

irradiation from a high energy lamp, several absorption transitions occur, although only one is shown. The excited states all decay non-radiatively to the ${}^4F_{3/2}$ level from which laser action occurs to the ${}^4I_{11/2}$ level with a wavelength of 10,600 Å for Nd-glass and 10640 Å for Nd³⁺-YAG. The ${}^4F_{3/2}$ state is long lived, $\sim 10^{-4}$ sec, but depends somewhat on the Nd³⁺ concentration. This again allows a large population inversion to build up and allows Nd³⁺ to be used in high power lasers.

Chapter 9

Synthesis Methods

9.1 General observations

Many methods can be used to synthesize solids. Some solids can be prepared by a variety of routes but others, especially those that are not thermodynamically stable, may be much more difficult to prepare and may require special methods. Solids can also be prepared in various forms, as fibres, films, foams, ceramics, powders, nanoparticles and single crystals; for several of these, optimization of the synthesis/fabrication procedure is crucially important.

Here we review some of the main methods used to synthesize solids, using as examples materials that have been discussed earlier in this book. A few new materials are also introduced, such as amorphous silicon and diamond films since these are important technologically and can be discussed easily within the framework of synthesis methods.

9.2 Solid state reaction or shake 'n bake methods

The oldest, simplest and still most widely used method is to mix together powdered reactants, perhaps press them into pellets or some other shape and then heat in a furnace for prolonged periods. The method is not very sophisticated, hence the use of alternative names such as shake 'n bake or, beat 'n heat! It is nevertheless very effective and, for instance, almost all the new high T_c superconductors were first prepared by solid state reaction methods. The method is intrinsically slow because, although the reactants may be well-mixed at the level of individual particles (e.g. on a scale of 1 μm or 10^{-2} mm), on the atomic level they are very inhomogeneous. An enormous amount of mixing of atoms or ions between particles is therefore required, either by solid state counterdiffusion or by liquid- or gas-phase transport, in order to bring together atoms of the different elements, and in the correct ratio, to form the desired product. Thus from a bird's eye view, perhaps a well-ground mixture of e.g. MgO and Al₂O₃ powders, from which it is desired to form MgAl₂O₄ spinel, may look homogeneous but on an atomic scale the mixture will still be completely segregated into the reactants. Let us briefly consider the steps involved in a solid state reaction, using the schematic example shown in Fig. 9.1.

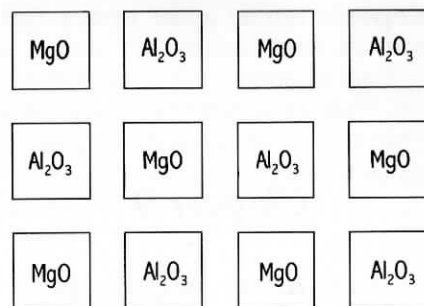


Fig. 9.1 Idealized reaction mixture composed of grains of MgO and Al₂O₃. In practice, their shapes may be irregular and of different size and they would not be arranged in such an orderly fashion

a) Nucleation and growth, epitaxy and topotaxy

At every interface between grains of MgO and Al₂O₃, all the ingredients necessary to form the MgAl₂O₄ product are present. The first stage, therefore, is *nucleation* of small crystals with the spinel stoichiometry and structure. For nuclei to be stable and not to spontaneously disintegrate as soon as they form, they must usually be several tens of angstroms across, i.e. they must be considerably larger than a single unit cell and must therefore contain many tens of atoms. The *critical size* of nuclei represents a balance between the negative free energy of formation of the spinel product, inside the nuclei and the positive surface energy of the nuclei. If the nuclei are too small, the surface area to volume ratio is too large and the nuclei are unstable. Nucleation tends to be a difficult process, therefore, simply because of the large number of ions that must get together, in the correct arrangement, to form a stable nucleus.

Nucleation is greatly facilitated if it is *heterogeneous* and the product nuclei can form on the surface of an existing structure, especially if there is some similarity in the two structures. The MgO/Al₂O₃ reaction to form spinel provides two examples of possible assisted or oriented nucleation, on the surfaces of either MgO or Al₂O₃ grains, Fig. 9.2.

At the MgO/MgAl₂O₄ interface, provided the MgAl₂O₄ nucleus and the underlying MgO are in the same crystallographic orientation, the oxide ion arrangement can continue unchanged since it is *ccp* in both structures, with an ABC stacking sequence (a). In MgO, the Mg²⁺ ions occupy fully the octahedral sites (rock salt structure) whereas in spinel, Mg occupies 1/8 of the tetrahedral sites with Al in 1/2 of the octahedral sites. Formation of a spinel nucleus on top of an MgO structure (or *substrate*) is easy because of the structural similarity of MgO and spinel and the absence of any necessity to create a stand-alone spinel nucleus with large surface area.

At a suitably-oriented Al₂O₃/MgAl₂O₄ interface, the situation is somewhat similar but now, the oxygen stacking sequence changes from *hcp* (AB) in Al₂O₃ to *ccp* in spinel (Al₂O₃ has the corundum structure with *hcp* oxide ions and

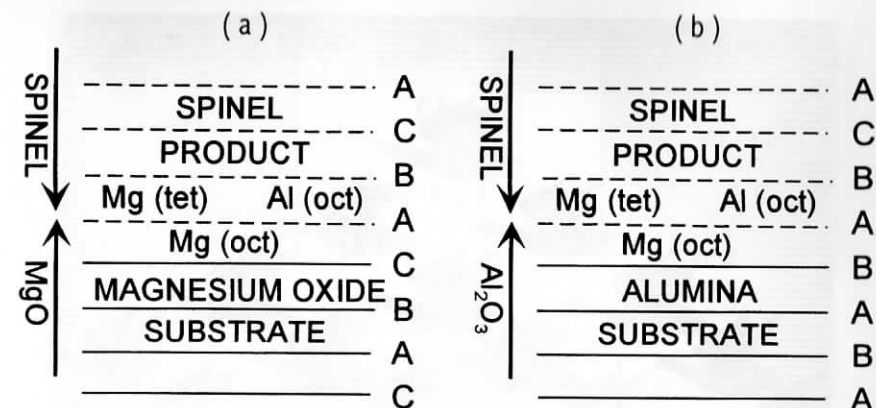


Fig. 9.2 Nucleation of MgAl₂O₄ spinel on (a) MgO and (b) Al₂O₃. Letters A, B, C refer to close packed layers of oxide ions

Al in 2/3 of the octahedral sites). Oriented nucleation of spinel on an alumina substrate is still easy (the change in stacking sequence resembles that found in stacking faults, Chapter 5) therefore.

In the latter, Al₂O₃/spinel case, the structural similarity between substrate and nucleus is limited to the 2D interface and is referred to as *epitaxy*. In the MgO/spinel case the structural similarity extends to 3D since there is a common oxygen packing arrangement; this is referred to as *topotaxy*. Epitactic and topotactic phenomena are very common in solid state reactions, crystal growth, oriented thin film deposition, intercalation reactions and phase transformations. They are fascinating phenomena and often the two structures to either side of a common interface have quite different properties or can transform imperceptibly from one to the other. A beautiful analogue is provided by the 'fishes to birds' transformation in one of the Escher drawings, Fig. 9.3.

Oriented nucleation, of the kinds described above is relatively easy provided (a) the appropriate atoms to form the product nuclei are nearby and (b) there is good *lattice matching* between substrate and nucleus; for instance the separation of O²⁻ ions should be similar in both structures. If lattice matching is good, a *coherent interface* may form; if lattice matching is not good, large strains rapidly develop and the coherent interface may be lost and the nucleus becomes detached from the substrate. In our MgO/Al₂O₃ reaction mixture, Fig. 9.1, we may expect thin nuclei of spinel to form whenever grains of MgO and Al₂O₃ are close together or touching because all three structures have close packed oxide arrangements and lattice matching across either or both interfaces should be reasonably good.

Although the first few atomic layers of product nuclei may form relatively easily, subsequent growth or thickening of the product is much more difficult because, effectively, the two reactants, MgO and Al₂O₃ are no longer in contact but are separated by a rather impenetrable spinel layer. A complex counter-diffusion process is therefore required in which Mg²⁺ ions diffuse away from

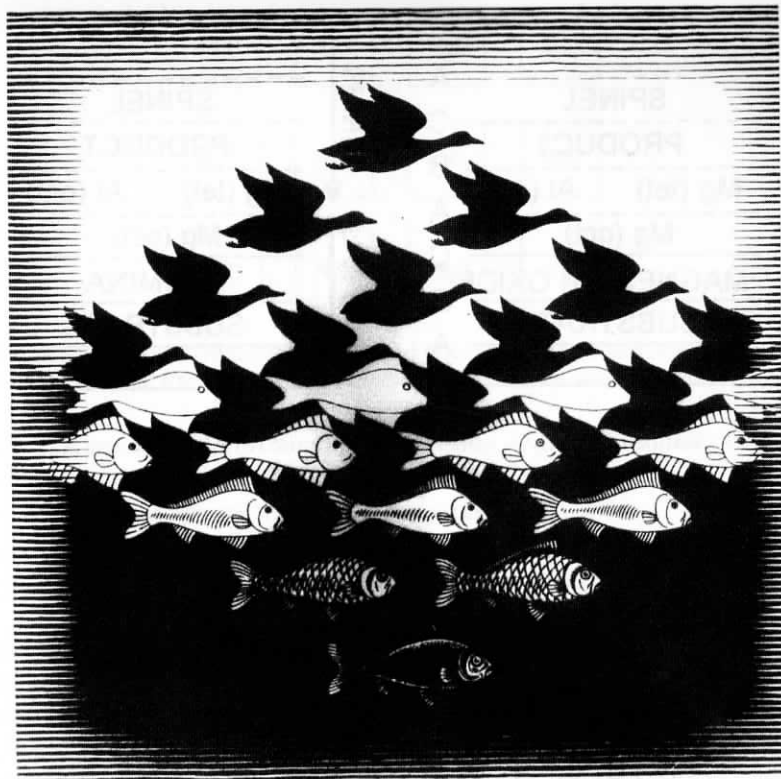
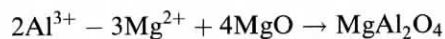


Fig. 9.3 Fishes to birds. Escher drawing. (Reproduced by permission from Escher, M.C. 'The Graphic Work'.)

and Al^{3+} ions diffuse towards the $\text{MgO}/\text{MgAl}_2\text{O}_4$ interface and vice versa for the $\text{MgAl}_2\text{O}_4/\text{Al}_2\text{O}_3$ interface. Assuming for the moment that there is no way for the ions to bypass the long diffusion pathway through the spinel product layer, then we have the scenario summarized in Fig. 9.4. As reaction proceeds the spinel layer thickens, the diffusion pathlength increases and hence, the reaction slows down.

In order to preserve local electroneutrality during the reaction and throughout the product it is necessary that, for every three Mg^{2+} ions that diffuse to the right hand interface, two Al^{3+} ions must diffuse to the left hand interface. The reactions that occur at the two interfaces may be written, ideally, as:

Interface $\text{MgO}/\text{MgAl}_2\text{O}_4$



Interface $\text{MgAl}_2\text{O}_4/\text{Al}_2\text{O}_3$

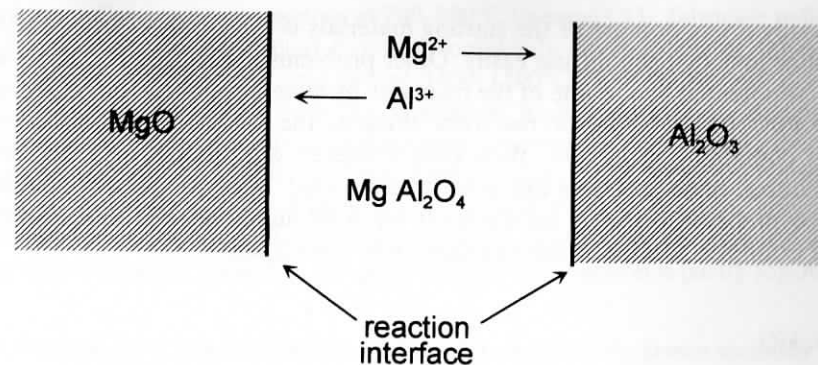
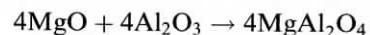


Fig. 9.4 Spinel product layer separating MgO and Al_2O_3 reactant grains

Overall reaction



from which we can see that the right hand interface should move three times as quickly as the left hand interface. In cases where the reactant(s) and product are of different colour, it may be possible, in carefully designed experiments, to observe visually the displacement of the interfaces; using the interfaces in this way as a marker is known as the *Kirkendall effect*.

The spinel formation reaction is particularly slow because ions such as Mg^{2+} and Al^{3+} diffuse very slowly; typically, heating for 1 week at 1500°C would be required to form a fairly pure spinel product. Defects are required, particularly vacant sites for adjacent ions to hop into. Very high temperatures are also required so that ions have sufficient thermal energy to, occasionally, vibrate or hop out of one site into an adjacent vacancy or interstitial site. Consequently, it can be difficult for solid state reactions to proceed to completion as the remaining reactants become increasingly separated from each other. One important way to accelerate reactions is to frequently grind the partially-reacted mixtures; this acts to break up reactant/product interfaces and to bring fresh reactant surfaces into contact. Another is if gas- or liquid-phase assisted transport of matter can occur, in which case reactants may be brought together without the need for long-range solid state diffusion. A small amount of liquid or gaseous transporting agent may be very effective in giving enhanced reaction rates.

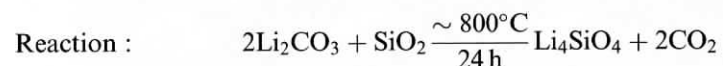
b) Examples of solid state reactions

Although the problems associated with spinel synthesis by solid state reaction have been clearly set out, spinel synthesis does represent a particularly problematic reaction since the two reagents, MgO and Al_2O_3 are both inert, non-reactive solids. Most other solid state reactions are considerably easier,

especially if one or more of the starting materials is chemically reactive and/or contains ions that can diffuse easily. Other problems may then arise, however, such as potential loss of one of the reactants by evaporation (e.g. alkali oxides, Tl_2O , PbO , Bi_2O_3 , HgO), or reactivity towards the container (e.g. transition metal containing materials). With care, however, and attention to synthesis procedures, these problems can usually be avoided. Many thousands of solids can be prepared perfectly satisfactorily by solid state reaction; here are just three examples, each of which requires some special care.

i) Li_4SiO_4

Li_4SiO_4 is the parent phase for a large family of Li^+ ion conductors.



Problem: Li_2CO_3 melts and decomposes readily above $\sim 720^\circ C$ and is reactive towards most container materials, including Pt and silica glass crucibles.

Solution: use Au containers; carry out pre-reaction and decomposition of Li_2CO_3 at $\sim 650^\circ C$ for a few hours before final firing at $800\text{--}900^\circ C$ overnight.

ii) $YBa_2Cu_3O_7$

$YBa_2Cu_3O_7$, YBCO, is the classic 90 K superconductor.

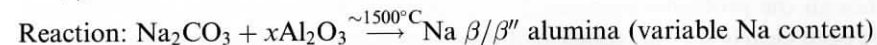


Problems: BaO readily picks up CO_2 from the atmosphere to form $BaCO_3$ which, once formed, is difficult to decompose; CuO is very reactive to most container materials at high temperatures; the oxygen content of the YBCO product is variable and must be controlled to optimize T_c .

Solutions: react in CO_2 -free atmosphere, with $Ba(NO_3)_2$ as a source of BaO; make pellets of reaction mixture (after decomposition of $Ba(NO_3)_2$) and react these on a bed of prepared YBCO; after reaction at $\sim 950^\circ C$, carry out final heating at $\sim 350^\circ C$ to allow O_2 uptake to occur and achieve the desired stoichiometry, $YBa_2Cu_3O_7$.

iii) Na β/β'' alumina

Na β/β'' alumina is the classic Na^+ ion conducting solid electrolyte.



Problem: Na_2O is volatile at the required reaction temperatures; lower temperatures cannot be used because of the inertness of Al_2O_3 .

Solution: Carry out pre-reaction at $700\text{--}800^\circ C$ to expel CO_2 ; fabricate pellets or tubes of the partially reacted mixture; completely cover pellets or tubes with prereacted β/β'' alumina and fire at $1400\text{--}1500^\circ C$. This 'buffering' prevents significant loss of Na_2O from the samples at high temperatures. Reaction is also speeded up by using high surface area, reactive alumina starting materials such as boehmite or $\gamma\text{-}Al_2O_3$. These have a defect spinel structure (similar to that in the β/β'' alumina product) and the first stage of reaction appears to involve intercalation of Na^+ into the particles of alumina. This greatly assists the nucleation and growth of the product since the reaction is partly topotactic.

c) Problem: how to homogenize reaction mixtures? Chimie Douce methods

Clearly, the biggest drawback of solid state reactions is that reactants are not mixed on an atomic scale. All the alternative methods described in the rest of this chapter address this problem by achieving atomic scale mixing of reactants, in gas, liquid or even solid phases. Most are low temperature methods, often referred to as Chimie Douce or soft chemistry methods, although a final firing at high temperatures may be needed, especially for ceramic-type products. Consequently, greater purity may be attainable, especially if prolonged heating at high temperature can be avoided. If the reaction conditions are optimized, products with high chemical and textural homogeneity are possible, which often leads to improved properties. It is also possible to use a variety of non-powder feedstocks and products may be produced in a variety of forms, such as fibres or coatings. Disadvantages of these alternative methods are that often, the reagents are costly and difficult to handle on a large scale, considerable research may be required to optimize the synthesis of a particular material and once conditions have been found, these may not then be suitable for synthesis of other materials. For these reasons, solid state reactions, which are relatively quick, easy and versatile, are usually tried first.

9.3 Sol-gel methods

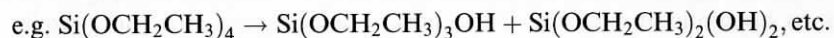
The starting point in these methods is to prepare a homogeneous solution containing all the cationic ingredients. The solution is gradually dried and, depending on the species present, it may transform to a viscous sol containing particles of colloidal dimensions and finally, to a transparent, homogeneous, amorphous solid known as a gel, without precipitation of any crystalline phases. The gel is then fired at high temperatures to remove various volatile components trapped in the pores of the gel or chemically-bonded organic-side groups and crystallize the final product.

The reagents for sol-gel syntheses are usually metal-organic compounds, especially alkoxides such as tetraethylorthosilicate (TEOS), $Si(OCH_2CH_3)_4$ as a source of SiO_2 , titanium isopropoxide, $Ti(O^iPr)_4$ as a source of TiO_2 and aluminium butoxide, $Al(OBu)_3$ as a source of Al_2O_3 . These are usually covalent liquids, which are mixed in the appropriate ratios, often with an alcohol to promote miscibility of the alkoxide and H_2O . Water is a key reagent since this

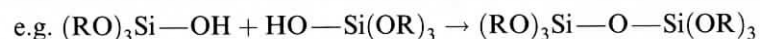
hydrolyses the alkoxides, usually in the presence of either acid or base as a catalyst to speed up reaction.

Hydrolysis may be regarded as occurring in two steps.

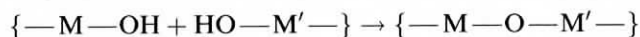
(i) replacement of $-OR$ groups by $-OH$



(ii) condensation polymerization with the elimination of H_2O

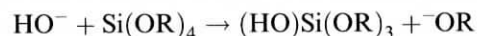


The composition, structure and viscosity of the reaction products depend very much on the degree of hydrolysis/condensation and careful control of the reaction variables is required to achieve the desired product. For the synthesis of complex oxides containing more than one cation, M, M' , cross-condensation is required,

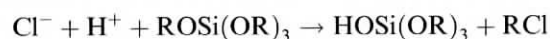


and clearly it is essential to achieve this instead of condensation of the components separately.

Hydrolysis may be base-catalysed, with nucleophilic substitution of OH^- ,



or acid-catalysed with electrophilic attack by H^+ (or H_3O^+)



The final stage of synthesis is to heat, or *calcine* the gel, burning off organic matter and leaving an oxide product.

The sol-gel method is extremely versatile and can incorporate most elements of the periodic table. A selection of examples follows.

a) Synthesis of MgAl_2O_4

Appropriate reagents are $\text{Mg}(\text{OCH}_3)_2$ and $\text{Al}(\text{O}^s\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$. On mixing, hydrolysis, condensation and drying, an amorphous gel is obtained that decomposes to form very fine particles of spinel after a final heating at 250°C . Clearly this compares very favourably, in energy terms, with heating for several days at 1500°C , but the reagents are expensive and difficult to use.

b) Synthesis of silica glass

Pure silica glass is difficult, and expensive, to prepare by the traditional melt route since molten SiO_2 is extremely viscous, even at 2000°C (melting

point of SiO_2 is $\sim 1700^\circ\text{C}$). Starting from TEOS, it is possible by the sol-gel route to prepare an amorphous product which, to all intents and purposes, resembles silica glass but which has never been heated above 1200°C . Both silica glass and this amorphous silica look-alike are metastable and care is required to avoid some crystallization at the final processing temperature of 1200°C .

c) Spinning of alumina fibres

We normally encounter Al_2O_3 as a powder or a ceramic. By the sol-gel route it can be prepared as fibres which, in its ICI tradename 'Saffil', is used as a thermal insulation to replace asbestos. The starting material is $\text{Al}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$. To produce fibres, it is crucial to control the viscosity at the stage of drawing fibres. Also, the polymer intermediates should be linear rather than branched chain; for this, acid catalysis is used since base catalysis tends to give 3D polymers (with base catalysis, there is an increase in the rate of substitution of OR by OH groups; with each additional OH group, which is electron withdrawing, the Si carries an increasing δ^+ charge and is therefore more susceptible to further nucleophilic attack by OH^- groups. This leads to a high concentration of Si atoms containing several OH groups and therefore, a high concentration of silanol groups that will lead to cross-linked structures on condensation polymerization).

d) Preparation of indium tin oxide (ITO) and other coatings

Semiconducting ITO is widely used as an electrode, especially as a thin film coating. It is also used as a coating on glass for energy control of buildings since it transmits visible light and reflects infrared radiation. The coatings are prepared by the sol-gel route; starting with In and Sn alkoxides a thin film is poured onto the substrate or alternatively, the substrate is dipped into the liquid precursor mixture. The coating is then processed *in situ* giving finally, an amorphous, thin, transparent, adherent layer.

Other coatings that are prepared in this way include

- Ta_2O_5 (from $\text{Ta}(\text{OCH}_2\text{CH}_3)_5$) on Si: Ta_2O_5 is an insulator and is used in $\text{Ta}_2\text{O}_5/\text{Si}$ capacitors;
- $\text{SiO}_2/\text{TiO}_2$ on Si wafers: the refractive index depends on the TiO_2 content and $\text{SiO}_2/\text{TiO}_2$ anti-reflective coatings are used to increase the efficiency of Si solar cells.

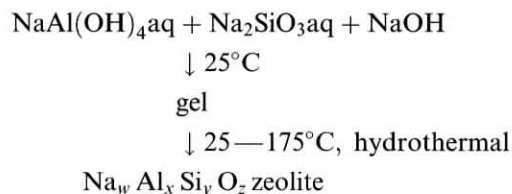
One of the major concerns in preparing coatings is to control the drying conditions such that the coatings remain crack-free and adherent. Generally, a large reduction in volume occurs on drying/decomposition of a gel, because of its high content of water and other volatiles. Thin coatings are better able to sustain these losses and retain their integrity than are thick coatings or bulk samples which experience large tensile stresses as a result of differential drying and shrinkage rates in the bulk and at the surface.

e) Fabrication of YSZ ceramics

YSZ (yttria-stabilized zirconia) is an important oxide ion conducting ceramic used in gas sensors and solid oxide fuel cells (Chapter 7). It can be prepared by the sol-gel route starting from precursors $Y(OCH_2CH_2CH_3)_3$ and $Zr(OCH_2CH_2CH_3)_4$.

f) Synthesis of zeolites

Zeolites are aluminosilicate framework structures containing large, interconnected voids and channels that permit either ready ion exchange processes or, in empty-channel structures, small organic molecules to enter where they can subsequently be induced to undergo various transformations or reactions. Recently, a range of other related framework materials have been synthesized, such as ALPOs (aluminophosphates) and also methods have been found to increase the size of the cavities, in the so-called MCM phases. Zeolites, or more generally *microporous solids*, are synthesized by sol-gel methods, often with a final treatment under hydrothermal conditions (heat in high pressure H_2O). A typical reaction is



The particular zeolite that forms depends not only on the starting composition, temperature and pressure but also on the particular *template* that is added. This is usually an alkylammonium cation, $(R_4N)^+$, around which the aluminosilicate structure crystallizes.

After crystallization of the zeolite, it is necessary to remove the template ions; this is done by heating to 300–400°C, where the organic material burns off leaving intact the inorganic framework. Although these open, aluminosilicate frameworks are not usually thermodynamically stable, they are kinetically stable up to 300–400°C and can therefore be used at lower temperatures in a range of applications as ‘molecular sieves’ and catalysts.

g) Preparation of alumina-based abrasives

Fine powders of doped Al_2O_3 are used as abrasive grit but to control the grade of performance, accurate control of particle size is necessary. The sol-gel method that is used is based not on alkoxides but starts from $AlOOH$ which is *peptized* or dispersed in dilute acid to give a sol which is then mixed with other cation-containing solutions of e.g. zirconyl acetate or $Mg(NO_3)_2$. The resulting mixtures polymerize to give a gel which is dried, crushed to give fine

particles with sharp edges caused by their fracture and then fired to convert the particles into their oxides.

h) Preparation of YBCO superconductor

A modified sol-gel method, known as the *citrate gel* method is used to prepare $YBa_2Cu_3O_7$. Starting materials are the nitrates of Y, Ba and Cu which are dissolved in water and mixed followed by addition of citric acid and ethylene glycol. On gradual heating of the mixture, H_2O evaporates and a gel forms which subsequently decomposes to give the $YBa_2Cu_3O_x$ product at temperatures as low as 700°C, considerably lower than required for solid state synthesis (Section 9.2bii).

9.4 Use of homogeneous, single source precursors

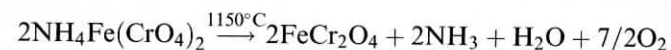
A solid state analogue of the sol-gel method is to prepare a crystalline, homogeneous, single phase precursor material that, upon decomposition, yields the desired product. These crystalline precursors cannot be prepared so readily and with such possibilities of compositional variation, as the sol-gel precursors, however and so the method is of more limited applicability. Some examples of crystalline precursors which have the desired properties of limited thermal stability and accurately-controlled stoichiometry with cations present in the desired ratio are as follows:

(a) $NH_4Fe(CrO_4)_2$ precursor to $FeCr_2O_4$

The precursor is synthesized by precipitation from aqueous solution:

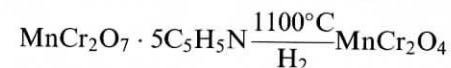


It decomposes on heating:



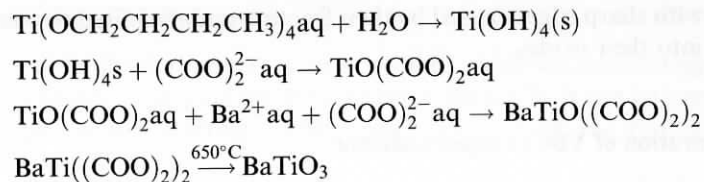
(b) $MnCr_2O_7 \cdot 5C_5H_5N$ precursor to $MnCr_2O_4$

The pyridinate precursor is precipitated from aqueous solution and then decomposed in H_2 :

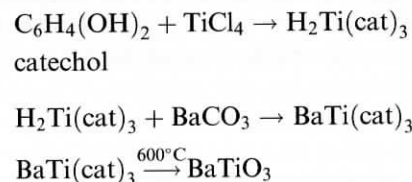


(c) $Ba(TiO)((COO)_2)_2$ precursor to $BaTiO_3$

Barium titanyl oxalate is prepared by a multistep route and is then decomposed by heating:



(d) BaTi catecholate precursor to BaTiO₃
Again, a multistep route is used:



9.5 Hydrothermal synthesis

This method involves heating the reactants in water/steam at high pressures and temperatures. The water has two functions, as a pressure-transmitting medium and as a solvent, in which the solubility of the reactants is P , T -dependent. The method is quite simple; reactants and water are placed inside a teflon-lined cylinder or 'bomb' which is either sealed or connected to an external pressure control. The bomb is then placed in an oven, usually at a temperature in the range 100–500°C. Pressure is controlled either externally or by the degree of filling in a sealed bomb, by making use of the P/T 'phase diagram', Fig. 9.5(a);

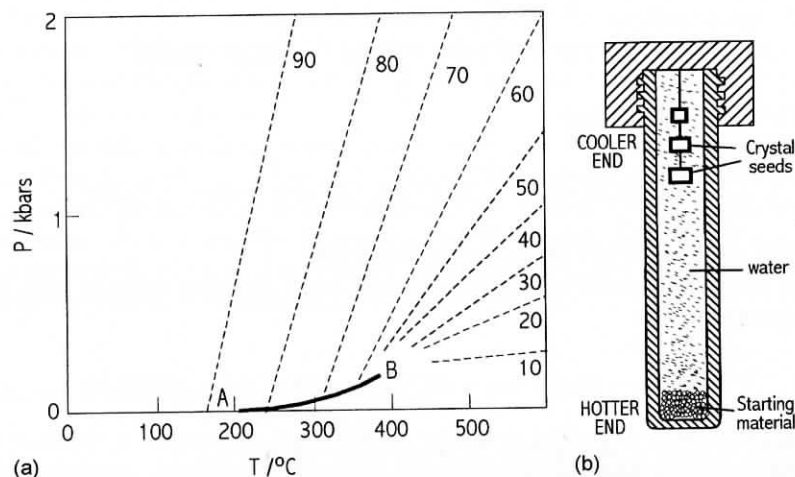


Fig. 9.5 (a) Pressure-temperature relations for water at constant volume. Dashed curves represent pressures developed inside a closed vessel; numbers represent the percentage degree of filling of the vessel by water at ordinary P , T . (After Kennedy, 1950). (b) Schematic hydrothermal bomb used for crystal growth

curve AB is the *saturated steam curve* and separates water (above) from steam (below); at temperatures above 374°C, point B, the water is in the *supercritical* condition and there is no distinction between liquid and vapour states.

Hydrothermal methods have a wide range of applications:

- (i) For zeolite synthesis, Section 9.3f, the final stage is to heat aluminosilicate gels hydrothermally to crystallize the zeolites.
- (ii) Single crystals of quartz, SiO₂, which are used as piezoelectrics in a range of applications, are grown hydrothermally in a temperature gradient using the arrangement shown in Fig. 9.5(b). The solubility of SiO₂ in NaOH solution increases with temperature; effectively, therefore, SiO₂ dissolves at the hot end, is transported to the cooler end by convection and crystallizes on the suspended seeds. In this reaction, NaOH acts as a *mineralizer*: SiO₂ is only sparingly soluble in H₂O, but solubility increases greatly when NaOH is dissolved in H₂O. Use of NaOH solution instead of pure H₂O greatly speeds up the growth of quartz crystals by hydrothermal treatment.

9.6 Intercalation and deintercalation

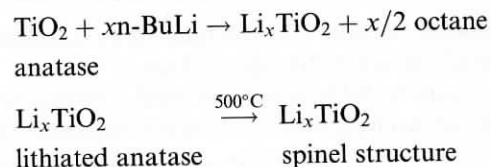
A very elegant way to synthesize new materials is to take an existing crystalline solid and either introduce new atoms into empty sites or selectively remove certain atoms, whilst keeping intact the overall original structure. These are examples of topotactic reactions in which there is a strong 3D similarity in the structures of the starting phase and the product.

Most intercalation and deintercalation reactions involve the addition or removal of ions (commonly Li⁺, Na⁺, H⁺, O⁼); to preserve charge balance, electrons must also be added or removed. These are, therefore, solid state redox processes and an automatic requirement is that the host materials should be mixed conductors so as to allow the migration of both ions and electrons. Numerous examples have been discussed already in Chapters 5 and 7, specifically,

- (i) intercalation of alkali metals or H⁺ into WO₃ to form tungsten bronzes, with electrochromic applications
- (ii) intercalation and deintercalation of Li into LiMn₂O₄ or Li_xCoO₂ cathode materials in solid state lithium batteries
- (iii) intercalation of O into YBa₂Cu₃O_x and other perovskite-related cuprates so as to optimize T_c of superconductors

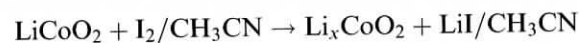
One other example that has to be mentioned because of the incredible change in properties that occurs is the topotactic conversion of the anatase polymorph of TiO₂, which is a white insulating solid, to a lithium titanate superconductor. The first step is to react anatase with n-butyl lithium dissolved in hexane. Li⁺ ions and electrons intercalate into the anatase structure, which has open, 1D channels not unlike those in rutile, Fig. 1.32; no significant structural changes occur on intercalation of Li. The second step is to heat the lithiated anatase to 500°C; this causes a structural reorganization to occur and gives a material with the same composition but with the spinel structure and which is

superconducting with a T_c of 13 K. This insulator to superconductor transformation is almost as miraculous as the 'fishes to birds' transformation crafted by Escher! The reactions that take place may be summarized:



Butyl lithium is a very powerful lithiating agent; effectively, it is a source of atomic Li.

A useful delithiating agent is I_2 dissolved in acetonitrile, CH_3CN ; it carries out reactions such as:



Products with a range of x values can be obtained by controlling the amount of I_2 used. The driving force for this reaction appears to be the formation of LiI which is soluble in CH_3CN .

Graphite is the classic example of a host crystal that is capable of intercalating a wide variety of atoms, ions and molecules and has been extensively studied. Graphite has a planar ring structure, shown in Fig. 9.6(a) and it is possible to intercalate, for example, alkali cations, halide anions, ammonia and amines, oxysalts and metal halides between the carbon layers.

Some typical reactions and conditions for the formation of graphite intercalation compounds are as follows:

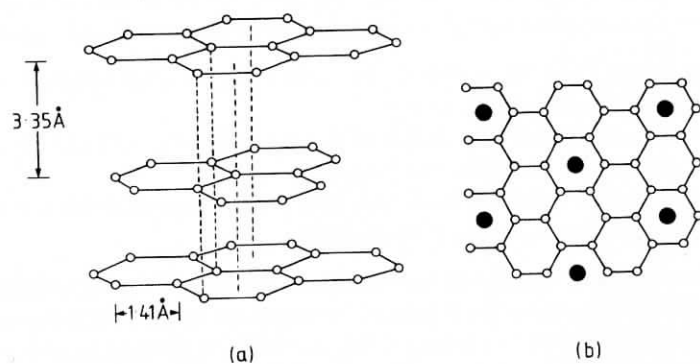
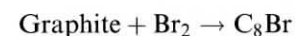
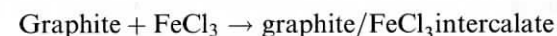
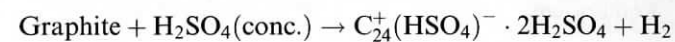
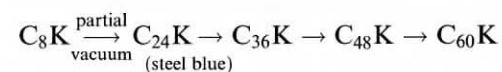
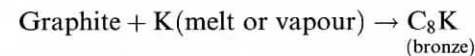
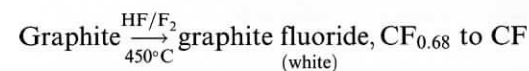
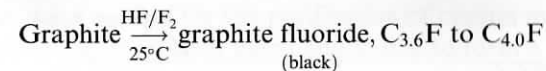


Fig. 9.6 Structures of (a) graphite, in oblique projection showing the two-layer stacking sequence and (b) graphite potassium, C_8K . In (b) the graphite layers are superposed in projection but the potassium atoms are not and various stacking sequences are possible. The structure in (b) is typical of many donor and acceptor complexes of graphite



Most of these reactions are reversible; thus C_8K forms on exposure of graphite to molten potassium and the potassium may be subsequently removed under vacuum. The reactions are readily reversible because the structure and planarity of the carbon layers are essentially unaffected by intercalation.

The structure and electronic properties of graphite are described in Section 2.15diii. Here, we note that bonding within the graphite layers is strong, with an average C—C bond strength of 1.5, but adjacent layers are held together by much weaker van der Waals bonds, as evidenced by the relatively large inter-layer spacing of 3.35 Å. This weak bonding permits suitable foreign atoms to intercalate between the layers and push them apart to, for example, 5.5 Å in C_4F , ~ 6.6 Å in CF and 5.41 Å in C_8K .

The structures of the intercalation compounds are often not known with certainty; the probable structure of one—graphite potassium, C_8K —is shown in (b). The relative positions of the carbon layers are different to those in pure graphite in that they now form an ...AAA... stacking sequence. Potassium ions are sandwiched between pairs of carbon rings, giving K^+ a coordination number of twelve. If all such sites were occupied, the stoichiometry C_2M would result, but in C_8K only one quarter are occupied, in an ordered fashion. The electronic structure of graphite is modified on intercalation of potassium atoms since partial electron transfer from potassium to graphite occurs, resulting in a polar structure which may nominally be represented as C_8K^+ , Fig. 2.27.

9.7 Vapour phase transport

The essential feature of this method is the formation of a volatile, unstable intermediate that contains at least one of the elements in the desired final product. The method may be used for the synthesis of new compounds, for the growth of single crystals or for the purification of a compound and involves

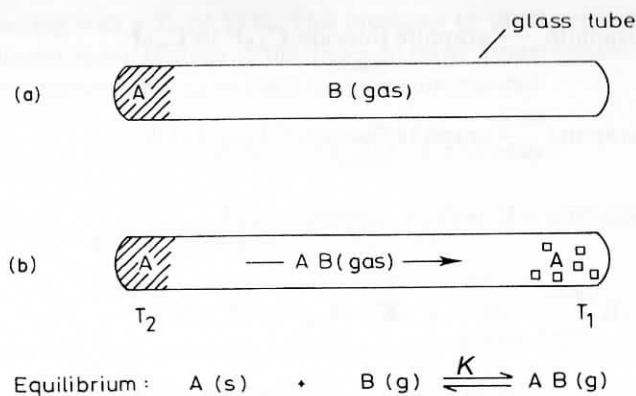
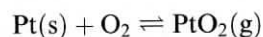


Fig. 9.7 Simple vapour phase transport experiment for the transport and growth of crystals of substance A via a volatile intermediate AB

chemical transport along a temperature gradient via the vapour phase. The method consists of a tube, usually of silica glass with the reactants, A, at one end and which is sealed either under vacuum or with a small amount of the transporting agent, B, Fig. 9.7(a). The tube is placed in a furnace such that a temperature gradient of e.g. 50 to 100°C exists inside the tube. In the simplest case, A and B react to form a gaseous intermediate AB which permeates the whole tube and decomposes somewhere else in the tube, at either higher or lower temperature to redeposit A, (b).

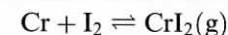
The method depends on the existence of a reversible equilibrium between A, B and AB. The equilibrium constant, K , should be small; if K is zero then no AB would form and vapour phase transport could not occur; if K is very large, AB would be stable and would not subsequently decompose. If the formation of AB is endothermic, it will tend to form at higher temperatures and decompose at lower temperatures, i.e. equilibrium will be displaced to the right with increasing temperature and to the left with decreasing temperature. The exact opposite will happen if AB forms exothermically. Hence, depending on whether AB forms endothermically or exothermically the tube is arranged for the reactants A to be at the hot end or cold end, respectively. Since K is temperature dependent, a concentration gradient of gaseous AB builds up along the length of the tube and this provides the driving force for gaseous diffusion and therefore, for chemical transport.

An example of an endothermic reaction which can be used for chemical transport is the formation of gaseous PtO_2 at 1200°C or higher:



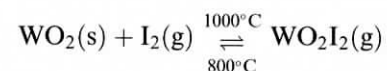
The PtO_2 diffuses to lower temperatures where it may deposit well-formed crystals of platinum metal. In furnaces that contain heating elements of platinum, it is common to find platinum crystals deposited on cooler parts of the furnace wall: these form by a process of vapour phase transport.

The *van Arkel* method for the purification of certain metals makes use of an exothermic reaction between metal and iodine to form a gaseous iodide, e.g.:

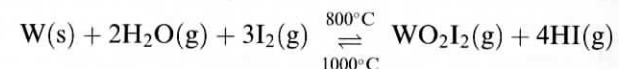


Since the formation of CrI_2 is exothermic, chromium metal is redeposited at a higher temperature. Other metals which may be purified by this method include Ti, Hf, V, Nb, Cu, Ta, Fe and Th. By this method, the metals may be extracted from their carbides, nitrides and oxides.

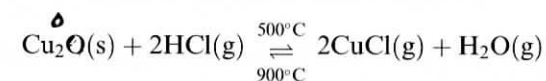
An elegant variation is to transport *two* substances in opposite directions along a temperature gradient; this is possible if one reaction is exothermic and the other endothermic. For instance, WO_2 and W may be separated by this means using I_2 and H_2O as the gas phase: W is deposited at 1000°C and WO_2 at 800°C. The reactions involved are:



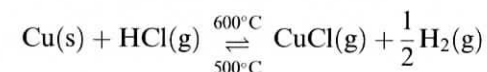
and



Another example is the separation of Cu and Cu_2O using HCl as the transporting agent. The reactions involved are:

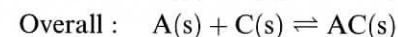
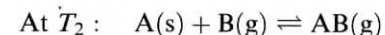


and



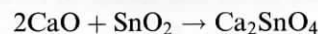
Since CuCl forms exothermically from Cu_2O and endothermically from Cu, the Cu_2O is redeposited at a higher temperature and Cu at a lower temperature.

The above examples are simple cases of transport in which reactant and product are the same. For use as a preparative method, the transport reaction is coupled with a subsequent reaction, represented schematically as:

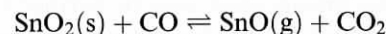


There are many examples of the use of this method for the preparation of binary, ternary and even quaternary compounds. Some examples (after Schäfer, 1971) are:

- (a) Preparation of Ca_2SnO_4 . CaO and SnO_2 react slowly according to:

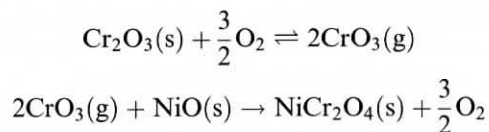


In the presence of gaseous CO , the reaction speeds up since SnO_2 converts to gaseous SnO and can be chemically transported:

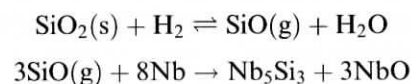


The gaseous SnO subsequently reacts with CaO and CO_2 .

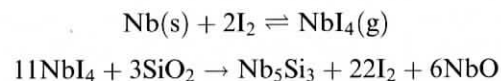
- (b) Preparation of nickel chromite, NiCr_2O_4 . Reaction of NiO and Cr_2O_3 is slow but speeds up in the presence of oxygen since gaseous CrO_3 forms which migrates to the NiO :



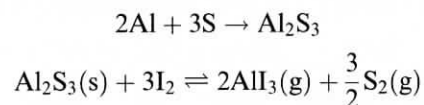
- (c) Preparation of niobium silicide, Nb_5Si_3 . Metallic Nb and SiO_2 do not react if heated under vacuum at, for example, 1100°C , but in the presence of traces of H_2 gaseous SiO forms which migrates to the Nb :



Alternatively, in the presence of I_2 , gaseous NbI_4 is formed and is transported to the SiO_2 :



- (d) Preparation of aluminium sulphide, Al_2S_3 . Al and S react only slowly at, e.g. 800°C , since liquid Al becomes coated with a skin of Al_2S_3 which acts as a diffusion barrier to further reaction. In the presence of I_2 , however, and a temperature gradient of 100°C , Al_2S_3 separates as large colourless crystals at the cool, 700°C , end. This is because the product, Al_2S_3 , is chemically transportable via the formation of gaseous AlI_3 :



- (e) Preparation of Cu_3TaSe_4 . The elements, Cu , Ta and Se , are heated at 800°C in the presence of I_2 ; transport occurs to give Cu_3TaSe_4 at 750°C , presumably by means of a gaseous complex iodide intermediate.

- (f) Preparation of zinc tungstate, ZnWO_4 . ZnO and WO_3 are heated at 1060°C in Cl_2 gas. Intermediate volatile chlorides form which are transported and crystals of ZnWO_4 are deposited at 980°C .

These examples illustrate the importance of the gas phase as a transporting agent and its subsequent influence on reaction rates. Gases react much more quickly than solids because mobilities are increased. In addition, the gaseous phase is often important in normal 'solid state' reactions under isothermal conditions, where it may act as a rapid means of transporting matter from one crystal to another.

9.8 Preparation of thin films; electrochemical methods, chemical vapour deposition, sputtering and laser ablation

Thin films, both crystalline and amorphous, are very important in modern technology. They may be used to form protective coatings on materials and they play a key role in the miniaturization of components in electronic devices. They also sometimes have special properties which derive from their thinness and, in particular, from their very large surface area to volume ratio: the structures and properties of the surfaces of solids are often quite different from the interior. Various methods are used to prepare thin films; some are described below.

a) Electrochemical methods

i) Cathodic deposition

This is a standard method of electroplating; two metal electrodes are dipped into an electrolyte solution and on application of an external field across the electrodes, metal ions from the solution are deposited on the cathode as a thin film. In order to maintain charge balance, the anodic metal gradually dissolves in the electrolyte.

ii) Electroless deposition

This is similar to cathodic deposition except that it takes place in the absence of an applied external field. It is commonly used for the deposition of nickel films. Both this and cathodic deposition suffer from the disadvantage that their use is limited mainly to the deposition of metallic films on to substrates that are electronically conducting, i.e. metals.

iii) Anodic oxidation

This is an electrolytic method for producing oxide films on the surfaces of metals such as Al , Ta , Nb , Ti and Zr . These metals form the anode that dips into a liquid electrolyte such as a salt or acid solution. Oxide ions are attracted

to the anode to form a thin layer of, for example, Al_2O_3 ; on increasing the field strength, more oxide ions diffuse through the oxide layer to the metal surface and, hence, the oxide layer grows thicker. An equilibrium thickness is usually reached which depends on the magnitude of the applied field. Anodic layers may also be formed by exposure of the metal to a glow discharge.

b) Thermal oxidation

Many substances oxidize in air, especially at high temperatures, and in some cases the product is an inert film which inhibits further oxidation. Thus, metallic aluminium forms an oxide film that is 30 to 40 Å thick at room temperature but whose thickness increases with temperature. The method is not restricted to oxide films; thus some metals, on exposure to, for example, ammonia at elevated temperatures, become coated with a metal nitride film.

c) Chemical vapour deposition (CVD)

The CVD method is developing into an extremely important way of making high purity thin films and coatings for industrial applications, especially in electronics, as well as for fundamental scientific research. Conceptually, it is simple; precursor molecules containing the elements of interest are decomposed in the gas phase and the products deposit as thin films on every available object in the vicinity.

Early work focused on simple precursor molecules such as volatile, unstable hydrides, e.g. SiH_4 and metal alkyls, e.g. $\text{Al}(\text{CH}_3)_3$. For the deposition of elements, e.g. Si, this is fine since only one precursor is necessary but to deposit compounds, e.g. GaAs, then a mixture of precursors is needed. Emphasis of research has now moved to the synthesis of suitable single-source precursors which contain all the elements of interest and in the correct ratio. This necessitates the design of increasingly exotic organometallic molecules which decompose cleanly to give the desired product.

There are various acronyms used to describe variations on the CVD technique; a commonly-used one is MOCVD which refers to the *metal-organic* nature of the precursors. The precursors can be decomposed in various ways, by the action of heat or by irradiation. Some simple examples are:

1. $\text{Si}(\text{CH}_2\text{CH}_3)_4 \xrightarrow{\text{heat in air}} \text{SiO}_2$
2. $\text{GeH}_4 \xrightarrow{h\nu} \text{Ge} + 2\text{H}_2$
3. $\text{CrCl}_2 + \text{H}_2 \xrightarrow{600^\circ\text{C}} \text{Cr} + 2\text{HCl}$
4. $\text{W}(\text{CO})_6 \rightarrow \text{W}$
5. $\text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{Fe}$
6. $\text{Ga}(\text{CH}_3)_3 + \text{AsH}_3 \xrightarrow[h\nu]{\text{heat}} \text{GaAs} + 3\text{CH}_4$

In many applications, such as the fabrication of multilayer semiconductor devices, it is necessary for the deposited films to have the correct structural orientation and to be coherent with the underlying layer. Hence *vapour phase epitaxy* is essential in the growth mechanism.

There is now a wide range of reactant or precursor molecules available for MOCVD. General problems associated with the precursor molecules include: (i) the pyrophoric nature of alkyls; (ii) water sensitivity of alkyls leading to possible oxygen contamination of the thin film product; (iii) toxicity of hydrides; (iv) nucleation of reaction products inside the reaction chamber prior to deposition as a growing film, the so-called snowing effect, which occurs because the alkyls, with their coordinative unsaturation, react readily with electron pair donors such as Group V and VI hydrides; (v) the need to control accurately the precursor mix to achieve the desired film stoichiometry and homogeneity; and (vi) variations in volatility or reactivity of the reactants. These problems are not insurmountable, however, and high quality GaAs films have been prepared and used in devices.

As an alternative to using precursor mixtures, complex single source precursors are being continually developed. The attributes required for their use in MOCVD are that they should be volatile, have stable ligands (to avoid charring), pyrolyse the metal-ligand bonds cleanly (to retain desired stoichiometry of product and avoid contamination) and be of low toxicity. They also often have other natural advantages in that pre-reaction and snowing is less of a problem and the precursors are less reactive towards O_2 and H_2O since they are less coordinatively unsaturated than metal alkyls.

Some examples of single source precursors, their synthesis and decomposition products are given in Fig. 9.8. Next, we deal with two materials prepared by CVD methods that are of great technological importance.

i) Amorphous silicon

Amorphous silicon, a-Si, is the key materials component in a variety of technologies that utilize photoconductivity. The critical advance which made possible these technologies was the discovery by Dundee physicists, Spear and Le Comber, that a-Si, when contaminated by hydrogen impurity, could be doped to make it n- or p-type, in the same way that crystalline Si can be doped. This, coupled with the ready possibility to make a-Si as large area, thin films lead to applications of a-Si in, for instance, photocopiers and solar panels.

First, let us review the characteristics of crystalline Si. Pure, crystalline Si has a band gap of ~ 0.7 eV and can be made n- or p-type by doping with e.g. P or Al, Figs 7.11 and 7.12. For device applications, high purity, defect-free crystals are required which are doped selectively to create, for instance, pn junctions. These are used either as thin wafers cut from a single crystal boule or are prepared as epitaxial layers. There is, however, an inherent practical limitation to the size (area) that such single crystals, of acceptable quality, can be grown. Large area, thin films of Si can be deposited by CVD techniques but these are usually amorphous. Early attempts to add Group III or Group V dopants to induce p- or n-type semiconductivity were unsuccessful since, although the dopants could be added, they had little effect on the electrical properties.

The discovery that triggered the revolution in a-Si technology and its applications resulted from the (unintentional) fabrication of impure, hydrogen-doped

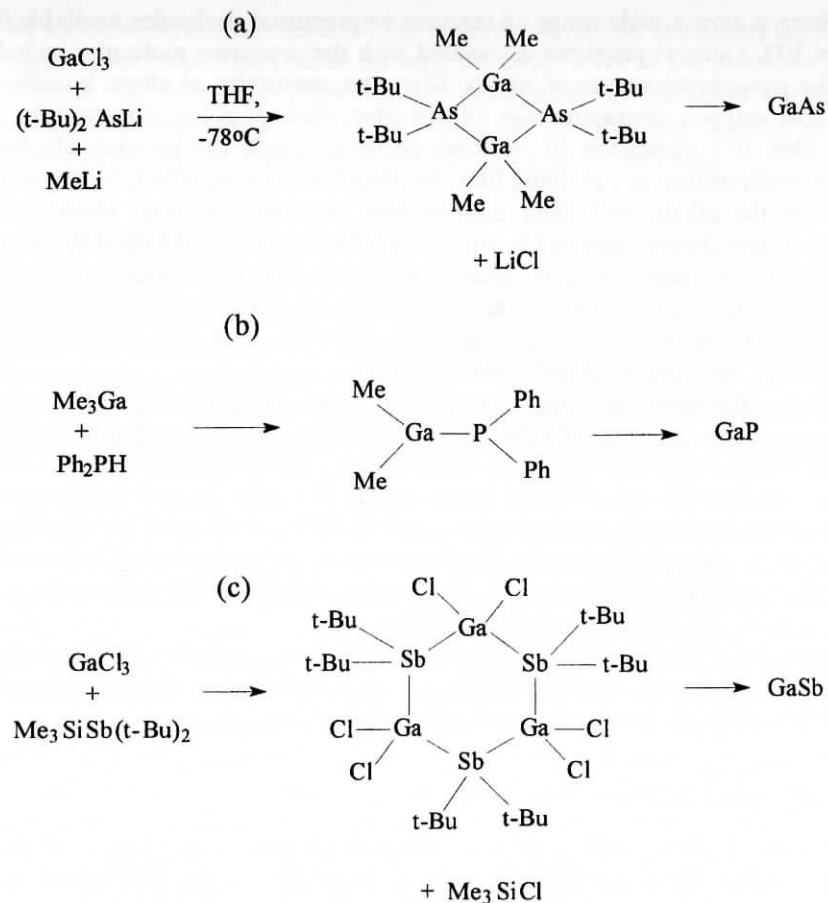


Fig. 9.8 Single source precursor molecules for MOCVD: Me = CH₃, t-Bu = t-CH₂CH₂CH₂CH₃, Ph = C₆H₅

a-Si. SiH₄ was used as a precursor, which decomposed in a CVD chamber, under the action of an rf plasma, to yield hydrogenated amorphous silicon, a-Si:H; unlike pure a-Si, it was found that a-Si:H can be doped to make it n- or p-type.

We can appreciate the differences between a-Si and a-Si:H by comparing their schematic structures and energy bands, Fig. 9.9. Both a-Si and a-Si:H are built of random networks of tetrahedrally-coordinated Si atoms, i.e. they are non-crystalline analogues of the diamond structure adopted by crystalline Si in which each bond may be regarded as an electron-pair, covalent single bond. In a-Si, some of the bonds are broken, leaving 3-coordinate Si with an additional, single, unpaired electron (a). These unpaired electrons, often referred to as 'dangling bonds' are readily available for covalent bond formation and in a-Si:H, most form Si-H bonds (b). The band structures are shown in (c), (d);

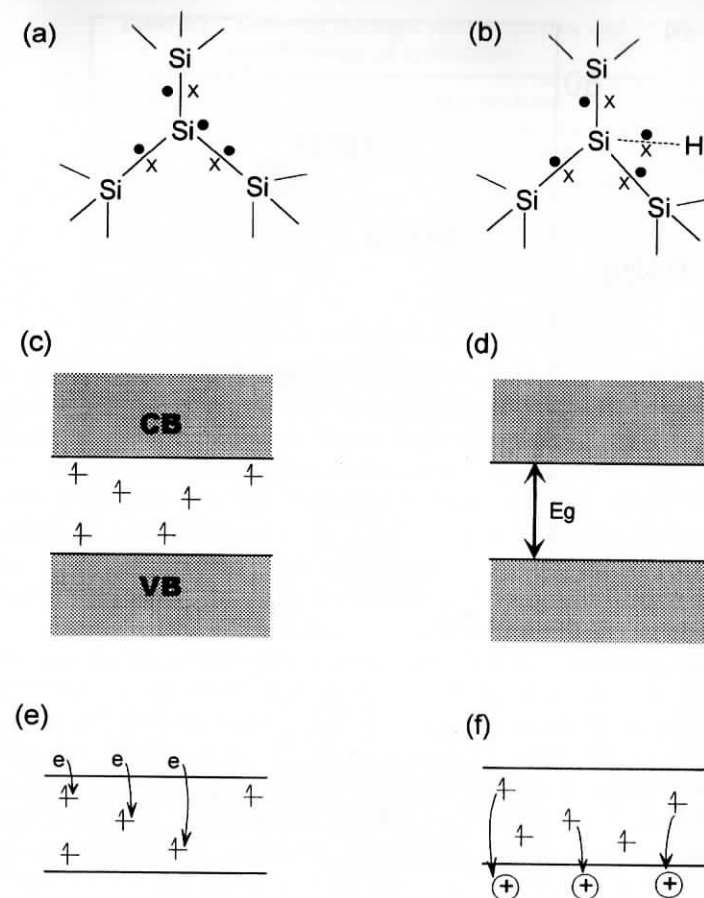


Fig. 9.9 (a) A 3-coordinate Si atom in a-Si, (b) an Si-H bond within the structure of a-Si:H, (c) and (d) band structures of a-Si and a-Si:H, and (e) and (f) interband levels in a-Si can act as either traps or donors

valence and conduction bands are present, as with crystalline Si. In a-Si, however, the dangling bonds form localized states, or discrete energy levels at various energies within the forbidden band gap; these can act as either trap states or donor states on attempting to dope a-Si and make it n- or p-type. Thus, if n-type (Group V) dopants are added, the donor electrons enter initially the conduction band but subsequently fall into one of the lower energy, inter-band traps associated with a dangling bond (e). Similarly, attempts to create p-type a-Si are ruined because electrons in the inter-band levels can drop down into the positive holes that have been generated in the valence band (f).

The band structure of a-Si:H differs from that of a-Si because the band gap is 'clean' and there are no inter-band levels associated with dangling bonds (d). Consequently, a-Si:H can be doped to make it n- or p-type.

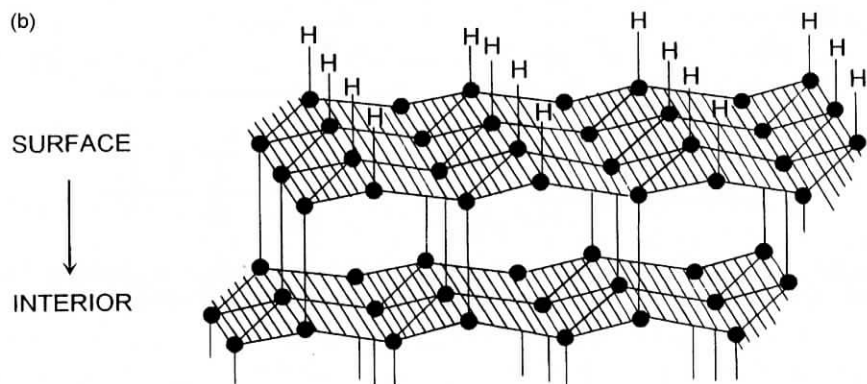
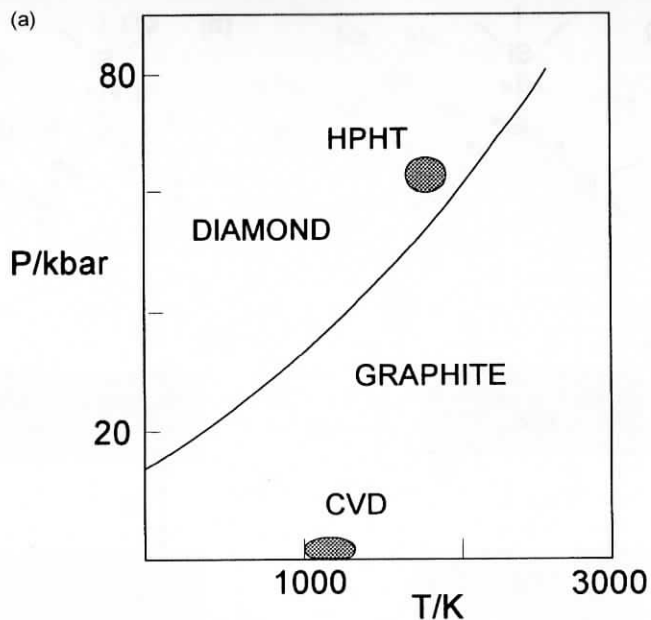


Fig. 9.10 (a) Phase diagram for carbon and (b) schematic surface of diamond film and growth mechanism

ii) Diamond films

Synthetic diamonds were first prepared in the 1950s by scientists at GE in the United States of America. From the phase diagram for carbon, Fig. 9.10(a), diamond is the equilibrium, thermodynamically stable polymorph only at high pressures and temperatures (HPHT) and in order to prepare synthetic diamonds, very extreme conditions: 60,000 atm pressure at 1500°C, are required. The resulting 'industrial' diamonds have found a variety of applications in, for instance, machine tool tips.

Table 9.1 Diamond coatings, their properties and possible areas of application

Property	Application
Hardness	Machine tools
Low thermal expansion	Electronic substrate
High thermal conductivity	Abrasive
Semiconductivity (doped)	Electronic devices
Transparent in visible/IR	Window/lens
Radiation resistance	Microwave devices
Large refractive index	Electro optic devices

At the time, it was thought that HPHT conditions were essential for diamond synthesis and there seemed no way in which the constraints imposed by the phase diagram could be avoided. Now, however, the situation has changed totally and it is possible to prepare diamond films under ordinary laboratory conditions, essentially by CVD by burning certain gas mixtures in an oxyacetylene flame. The individual crystals in the films are usually small and not of gem quality but nevertheless, the films offer many possibilities for industrial applications, Table 9.1. This is because diamond has many unique and useful properties. Thus, its thermal conductivity is several times higher than that of metals such as Ag but electrically, it is an insulator. It is therefore an excellent material to use as an insulating, heat sink. Diamond also has the highest transparency in the IR region of the electromagnetic spectrum of any substance prepared to date and this gives rise to applications in IR-transmitting windows or lenses. These properties, coupled with more well-known properties such as its legendary hardness (it is the reference material, with a hardness of 10 on the Moh's scale), resistance to chemical attack and radiation damage, make it an exceptionally valuable material technologically, provided it can be made cheaply and in a suitable form.

The CVD synthesis of diamond requires a hydrocarbon precursor such as methane, CH_4 or acetylene, C_2H_2 , hydrogen and a means of activation such as microwaves, heating or RF induction. Typically, the process operates at 600–1000°C at a reduced pressure of 0.1 atm, and diamond films are deposited inside the reaction chamber on a substrate, such as a glass slide with growth rates of 1 to 10 $\mu\text{m hr}^{-1}$. It is possible to avoid the phase diagram constraints referred to earlier since first, this synthesis method does not involve the transformation of graphite to diamond but instead involves deposition from the gas phase onto a growing surface and second, the deposition proceeds by a surface-controlled mechanism and surface free energies may be very different to bulk free energies. Under certain conditions, therefore, it is easier, kinetically, for the depositing carbon atoms to form a diamond-like rather than a graphitic structure. The resulting diamonds are in a metastable state, rather than the thermodynamic equilibrium state, as illustrated in Fig. 6.2.

The mechanism by which diamonds grow from the gas phase is illustrated in Fig. 9.10(b). Carbon is tetrahedrally-coordinated, sp^3 hybridized in diamond and the outermost surface of the diamond crystallites in a film is likely to be

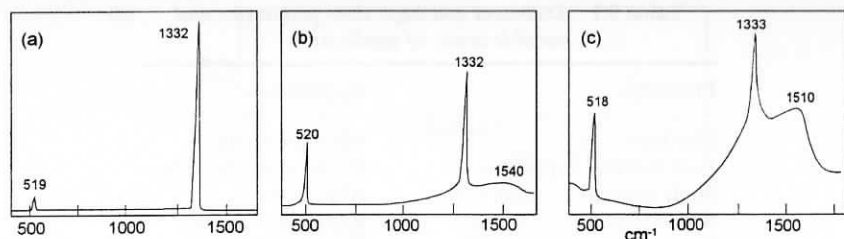
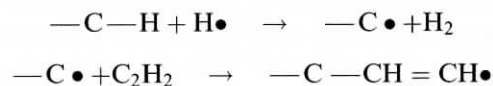


Fig. 9.11 Laser Raman spectra of diamond films of variable quality

composed of C–H bonds. An important component of the gas mixture in the CVD chamber is H_2 which, ‘under activation’ dissociates to give atomic hydrogen or hydrogen radicals, H. These radicals abstract H atoms from the diamond surface, leaving carbon radicals that then readily react with species such as acetylene:



In this way, the diamond surface grows by the gradual attachment of hydrocarbon species which subsequently reorganize to form a fresh layer with the diamond structure. Various other organic radicals and molecules may also be involved in diamond nucleation and growth and further research is needed for the mechanisms to be fully understood.

One of the most useful experimental techniques for assessing the quality of diamond films is laser Raman spectroscopy; sp^3 carbon has a characteristic peak at 1332 cm^{-1} whereas sp^2 carbon has a broad band at $1500\text{--}1600\text{ cm}^{-1}$. Spectra are shown in Fig. 9.11 for three films of variable quality: (a) is a high quality diamond film; (b) has some graphitic impurity but is largely diamond-like; and (c) is mixed diamond and graphite-like. This provides an excellent example of the use of laser Raman spectroscopy as a fingerprint technique for inorganic solids.

d) Sputtering and evaporation

The apparatus used for sputtering is outlined in Fig. 9.12(a). Basically, it consists of a bell jar which contains a reduced pressure— 10^{-1} to 10^{-2} torr—of an inert gas, argon or xenon. This gas is subjected to a potential drop of several kilovolts creating a glow discharge from which positive ions are accelerated towards the cathode (target). These high energy ions remove material from the cathode which then condenses on the surroundings, including the substrates to be coated, which are placed in a suitable position relative to the cathode. The mechanism of *sputtering*, or removal of material from the cathode, involves the transfer of momentum from the gaseous ions to the cathode in such a way that atoms or ions are ejected from the cathode. Modern sputtering

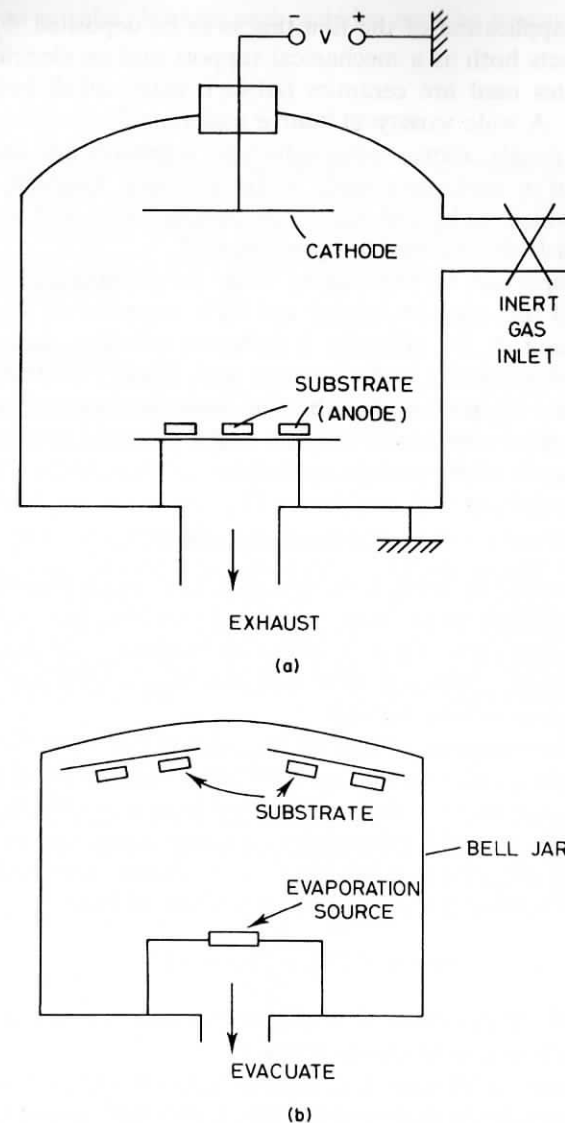


Fig. 9.12 (a) Cathode sputtering equipment for thin film deposition. (b) Vacuum evaporation equipment for thin film deposition

equipment has various refinements, including the means to prevent permanent contamination of the substrate by inert gas atoms or ions.

The simpler, vacuum evaporation method, is shown in (b). The system operates under a high vacuum, 10^{-6} torr or better. Material from the evaporation source is converted into the gaseous phase by heating or electron bombardment and gaseous material then deposits on the substrate and its surroundings as a film. Various substrate materials are used, depending on

