al_2O_3, Mo	Mo, Ta	
Tin	Sn	232	7,75	0,724	682	807	997	eBeam (xlnt), Thermal	Al_2O_3, Ta	Mo	Wets Mo
Titanium	Ti	1675	4,5	0,628	1067	1235	1453	eBeam (xlnt), Thermal	TiC	W	Alloys with refractory metals.
Tungsten	W	3410	19,3	0,163	2117	2407	2757	eBeam (good),	--	--	Forms violate oxides. Films hard & adherent.

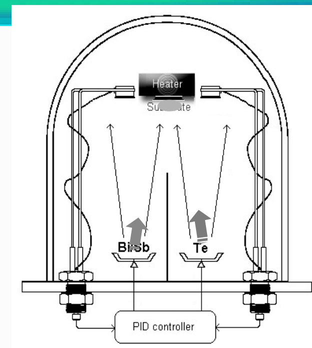
Co - evaporação

- Dois ou mais sistemas de deposição ao mesmo tempo (normalmente do mesmo tipo)
  - Permite criar compostos, controlando a composição
  - Controlo da taxa de deposição em cada sistema
  - Através do controlo da potência

  - Ex: Bi2Te3



Thermal Co-evaporation



- 2 crucibles
- Power controlled by PID
- Constant evaporating rate
- Two oscillating crystals
- Substrate heated
- Deposition slow: few μm/h

Recomendações dos fabricantes de equipamentos

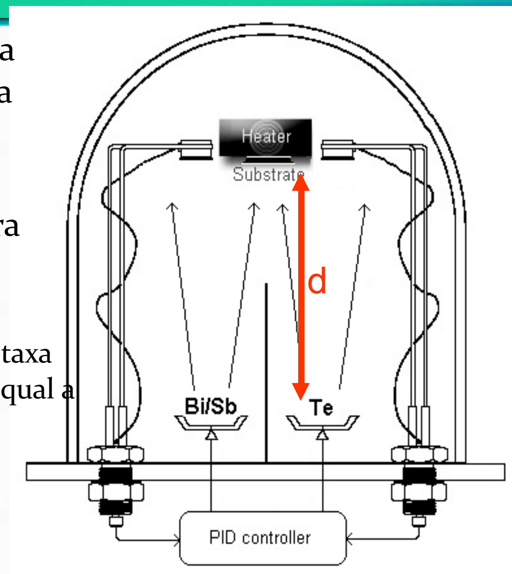
Thermionics Laboratory Inc.

NAME	SYMBOL	MELTING POINT °C	DENSITY g/cc	10^{-8} TORR	10^{-6} TORR	10^{-4} TORR	LINER	NOTES N=INDEX OF REFRACTION
Aluminum	Al	660	2.70	677	821	1010	BN, CG	Alloys and wets May fill volume 70% [1]
Aluminum Carbide	Al_4C_3	1400	2.36			~800		N=2.7 [3]
Aluminum Floride	AlF_3	1257 Subl.	3.07	410 Subl.	490 Subl.	700 Subl.	G, W, MO	N=1.38 @ .55μ [4]
Aluminum Nitride	AlN	Subl.	3.26			~1750		Decomposes Reactive evaporate in $10^{-3}N_2$ with glow discharge [3]
Aluminum Oxide (alumina)	Al_2O_3	2045	3.97			1500		N=1.66 forms smooth hard films [1]
Antimony	Sb	630	6.68	279 Subl.	345 Subl.	425 Subl.	BN, G, Al_2O_3	Toxic. Evaporates well, film structure is rate-dependent [1]
Antimony Trioxide	Sb_2O_3	656	5.2 or 5.76	Subl.	Subl.	Subl.	BN, Al_2O_3	Toxic, decomposes on W.n=2.05 [3]
Antimony	Sb_2S_3	550	4.64			~200	Al_2O_3	N=3.01 @ .55μ .

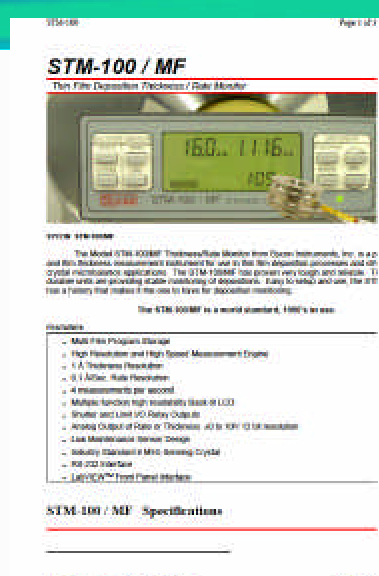
Exercício

- Demonstre como varia a taxa de deposição com a distância ALVO – SUBSTRATO
- E como varia a espessura final obtida?

- Ex: se à distância de 10cm a taxa de deposição é de 1nm/seg, qual a taxa de deposição a 20cm?



Medição de espessura e taxa de deposição


STM-100 / MF

Thin Film Deposition Thickness / Rate Monitor

STM-100 / MF Specifications

Medição de espessura e taxa de deposição

The sensor uses the resonant frequency of an exposed quartz crystal to sense the mass of deposited films attached to its surface. The presence of mass of the deposited film on the surface of the crystal decreases its resonant frequency. The relationship between the mass of the film and the frequency of the sensor crystal is given by [10]:

$$h = \left(\frac{N_Q d_Q}{\pi d_F Z f} \right) \arctan \left[Z \tan \left(\frac{\pi (f_Q - f)}{f_Q} \right) \right], \quad (1)$$

where the terms used in the equation are defined as:

h - film thickness;

N_Q - frequency constant for AT-cut quartz crystal (1.668×10^{13} $Hz.$Å);

d_Q - density of quartz ($2.648\ g.cm^{-3}$);

d_F - density of film material;

Z - Z-Factor of film material;

f_Q - frequency of crystal prior to depositing any film on it;

f - frequency of loaded crystal.

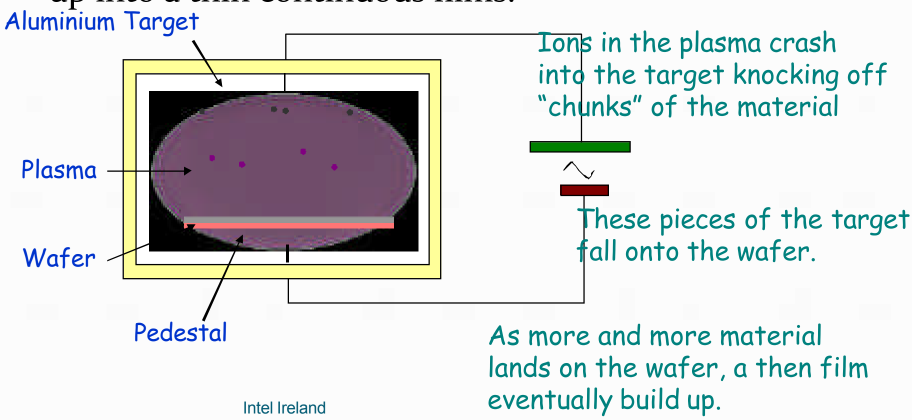
Physical Vapour Deposition

- This method of thin film deposition refers to several different deposition techniques.

1. Evaporation systems
    - Thermal evaporation
    - Electron beam evaporation
2. Sputtering systems
    - DC
    - Pulsed
    - RF

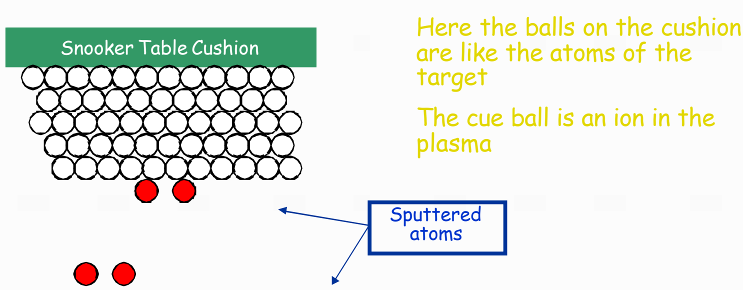
PVD - Sputtering

- Sputtering is a process whereby atoms are knocked off a target in a plasma and made to land on the wafer. As more of the target lands on the wafer, the layers build up into a thin continuous films.



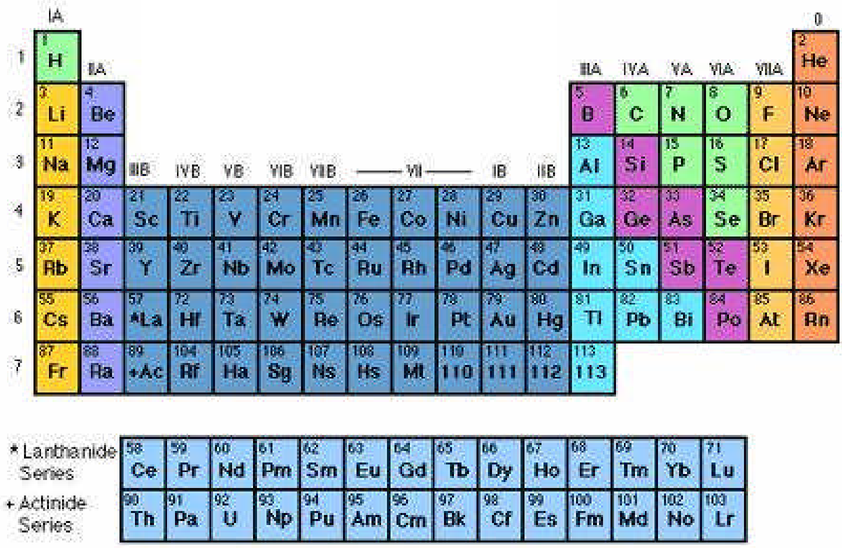
Sputter process – atomic snooker

- As an example take some snooker balls and line them along the cushion as shown. Then hit them with cue ball at various speeds



- Energy is a very important parameter in this process.
- If the energy is too low the cue ball won't be able to break the target atoms apart and so no atoms will be sputtered
- At higher energy though the cue ball (ion) is able to break the atoms of the target apart, causing many of the atoms to be sputtered from the target

Sputter process – atomic snooker



States of Matter

- Matter can exists in 4 different states :
  - Solid, Liquid, Gas & Plasma
- Using
  - cules
    re
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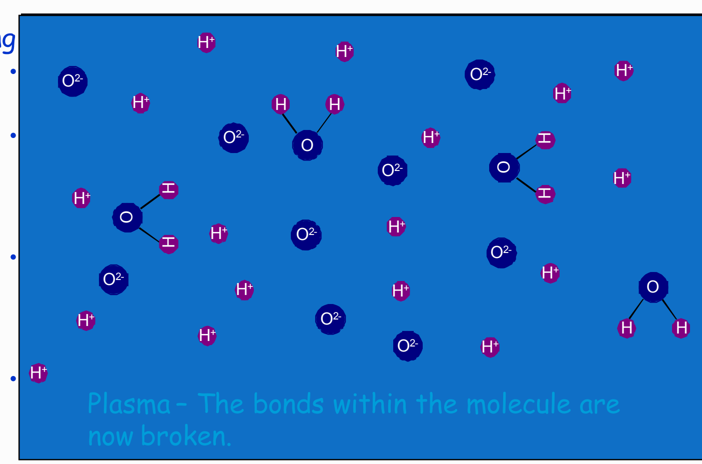
  - ill turn
    nergy
  - single
    nt

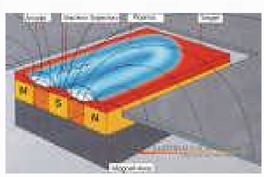
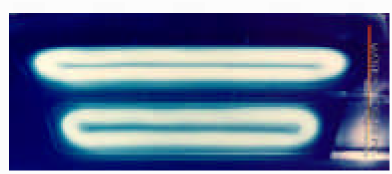


Sputtering in a Plasma

- By applying a large voltage to gas usually under vacuum, a plasma can be created. For sputtering processes this gas tends to be Argon.

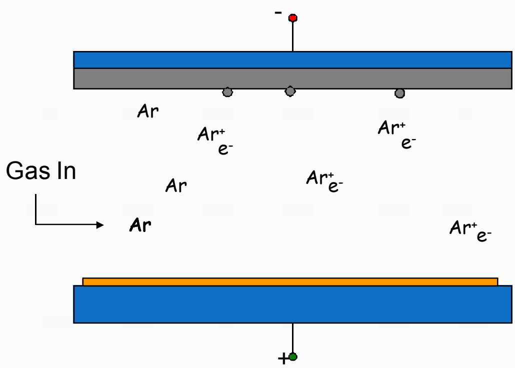
- Why Argon ?
  - It's a large molecule, on a par with the size of the atoms that we tend to want to deposit.
  - Its inert, so it won't react with the target to form an unwanted substance.
  - Its easily pumped out of the system.
  - Its not an overly dangerous gas.

Magnetrão para sputtering

Argon Sputter Process

- Argon gas is fed into the chamber which is under vacuum.
- A large voltage is applied causing some electrons on the argon molecules to break free, leaving positively charged argon ions.



The argon ions will be attracted to the negative potential, so that's where the target material is placed.

The wafer is placed on the positive/neutral electrode.

The argon bombards the target causing chunks of material to fall on the wafer.

The free electrons collide with the argon atoms producing more ions and so sustaining the plasma and the sputtering process

Reactive Sputtering

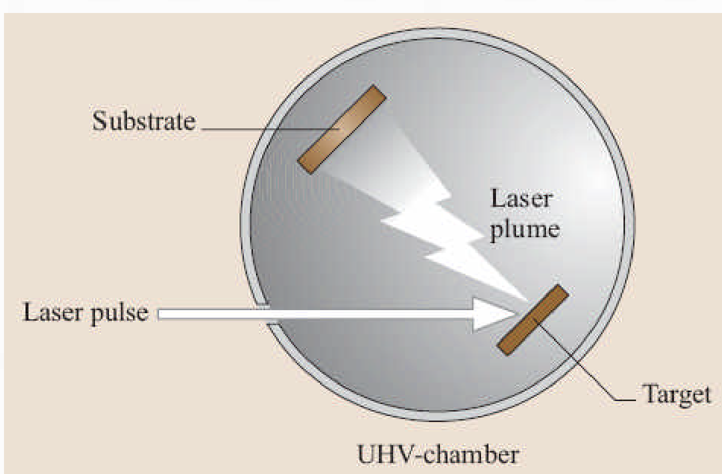
Azoto
Oxigénio

- Although argon is used in all of our sputtering processes, sometimes other gases are introduced that can be incorporated into the film.
- The titanium nitride films that is deposited as part of the metal stack is produced through a reactive sputtering process.
- This means that while argon is used to sputter the titanium material off the target, another gas (nitrogen) is introduce to react with those titanium atoms and produce titanium-nitride.
- While it would be possible to use the nitrogen to perform the sputtering process also, the deposition time required to produce the film would be way to long, hence argon is added to speed up the process.

Comparação

- Térmico:
  - Exige baixa temperatura de evaporação do material
  - O eq. mais simples, barato e eficaz (quando funciona)
  - Os compostos podem decompor ao evaporar
- E-beam
  - Permite maiores temperaturas de evaporação que o térmico.
  - Eq. mais complexo e mais caro.
  - Os compostos podem decompor ao evaporar
- Sputtering
  - Qualquer material (....)
  - Eq. simples
  - Alvos caros (muito material)
  - Compostos podem ser depositados (mas pode alterar composição)

PLD – Pulsed Laser Deposition



CVD
Chemical Vapour Deposition

Chemical Vapour Deposition

- This is a process where gaseous chemicals are introduced to a system, have a reaction on the surface of the wafer which results in a thin film being deposited.
- All other by-products of the reactions are gaseous and so are pumped away and out of the system.
- Plasmas can be used to help generate the reactive species.

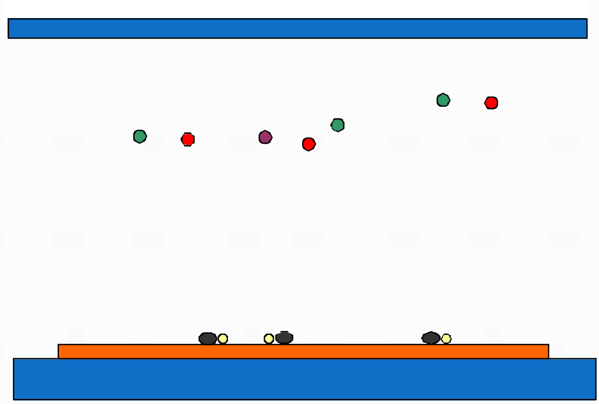
- CVD is used for a large number of deposition processes in the semiconductor industry:
  1. Epitaxial film – top layer of a silicon wafer where the transistors are formed.
  2. Polysilicon – Connection to the gate oxide
  3. Interlayer Dielectrics – Layers of insulating material between the metal layers
  4. Some metal films – Tungsten plugs and seedlayer TiN layer

CVD Process Overview

- Step 1: Gases are introduced into the system which may be at atmospheric or low pressure.
- Step 2: The precursors diffuse through the system to the stagnant gas flow above the wafer surface where they are adsorbed.
- Step 3: These precursors migrate on the surface so that chemical reactions can begin and produce solid by-products.
- Step 4: These solid by-products form nuclei which grown into islands that eventually merge together so that a continuous film is produced.
- Step 5: Other gaseous by-products desorb from the surface and are pumped away, out of the system

The CVD Process

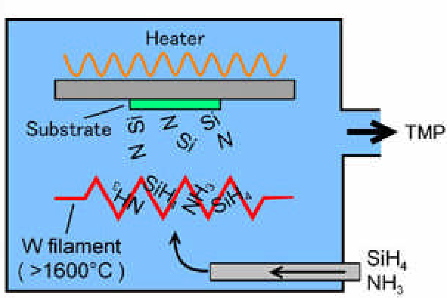
[illegible]
adsorbed.

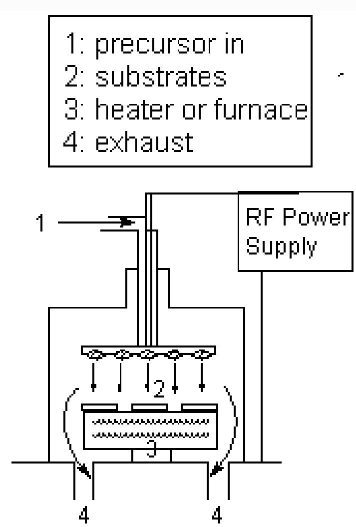


CVD @Physics, UMinho

Intel Ireland

Hot Wire (cat) / RF CVD



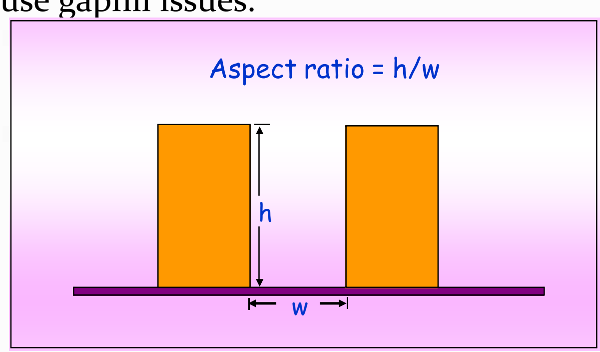


Films and their Precursors

Films	Precursors
Polysilicon	SiH_4 (Silane)
Oxynitride	$SiH_4, N_2), NH_3, N_2$
Silicon Nitride	$C_8H_{22}N_2Si$ (BTBAS), NH_3
Tungsten	SiH_4, H_2, WF_6
Ti-Nitride	$Ti[N(CH_3)_2]_4$ (TDMAT)

Step Profile and Coverage

- Step coverage is the most important specification for a CVD process.
- It is determined by the arriving angle and the precursor surface mobility.
- In a situation where aspect ratio is very tight this could cause gapfill issues.

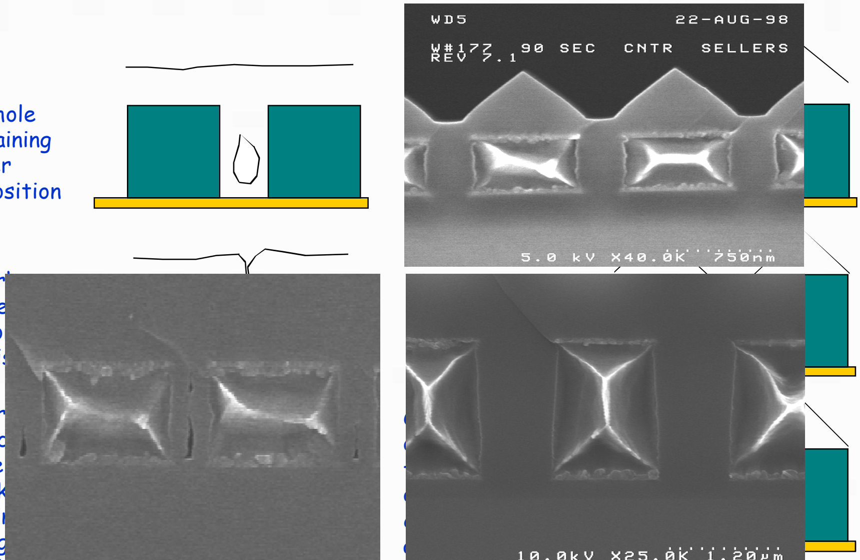


CVD dep in a standard process — CVD dep in a HDP system

Keyhole remaining after deposition

Over close befo gap i

Over the c deve quick maki the g difficult



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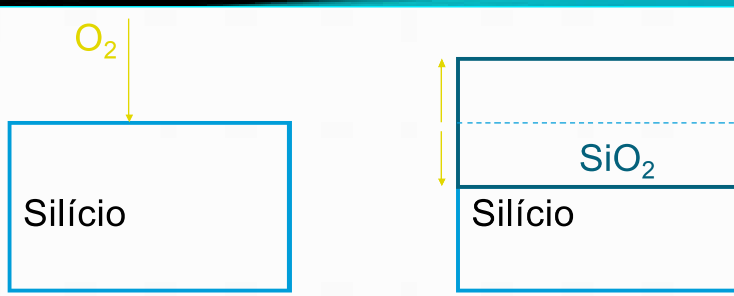
Aspectos da deposição - Compatibilidade

- Compatibilidade térmica
  - A oxidação térmica e os filmes LPCVD são mutuamente compatíveis
  - A oxidação térmica e o LPCVD não são compatíveis com polímeros (derretem/ardem) e com a maioria dos metais (formação eutéctica, difusão, contaminação do forno)
- Compatibilidade topográfica
  - Não se pode fazer spin-coat sobre degraus elevados
  - Deposição sobre rasgos profundos deixa buracos

Aspectos da deposição - Conformabilidade

- Um coating (cobertura) *conformal* cobre todas as superfícies com uma película uniforme
- Um coating planarizador tende a reduzir o degrau vertical da secção transversal
- Um coating não-*conformal* deposita mais nas superfícies do topo do que nas superfícies da base e/ou laterais

Oxidação térmica



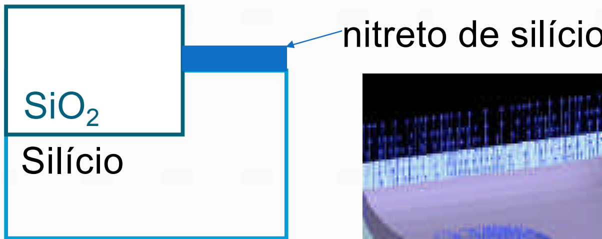
O silício é consumido à medida que o dióxido de silício cresce.

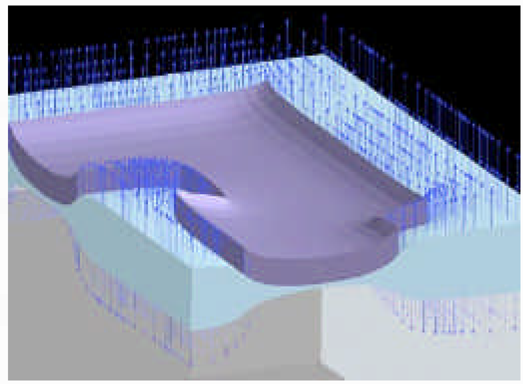
O crescimento ocorre em oxigénio e/ou vapor a 800-1200 ºC

Filmes com ~2um é o máximo valor prático possível

Oxidação térmica

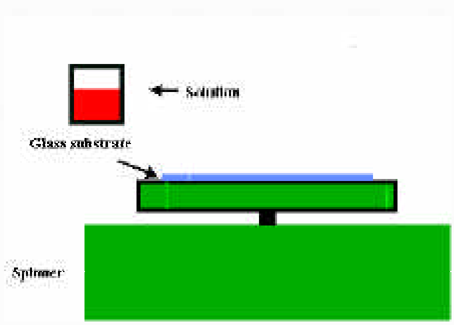
- A oxidação pode ser mascarada com nitreto de silício, que evita a difusão do O_2

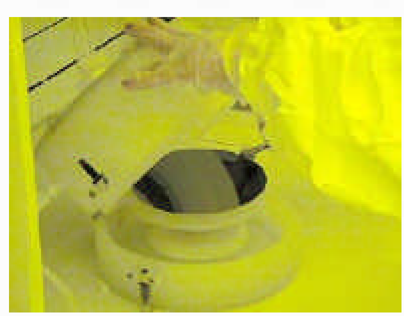




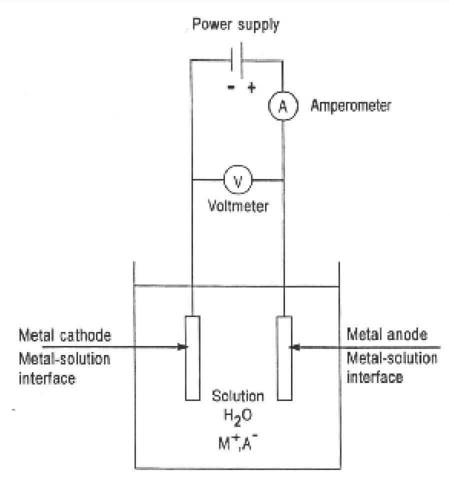
Spin Coating

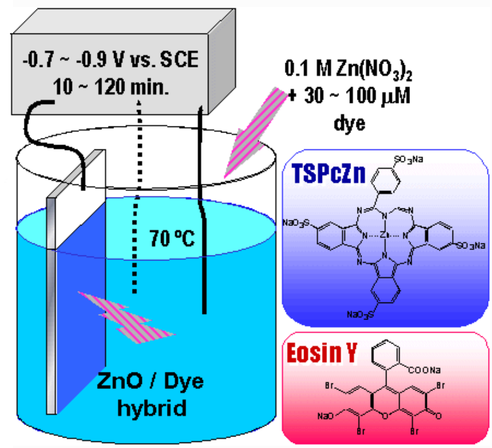
- Um liquido viscoso é colocado no centro do wafer
- O wafer roda entre 1000-5000 RPM, 30 s
- Baked (levar ao forno) em pratos quentes 80-500 ºC, 10-1000s
- Aplicação de corrosivos e solventes, secar



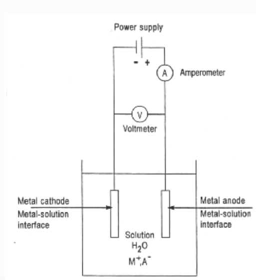


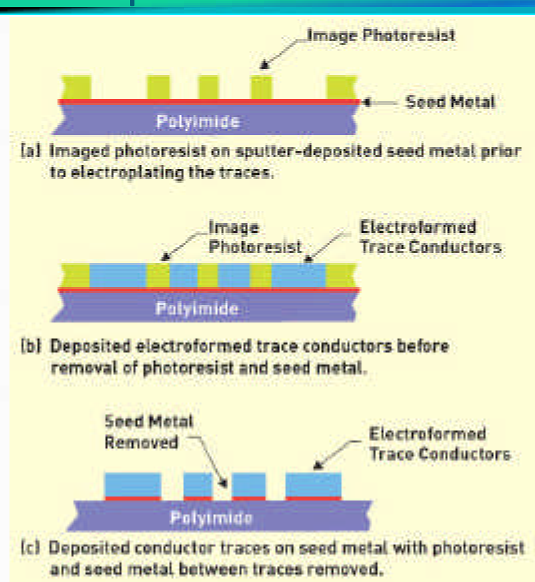
Deposição electroquímica





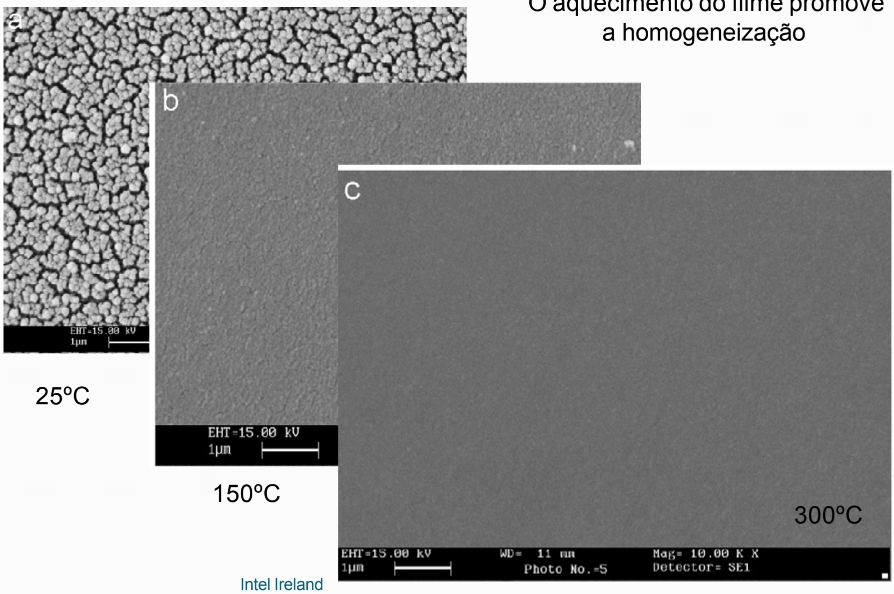
Deposição electroquímica





Annealing

O aquecimento do filme promove a homogeneização



25ºC

150ºC

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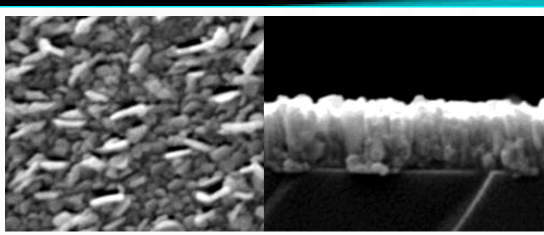
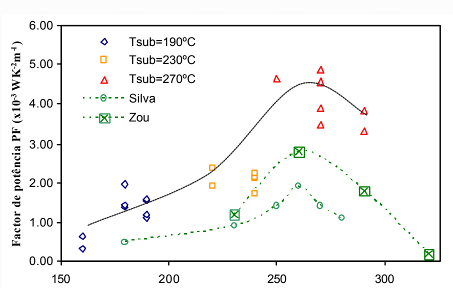
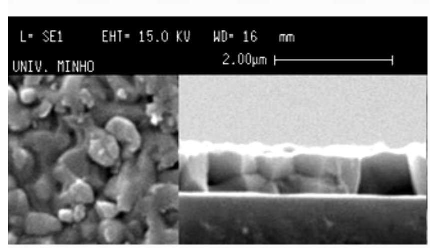
Annealing



150ºC

O aquecimento do filme promove a aglomeração de átomos, formando cristais de dimensão maior, alterando as propriedades dos materiais





300ºC

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O Silício

- Si, existente em grande quantidade na Terra.
- Processo de Czochralski (crescimento de cristais de Si) para formação de wafers de silício.
- Facilidade de obtenção do SiO_2 (um bom isolante) a temperaturas médias na presença de oxigénio.

Estrutura

- Amorfo – CVD ou outros
- Nanocristalino - CVD
- Policristalino - CVD
- Monocristalino - Czochralski

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Processo de Czochralski – Si monocristalino