CHAPTER II

THEORY

2.1 Polyimides

2.1.1 Synthesis of Polyimides

The two-step poly(amic acid) process is the most commonly practiced procedure of making polyimides. In this process, dianhydride and diamine react at ambient temperature in a dipolar aprotic solvent such as N-methyl- 2-pyrrolidinone (NMP) or N,Ndimethylacetamide (DMAc) to form a poly(amic acid), which is then cyclized into the polyimide product.

2.1.1.1 Formation of poly(amic acid)s

When a diamine and a dianhydride are mixed in a dipolar aprotic solvent such as N,N-dimethylacetamide, poly(amic acid) is rapidly formed at ambient temperatures. The reaction mechanism involves the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group, followed by the opening of the anhydride ring to form amic acid group as illustrated in Figure 2.1.
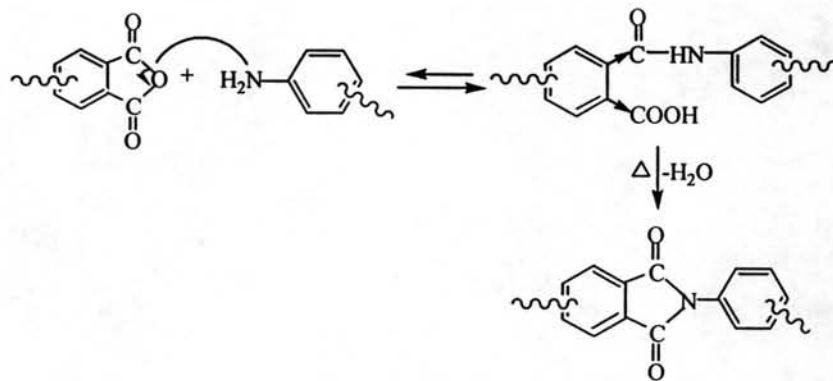

Figure 2.1 Reaction mechanism of imide formation [1]

2.1.1.2 Thermal Imidization of Poly(amic acid)

The most common conversion method of poly(amic acid)s to the corresponding polyimides is thermal curing. The two step method is suitable for preparation of thin objects such as films, coatings, fibers, and powders in order to allow the diffusion of by-product and solvent without forming voids in the final polyimide products. The suitable curing temperature should be between 250-350°C, depending upon the stability and glass transition temperature (T_g) of each polyimides. In stead of rapidly increasing temperature which may cause bubbles, the temperature should be raised slowly to prevent bubble forming in the sample. In the subsequent heating, imidization reaction takes place not in a true solid state but rather in a very concentrated viscous solution, at least during the initial and the intermediate stages of thermal imidization.[1]

2.1.2 Fluorinated Polyimides for opto-electronic application

Adding fluorine atoms in polyimide can improve several properties such as radiation durability against UV light, transparency in the visible and NIR regions, lower the glass transition temperature and increase in thermal expansion coefficient. Therefore fluorinated polyimide are expected to be used as optical polymers.[1] Especially, fluorinated polyimides from 6FDA exhibit good optical properties due to the introduction of a hexafluoroisopropylidene group into the polyimide unit which greatly improves the optical transparency of polyimides.

2.2 Zinc oxide (ZnO)

ZnO is a semiconductor compound with a wide band gap of 3.44 eV [10] The bandgap of ZnO can be tuned via divalent substitution on the cation site. It has attracted much attention as promising candidates for future developmental technology. It is a useful material with many applications in various fields such as solar cells, transparent electrodes, gas sensors, transducers and blue/UV light emitting devices. The large ZnO exciton binding energy of 60 meV give it a very high potential for room temperature light emission[11,12].

The hexagonal (wurtzite) crystal structure is a general type of ZnO with a = 3.25 Å and c = 5.205 Å as shown in figure 2.2. The Zn atoms are tetrahedrally coordinated to four O atoms, where the Zn d-electrons hybridize with the O p-electrons. The wurtzite structure family has a few important members such as ZnO, GaN, AlN, ZnS, 6H-SiC and CdSe. ZnO shows various physical properties which are listed in Table 2.1.
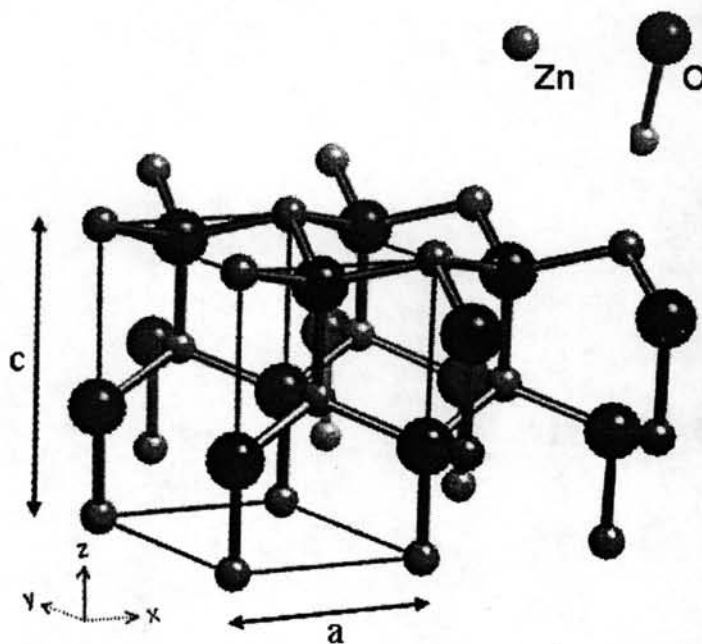
Figure 2.2 Crystal structure of zinc oxide [13]

Table 2.1 The physical properties of zinc oxide [*14*]

Properties	
Molecular mass	81.389
Melting point (K)	2250
Color	white
Specific gravity at room temperature (g/cm^3)	5.642
Lattice constants at room temp	a=3.250, c=5.205
Electron mass	0.28
Bandgap energy at room temp (eV)	3.44
Exciton binding energy (meV)	60
Density (g/cm^3)	5.606
Specific heat (cal/gm)	0.125
Thermal conductivity (cal/cm/K)	0.006
Thermoelectric constant at 573 K (mV/K)	1200
Coefficient of expansion (x10^{-6}/°C)	4
Point group	6mm (Wurtzite)
Crystal structure	hexagonal, wurtzite

2.3 The Electromagnetic Spectrum

The electromagnetic spectrum is the range of all possible electromagnetic radiation. When white light is shone through a prism, it is separated out into all the colors of the rainbow which are violet, blue, cyan, green, yellow, orange and red. This is the visible spectrum so white light is a mixture of all colors.

The electromagnetic spectrum shown in figure 2.3 is the whole spectrum. These electromagnetic waves are made of two parts, that is, an electric and magnetic field. The visible spectrum is just one small part of the electromagnetic spectrum.

Electromagnetic energy at a particular wavelength λ (in vacuum) has an associated frequency v and photon energy E. Thus, the electromagnetic spectrum may be expressed equally well in terms of any of these three quantities. They are related according to the following equations.

$$\lambda = \frac{c}{v} \tag{1.1}$$

and
$$E = hv \tag{1.2}$$

where c is the speed of light which equals to 299,792,458 m/s

$$c \approx 3 \cdot 10^8 \text{ m/s}$$

h is Planck's constant, $h \approx 6.626069 \cdot 10^{-34}$ J · s

In this research, only infrared, visible and ultraviolet light interest us.

Frequency (Hz) Wavelength (M)

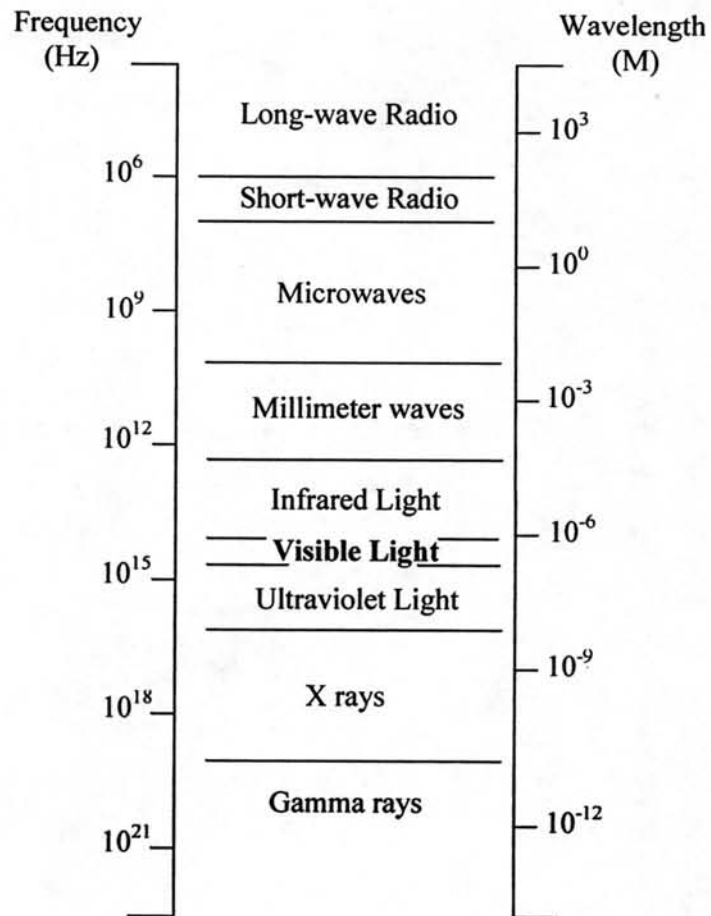| Frequency (Hz)	Band	Wavelength (M)
	Long-wave Radio	10^3
10^6	Short-wave Radio	
	Microwaves	10^0
10^9		
	Millimeter waves	10^{-3}
10^{12}	Infrared Light	
	Visible Light	10^{-6}
10^{15}	Ultraviolet Light	
	X rays	10^{-9}
10^{18}		
	Gamma rays	10^{-12}
10^{21}		

Figure 2.3 The electromagnetic spectrum

2.3.1 Infrared light

The infrared part of the electromagnetic spectrum covers the range from roughly 300 GHz (1 mm) to 400 THz (750 nm). It can be divided into three parts:

2.3.1.1 Far-infrared, from 300 GHz (1 mm) to 30 THz (10 μm). The lower part of this range may also be called microwaves. This radiation is typically absorbed by so-called rotational modes in gas-phase molecules, by molecular motions in liquids, and by phonons in solids.

2.3.1.2 Mid-infrared, from 30 to 120 THz (10 to 2.5 µm). Hot objects (black-body radiators) can radiate strongly in this range. It is absorbed by molecular vibrations, that is, when the different atoms in a molecule vibrate around their equilibrium positions.

2.3.1.3 Near-infrared, from 120 to 400 THz (2,500 to 750 nm). Physical processes that are relevant for this range are similar to those for visible light.

2.3.2 Visible light

Above infrared in frequency comes visible light. This is the range in which the sun and stars emit most of their radiation. It is probably not a coincidence that the human eye is sensitive to the wavelengths that the sun emits most strongly. Visible light (and near-infrared light) is typically absorbed and emitted by electrons in molecules and atoms that move from one energy level to another. The light we see with our eyes is a very small portion of the electromagnetic spectrum (the range of wavelengths approximately from 380 nm to 740 nm). A rainbow shows the optical (visible) part of the electromagnetic spectrum; infrared and ultraviolet lights are located just beyond the visible part. Infrared would be located upper 740 nm (red side) and ultraviolet appearing just lower 380 nm (violet side). Spectrum is then a distribution giving its intensity at each wavelength that gives different colors as shown in table 2.2.

2.3.3 Ultraviolet light

This is radiation whose wavelength is shorter than the violet end of the visible spectrum.

Table 2.2 Optical wavelength of the electromagnetic spectrum

Color	Wavelength interval	Frequency interval
violet	~ 380 to 430 nm	~ 790 to 700 THz
blue	~ 430 to 500 nm	~ 700 to 600 THz
cyan	~ 500 to 520 nm	~ 600 to 580 THz
green	~ 520 to 565 nm	~ 580 to 530 THz
yellow	~ 565 to 590 nm	~ 530 to 510 THz
orange	~ 590 to 625 nm	~ 510 to 480 THz
red	~ 625 to 740 nm	~ 480 to 405 THz

2.4 Fluorescence and phosphorescence (photoluminescence)

Luminescence is the emission of light by a substance. It occurs when an electron returns to the electronic ground state from an excited state and loses its excess energy as a photon. It has several types in term of excited molecule source. When light is an excited molecule it is called photoluminescence. Photoluminescence can be divided into two parts that are fluorescence and phosphorescence.

The electronic states of most organic molecules can be divided into two types that are singlet states and triplet states. In singlet states, all electrons in the molecule are spin-paired and in triplet states, one set of electron spins is unpaired as shown in figure 2.4.
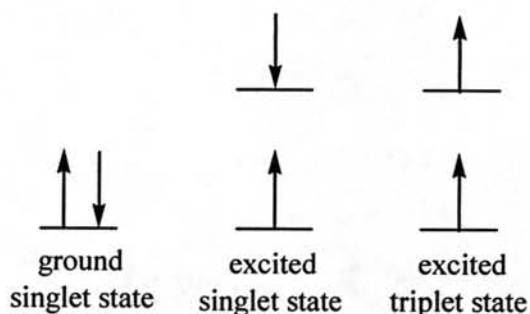
Figure 2.4 Electrons spin in molecule

2.4.1 Fluorescence

In absorption of UV radiation, a molecule was excited and returned to an electronic ground state by deexcitation or deactivation process which has radiationless process and radiation process. A molecule in a high vibrational level of the excited state will quickly fall to the lowest vibrational level of this state by losing energy to other molecules through collision. After molecules lose energy from collision then an electron returns to the electronic ground state, from the excited singlet state, by emission of a photon which are called fluorescence. Other than fluorescence is emission process, phosphorescence is also emission process too. If a molecule which absorbs UV radiation does not fluoresce, it must have lost energy in some other ways such as heat. These processes are called radiationless transfer of energy as shown in figure 2.5.
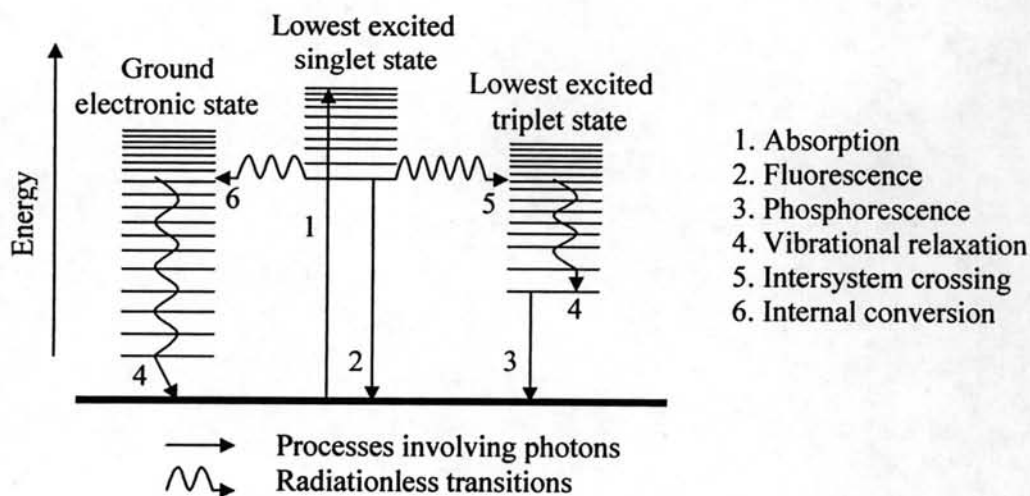
Figure 2.5 Possible physical processes following absorption of a photon by a molecule.

2.4.2 Internal conversion

The electrons in a molecule return to the electronic ground state in which the excess energy is converted to vibrational energy, and the molecule is placed in an extremely high vibrational level of the electronic ground state, this process rapidly occurs in 10^{-2} seconds.

2.4.3 Vibrational relaxation

The vibrational relaxation occurs when the electrons in molecule in high vibrational level of the electronic ground state return to the lowest electronic ground state. The excess vibrational energy is lost by collision with other molecules. The conversion of electronic energy to vibrational energy is helped if the molecule is "loose and floppy", because it can reorient itself in the way which aids the internal transfer of energy.

2.4.4 Intersystem crossing

Intersystem crossing occurs from the spin of an excited electron which can be reversed. These processes involve molecule transfer from excited singlet state to excited triplet state. The triplet state is of a lower electronic energy than the excited singlet state. The probability of intersystem crossing occurrence is increased if the vibrational levels of these two states overlap. For example, the lowest singlet vibrational level can overlap one of the higher vibrational levels of the triplet state. A molecule in a high vibrational level of the excited triplet state can lose energy in collision with solvent molecules, leaving it at the lowest vibrational level of the triplet state. It can then undergo a second intersystem crossing to a high vibrational level of the electronic ground state. Finally, the molecule returns to the lowest vibrational level of the electronic ground state by vibrational relaxation.

2.4.5 Phosphorescence

A molecule in the excited triplet state return to the ground state then losing energy by emission of a photon called phosphorescence. A triplet/singlet transition is much less probable than a singlet/singlet transition. The lifetime of the excited triplet state has long time periods between 10^{-4} to 10 seconds, in comparison with 10^{-5} to 10^{-8} second average lifetime of an excited singlet state. Emission from triplet/singlet transitions can continue after initial irradiation. Internal conversion and other radiationless transfers of energy compete so successfully with phosphorescence that it is usually seen only at low temperature or in highly viscous media.