CHAPTER 2

LITERATURE REVIEW

To understand the sparked zinc oxide and its applications, the understanding of the electrical, optical and photocatalytic properties of materials is the first necessary and therefore these properties were described in detail in this chapter.

2.1 Electrical properties of materials

2.1.1 Conduction and Charge Carrier

Inside metal, electrons are free to move in a sea of electron throughout the lattice. In the absence of an applied field, the electron motion is random. The current (I_A) in a metal segment of length L is defined to be proportional to the voltage drop (V) across that segment i.e.

$$I_A = V/R_\Omega \qquad (2.1)$$

The resistance R_Ω is related to the length of the segment and is inversely proportional to the cross-sectional area (A) i.e.

$$R_\Omega = \frac{\rho L}{A} \qquad (2.2)$$

where ρ is the resistivity (Ω cm). For a uniform electric field (E) across L, V=EL and therefore,

$$I_A = V/R_\Omega = \frac{EL}{(\rho L / A)} = \frac{EA}{\rho} \qquad (2.3)$$

Upon applying an electric field, electrons will be accelerated in an opposite direction to the electric field. The summation of the time between acceleration of electrons (due to electric field) and deceleration of electrons (due to collisions and lattice scattering events caused by phonons, crystal defects, impurities, etc.) over the mean free path between scattering events results in the electrons having an average drift velocity. Electron mobility is a quantity relating the drift velocity of electrons to the applied electric field across a material, according to the formula:

$$\upsilon_d = \mu E \qquad (2.4)$$

where μ is the mobility.

In addition, the current is also related to the number of electrons per unit volume ($n_e=N_e /V_{vol}$), the drift velocity (υ_d), the electron charge (e) and the cross-section (A). Therefore,

$$I_A = n_e e A \upsilon_d \text{ or } \rho = E/(n_e e \upsilon_d). \qquad (2.5)$$

Note that, based upon Ohm's law, ρ must be independent of E. Therefore, the drift velocity (υ_d) must be proportional to E. In the presence of an external electric field, a free electron feels a force of magnitude eE. If this were the only force, the electron of mass m_e would have an unbounded acceleration eE/m_e.

2.1.2 Metals and insulators

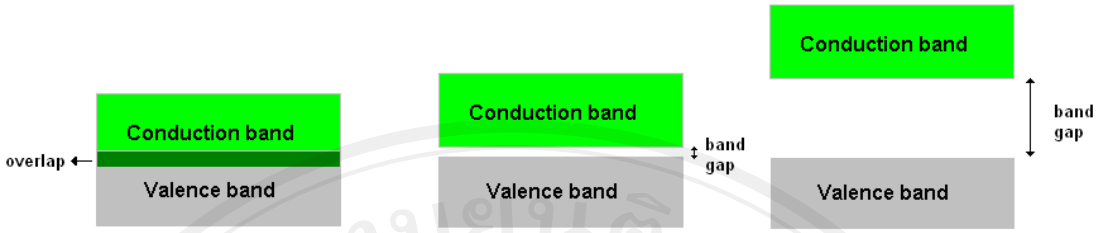
Metals are able to conduct electricity while other materials, such as plastics and ceramics always cannot (except at high voltage). A simple explanation of this phenomenon is that different elements have atoms with different numbers of electrons. These electrons can only move in specific places around the atom. In an

insulator, the electrons rarely move out of their usual orbit. No moving electron means no electricity can pass through. In a metal, the outer electrons are lowly attracted to the nucleus of the atom and readily wander off to other atoms. Due to the large number of many moving electrons, metals can therefore conduct electricity.

The difference between conductors and insulators can be properly explained using band theory. Electrons occupy energy levels in an atom starting from the lowest energies and upwards. The highest filled level is known as the valence band. Electrons in the valence band do not participate in the conduction process. The first unfilled level above the valence band is known as the conduction band. In metals, there is no forbidden gap, between valence and conduction band, since the conduction band and the valence band overlap, allowing free electrons to participate in the conduction process. For insulators, on the other hand, have an energy gap that is far greater than the available energy of the electron.

2.1.3 Semiconductor

There are materials that have conductivity levels between metals and insulators. Shining a light on them, or injecting charges, can modify their conductivity briefly. These materials are known as semiconductors. Semiconductors have small band gaps between their valence and conduction bands shown in fig. 2.1.



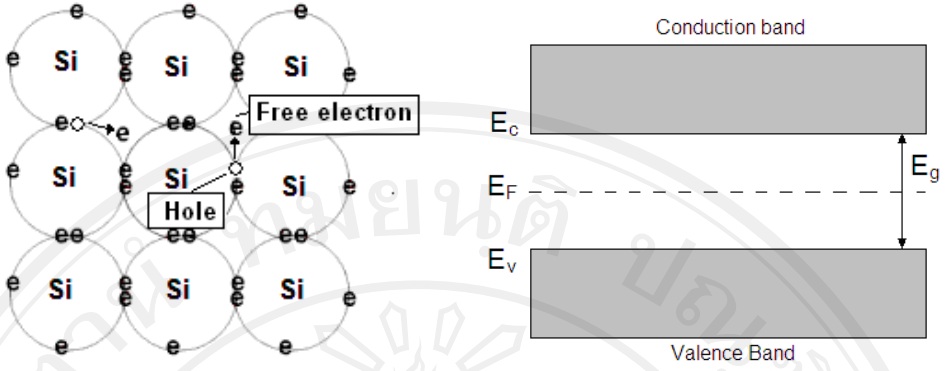
(a) (b) (c)

Fig. 2.1 Band gap of materials i.e. (a) conductor where the conduction band and the valance band overlap slightly, (b) semiconductor where the conduction band and the valance band are separated and (c) insulator where the conduction band and the valance band are widely separated.

The conductivity of semiconductor is much lower than that of metals because there are fewer free electrons. In general, the conductivity depends on temperature. For instance it can be increased by increasing temperature. Moreover, the conductivity can also be increased by applying light onto it. This is as the photons in the light provide energy to electrons in valence band, enabling them to jump into conduction band. Such semiconductor refers to photoconductor. However, the most effective way of increasing the conductivity of semiconductor is by doping it with an impurity. This property allows semiconductor to be used in electronic devices. Their conductivity may easily be modified by introducing impurities into their crystal lattice. The amount of impurity, dopant, added into intrinsic (pure) semiconductor dranges its conductivity. Doped semiconductors are often referred as extrinsic semiconductor.

2.1.4 Intrinsic semiconductor

Intrinsic semiconductor is an undoped semiconductor. Elemental and compound semiconductors can be intrinsic semiconductors. The number of charge carriers is therefore determined by the properties of the material itself. At very low temperatures all the bonds are intact and there are no free charge carriers. At room temperature some of the bonds are broken by thermal ionization so the resistance of semiconductor material decreases when temperature increases. Few electrons possess enough thermal energy to be excited into the conduction band. The excited electrons leave behind unoccupied energy levels, or hole, in the valence band. Electron and the hole are created by the excitation of a valence band to the conduction band, they are called an electron-hole pair and known as intrinsic charge carriers as shown in fig. 2.2 (a). In intrinsic semiconductors the number of excited electrons and the number of holes are equal, the Fermi's level of intrinsic semiconductor is at the middle between valence and conduction band as shown in fig. 2.2(b).



(a) (b)

Fig. 2.2 (a) The atoms of Si have four valence electrons which are bound together to form tetrahedral crystals, where each atom has four nearest neighbours, and thermal energy can create few electron hole pairs resulting in weak conduction and (b) energy gap (E_g) with Fermi level at the middle.

2.1.5 Extrinsic semiconductor

An extrinsic semiconductor is a semiconductor that has been doped, which has different electrical properties than the intrinsic semiconductor. Doping involves adding dopant atoms to an intrinsic semiconductor, which changes the electron and hole concentrations of the semiconductor at thermal equilibrium. To take the simplest example, consider Silicon. When small quantities of phosphorous are incorporated into the crystal, the atoms form a substitutional with silicon.

Phosphorus has five valence electrons, one valence electron more than silicon. Four of these valence electrons form regular electron-hole pair bonds with their neighbor silicon atoms (fig. 2.3 (a)). The fifth electron is only loosely bound to silicon. At slightly elevated temperatures this extra electron becomes dissociated from its atom and drifts through the crystal as a conduction electron when a voltage is

applied to the crystal Extra electron of this type are called “donor electrons.” It has to be note that at sufficiently high temperature, in addition to these donor electrons, some elecrons from the valence band are also excited into the conduction band in an intrinsic manner. The conduction band contains electron from two sources, the amount of which depends on the device temperature. Since the conduction mechanism in semiconductors which donor impurities (P, As, Sb) is predominated by negative charge carriers (electrons) these maerials are called n-type semiconductor. The electrons are majority carriers.

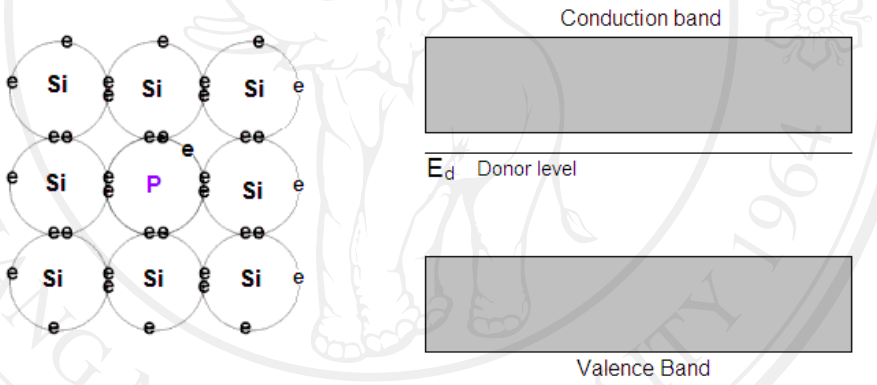


Fig. 2.3 (a) Schematic diagram shows n-type silicon (doped with phosphorous), and (b) energy level diagram of n-type semiconductor.

Consider the effect of adding an element with less than enough electrons to satisfy the covalent bonds of silicon. Boron is such an atom. There is an electron missing (fig. 2.4 (a)). Boron is an acceptor element, and the structure is calling a p-type semiconductor.

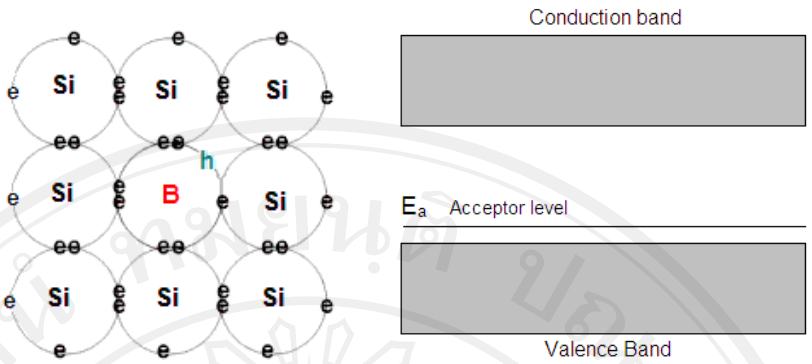


Fig. 2.4 (a) Schematic diagram shows p-type silicon (doped with boron), and (b) energy level diagram of p-type semiconductor.

The band structure of impurity or extrinsic semiconductors is essentially the same as for intrinsic semiconductors. It is desirable the represent in the same way the presence of the impurities atoms by impurity states. It is common to introduce into the forbidden band so-call donor (fig. 2.3(b)) or acceptor (fig. 2.4(b)) levels. The distance between the donor level and the conduction band represent the energy that it needed to transfer the extra electrons into the conduction band. The same is true for the acceptor level and valence band. It has to be emphasized that the introduction of these impurity levels does not mean that mobile electrons or hole are found in the forbidden band of silicon. The impurity states are only used as a convenient means to remind the reader of the presence of extra electrons or holes in the crystal.

2.1.6 p-n junction

By joining n-type and p-type together, coupled semiconductor is made with there doped differently on the opposite side of the junction. Free electrons on the n-side and free holes on the p-side can initially wander across the junction. When a free electron meets a free hole it cancels each other and vanish (shown in fig. 2.5). As a result, produce a depleted region of moving charges. This is called the depletion zone.

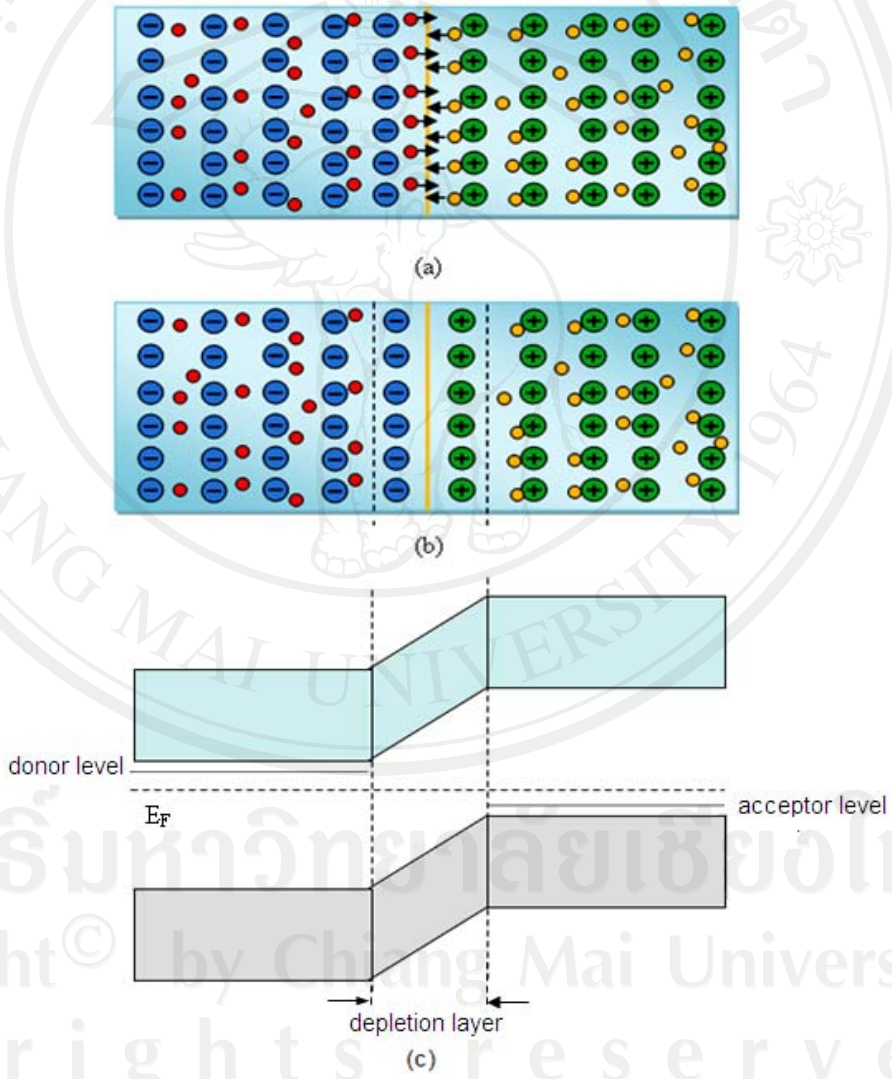
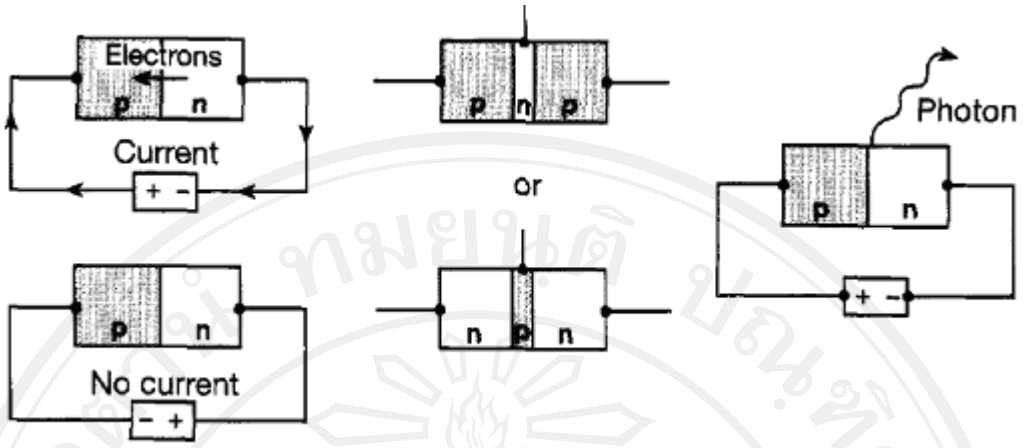


Fig. 2.5 Formation of the p-n junction which shows (a) holes and electrons diffuse across junction, (b) depletion layer, and (c) energy band diagram for a p-n junction at thermal equilibrium.

There are a lot of positive charges on the n-type side and a lot of negative charges on the p-type side. These exert a force on the free charge to drive it back to its original side of the junction. The acceptor and donor atoms cannot move around and the depletion zone has formed. A free charge now requires some extra energy to overcome the barrier (from the donor or acceptor atoms) to cross the zone. The energy required by the free holes and electrons can be supplied by a sufficient voltage between the ends of the p-n junction diode. This voltage must be supplied in the correct direction to push the charges across the barrier. However, if applied voltage is in wrong direction, it pulls free charges away from the junction.

Another complex junction arrangement is to have n-p-n or p-n-p junctions with a thin middle region. This is known as a transistor and has the property that the electric potential on the middle section can be used to control the flow of current through the device. As current flow through p-n junction, electrons frequently fall into holes and energy is released. In some materials this energy is large enough to emit visible photon. This is the basis of LEDs (light emitting diodes) which are used in the visual displays of many electronic devices. Conversely, if light shines onto the junction, electrons can be excited into the conduction band and these produces the holes. This lead to flow of current if an external circuit is connected. This is the mechanism of solar cells used for the generation of electricity. Examples of semiconductor devices were shown in fig. 2.6.



(a) (b) (c)

Fig. 2.6 Semiconductor devices e.g. (a) diode, (b) transistor, and (c) Light Emitting Diode (LEDs) [13].

2.1.7 Metal – semiconductor contact

Metal to semiconductor contact can behave either as a rectifying or as an ohmic contacts depending on the type of metal used.

(1) Rectifying contacts (Schottky barrier contacts)

When a metal and an *n*-type semiconductor are joined and the work function of metal is less than that of the semiconductor, i.e. $\Phi_M > \Phi_S$ (fig. 2.7(a)), electrons start to flow from the semiconductor "down" into the metal until the Fermi energies of both solids are equal (fig. 2.7(b)). As a consequence, the metal will be charged negatively and the potential barrier is form. This means that the energy bands in the bulk semiconductor are lower by the amount $\Phi_M - \Phi_S$.

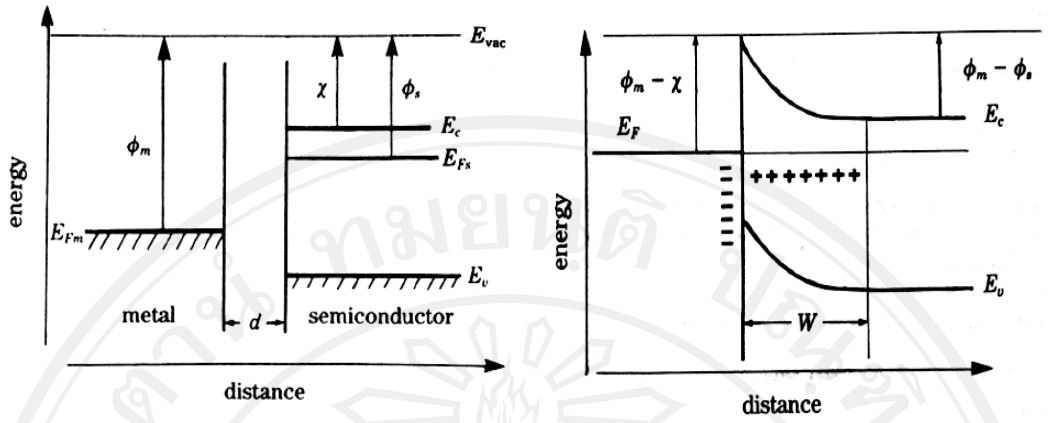


Fig. 2.7 Energy band of the metal and n-type semiconductor, $\Phi_M > \Phi_S$, (a) before and (b) after contact is made. [14]

In the equilibrium state, electron from both side cross the potential barrier. This electron flow calls diffusion current.

The potential barrier height for and electron diffusing from the semiconductor into the metal is $\Phi_M - \Phi_S$. This potential difference is called the contact potential. The height of the potential barrier from the metal side is $\Phi_M - \chi$, where χ is the electro affinity, measured from the bottom of conduction band to the ionization energy (vacuum level).

When a metal and an n-type semiconductor are connecting to a DC source, the net current that flows across the potential barrier can be estimated. At first, the metal is assumed to connect to the negative. The metal is charged even more negatively than without bias. Thus, the electrons in the semiconductor are repelled even more, depletion region becomes wider and the potential barrier is increased (fig 2.8 (a)). Further, the depletion layer becomes wider. Because both barriers are now relatively high, the diffusion current in both directions are negligible.

If the polarity of the battery is reverse, the potential barrier in semiconductor is reduced. The electrons are driven across the barrier and the results in a large net current from the semiconductor into the metal. The depletion layer is narrow (fig. 2.8 b). The voltage current characterization of rectifier is shown in figure 2.9 (a). Rectifiers of this type are used to convert alternating current into direct current.

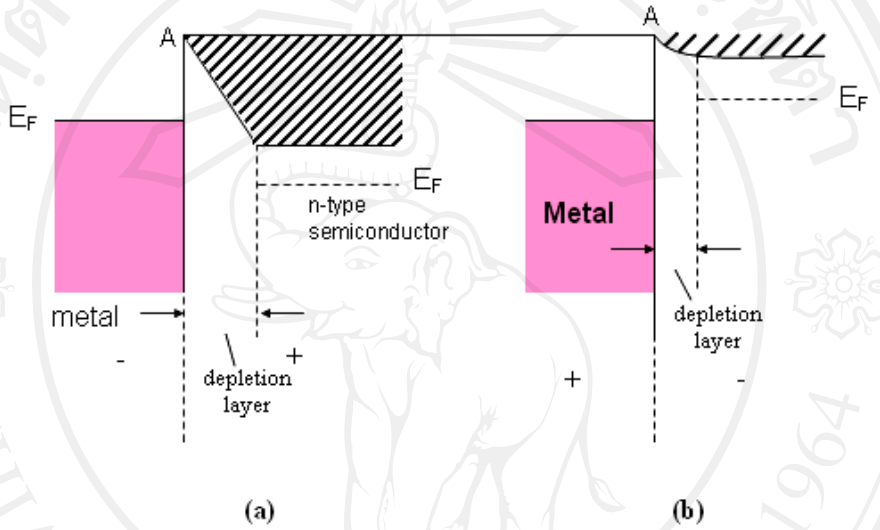


Fig. 2.8 Metal-semiconductor contact with two polarities: (a) reverse bias and (b) forward bias. The number of electron that flow in both directions and the net current is indicated by the range of the arrows. The potential barriers are marked by heavy lines [14].

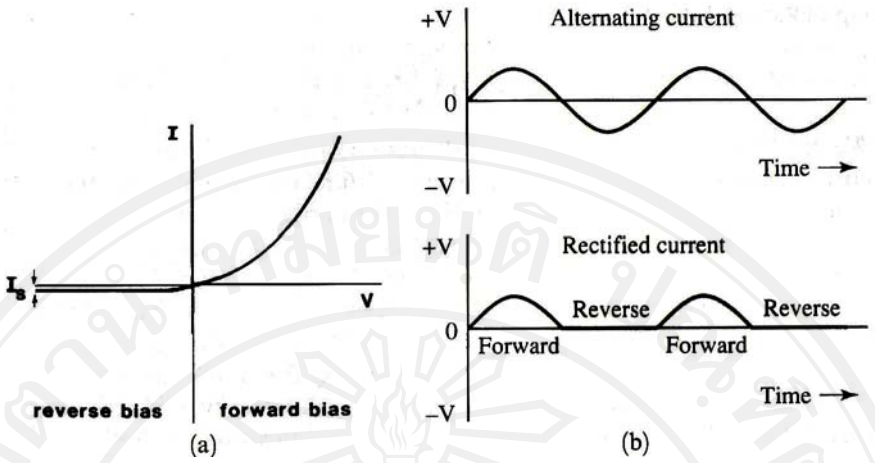


Fig. 2.9 (a) Characteristic of rectifier and (b) Voltage versus time curves to demonstrate behaviour of and alternating current and a current for which the negative voltage has been eliminated [14].

(2) Ohimic contacts (metallizations)

For the case where a metal is brought into contact with an n-type semiconductor which $\Phi_M < \Phi_S$ (shown in fig. 2.10.) the electrons now flow from the metal into the semiconductor, which charges the metal positively. The energy band of the semiconductor bends downward and no barrier exists for the flow of electrons in either direction. In other words, the configuration allows the injection of a current into and out the semiconductor without suffering a sizable power loss. The current increases linearly with increasing voltage and the systematic behaviour about the origin is as Ohm's law. Accordingly, this junction is called an ohmic contact. A similar situation exists for p-type semiconductor and $\Phi_M > \Phi_S$.

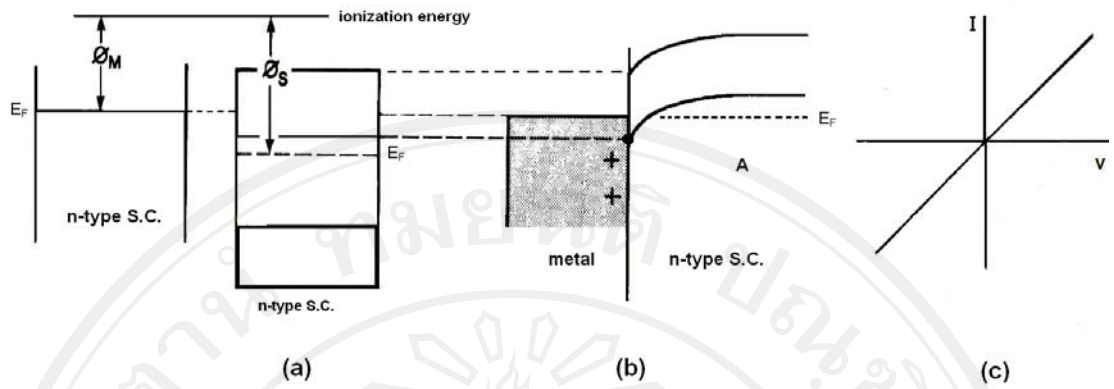


Fig. 2.10 (a) Ohmic contact between metal and n-type semiconductor ($\Phi_M < \Phi_S$), where metal and semiconductor are separated, (b) when metal and semiconductor are in the contact, and (c) the current voltage characteristic [14].

2.2 Optical properties of materials

The spectrum of electromagnetic wave covers wavelengths from thousands of meters down to the size of an atom. Visible light comprises only an extreme small segment of the entire spectrum, as depicted in fig. 2.11.

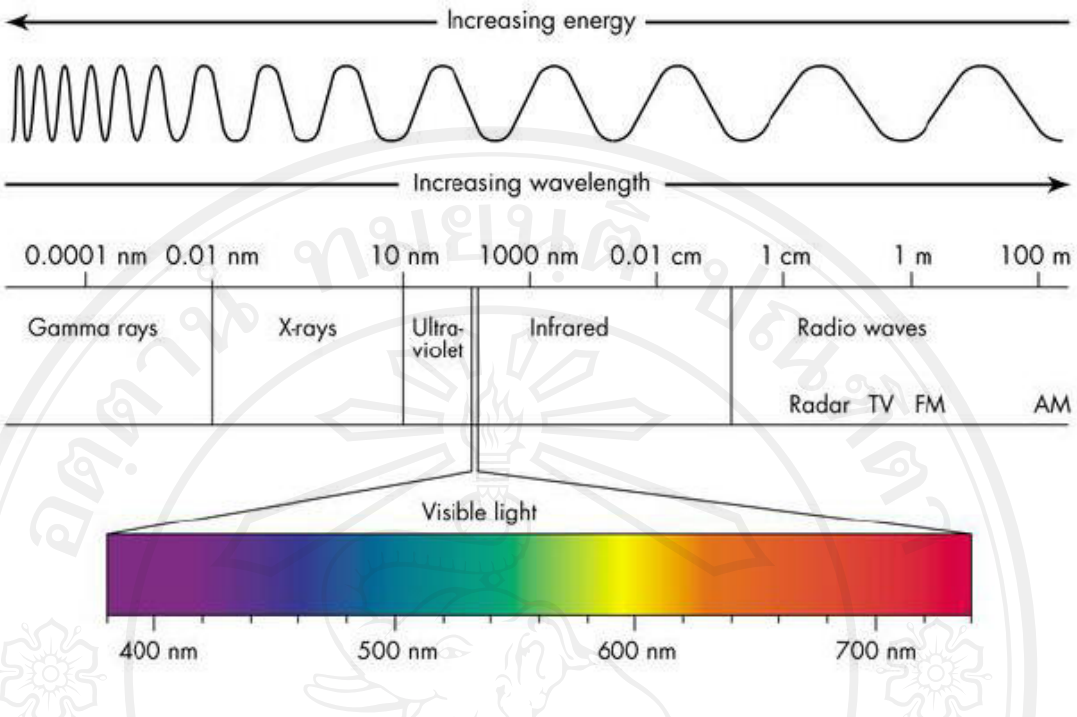


Fig. 2.11 The electromagnetic spectrum [15].

Base on Plank's famous hypothesis that a certain minimal energy of light at lease one light quantum, a phonon, is

$$E = h\nu, \qquad (2.6)$$

where E is the photon energy, h is Planck's constant and ν is the frequency of light given in the number of vibration per second or hertz (Hz).

When light passes into material medium, there are the optical processes occur such as reflection, absorption, transmission, refraction and emission (some shown in fig. 2.12.).

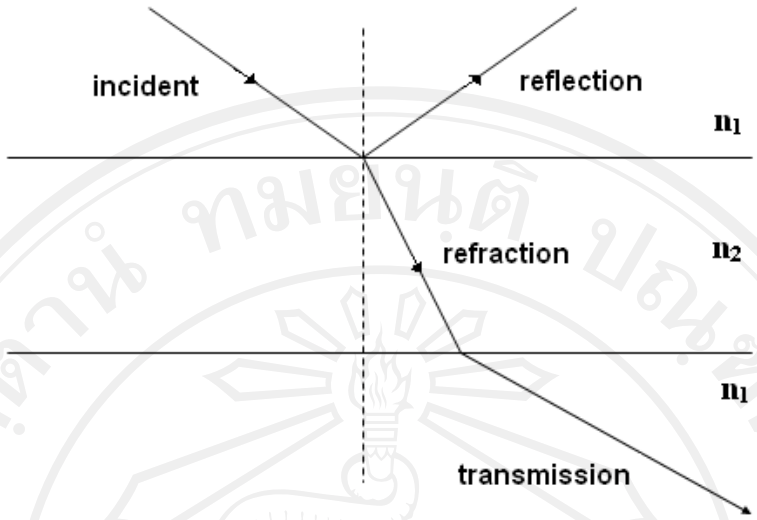


Fig. 2.12 Diagram of reflection, refraction and transmission of light (refractive index, $n_2 > n_1$).

2.2.1 Refraction

Whenever light waves propagate in a matter, their wavelength is decreased. The ratio of the speed of light in the vacuum to the observed materials is called the refractive index (n) of the medium. i.e.

$$n = c/v, \qquad (2.7)$$

where c is velocity of light in vacuum and v is velocity of light in medium.

2.2.2 Reflection

When light incident upon a surface it will in general be partially reflected and partially transmitted as a refracted ray. A light ray incident upon a reflective surface will be reflected at an angle equal to the incident angle. Both angles are typically measured with respect to the direction normal to the surface.

The ratio between reflected intensity I_R and the incoming intensity I_0 of the light serves as a definition for the reflectivity i.e.

$$R = I_R / I_0 \qquad (2.8)$$

In general, metals have large reflectivity. In contrast, for glass and many other dielectrics, light penetrates into much farther than into metals. Otherwise, very thin metal film (up to about 50 nm thickness) may allow some light to be transmitted.

The reflection losses encountered in optical instrument such as lenses can be reduced by coating the surfaces with a thin layer of dielectric material such as magnesium fluoride. This result is well known as blue hue on lenses for cameras.

2.2.3 Transmission

Quite similar to reflection, one defines the ratio between the transmitted intensity, I_T, and the impinging light intensity as the transmissivity e.g.

$$T = I_T / I_0 \qquad (2.9)$$

2.2.4 Absorption

Light passing through an optical system can be attenuated by absorption. The exponential law of absorption is the basic working relationship. The absorption of light by the medium is quantified by its absorption coefficient α via

$$I/I_0 = e^{-\alpha t} \text{ or } I = I_0 e^{-\alpha t} \qquad (2.10)$$

where I_0 is the incident light intensity, I is defined as the transmitted intensity through the material and t is thickness.

Absorption coefficient is high for metals but small for ceramics and polymers and it varies with wavelength. The absorption can be described in terms of the optical density (O.D.) which in also called the absorbance, i.e.

$$O.D. = - \log (I_T/I_0) \qquad (2.11)$$

Base on Eq. (2.11), this can be written in terms of α i.e.

$$O.D. = - \log (e^{-\alpha t}) = \alpha t \log e = 0.434\ \alpha t \qquad (2.12)$$

As can be seen, OD can be used as a characteristic property for filters but not very useful as a general characterization of a material because the value depends on thickness (t).

2.2.5 Scattering

Scattering is a general physical process where some forms of radiation, such as light, sound, or moving particles, are forced to deviate from a straight trajectory by one or more localized non-uniformities in the medium. The are many causes of scattering of light such as the residual porosity in ceramics materials, gain boundaries which have small variation in refractive index compared to the matrix, finely dispersed particles and boundaries between crystalline and amorphous regions in polymers.

2.2.6 Emission

An excited electron must revert back into a lower energy state. This occurs within a fraction of a second and this is accompanied by the emission of photon and/or the dispersion of heat. The emission of light due to reversion of electrons from a higher energy state is called luminescence. If the electron transition occurs within

nanoseconds or faster, this process is call fluorescence. In some materials, the emission takes place after microseconds or milliseconds. This process is referred to phosphorescence.

Photoluminescence is observed when the light impinges on a material which in turn re-emits light of lower energy. Electroluminescence materials emit light as a consequence of an applied voltage or electric field. Cathodoluminescence is the term used to describe light emission from a substance that has been showered by electron of higher energy.

In luminescent materials which contain a small amount of an impurity, this impurity is the key of to luminescence. There are essentially three steps in this process. First, a photon or electron is shot at the solid, and its energy is absorbed. This enables an electron of the solid to rise to the conduction band and a hole is created in valences band as well. Second, the electron wanders through the structure until it falls into a trap or luminescent center. These traps are produced by the impurity. The energy level traps lie between the more elevated conduction band and valence band. Finally, after a time the electron acquires enough energy to leave the trap and fall to valence band, giving rise to a photon of definite wavelength related to the ion producing the trap.

Phosphorescence occurs when materials have deep traps. Therefore it takes more time for the trapped electrons to receive enough energy to escape. As a consequence, they are liberated over a longer period.

2.3 Transparent conducting oxide films

Transparent conducting oxides (TCO) are materials which have high conductivity and high optical transmittance. They have optical and optoelectronic applications such as a transparent conducting electrode in flat-panel displays (FPDs), organic light-emitting diodes (OLEDs) and solar cells. Highly conductive materials not normally transmit visible light, while highly transparent media like oxide glasses behave as insulators.

Semiconductor thin films are the consideration for reduce optical scattering and reflection losses at the interfaces. A quantitative measure of performance of a TCO can be written in terms of the ratio of the electrical conductivity (σ) to the optical absorption coefficient (α) or [16],

$$\sigma/\alpha = 1/ [R_s \ln(T+R)] \quad \text{.....(2.13)}$$

where, T and R are transmittance and reflectance of the material, and R_s is the sheet resistance (= resistivity / film thickness).

The first TCO material occurred a century ago when a thin film of sputter deposited cadmium metal underwent incomplete thermal oxidation upon post-deposition heating in air [17]. This show n-type electrical conductivity provided that electrons can be promoted to the conduction band of the metal oxide from defect energy levels lying close to the conduction band. Since this early discovery, appreciable values of electrical conductivity have been observed in many single, binary, ternary and quaternary metal oxide systems.

Recently, p-type conductivity has been reported in certain metal oxide systems where the defect energy levels lie approximately equal to the valence band of the

metal oxide [18]. In such materials, electron promotion to these defect levels creates holes in the valence band thereby promoting conductivity. Again, good transmission in the visible region of the spectrum can be achieved but measured conductivities are considerably smaller than those exhibited by the n-type materials.

2.4 Photocatalytic activity of semiconductor

Semiconductors are usually selected as photocatalysts, because they have a narrow gap between the valence and conduction bands. In order for photocatalysis to proceed, the semiconductors need to absorb energy equal to or more than its energy gap. This generates a positive hole in the valance band due to loss of an electron and a lone pair of electron and the conduction band gains an electron. In electrical conducting materials, such as metal, the produced charge carriers are immediately recombined. In semiconductor, electron hole pairs diffuse to the surface of catalytic particle. These highly unstable hole (h^+) and electron (e^-) have strong oxidation and reduction powers and converts water and oxygen into reactive oxygen species, depicted in equation 2.14 [19].

$$\left.\begin{array}{l} \text{Semiconductor photocatalyst } (ZnO, TiO_2) \xrightarrow{\text{Sunlight}} h^+ (VB) + e^- (CB) \\ H_2O + h^+ \longrightarrow OH^- + H^+ \\ O_2 + e^- \longrightarrow O_2^- \\ OH^- + h^+ \longrightarrow HO^\bullet \\ OH^\bullet + \text{Organics} \longrightarrow H_2O, CO_2, \text{etc.} \end{array}\right\} \quad (2.14)$$

Positive holes (h^+) that cause oxidative reaction have very strong oxidative power. They directly oxidize water and produce a highly reactive hydroxyl radical [$OH^\bullet$]. In some cases, they directly oxidize organic matter attached to the surface. Under some conditions, organic compounds can react directly with the positive holes, resulting in oxidative decomposition.

Electrons transfer to adsorbed oxygen and forms superoxide anions (O_2^-). In many cases, this transfer is also associated with photocatalytic reduction. The Superoxide anions attach to the intermediate product in the oxidative reaction, form peroxide or change to hydrogen peroxide and then to water.

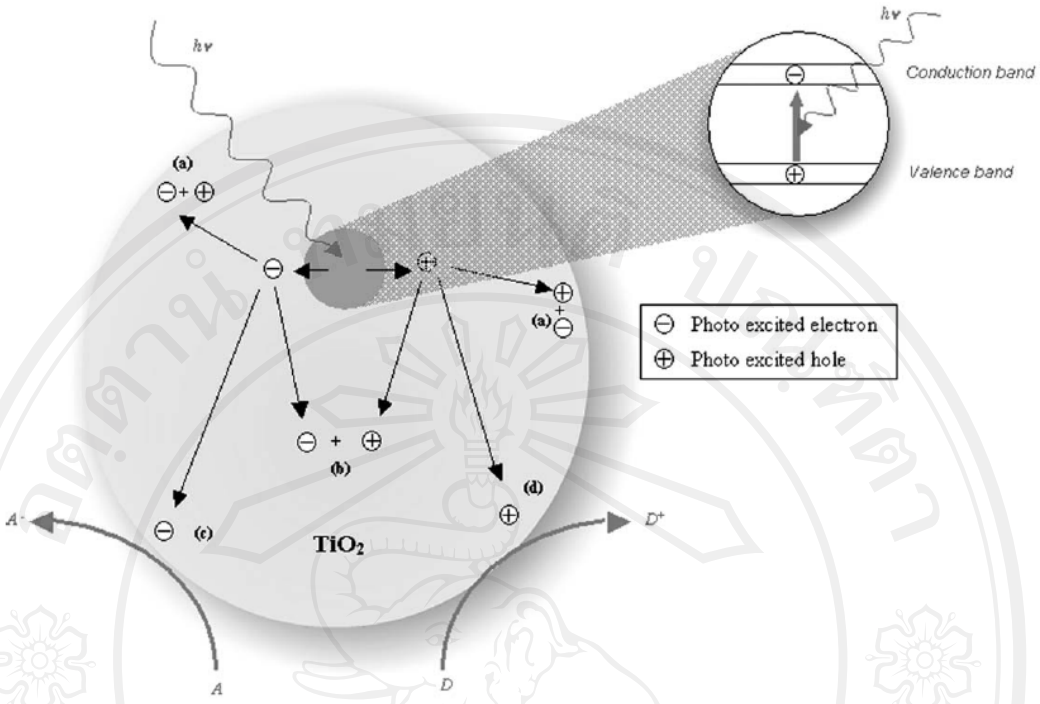


Fig. 2.13 Upon irradiation of semiconductor photocatalyst by ultra band gap light, the semiconductor undergoes photo-excitation. The electron and the hole can result one of several pathways: (a) electron–hole recombination on the surface; (b) electron–hole recombination in the bulk reaction of the semiconductor; (c) electron acceptor A reduction by photogenerated electrons; and (d) electron donor D is oxidation by photogenerated holes. [20]

The energy of a semiconductor's band gap is equal to the difference in energy between the conduction band edge and the valence band edge. Knowledge of band edge positions is useful when synthesizing and analyzing semiconductor photocatalysts. For example, if the oxidation of an organic compound is desired by the photocatalyst, then the valence band edge of the semiconductor must be positioned favorably relative to the oxidation potential of the organic compound. On the other

hand, if the reduction of a molecule such as O_2 is required, then the conduction band edge of the semiconductor must be positioned favorably relative to the reduction potential of the O_2 molecule. The band gaps of most semiconductors are well known; however, the respective energy levels of the valence (E_v) and conduction bands (E_c) have not been accurately determined for many of these semiconductors. For those semiconductors, the values of E_v and E_c can be determined by a simple relationship if a semiconductor's band gap (E_g, units of eV) and absolute electronegativity ($-\chi$, units of eV) are known. The absolute electronegativity is essentially Fermi level of a pristine semiconductor [21]. Therefore, Ec and Ev can be defined as

$$E_C = -\chi + 0.5 \bullet E_g, \qquad (2.15)$$

$$E_V = -\chi - 0.5 \bullet E_g, \qquad (2.16)$$

Figure 2.14 shows the band-edge positions of several dominant photocatalysts in relation to the oxidation and reduction potentials of H_2O. It should be noted that, although the bulk electronic structure of the semiconductor photocatalysts changes only faintly with pressure and temperature, the pH of the electrolyte used during the study has a direct effect on the flatband potential, flatband potential (at the semiconductor and solution interface) is a certain potential which the Fermi energy (of semiconductor) lies at the same energy as the solution redox potential so there is no net transfer of charge, and therefore proportionally on the band-edge positions. As a result, the potentials shown in fig. 2.14 can vary slightly.

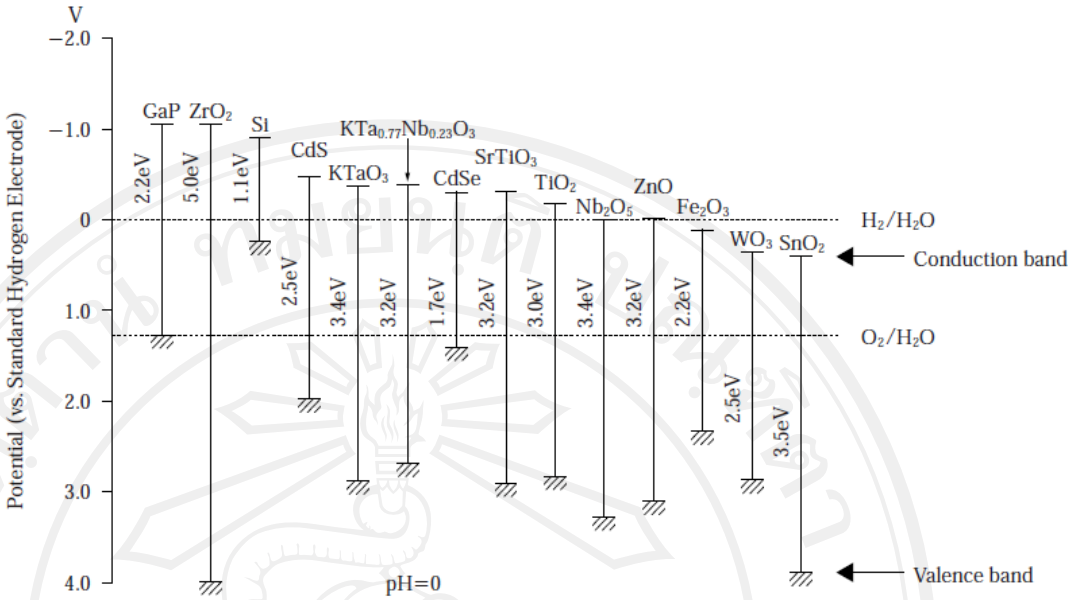


Fig. 2.14 Energy structures of various photosemiconductors. [22]

Figure 2.14 show energy structure of semiconductor in pH = 0 solution. Therefore a unique feature of metal oxide semiconductors, such as TiO_2, SnO_2, ZrO_2, and ZnO, is the dependence of conduction band edge position on the pH of the solution according to the Nernst-like equation [23]:

$$E_{cb}\ (pH) = E_{cb}\ (pH\ 0) - 0.059 \bullet pH \quad \ldots\ldots\ldots\ldots\ (2.17)$$

2.4.1 Definition of pH

The pH unit were used for measures the degree of acidity or basicity of a solution. To be more exact, pH is the measurement of the hydrogen ion concentration, $[H^+]$. Every aqueous solution can be measured to determine its pH value. This value ranges from 0 to 14 pH. Values below 7, pH exhibit acidic properties, and values above 7 pH exhibit basic properties. Since pH=7 is the center of the measurement

scale, it is neither acidic nor basic and is, therefore, called "neutral."

pH is defined as the negative logarithm of the hydrogen ion concentration. It is expressed mathematically as

$$pH = -\log [H^+] \quad \ldots\ldots\ldots\ldots\ldots \quad (2.18)$$

where: $[H^+]$ is hydrogen ion concentration in mol/L.

The pH value is an expression of the ratio of $[H^+]$ to $[OH^-]$ (hydroxide ion concentration). Hence, if the $[H^+]$ is greater than $[OH^-]$, the solution is acidic. Conversely, if the $[OH^-]$ is greater than the $[H^+]$, the solution is basic. At 7 pH, the ratio of $[H^+]$ to $[OH^-]$ is equal and, therefore, the solution is neutral.

When pH = 0, the $[H^+]$ = 1 mol/L.

$$pH = -\log (1 \times 10^0)$$

$$= 0$$

When determining the pH of a solution, even though the hydrogen ion concentration is being measured, the hydroxide ion concentration can be calculated:

$$[H^+][OH^-] = 10^{-14} \quad (2.19)$$

At pH =0 hydrogen ion concentration is 1 mol/L and hydroxide ion concentration ion is 10^{-14} mol/L.

Obviously electron and hole recombination is detrimental to the efficiency of a semiconductor photocatalyst. Modifications to semiconductor surfaces such as addition of metals, dopants, or combinations with other semiconductors are beneficial in decreasing the electron and hole recombination rate and thereby increasing the yield of the photocatalytic process.

2.4.2 Metal doping semiconductor photocatalyst

Some good conducting metals, such as silver, gold and copper, were added to semiconductor photocatalyst to inhibit the recombination of carriers and improve the photocatalytic efficiency. For example, incorporate gold as a support to titanium dioxide powder. As the surfaces of photocatalytic particles are allowed to carry gold metal as a support (shown in fig. 2.15), higher photocatalytic action is achieved. When a photocatalyst is exposed to ultraviolet rays, electrons and positive holes are produced and generate catalytic action. However electrons and positive holes can recombine very easily. When photocatalytic particles are allowed to carry gold, electrons are drawn to the gold (shown in fig. 2.16). This inhibits the recombination of electrons and holes, thereby ensuring the stable formation for emitting radicals more effectively than a photocatalyst without gold.

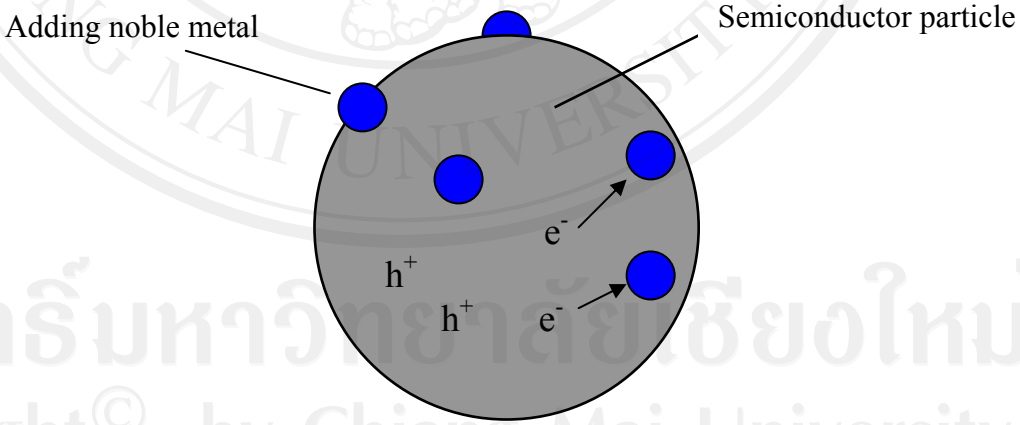


Fig. 2.15 Semiconductor photocatalyst particle with adding noble metal for trapped electron.

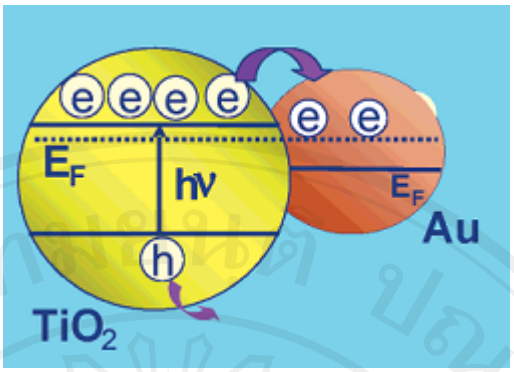


Fig. 2.16 Design of semiconductor-metal nanocomposites using couple geometry [24].

2.4.3 Coupled semiconductor photocatalyst

The composite of nano-semiconductor is an alternative way to improve the photocatalytic efficiency. The coupling of two semiconductors (possessing different energy levels for their corresponding conduction and valence bands) allows the vectorial displacement of holes and electrons from one semiconductor to another and retards the recombination of the electron-hole pairs.

For example, in ZnO-TiO_2 composite, when the ZnO-TiO_2 film absorbs photons with energy higher than the energy gap, electrons are excited from valence band to the conduction band of ZnO and TiO_2 (shown in fig. 2.17), leading to the generation of electron hole pairs. The electrons transfer from the conduction band of TiO_2 to the conduction band of ZnO, and conversely, the holes transfer from the valence band of ZnO to the valence band of TiO_2 giving rise to the decrease in the pairs' recombination rate.

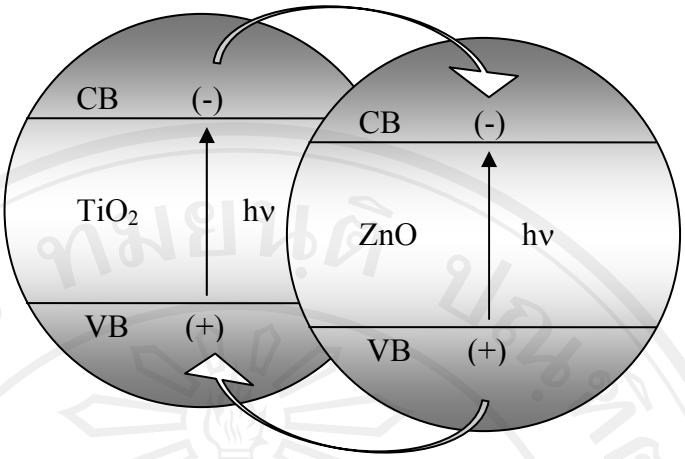


Fig. 2.17 The proposed mechanism of photocatalytic ZnO-TiO_2 composite.

2.5 Solar irradiation on earth

Solar radiation is an essential source of energy for life on Earth. The amount of solar radiation arriving at the top of the Earth's atmosphere is called the solar constant, G_{sc} = 1367 W/m^2 [25]. This amount can be readily derived from an energy balance between concentric spheres (i.e., outer edge of the sun and a sphere encompassing the Earth's orbit). The spectral distribution, as shown in fig. 2.18, of this extraterrestrial irradiation (outside of the Earth's atmosphere).

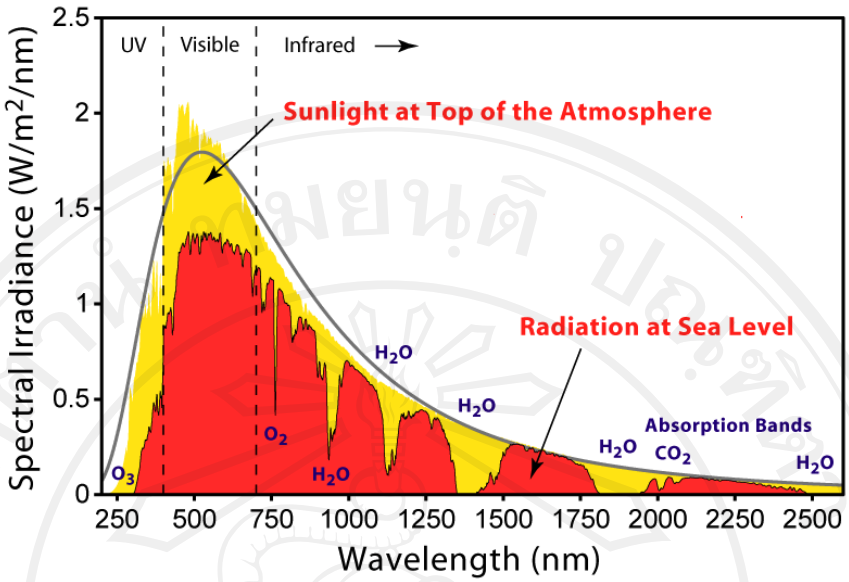


Fig. 2.18 The solar radiation spectrum for direct light at both the top of the Earth's atmosphere and at sea level [26]. These curves are based on the American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra, which are standards adopted by the photovoltaics industry to ensure consistent test conditions and are similar to the light that could be expected in North America. Regions for ultraviolet, visible and infrared light are indicated.

The solar constant represents the energy flux (per unit surface area) in the direction of the incoming radiation from the sun. However, the radiation component actually passing through the top of the atmosphere, G_o, is the component normal to the relevant surface. In other words, G_{sc} must be multiplied by cos θ ; where θ refers to the angle between the incident radiation and the tangent to the top surface of the atmosphere, as shown in fig. 2.19. This can be envisioned by a plate of an area of 1 m^2 held at the top of the atmosphere. In this case, the plate is nearly parallel to the sun's incoming radiation near the north and south poles of the Earth, and thus cos θ ~

0 correctly yields little or no heat passing downwards through the atmosphere there. On the other hand, near the equator, cos θ ~1 and the full amount of solar radiation pass through the top of the atmosphere.

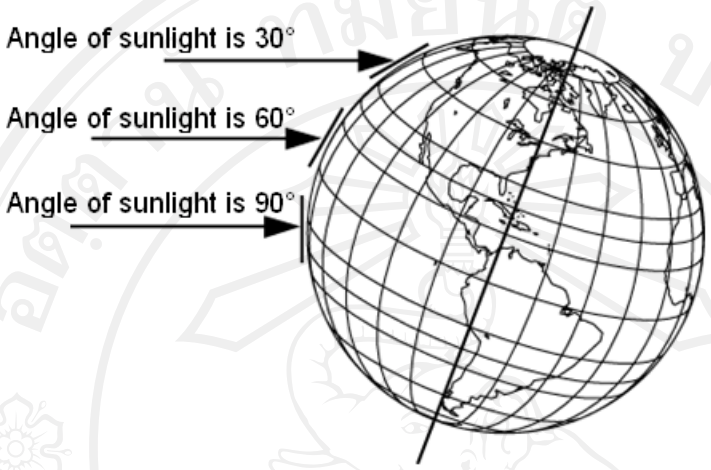


Fig. 2.19 Angle of the sunlight [27].

The dependence of radiation on time of year is a simple equation is given by equation 2.20a, as provides a more accurate equation in the form of equation 2.20b.

$$G_{on} = \begin{cases} G_{sc}\left(1+0.033\cos\dfrac{360n}{365}\right) & \text{(2.20a) [28]} \\ G_{sc}\left(\begin{matrix}1.000110+0.034221\cos B+0.00128\sin B+0.000719\cos 2B \\ +0.000077\sin 2B\end{matrix}\right) & \text{(2.20b) [29]} \end{cases}$$

where G_{on} is the extraterrestrial radiation incident on the plane normal to the radiation on the n^{th} day of the year and B is given by

$$B = (n-1)\frac{360}{365} \qquad (2.21)$$

In free space (i.e., evacuated space outside of the atmosphere), the intensity of emitted radiation, I_λ, from the sun remains constant in a particular path of travel since little or no scattering or absorption of radiation occurs there. However, once the radiation passes through the top of the atmosphere, absorption and scattering of radiation by dust particles, moisture, etc. reduces the radiant intensity with distance traveled. If 100% of the incident radiation arrives at the top of the atmosphere, the remaining parts of the radiation are distributed as follows:

- 1- 6% is scattered back to space.
- 11-23% is absorbed by the atmosphere (i.e., gases such as O_3, O_2, H_2O, CO_2, dust, and aerosols).
- 5- 15% is diffuse (scattered throughout the sky and arriving on the surface of the Earth).
- 56-83% is radiation arriving directly on the Earth's surface.

2.6 Zinc Oxide (ZnO)

Zinc oxide (ZnO) is a chemical compound with hexagonal crystals (shown in fig.2.20). It is nearly insoluble in water but soluble in acids or alkalis. The close-packed (0001) planes are made up of two subplanes, each consisting of the cationic (Zn) and the anionic (O) species, respectively. Such that each Zn ion is surrounded by a tetrahedra of O ions, and vice-versa. This tetrahedral coordination gives rise to polar symmetry along the hexagonal axis. This polarity is responsible for a number of the properties of ZnO, including its piezoelectricity and spontaneous polarization, and is

also a key factor in crystal growth, etching and defect generation. ZnO decomposes into zinc vapor and oxygen at around 1975 °C. High-quality single-crystalline ZnO is almost transparent. Zinc oxide occurs in nature as the mineral zincite.

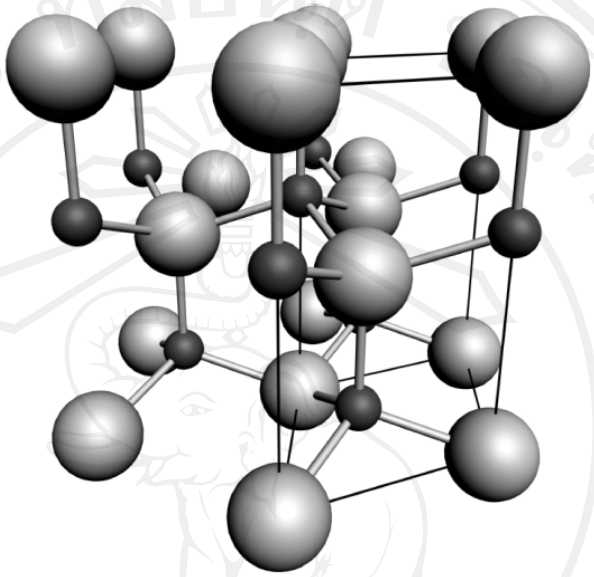


Fig. 2.20 The hexagonal wurtzite structure of ZnO. O atoms are shown as large white spheres, Zn atoms as smaller black spheres. One unit cell is outlined for clarity. [30].

ZnO can be doped to both p-type and n-type semiconductor. N-type doped films are often used in thin film technology. N-type doping is possible by introduction of aluminum, gallium, indium, silver and gold [31-33]. On the other hand, p-type can be doped using nitrogen, lithium, antimony, phosphorous and arsenic [34-37].

Some important physical properties of bulk ZnO can be detailed as the following: [13]

1. Appearance white solid
2. Crystal structure hexagonal

3. Melting point	1975 °C
4. Lattice constants at 300K (nm)	a = 0.32495
	c = 0.52069
5. Thermal expansion coefficient($10^{-6}K^{-1}$)	a = 6.5
	c = 3.02
6. Thermal conductivity (cal/cm/K)	0.006
7. Heat Capacity (cal/g)	0.125
8. Density at 300K (g cm^{-3})	5.606
9. Bandgap (eV) at 300K	3.37
10. Exciton binding energy (meV)	60
11. Molecular Mass	81.4
12. Shear Modulus (Gpa)	45.5

ZnO thin films are a multifunctional material that is used as polycrystalline material industrialized as transparent conductive oxide. Also, the piezoelectric properties of crystalline material are employed in surface acoustic wave devices. Moreover, it can be used in thin film solar cells and flat panel displays. It is used as a pigment in paints and also used in coatings for paper. Moreover, it has a common application in gas sensors.

2.7 Titanium Dioxide

Titanium dioxide is one of the basic materials in everyday life. It has been widely used as cosmetic products, food stuffs and white pigment in paint**.** TiO_2 exists in three crystalline modification: rutile, anatase and brookite. Titanium dioxide is

semiconducting material with can be chemically activated by light. It is also a potent photocatalyst that can break down almost any organic compound when exposed to sunlight.

Titanium dioxide is commercially available in two crystal structures: anatase and rutile (shown in fig. 2.21). Rutile has density if 4.2 g/cm^3 while anatase has density of 3.9 g/cm^3. Rutile possesses a more compact atomic structure which provides a higher refractive index and stability than anatase. However, the TiO_2 used in industrial products is almost exclusively from anatase type because it is less expensive. Anatase is a typical n-type semiconductor and requires about 3.20 eV to be an electrical conductor. Throughout the years, anatase has been the popular choice as semiconductor photocatalyst in research efforts, due to its non-toxicity and high photo-activity.

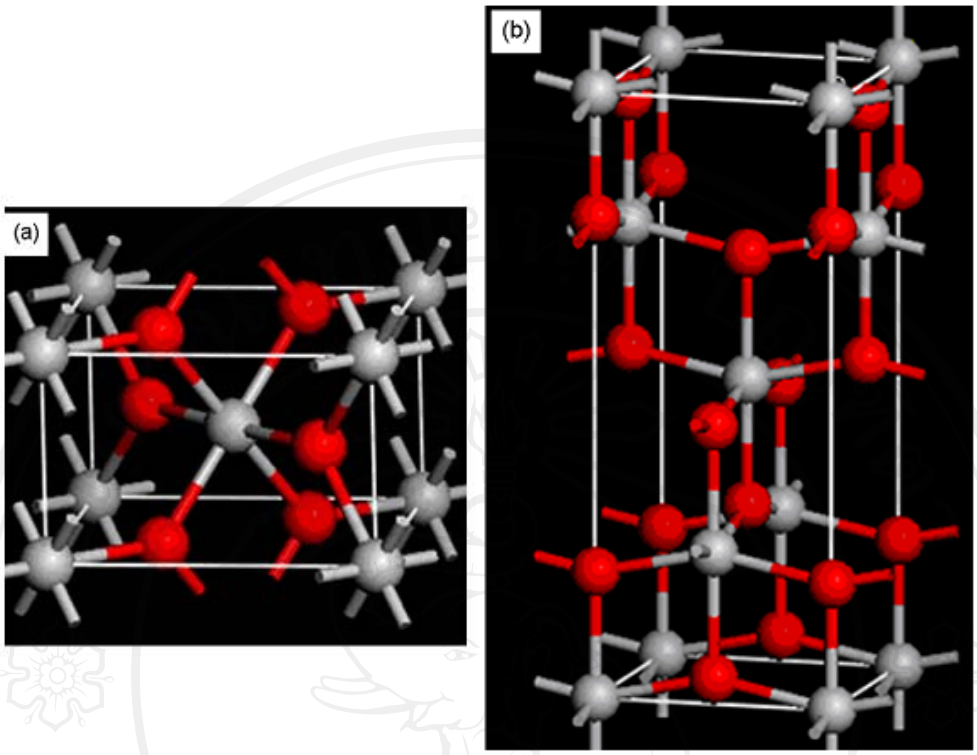


Fig. 2.21 Unit cell of (a) rutile and (b) anatase phase of TiO_2. The red circles are titanium and the white circles are oxygen. Both forms are tetragonal with lattice constants a and c of 0.4594 nm and 0.2958 nm for rutile and 0.3785 nm and 0.9514 nm for anatase. **[**38**]**

2.8 Surface tension (γ)

Surface tension is an attractive property of the surface of a liquid. It is caused by the attraction between the liquid's molecules by various intermolecular forces. In the bulk of the liquid, each molecule is pulled equally in all directions by neighbouring liquid molecules, resulting in a net force of zero. At the surface of the liquid, the molecules are pulled inwards by other molecules deeper inside the liquid and are not attracted as intensely by the molecules in the neighbouring medium

(vacuum, air or another liquid). Therefore, they exhibit stronger attractive forces upon their nearest neighbours on the surface. This enhancement of the intermolecular attractive forces at the surface is called surface tension (shown in fig. 2.22).

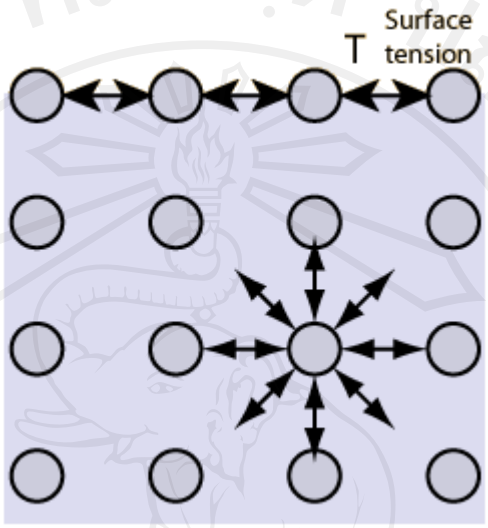


Fig. 2.22 Diagram of force on molecules of liquid. [39]

Surface tension has the dimension of force per unit length or of energy per unit area. The two are equivalent, but when referring to energy per unit of area, always use the term surface energy. In materials science, surface tension is used for either surface stress or surface free energy.

2.8.1 Influence of temperature

Surface tension is dependent on temperature. For that reason, when a value is given for the surface tension of an interface, temperature must be explicitly stated. The general trend is that surface tension decreases with the increase of temperature, reaching a value of 0 at the critical temperature [40]. There are only empirical equations to relate surface tension and temperature

2.8.2 Influence of solute concentration

Solutes can have different effects on surface tension depending on their structure.

- No effect, for example sugar
- Increase of surface tension, inorganic salts
- Decrease surface tension progressively, alcohols
- Decrease surface tension and once a minimum is reached, no more effect, surfactants

2.8.3 Influence of particle size on vapour pressure

Because of surface tension, the vapor pressure for small droplets of liquid in suspension is greater than standard vapor pressure of that same liquid when the interface is flat. That is to say that when a liquid is forming small droplets, the equilibrium concentration of its vapor in its surroundings is greater. This arises because the pressure inside the droplet is greater than outside. [41]

2.9 Enhance field factor (β)

The enhance field factor is a parameter which estimates the electric field intensity near the tip of an emitter. The value of the field enhancement factor depends on the geometry of the emitter and the anode-cathode spacing. The emitters always have a cylindrical or the conical configuration. Typically, the latter could be described by geometrical parameters, such as the length (L), radius of the tip (r), and angle of the cone (Θ), schematically shown in fig. 2.23.

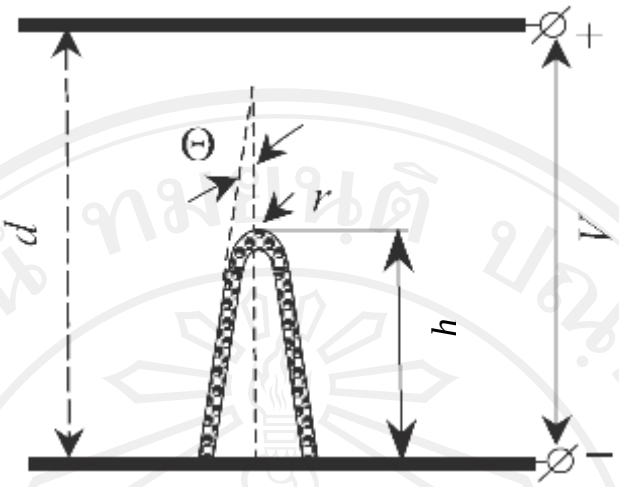


Fig. 4.23 Geometry of an individual emitter in diode system. L height of emitter; r radius of curvature; Θ-tip semi-angle for cone form. [42]

For the conical tip metal emitter, the enhance field factor was shown by Charbonnier [43]

$$\beta \cong \frac{1.4}{r^{\frac{2}{3}}(d-h)^{\frac{1}{3}}(\tan\Theta)^{0.2}(d/h)^{0.5}} \qquad [2.20]$$

where d-tip-anode distance, h-height of the emitter cone, Θ- half-angle at the cone apex.

From the equation, β increase when Θ decrease so the electric field near the sharp tip is larger than the dull tip (Θ of sharp tip is smaller than dull tip). Therefore, the shape tip produces the smaller nanoparticle than the dull tip.

2.10 Literature review

Guha et al. (1998) [44] fabricated ZnO thin films by Metal-organic chemical vapor deposition (MOCVD) method. The ZnO films were deposited on the substrate using Zn source such as $Zn(C_2H_5)_2$ and O_2 gas as source gases and Ar was used as a carrier gas. MOCVD is widely employed to achieve high-quality epilayers of various semiconductor materials but it is expensive than the sparking process.

Kim et al. (2003) [45] reported ZnO film prepared by spin coating process. A typical process involves depositing a small puddle of a dissolving zinc acetate dihydrate ($Zn(CH_3CO_2)_2$ $2H_2O$) into anhydrous ethanol onto the centre of a substrate and then spinning the substrate at high speed (typically around 3000 rpm). Centripetal acceleration will cause most of the solution to spread to, and eventually off, the edge of the substrate, leaving a thin film of solution on the surface. Spin coating process offers a simple and low-cost but it hardly produce very thin film and control film thickness. On the other hand, like sparking process allow to produce a very thin film by control the sparking time.

Gui et al. (2003) [46] investigated titanium oxide (TiO_2)-doped zinc oxide (ZnO) thick film. The paste of mixed powder of Zn nanoparticles with content of 1, 5, and 10 wt% commercial TiO_2 (99.9% purity) were formed by adding suitable amount distilled water and then to be coated on Al_2O_3 tubes on which Pt electrode wires had been fixed at each end. The thick film element and the remainder of the paste were both sintered at 650 °C for 2 h, and TiO_2-doped ZnO thick film were obtained. The films consist of ZnO, Zn_2TiO_4 and TiO_2. The sintering method is simple way to produced thick film or rod and needle-like structure.

Kim et al. (2007) [47] produced heterojunction films composed of ZnO and TiO_2 layers for improve photoelectrocatalytic properties. TiO_2 powder was prepared by precipitation of titanium isopropoxide in de-ionized (DI) water ZnO powder was synthesized via hydrothermal process after stirring zinc acetate solution with KOH. Slurries for film deposition were prepared by mixing TiO_2 or ZnO nanoparticles. ZnO and TiO_2 colloids were coated on the substrates by using a spin-coater. For the thin ZnO layers on the TiO2 films, the photocurrent and the resulting photoelectrocatalytic properties decreased as the thickness of the thin layer increased.

Vaezi (2008) [48] reported ZnO/TiO_2 nano-composite by two step solochemical synthesis. The zinc solution was prepared by mixing concentrated NH_4OH with $ZnCl_2$ until white $Zn(OH)_2$ was precipitated. TiO_2 powder was produced by dissolving an alkoxide together with a polyhydroxy alcohol and a chelating agent, such as citric acid. Two prepared sols were mixed in an appropriate ratio to obtain the nano-composite with 50 mol% of Zn and 50 mol% of Ti. The nano-composite thin films were prepared by depositing the mixture of two sols of zinc and titanium by the dip-coating method. The films consist of ZnO, Rutile and Anatase TiO_2. The two step solochemical synthesis, so-gel and dip coating, is more inexpensive way to synthesis ZnO/TiO_2 film than sparking process but it must used hazardous solution in the process and the film porous is less than sparking film.

Wang et al. (2008) [49] prepared nanoparticle zinc-titanium oxide materials by the aerogel approach. Zinc acetate and titanium butoxide were used as precursors and dissolved in ethanol. The Pyrex glass liner containing the solution was then placed into a 316 stainless steel autoclave, and heating commenced till the temperature and pressure reached supercritical points (normally peak condition at 265 °C and 110 bar)

with respect to ethanol. Then the reactor began to depressurize to ambient, the heating stopped, and a purge flow of nitrogen gas through the vessel and pipeline followed. The surface area is a function of Zn/Ti mole ratio, the Zn/Ti = 0.7 aerogel has the largest surface area around 210.4 m^2g^{-1} and the lowest packing density of 0.080 g cm^{-1}. The powders consist of ZnO, TiO_2, Zn_2TiO_3 and $Zn_2Ti_3O_8$. This technique is convenient to control Zn/Ti ratio.