

IB Paper 8 Electrical Engineering

Lecture 9 Fabricating Devices: Crystalline Silicon & Alloys

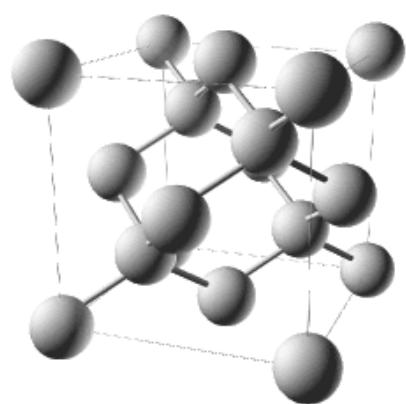
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Crystalline Silicon Introduction

- Silicon has dominated the last 50 years of semiconductor device technology
 - In many senses this is surprising as silicon is far from being the best semiconducting material
 - It has a relatively low carrier mobility (the speed with which electrons and holes moves under the application of an electric field) so devices switch relatively slowly
 - It is an indirect gap semiconductor, and so has difficulty in absorbing and emitting photons making it unsuitable for most optoelectronic applications
 - Many compound semiconductors, such as GaAs, have far better electrical characteristics, including a direct gap, and yet the fall of silicon has not happened, with compound semiconductors only gaining a real foothold in high speed and optoelectronic applications
 - Silicon has maintained its dominance because
 1. it is cheap (as cheap as sand!)
 2. it forms good quality insulators (SiO_2 , Si_3N_4)
 3. ***there is sixty years of experience in how to process silicon and fabricate devices!***

Crystalline Silicon Structure and Properties

Group → 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H														2 He			
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 57 La	* 72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	* 89 Ac	* 104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				* 58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				* 90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	



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- Silicon is a Group IV element

- It has four valence electrons, but would like to have eight, and so it naturally forms four covalent bonds to its nearest neighbours by hybridising its two 3s electrons and two 3p electrons to form four sp^3 states
- All four bonds are ‘equal’ and there are no ‘lone pair’ electrons, and so crystalline silicon (c-Si) has a tetrahedral structure
- The covalent Si—Si bond is very strong indeed, and this results in a material which has very interesting properties
 - High melting point ($>1400^\circ \text{C}$)
 - Resistant to most acids
 - Harder and stronger than steel
 - Less dense than aluminium
 - Elastic modulus similar to steel

Property	Value
Atomic weight	28.1
Atomic density	$5 \times 10^{28} \text{ m}^{-3}$
Band gap at 300 K	1.12 eV
Chemical resistance	High (resistant to most acids and some bases)
Density	2400 kg m ⁻³
Dielectric constant	11.8
Dielectric strength	$3 \times 10^8 \text{ V m}^{-1}$
Electron mobility	0.150 m ² V ⁻¹ s ⁻¹
Hole mobility	0.040 m ² V ⁻¹ s ⁻¹
Intrinsic carrier concentration	$1.45 \times 10^{16} \text{ m}^{-3}$
Intrinsic resistivity	$2.3 \times 10^3 \text{ W m}$
Knoop hardness	850 kg mm ⁻²
Lattice constant	0.543 nm
Linear coefficient of thermal expansion at 300 K	$2.6 \times 10^{-6} \text{ K}^{-1}$
Melting point	1688 K
Minority carrier lifetime	$2.5 \times 10^{-3} \text{ s}$
Poisson ratio	0.22
Relative permittivity	11.8
Specific heat at 300 K	713 J kg ⁻¹ K ⁻¹
Thermal conductivity at 300 K	156 W m ⁻¹ K ⁻¹
Tempertaure coefficient of the Young Modulus at 300 K	$90 \times 10^{-6} \text{ K}^{-1}$
Thermal diffusivity	$0.9 \times 10^{-4} \text{ m}^2 \text{ s}^{-2}$
Yield strength	7 GPa
Young modulus	190 GPa

Crystalline Silicon Growth

- Whilst the high melting point of c-Si makes this material very attractive for high temperature applications, it makes growth of silicon crystals more complicated
- The most common method for producing crystalline silicon is the ***Czochralski process***
 - Quartzite, a pure form of SiO_2 , is placed in a furnace with a carbon-releasing reducing agent, such as coke or coal, so produce ***metallurgical grade silicon*** with about 2% impurities by the reaction



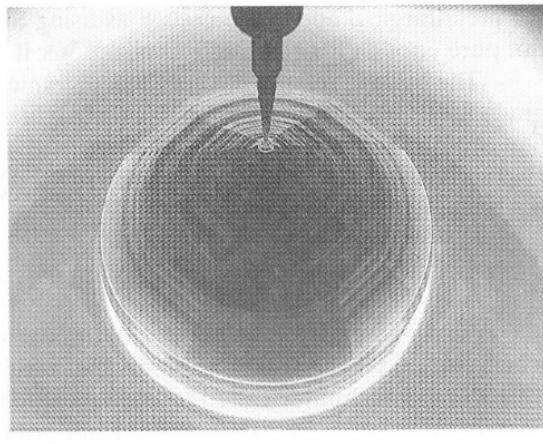
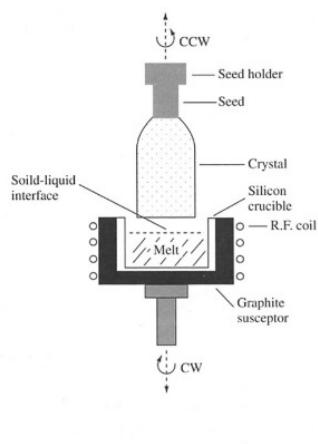
- The silicon is reacted with HCl to form liquid trichlorosilane



- The SiHCl_3 can be fractionally distilled to remove impurities before being reduced in a hydrogen atmosphere to produce polycrystalline ***electronic grade silicon***,



Figure 1–10
Pulling of a Si crystal from the melt (Czochralski method): (a) schematic diagram of the crystal growth process; (b) an 8-in. diameter, $\langle 100 \rangle$ oriented Si crystal being pulled from the melt. (Photograph courtesy of MEMC Electronics Int'l.)



(b)

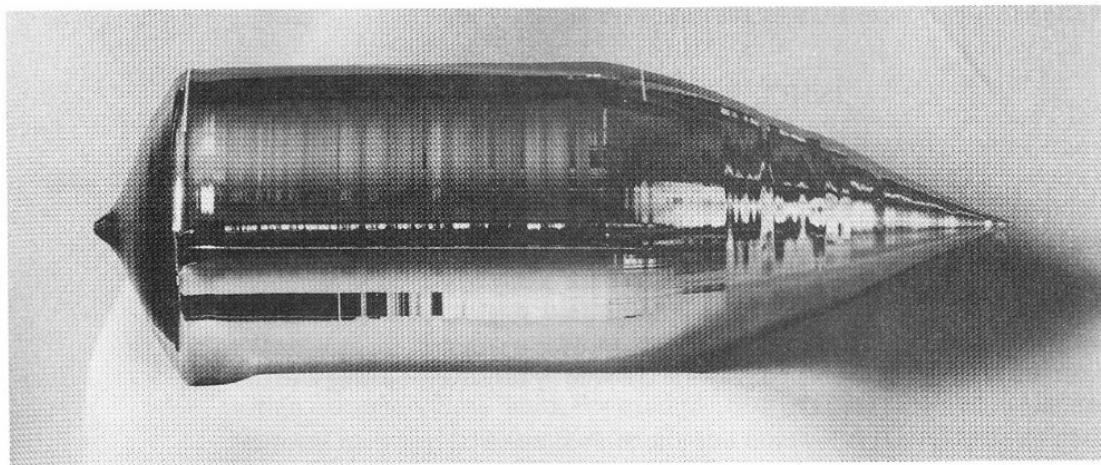
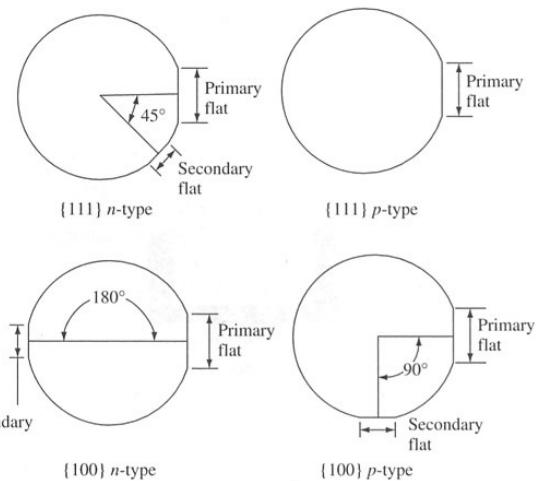
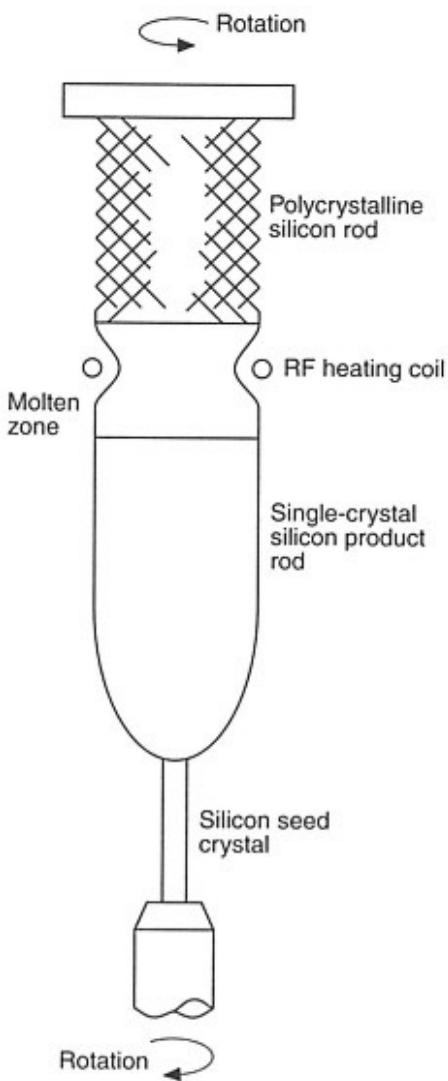


Figure 1–11

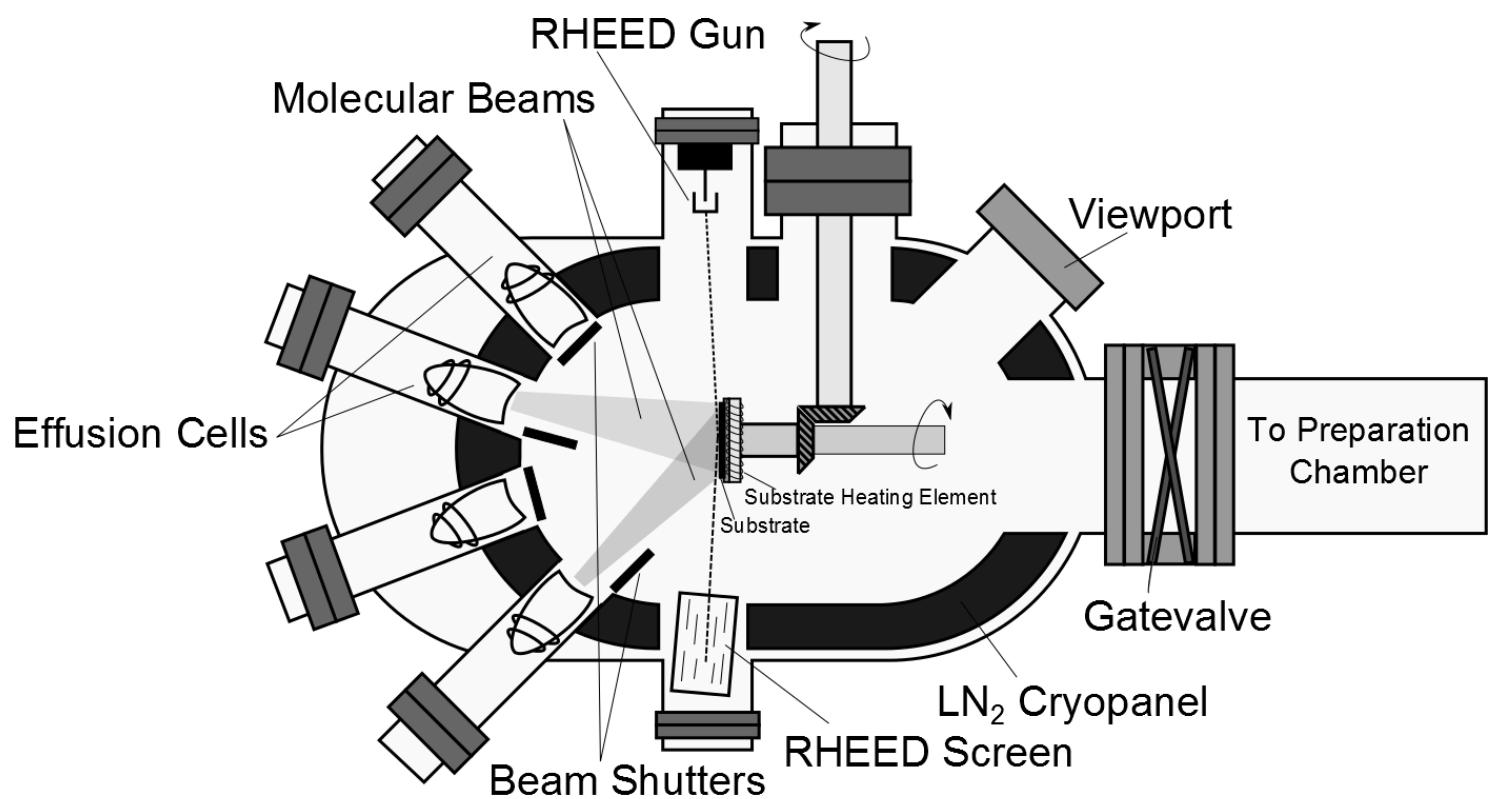
Silicon crystal grown by the Czochralski method. This large single-crystal ingot provides 300 mm (12-in.) diameter wafers when sliced using a saw. The ingot is about 1.5 m long (excluding the tapered regions), and weighs about 275 kg. (Photograph courtesy of MEMC Electronics Int'l.)

- The polycrystalline silicon is then melted in a fused silica crucible
 - A seed crystal of the correct orientation is partially dipped into the melt
 - It is then withdrawn at a rate of a few millimetres per minute, whilst being rotated, causing the silicon to solidify around the seed, thereby producing a solid silicon ingot
 - The disadvantage of this technique is its susceptibility to oxygen contamination, particularly from the crucible

- To produce a higher purity material, the ***float zone growth*** technique may be used
 - In this case, the polycrystalline silicon is counter rotated over a crystalline silicon seed
 - The polycrystalline silicon is locally melted by an rf heating element, and then crystallises on the seed
 - The silicon melt is not in contact with any crucible, and so the impurity concentration is reduced
- Wafer production continues by grinding the ingot to the correct diameter on a lathe
 - The orientation of the crystal is determined by x-ray diffraction, and flat edges ground onto the ingot which can later be used to determine the doping and orientation of the wafer
 - The ingot is then sliced and lapped using Al_2O_3 powder in glycerin, and the edges rounded to reduce cracking



- Epitaxial growth allows layers of c-Si to be grown on top of a wafer, which is used as the seed, at temperatures below the melting point of Si
 - In **vapour phase epitaxy** (VPE) the silicon wafer is heated to ~ 1200 °C in an atmosphere of SiCl_4 , SiHCl_3 , SiH_2Cl_2 or SiH_4 , all of which are gases, leading to silicon deposition on the wafer
 - **Molecular beam epitaxy** (MBE) uses a stream of Si atoms from a heated cell that travel by line of sight to a heated Si substrate ($400 - 800$ °C)
 - This provides excellent control of the deposition, but the rate of growth is very slow (~ 0.25 nm s $^{-1}$)
 - Usually combined with in-situ characterisation like reflection high energy electron diffraction (RHEED)

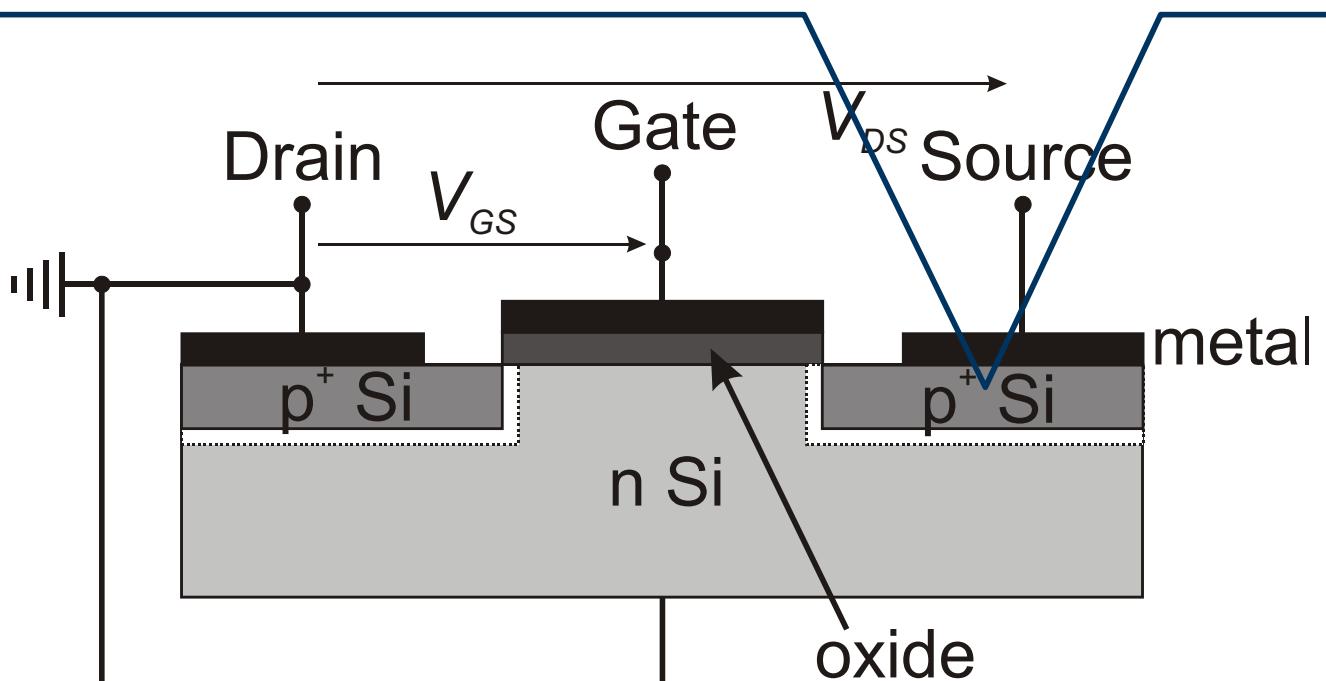


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Doping

- There are several ways in which impurities may be introduced into silicon to achieve doping
 - A whole wafer may be doped by introducing the impurity to the Czochralski melt
 - In the case of **epitaxial growth**, this may be done by introducing the impurity atom into the feed
 - This allows a very precise control of dopant concentration and freedom to vary the doping density through the depth of the silicon
- The above methods may only be used during growth of the silicon layer, but frequently we wish to introduce an impurity to a thin layer that has already been formed

- For example, in a MOSFET we need to create a pn junction at the source and drain with the channel semiconductor



- We may overcome this problem by allowing the **diffusion** of dopants into bulk silicon
 - The impurity is introduced in the gas phase with an inert gas carrier into a furnace containing the silicon wafer at a temperature between 800 and 1200 °C
 - Diffusion is controlled by the Fick Law,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (9.1)$$

- where C is the impurity concentration
- D is the diffusion coefficient, which is temperature dependent, as the process is thermally activated and

$$D = D_0 \exp\left(\frac{-E_a}{kT}\right) \quad (9.2)$$

- where E_a is the activation energy of diffusion, k is the Boltzmann constant and D_0 is the diffusion coefficient
- For the case of an infinitely deep medium where $C \rightarrow 0$ as $x \rightarrow \infty$ and there is a constant concentration of impurities at the surface as a function of time, C_s , then the solution to equation 9.1 is

$$C(x, t) = C_s \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (9.3)$$

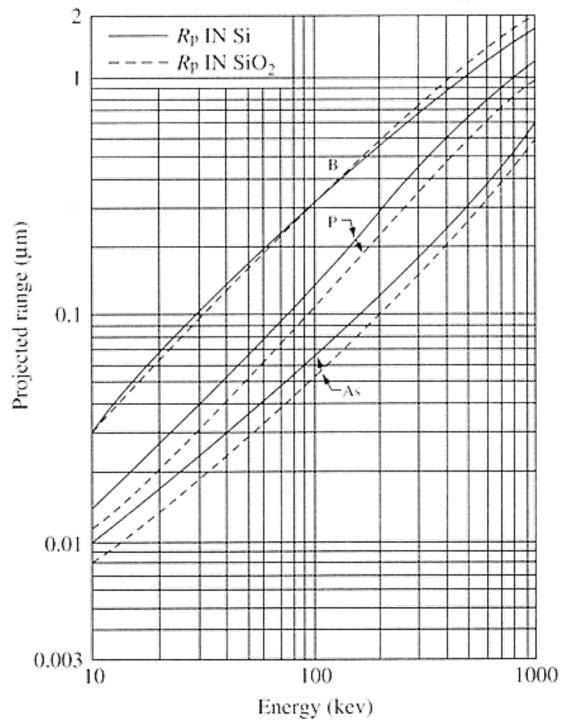
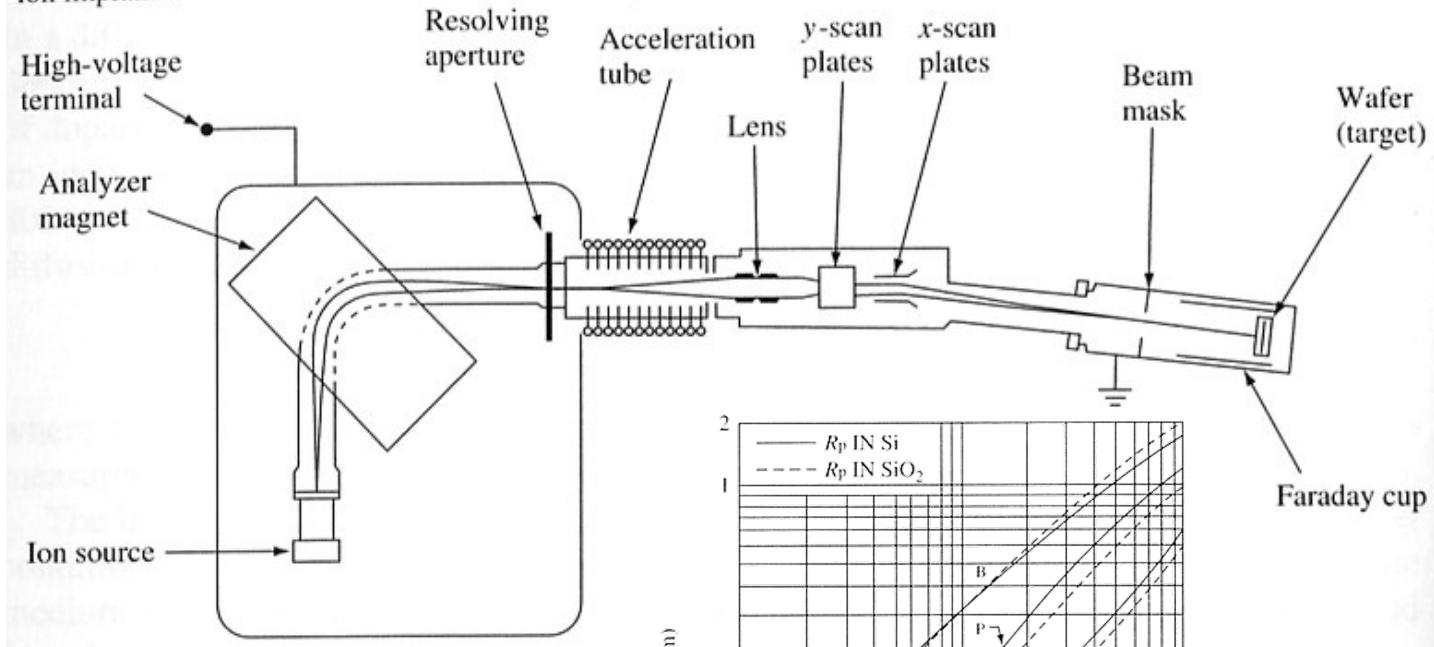
- This relationship holds for most impurity concentrations (**intrinsic diffusion**), but at very high concentrations, the system becomes non-linear (**extrinsic diffusion**), and look-up tables must be used to predict the diffusion process

- Dopant diffusion may be restricted to certain areas through the use of a silicon dioxide mask layer, as dopants diffuse less readily through this material, however, some lateral diffusion will take place under edges of the oxide
- An alternative to dopant diffusion is ***ion implantation***
 - In this technology, ionised impurity atoms filtered to a specific mass to charge ratio before being accelerated by an electric field to energies between 20 and 200 keV
 - The ions are then focussed by an electrostatic lens before being scanned over the area to be doped
 - The ions hit the substrate and are implanted into the bulk
 - Post implantation, the samples undergo a rapid thermal annealing to ‘activate’ the dopants by removing defects and allow bonding in the doping configuration
 - The dopants are implanted with a Gaussian distribution,

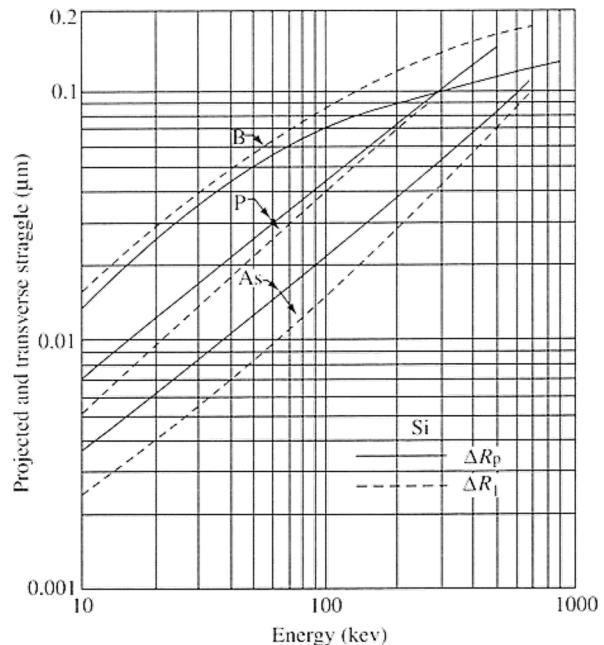
$$N_i(x) = \frac{Q_i}{\sqrt{2\pi}\Delta R_p} \exp \left[\frac{-1}{2} \left(\frac{x - R_p}{\Delta R_p} \right)^2 \right] \quad (9.4)$$

- where N_i is the number of implanted ions, Q_i is the total implanted dose (in ions m^{-2}), R_p is the projected range and ΔR_p is the fluctuation in the projected range
- As with diffusion, there is lateral motion of ions also underneath any implantation masking layer

Schematic of a medium-current ion implanter



(a)

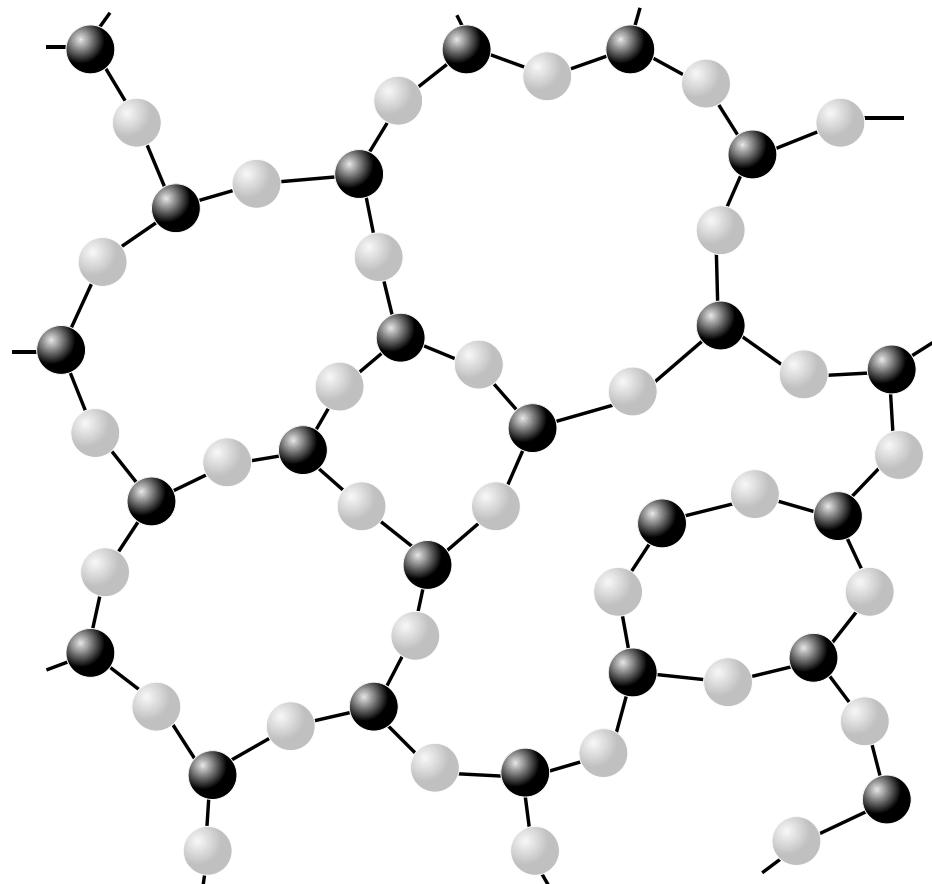


(b)

Figure 2.19 Projected range (a) and straggle; (b) of boron, phosphorus and arsenic ions implanted in silicon at different ion energies (Sze 1985)

Silicon Dioxide

- Silicon oxide is another frequently used electronic material as it is an excellent dielectric (insulator)
 - Also, the fact that this material is readily etched by hydrofluoric acid (HF) makes it an excellent sacrificial layer for releasing structures fabricated from c-Si, which is almost impervious to HF
- It forms as an amorphous material ($a\text{-SiO}_2$)
 - This means that although there is short-range order on an atomic scale, there is no long-range order
 - The structure is also quite ‘open’ and so it is easy for small elements (e.g. Na) to diffuse through the network



Property	Value
Band gap at 300 K	9 eV
Density	2200 kg m ⁻³
Dielectric constant	3.9
Dielectric strength	10 ⁹ V m ⁻¹
Etch rate in buffered HF	100 nm min ⁻¹
Melting point	~1600° C
Poisson ratio	0.20
Resistivity	10 ¹² - 10 ¹⁴ W m
Refractive index	1.46
Residual Stress	~350 MPa (Compressive)
Thermal conductivity	1.4 W m ⁻¹ K ⁻¹
Thermal expansion coefficient	0.35×10 ⁻⁶ K ⁻¹ (Thermal) 2.3×10 ⁻⁶ K ⁻¹ (PECVD)
Young modulus	70 GPa

- Thermal Oxidation
- For the special case of silicon oxide formation on crystalline silicon, thermal oxidation may be used to produce an oxide of exceptionally high quality
 - In dry oxidation, the silicon wafer is heated in a furnace at atmospheric pressure in an atmosphere of nitrogen and oxygen at a temperature between 700 and 1250 °C
 - The high temperature aids the diffusion of oxygen into the silicon bulk (see Transparency 10 on diffusion) where a reaction takes place of the form



- In the case of wet oxidation, the O₂/N₂ gas mixture is bubbled through a simmering water bath to add steam to the mixture
- This changes the reaction to



- and a faster oxidation rate results
- The silicon substrate is consumed in this reaction, and 460 nm of silicon is required to produce a 1000 nm thick silicon dioxide layer

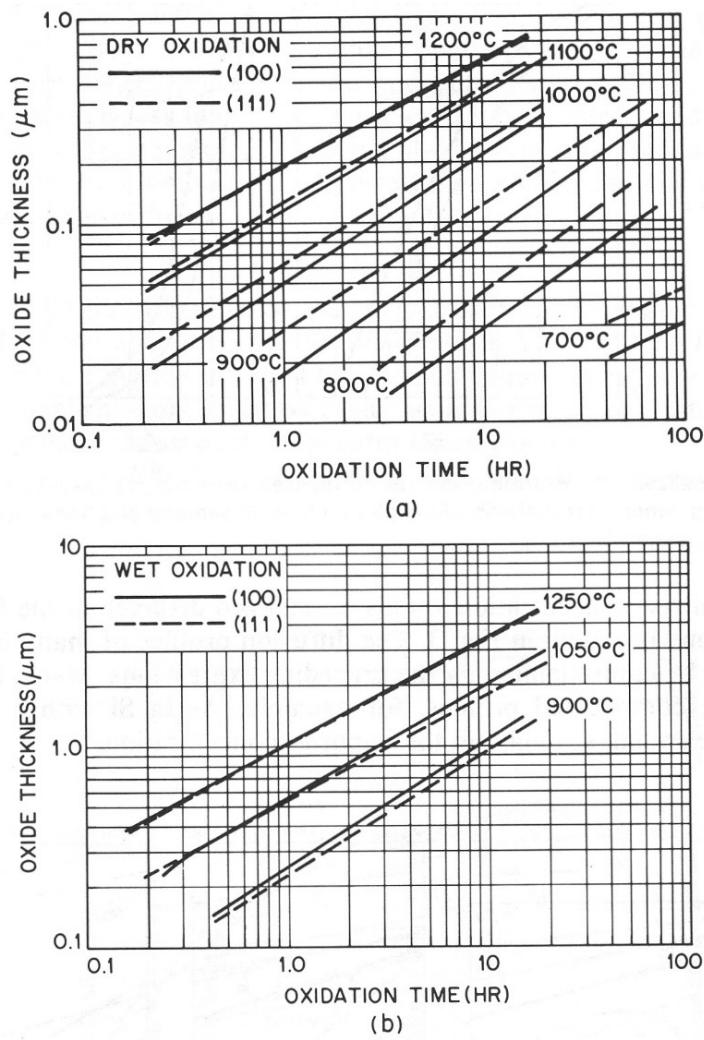
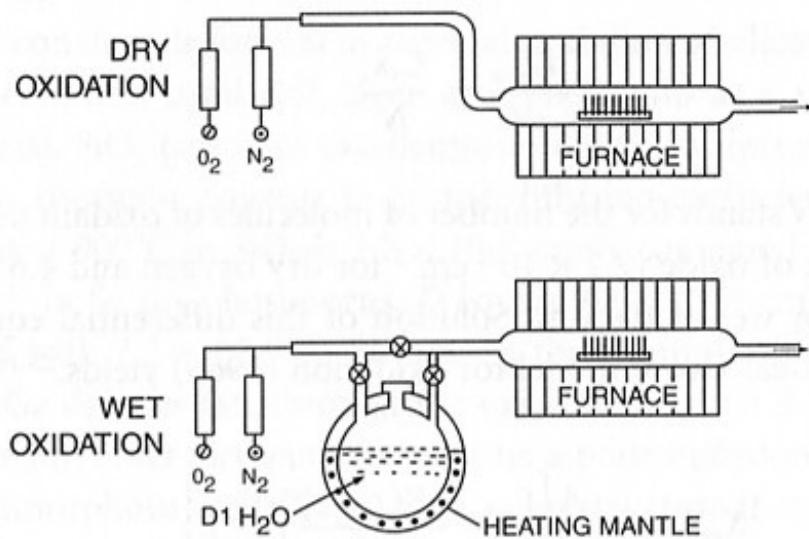
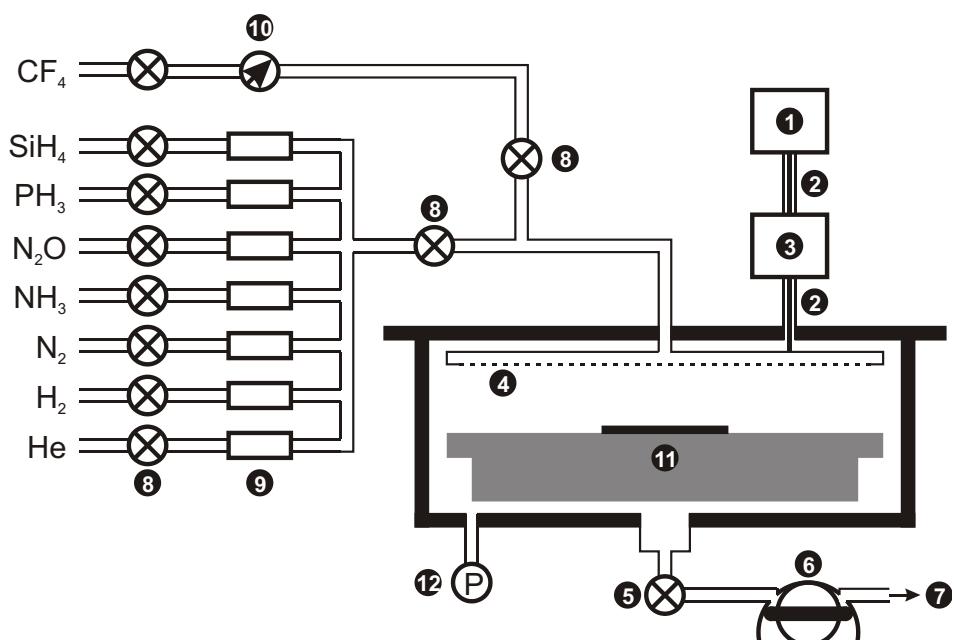


Fig. 2 Experimental results of silicon dioxide thickness as a function of the reaction time and temperature for two substrate orientations. (a) Dry oxygen growth. (b) Steam growth. (After Meindl et al., Ref. 16.)



• rf-PECVD

- Silicon dioxide can also be grown on a wafer
 - Thin film coatings of materials are most frequently achieved by condensing a gas phase precursor onto a substrate, and silicon dioxide films are no exception
 - One common technique for achieving this is ***radio frequency (rf) plasma enhanced chemical vapour deposition (PECVD)***
 - Silane (SiH_4) is the silicon equivalent of methane
 - It is a gas at room temperature, and can be readily dissociated into reactive species which will react with N_2O to form silicon dioxide on a surface



- | | |
|--------------------|---------------------------------|
| ① rf generator | ⑦ Exhaust |
| ② Coaxial cable | ⑧ Valves |
| ③ Matching network | ⑨ Mass flow controllers |
| ④ Gas shower head | ⑩ Rotameter |
| ⑤ Baffle valve | ⑪ Heated sample stage (earthed) |
| ⑥ Vacuum pumps | ⑫ Pressure gauge |

- The SiH₄ and N₂O gas flows are regulated by a ***mass flow controller (mfc)*** before passing into the top of vacuum chamber through a large, flat, stainless steel plate
 - The plate, known as the showerhead, is covered in small holes to ensure a uniform flow of gas over the whole area
 - The sample sits on a heated (~200 – 300 °C) plate a few cm below the showerhead and is grounded
 - A valve on the gas outflow pipe to the vacuum pumps allows the pressure of the gas in the chamber to be controlled
 - Normal deposition pressure are in the range of 1 to 10 Pa
 - Radio frequency radiation (normally at 13.56 MHz) is applied to the showerhead
 - The oscillating electric field causes the unstable silane molecule to dissociate, producing a mixture of ions, electrons and radicals – a ***plasma***
 - This induces the deposition of silicon dioxide
 - The pyrophoric nature of SiH₄ precludes the use of O₂ for oxide deposition by rf-PECVD, however te high reactivity of O relative to N means that nitrogen from the N₂O is not incorporated

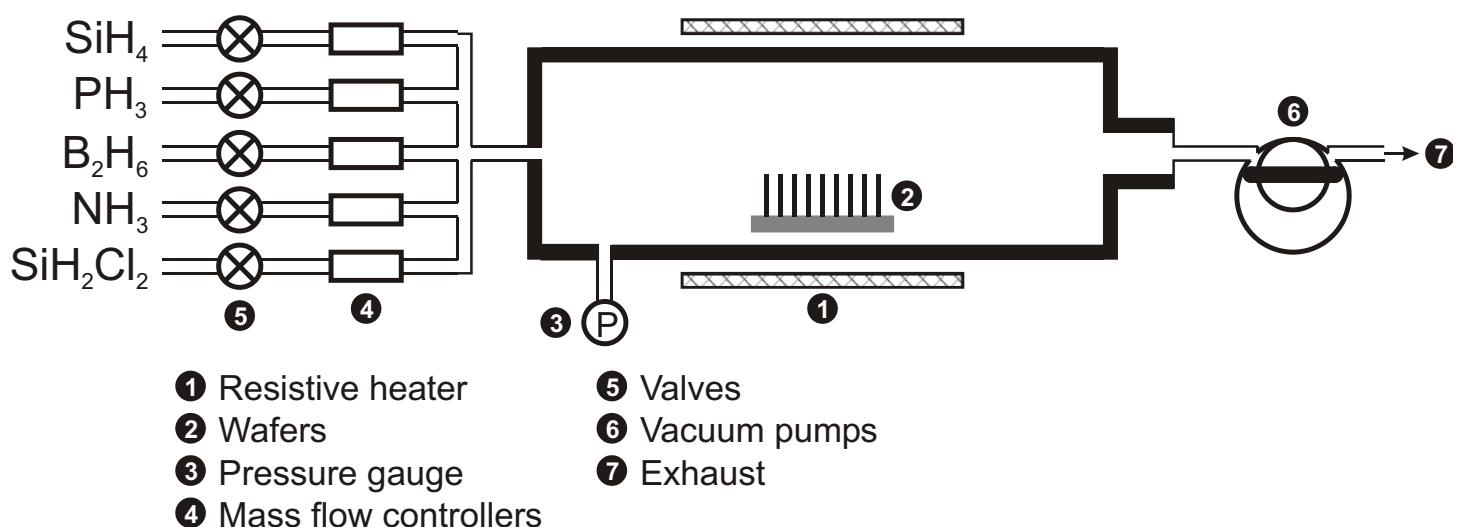
Silicon Nitride

- Silicon nitride (a-SiN) is another insulating amorphous material
 - In its stoichiometric form it has three Si atoms to every four N atoms
 - The strong nature of the Si—N bond means that this material is extremely hard, and is therefore ideally suited for wear-resistant coatings (for example, in MEMS with moving parts)
 - In addition, the structure of the material is very dense, and so it can form an excellent diffusion barrier, and even blocks the migration of sodium ions
 - a-SiN can be produced by rf-PECVD using a similar recipe to that for a-Si:H, but with the addition of ammonia (NH_3) as a source of nitrogen (as this is also an unstable molecule) and sometimes with N_2 as well, although this acts mainly as a dilutant to control the growth rate
 - This results in a hydrogen containing material

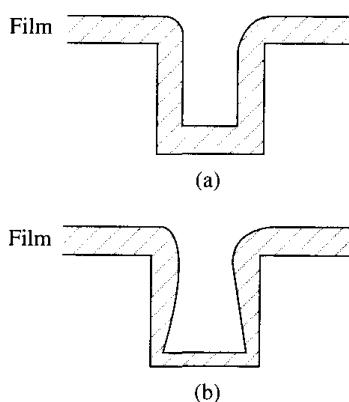
Property	Value
Band gap at 300 K	5.3 eV
Density	3440 kg m ⁻³
Dielectric constant	7.5
Dielectric strength	10 ⁹ V m ⁻¹
Etch rate in concentrated HF	20 nm min ⁻¹
Etch rate in buffered HF	1 nm min ⁻¹
Hydrogen content	4 – 8 at. % (LPCVD) 20 – 25 at. % (PECVD)
Melting point	3440° C
Resistivity	10 ¹² - 10 ¹⁴ W m
Refractive index	2.01
Thermal conductivity	19 W m ⁻¹ K ⁻¹
Thermal expansion coefficient	1.6×10 ⁻⁶ K ⁻¹
Yield strength	6.9 Gpa
Young modulus	380 GPa

• LPCVD

- A disadvantage of rf-PECVD a-SiN can be the presence of the H which leads to a material with a high residual stress
 - In addition, coverage of step edges by rf-PECVD tends not to be conformal
 - Therefore, low pressure chemical vapour deposition (LPCVD) tends to be preferred for this material
 - In this case a mixture of SiH_2Cl_2 and NH_3 is fed into a chamber at a pressure of $\sim 70 \text{ Pa}$
 - In this case, the substrates, which are stacked vertically, are heated at $\sim 800^\circ \text{ C}$, which is sufficient to thermally induce a chemical reaction on the surface of the substrate forming a-SiN by



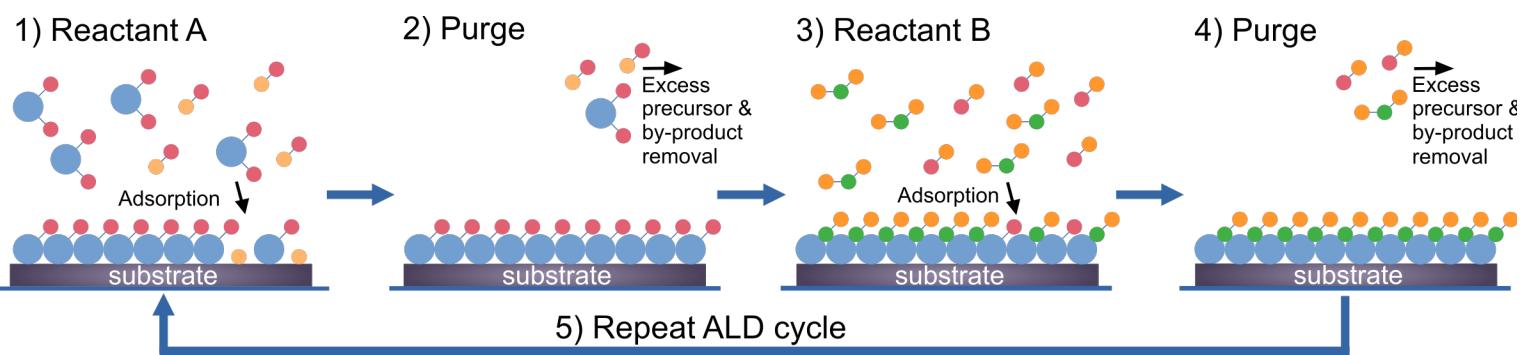
- Stoichiometric LPCVD a-SiN (with a high resistivity) produced with a $\text{SiH}_2\text{Cl}_2:\text{NH}_3$ flow ratio of 1:10 suffers a high tensile stress
 - However, material which is stress free or even compressive can be produced by increasing the silicon content of the nitride, although this compromises the high resistivity
 - A $\text{SiH}_2\text{Cl}_2:\text{NH}_3$ flow ratio of 1:6 is found to produce stress-free material
- LPCVD tends to yield conformal coating of step edges without pinholes
 - However, the high deposition temperature severely restricts the use of this technique, as many materials are damaged (or melt) at such a high temperature
 - Therefore, although LPCVD is preferred over rf-PECVD, use of the latter is frequently a necessity



(a) Conformal (i.e. ideal); (b) nonconformal

• Atomic Layer Deposition

- ALD has been emerging in recent years as a new deposition technique which allows very precise control of stoichiometry of thin film materials where conformality is important
- It is a cyclic deposition process where reactants are introduced and purged in order



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- In thermal ALD, heat is used to decompose the reactant gases which then chemically bond to the surface
 - Once a layer has grown, the process self-terminates
 - A second reactant (e.g. an oxidant such as water) is then introduced
 - A highly stoichiometric and conformal layer results
- In plasma-enhanced ALD, a plasma assists with decomposition of the reactants
 - This gives a higher growth rate by reduces conformality