

CHAPTER III

THEORY



3.1 Defect structure of crystal material

Defects can be broadly divided into two groups: stoichiometric defects in which the crystal composition is unchanged on introducing the defects and non-stoichiometric defects, which are a consequence of a change in crystal composition. Some phenomena cannot be explained without invoking the presence of defects. These include:

1. Understanding the forces required fracturing a crystal. If one simply calculated the force required to separate two layers of atoms in a crystal, the result would come out to be much larger than the actual force required fracturing a solid. It therefore appears as if a crystal breaks in stages, with each stage requiring a rather smaller force.

2. The ability of a crystal to deform irreversibly under stress. The primary example is called slip. Where application of a stress acts as a shear stress on particular crystal planes that appear to slide over each other.

3. The origin of color in many materials that would otherwise be transparent. A well-known example is the red color of ruby, Al_2O_3 , which is caused by Cr^{3+} impurities on the Al sites

4. The presence of a small but non-zero electrical conductivity in insulators, these are caused by the motion of charged ions as in a salt solution. Ionic conductivity is much higher in materials that contain vacant sites as defects.

5. The ability of atoms to diffuse within a solid, such as the diffusion of carbon atoms in iron. The processes are related to those that allow electrical conductivity.

6. Crystal growth, which often appears to proceed through a process that, involves the formation of a spiral defect.

The presence of defects can be exploited in applications, and in other cases the presence of defects causes technological problems, and both mean that it is important to understand the behavior of defects. Two such defects particular importance is the Frenkel and Schottky defects. Only point defect that concerns our work thus large-scale imperfections will not mentioned in details. The details of point defects are following

3.1.1 Vacancies: Schottky defects

Consider the simplest crystal defect, namely that of an atomic site becoming vacant, with the missing atom migrating to the crystal surface. This process will be energetically unfavorable, costing the system a change in energy.

The simple case of a vacant site is called a Schottky defect. In order to maintain a neutral charge distribution across a local length scale, it is common for both positive and negative vacant sites to be produced in thermal equilibrium and to be evenly distributed throughout the sample. This is represented in Figure 3.1.

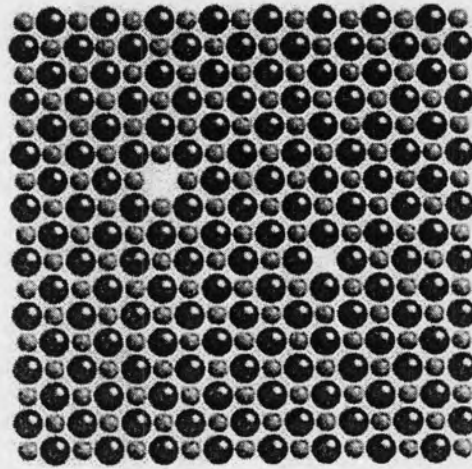


Figure 3.1: Cation and anion charge-balanced Shottky defects in NaCl.

3.1.2 Interstitial defects: Frenkel defects

In crystals that not pack with high efficiency, it is possible for atoms to occupy sites that are normally vacant, called interstitial sites. A Frenkel defect occurs when an atom leaves its normal site to create a vacancy, and is then displaced into one of the interstitial sites. This process is illustrated in Figure 3.2.

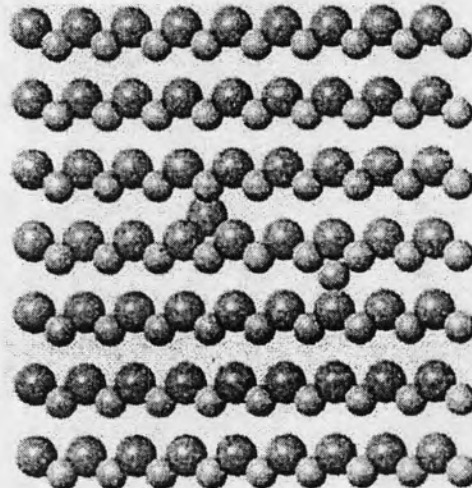


Figure 3.2: Pair of charge-balanced Frenkel defects in AgI.

3.1.3 Coupled charge substitutions and vacancies

The vacancies that mentioned above occur as equilibrium processes. Other point defects can be produced as non-equilibrium structures through the process of crystal growth. A common defect is the substitution of a different type of atom, usually one of similar charge. For example, NaCl can contain K^+ defects substituting for the cation sites, or F^- substituting on the anion sites. A substitution of a different charged cation will require production of a compensating charge defect. For example, substituting a Ca^{2+} cation in NaCl will require the formation of a charge-compensating cation vacancy. This structure is illustrated in Figure 3.3.

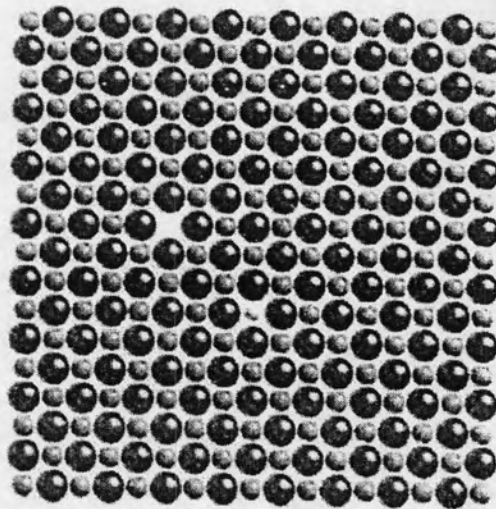


Figure 3.3: Substitution of a Ca^{2+} cation for a Na^+ cation in NaCl, accompanied by the formation of a vacant cation site in order to maintain charge neutrality.

3.1.4 Color centers

The charge substitutions that have been considered have been restricted to ions. It is also possible for electrons to occupy vacant anion sites in order to maintain charge neutrality. The electron forms its own energy bands. The color center is able to absorb electromagnetic radiation in the visible spectrum, and this gives color to what would otherwise be a transparent crystal. As a result, the presence of the color center can be detected in an optical absorption experiment.

3.2 Surface defects

There is a sense in which the surface itself with its coordinatively atoms is the most numerous type of defect. The bulk of the experimental results, spectroscopic or otherwise, necessarily relate to adsorption on the more numerous and expected sites on oxide surface, such as coordinatively unsaturated cations or anions, hydroxyls, acid-base pair, etc. However the most active sites will be connected with defects in the normal surface, which have unusual geometrical and/or local chemical compositional features. These may be present in concentrations that are one or two orders of magnitude less than those of the regular sites and their experimental detection can be correspondingly different.

In general, the majority of the experimental phenomena discussed above were connected with adsorption on the more numerous and expected sites on the oxide surface (coordinatively unsaturated cations, anions, hydroxyls, and their pair). However, the appearance of the most active surface centers suggests a connection with defects in the solid. The other factors influencing the properties of the real oxide surfaces are: (i) the presence of different lattice defects in the surface layer, and (ii) their chemical composition, which in many cases, may differ from that in the bulk.

In spite of the fact that the concentration of the defect centers on the surface is one or even two orders of magnitude less than the concentration of regular active sites, their reactivities are very often higher. This is why such defect centers can participate in the reaction.

The presence of the so-called dangling bonds (unsaturated valencies) at the surface creates electron energy states, usually named intrinsic states, which are present even in the case of pure and strictly stoichiometric surface. Additional structural defects on the surface which may be or may be not associated with adsorbed impurities, said to create extrinsic surface states.

The role of intrinsic defects in the activation of adsorbed molecules has not yet been elucidated. The physics of such defects is also still in development. In contrast, the influence of extrinsic defects on chemisorption and catalysis has been the object of many investigations.

Crystal with periodical arrangements of all of their structural elements cannot exist and real crystals show the presence of various imperfections described as defects. Those atoms into other sites or interstitial positions may due to (i) the displacement of atoms from the lattice sites normally occupy them, (ii) the presence of some vacant sites, or (iii) the displacement of part of a crystal with respect to another part along a crystal plane, etc. These defects are usually classified according to their dimensions into point defects (vacancies interstitial or foreign atoms), linear defects (dislocations) and spatial defects such as pores or foreign inclusion. For example, besides being a strong base, the highly dehydroxylated MgO surface is a good reducing agent. The reducing sites are apparently defects, possibly surface cation vacancies: the dissociative chemisorption of Bronsted acids blocks the reactivity of the reducing sites.

Investigation of small-surface-area bulk alkali earth-metal oxides, including MgO, e.g. as single crystal, show that their photoluminescence is caused by defects in the crystalline lattice, namely by the F^+ and F^\bullet centers, i.e. the oxygen vacancies have

captured one or two electrons, respectively. Such centers can be easily detected directly by EPR and/or by UV-Vis spectroscopic studies of the adsorption of molecules that easily form cation or anion radicals. Detailed analysis of such spectra obtained by using molecules which different but known values of ionization potential (IP) or electron affinity, allows us to obtain information about such an adsorption center, for example, on the basis of data on the transition to the radical state, and so to make a conclusion about its redox properties.

The main method used to investigate such centers is electron paramagnetic resonance (EPR) spectroscopy. It should be remembered that the formation of radicals could proceed on the surface of practically all oxide systems, when easily ionizable adsorbates which are able to cause the formation of both main and side-reaction products, are used.

A connection with the problem of defect sites, studies of mechanically activated oxide systems seem to be very interesting and useful. It is well known that mechanical activation (by grinding) affects an increase in the number of defects formed upon mechanical activation.

Mechanical treatment is an effective method for creating defects in solids. Various mechanical activation effects are related to the formation of such defects and their subsequent chemical transformations. Some of these defects are free radicals, for example in the case of SiO_2 ($=\text{Si-O-})_3\text{Si}^\bullet$ and $(=\text{Si-O-})_3\text{SiO}^\bullet$. A new type of natural defect, namely silanone (Si=O) groups was identified on the surface of mechanically activated SiO_2 . A study was carried out by using their thermal stabilities, optical properties (a characteristic absorption band was found with a maximum at 5.3 eV) and alcation, relative to simple molecules, such as CO_2 and N_2O , and radicals, such as H, D and CH_3 . Studies of the IR and Raman spectra of the oxides MgO , Cr_2O_3 , MoO_3 , Co_3O_4 and CuO in the regions of the cutoff vibrations allowed identification of sample amorphization during mechanical activation and also the decrease in the coordination number of both cations and anions as compared with nonactivated oxides. The latter

bring to increases in the reactivities. According to IR spectra of adsorbed CO in the case of CuO and Co₃O₄, the reduction of Cu²⁺ to Cu⁺ and Co³⁺ to Co²⁺ cations was observed during mechanical activation.

In the diffuse reflectance electron spectroscopy (DRES) spectra of MoO₃, the valence-to-conduction band transition exhibited a considerable blue shift with decreasing particle size. Excitonic absorptions observed in these spectra are also affected by the smaller particle size and by the altered crystallite surface. An increasing intensity of the bands was observed, and a linear dependence between the position of the band attributed to polaron conductance and the logarithm of the carrier concentration per Mo atom was obtained, both of these fact reveals that a sub-stoichiometric MoO_{3-x} species was formed upon mechanical treatment. According to the ESR data, both milled and non-milled MoO₃ samples contained Mo⁵⁺ centers interacting with OH groups in close vicinity, but their concentration was much smaller in the case of non-milled MoO₃. The main portion of these Mo⁵⁺ ions had C_{2v} or C_{4v} symmetry. These latter ions appear to result from the mechanical activation process and are suggested to be the precursors of a crystallographic shear structure. Exposure to O₂ reveals that all of these Mo⁵⁺ sites are located in the bulk and not necessarily on the surface, whereas free electrons are present at the surface. The high surface sensitivity of the IR technique when using adsorbed probe molecules revealed the formation of coordinatively unsaturated Mo⁴⁺ surface states in MoO₃ which was mechanically activated.

3.3 Titanium (IV) oxide

Titanium (IV) oxide occurs naturally in three crystalline forms: anatase, which tends to be more stable at low temperature, brookite, which is usually found only in minerals, and rutile, which tends to be more stable at higher temperatures and thus is sometimes found in igneous rock. These crystals are substantially pure titanium (IV) oxide but usually amounts of impurities, e.g., iron, chromium, or vanadium, which darken them. A summary of the crystallographic properties of the three varieties is given in Table 2.

Although anatase and rutile are both tetragonal, they are not isomorphous (Figure 3.4). Anatase occurs usually in near-regular octahedral, and rutile forms slender prismatic crystal, which are frequently twinned. Rutile is the thermally stable form and is one of the two most important ores of titanium.

The three allotropic forms of titanium (IV) oxide have been prepared artificially but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystal. The transformation from anatase to rutile is accompanied by the evolution of ca. 12.6 KJ/mol (3.01 kcal/mol), but the rate of transformation is greatly affected by temperature and by the presence of other substance which may either catalyze or inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is ca. 700°C, but this is not a transition temperature. The change is not reversible; ΔG for the change from anatase to rutile is always negative.

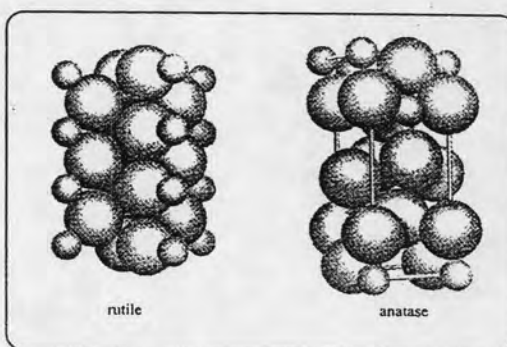


Figure 3.4: Crystal structure of TiO_2 . (Fujishima *et al.*,1999)

Brookite has been produced by heating amorphous titanium (IV) oxide, prepared from alkyl titanates of sodium titanate with sodium or potassium hydroxide in an autoclave at 200 to 600°C for several days. The important commercial forms of titanium (IV) oxide are anatase and rutile, and these can readily be distinguished by X-ray diffraction spectrometry.

Since both anatase and rutile are tetragonal, they are both anisotropic, and their physical properties, e.g. refractive index, vary according to the direction relative to the crystal axes. In most applications of these substances, the distinction between crystallographic directions is lost because of the random orientation of large numbers of small particles, and it is mean value of the property that is significant.

<i>Properties</i>	Anatase	Brookite	Rutile
Crystal structure	Tetragonal	Orthorhombic	Tetragonal
Optical	Uniaxial, negative	Biaxial, positive	Uniaxial, negative
Density, g/cm ³	3.9	4.0	4.23
Hardness, Mohs scale	5 ^{1/2} – 6	5 ^{1/2} – 6	7 – 7 ^{1/2}
Unit cell	D _{4a} ¹⁹ .4TiO ₂	D _{2h} ¹⁵ .8TiO ₂	D _{4h} ¹² .3TiO ₂
Dimension, nm			
a	0.3758	0.9166	0.4584
b		0.5436	
c	0.9514	0.5135	2.953

Table 3.1 Crystallographic properties of anatase, brookite, and rutile.

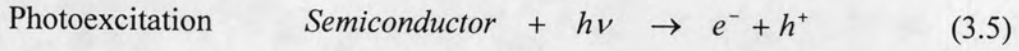
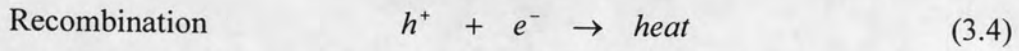
Measurement of physical properties, in which the crystallographic directions are taken into account, may be made of both natural and synthetic rutile, natural anatase crystals, and natural brookite crystals. Measurements of the refractive index of titanium (IV) oxide must be made by using a crystal that is suitably orientated with respect to the crystallographic axis as a prism in a spectrometer. Crystals of suitable size of all three modifications occur naturally and have been studied. However, rutile is the only form that can be obtained in large artificial crystals from melts. The refractive index of rutile is 2.75. The dielectric constant of rutile varies with direction in the crystal and with any variation from the stoichiometric formula, TiO₂; an average value for rutile in powder form is 114. The dielectric constant of anatase powder is 48.

Titanium (IV) oxide is thermally stable (mp 1855°C) and very resistant to chemical attack. When it is heated strongly under vacuum, there is a slight loss of oxygen corresponding to a change in composition to $\text{TiO}_{1.97}$. The product is dark blue but reverts to the original white color when it is heated in air.

3.5 Photocatalytic reaction

The primary photocatalytic process occurs upon irradiation of a semiconductor. A semiconductor is characterized by an electronic band structure, in which the highest occupied energy band, or valence band, and the lower empty band, conduction band, are separated by a band gap. The magnitude of the energy of band gap between the electronically populated valence band and the largely vacant conduction band governs the extent of thermal population of the conduction band in its intrinsic state. The band gap defines the wavelength sensitivity of the semiconductor to irradiation (Fox and Dulay, 1993). A photon of energy higher than or equal to the band gap energy is absorbed by a semiconductor particle. Then an electron from the valence band is promoted to the conduction band with simultaneous generation of an electronic vacancy or “hole” (h^+) in the valence band. This process is photoexcitation of electrons. Figure 3.1 shows the photocatalytic process occurring on an irradiated semiconductor particle.

In most materials that are electrically conductive, i.e., metals, two types of charge carriers, electrons (e^-) and holes (h^+), immediately recombine on the surface or the bulk of particle in a few nanoseconds and the accompanying energy is dissipated as heat (see Equation 3.4). On semiconductor such as titanium dioxide, however, they survive for longer periods of time to allow these carriers can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle (Equations 3.5, 3.6, and 3.7) (Litter, 1999). Subsequently, oxidation and reduction can be initiated.



Electron-hole recombination processes may be suppressed by bulk and surface traps. In Figure 3.5, the energy levels of the bulk and surface traps fall within the band gap. The surface and bulk traps are localized, and the electrons trapped in such states are thus associated with a particular site on the surface or in the bulk of the solid. The population of bulk and surface traps depend on two factors, namely, the decrease in entropy that occur when electrons are trapped, and the difference in relative energy between the traps and the bottom of the conduction band.

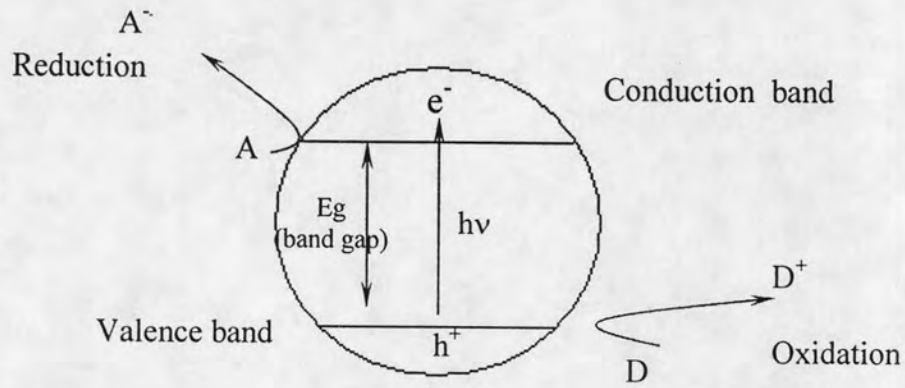


Figure 3.5: Photocatalytic process occurring on an illuminated semiconductor particle (Litter, 1999).

In aqueous solution, hydroxyl radicals ($\cdot\text{OH}$) production is favorable because of the abundance of hydroxyl groups and water molecules on the surface of catalyst. However, in the gas phase, organic substrates can themselves act as adsorbed traps for the photogenerated hole since in the gas phase, water molecules are not the predominant species in contact with the catalyst. Although in the presence of water vapor, OH groups are presented on the catalyst surface and their contribution to photooxidation can not be discarded (Alherici *et al.*, 1997).

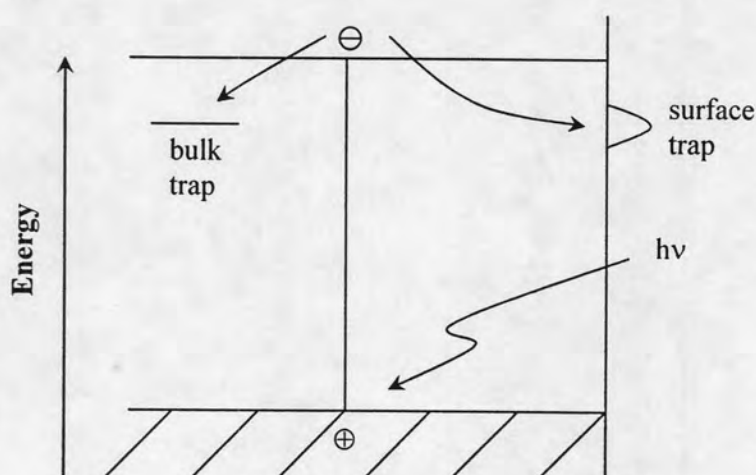
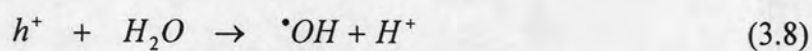


Figure 3.6: Surface and bulk electron trapping (Linsebigler *et al.*, 1995).

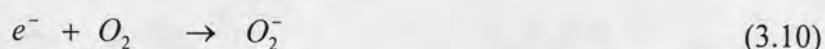
When adsorbed water molecules are oxidized by holes, hydroxyl radicals, which have strong oxidizing power, are formed (Equations 3.8 and 3.9).



The hydroxyl radicals can then react with organic components, initially producing free radicals. When molecular oxygen is present (reactions always occur in

the presence of oxygen from the air in the use of the photocatalyst for environment), It can react with these free radicals producing organic peroxy radicals. These radicals can then take part in chain reactions. In a short time, organic compounds are completely degraded, i.e., converted into carbon dioxide and water.

Meanwhile, the electrons that are produced in the electron-hole pairs are also put to work. These electrons are used to reduce (i.e., add electrons) to oxygen in air. Because oxygen is easier to reduce than water, it will tend to be reduced, producing the superoxide radical anion (O_2^-) Equation 3.10



The superoxide anion attaches itself to the peroxy radicals mentioned above. The resulting unstable product now contains at least four oxygens and can decompose to produce a carbon dioxide molecule. On the molecular scale, superoxide acts like a "supercharge ", greatly increasing the oxidation process, which is in fact a form of combustion. In addition to this mechanism, another interpretation proposed recently is that the formation of atomic oxygen (O^*), which is extremely reactive in air, leads to a direct attack on the carbon bonds in organic material.

In Figure 3.7, in terms of energy usage, the complete electrolytic decomposition of water is possible if the energy of the conduction band is at least as negative (i.e., higher in the diagram) as that required to reduce water to oxygen gas (0.0 V in acid solution), and the VB is at least as positive (i.e., lower) as that required to oxidize water to oxygen gas (+1.23 V). The complete decomposition of water is thus theoretically possible if a semiconductor that has the minimum band gap energy of 1.23 eV is illuminated with light, assuming that the energies of valence band and conduction band are located at appropriate positions. All of the semiconductors with small band gaps, however, have a strong tendency to decompose and dissolve when illuminated in aqueous solution.

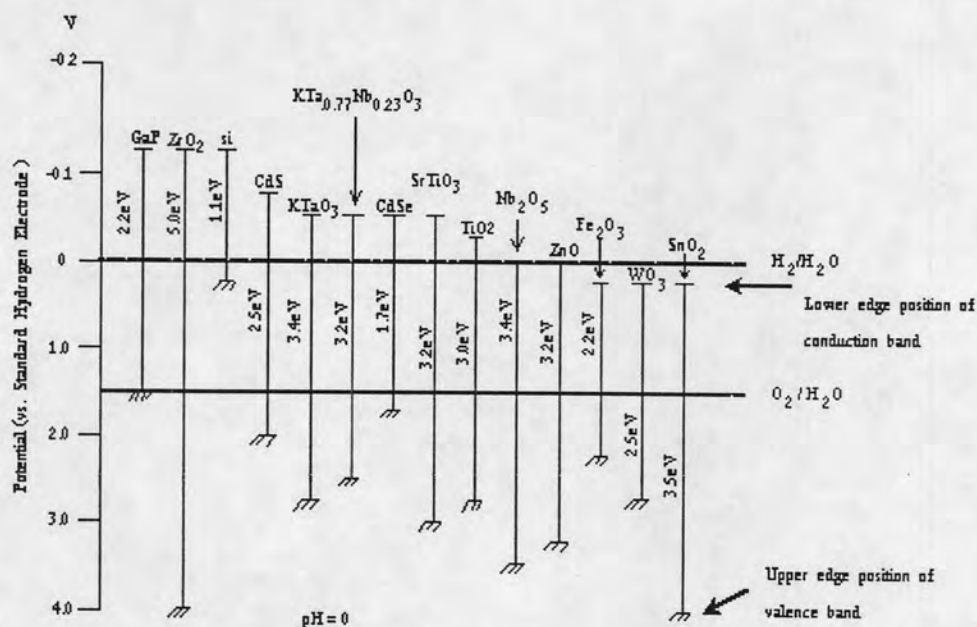
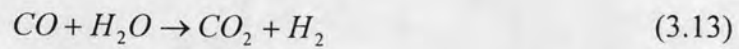
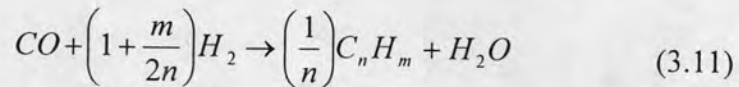


Figure 3.7: Energy diagram for typical semiconductors. (Fujishima *et al.*, 1999)

3.6 CO-hydrogenation

Fischer-Tropsch synthesis (FTS) that discovered by Fischer and Tropsch over 77 years ago, as an alternate process, can convert the synthesis gas (H_2/CO) derived from carbon sources such as coal, peat, biomass and natural gas, into hydrocarbons and oxygenates. During the past decades, FTS has been developed continuously by many researchers, although the rise and fall in research intensity on this process has been highly related to the demands for liquid fuels and relative economics. This synthesis is basically the reductive polymerization (oligomerization) of carbon monoxide by hydrogen to form organic products containing mainly hydrocarbons and some oxygenated products in lesser amounts. The main reactions of FTS are:



Equation (3.11) is the formation of hydrocarbons higher than C1, and the equation (3.12) is methanation. The water-gas shift reaction, which is undesirable for natural gas conversion, is shown in equation (3.13). The Boudouard reaction, which results in carbon deposition on the catalyst surface, is shown in equation (3.14).

The mechanism consists of surface steps in five categories: (1) the adsorption of reactants (H₂ and CO); (2) chain initiation; (3) chain propagation; (4) chain termination and desorption of products; (5) readsorption and secondary reaction of olefins. Depending upon the type of catalyst used, promoters, reaction conditions (pressure, temperature and H₂/CO ratios), and type of reactors, the distribution of the molecular weight of the hydrocarbon products can be noticeably varied.

Normally, catalysts used for this synthesis are group VIII metals. By nature, the hydrogenation activity increases in order of Fe < Co < Ni < Ru. Ru is the most active. Ni forms predominantly methane, while Co yields much higher ratios of paraffins to olefins and much less oxygenated products such as alcohols and aldehydes than Fe does.

With regards to the operating conditions, usually higher pressures will result in higher rates. Entrained bed reactors or slurry bubble column reactors are better than fixed-bed reactors for FTS since they can remove heat from this exothermic synthesis, allowing better temperature control.

The current main goal in using FTS is to obtain high molecular weight, straight chain hydrocarbons. However, methane and other light hydrocarbons are always present as less desirable products from the synthesis. According to the Anderson-Schulz-Flory (ASF) product distribution, typically 10 to 20% of products from the synthesis are usually light hydrocarbon (C_1 - C_4) these light alkanes have low boiling points and exist in the gas phase at room temperature, which is inconvenient for transportation. Many attempts have been made to minimize these byproducts and increase the yield of long chain liquid hydrocarbons by improving chain growth probability. It would be more efficient to be able to convert these less desirable products into more useful forms, rather than re-forming them into syngas and recycling them.