



## CHAPTER I INTRODUCTION

### 1.1 Problem Statement

Polyimide is well known as high temperature engineering polymers. When compared to most other organic or polymeric materials, polyimide exhibits an exceptional combination of thermal stability ( $>500^{\circ}\text{C}$ ), mechanical toughness and chemical resistance. In addition, it has excellent dielectric properties. Because of its inherently low thermal expansion coefficient (CTE), polyimide can be readily implemented into a variety of microelectronic applications. Thin film application on large silicon substrate can be achieved. In the past decade, the development of micromachine silicon-based devices, such as solid state gas sensor, have been rapidly growing because of their lower manufacturing cost, lower energy consumption and faster response. The sensor can be used to monitor the purity of microelectronic processing gases, environmental and automotive exhaust gases. The chemical vapor deposition (CVD) technique is used for preparing electrical conducting metal film coating on sensor units. The backside of the sensor is usually getting hot causing metal films to be shortened out during the CVD process. Polyimide is an appropriate protective material for backside of the sensor because it can fulfill almost all of the specific requirements which are high thermal stability, low CTE, electrical insulator, good adhesion, and low gas permeability.

Nowadays, it is difficult for the only single polyimide to meet all of requirements. Therefore, its properties can be further improved by adding inorganic filler to produce a nanocomposite material.

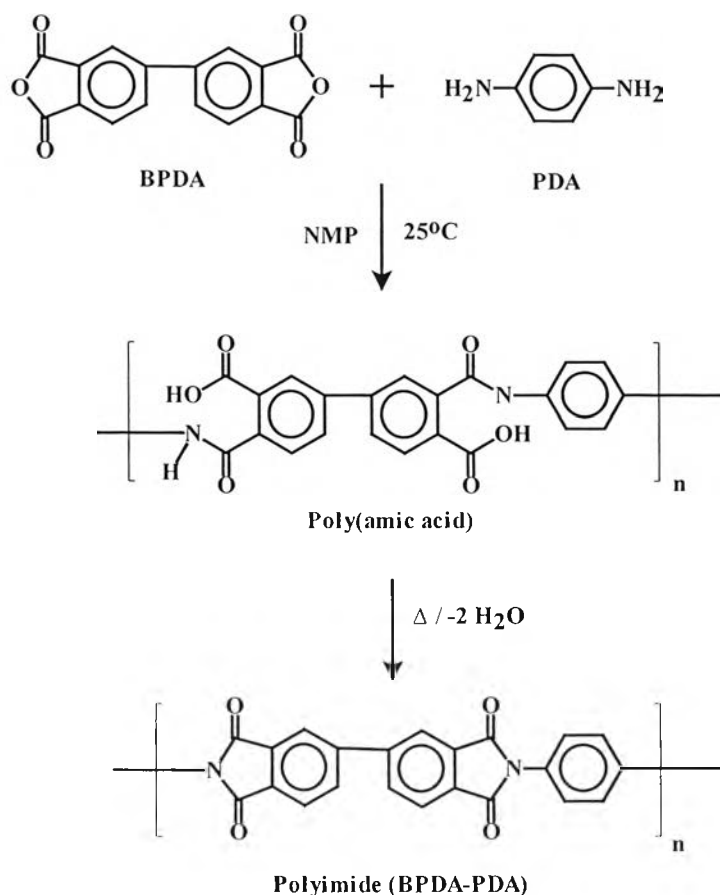
## 1.2 Background

### 1.2.1 Polyimides-Synthesis and Properties

Polyimides have found widespread application as microelectronic coating materials due to their excellent mechanical properties and chemical resistance in addition to the exceptionally high thermal stability up to 450 °C and electrical resistance. Polyimides can be synthesized by a two-stage classical method as described by Wilson *et al.* (1990). The first stage starts with a poly(amic acid) which is obtained from the polycondensation of diamine and dianhydride in a polar aprotic solvent, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), and N-methyl-2-pyrrolidone (NMP) at 15 to 75 °C. The poly(amic acid) is then cyclodehydrated to the corresponding polyimide by heating at elevated temperatures. A typical molecular structure of polyimide with a poly(amic acid) counterpart is shown in Figure 1.1. Since the polyimide is often insoluble and infusible, it is usually processed in the form of the poly(amic acid), which is thermally imidized in place.

Furthermore, polyimide can be synthesized by one-step synthesis method. In particular, the diamine and dianhydride are mixed together and stirred with a high-boiling point organic solvent at 180 to 220 °C. Chain growth and imidization essentially occur spontaneously under these conditions. The water generated in imidization step is usually allowed to distill from the reaction mixture. Nitrobenzene,  $\alpha$ -chloronaphthalene and *m*-cresol containing isoquinoline are the most widely used solvents. The one-step method is especially useful for the polymerization of unreactive dianhydride and diamine. For example, phenylated dianhydride cannot be used to prepare a high molecular weight poly(amic acid) involving the classical method. But these steric hindered monomers can react rapidly

with diamine at elevated temperatures to give a high molecular weight polyimide.



**Figure 1.1** The two-stage synthesis of polyimide from 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPDA) and *p*-phenylenediamine (PDA).

Polyimides have been prepared with various types of structures during the past decade. The physical properties of the polymers are usually varied with the molecular structure. The effects of structural changes in the polyimide backbone upon the properties have been extensively investigated. For example, the glass transition temperature ( $T_g$ ) was affected by isomeric attachments along the chain with *meta* catenation

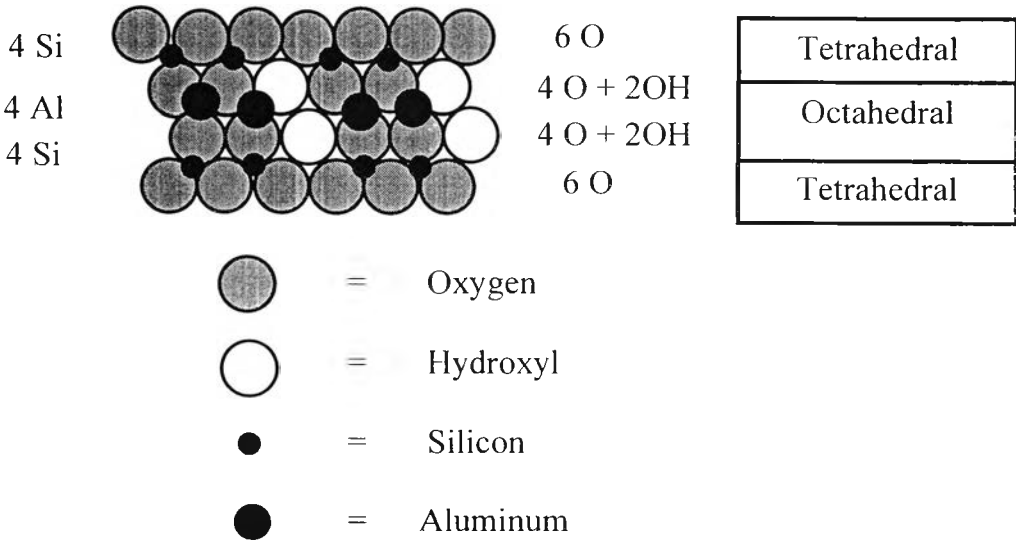
impairing the greatest lowering over the more common *para* catenation. *Ortho* catenation was not found to be effective in lowering  $T_g$ . Thermo-oxidative stability in polyimides can be related to the oxidation state of the constituent diamine and dianhydride moieties, with the diamine being more important than the dianhydride. Preferred units in the diamine would be bridging groups such as carbonyls, sulphones or highly fluorinated alkyls. The solubility of polyimides is related to their chemical structures. The *meta* and *ortho* catenation along the main chain can enhance the solubility of even highly aromatic systems. Color in polyimides is caused by chromophoric units or impurities in starting materials. The lowering of electronic interactions have been shown to give highly colored to colorless polymers.

Polyimide is useful as a very high performance coating material in semiconductor devices. The major concern for these applications is the mismatch between coating material and the substrate. It is suggested that a similar thermal expansion coefficient (CTE) can minimize this thermal mismatch. The polyimide structure is related to the CTE. The flexible polyimide containing many oxygen or sulphur linkages usually has higher CTE as reported by Numata *et al.* (1986). The tensile strength and modulus at 23 °C are other properties that can be related to the polyimide structure. The rigid-rod polyimide usually has a higher tensile strength and modulus but it exhibits a lower percent elongation. This result reveals that the rigid-rod polyimide is more brittle than the flexible one.

### 1.2.2 Clay Filler

Clay or layered silicate is a specific material in soil which consists of many kinds of minerals. The structure of smectite clay is composed of layer lattice structure of oxyanions and hydrated cation layer. Oxygen atoms reveal the layer edge of tetrahedral site and octahedral site.

The two-dimensional model illustrating the arrangement of each component in a unit of clay mineral is shown in Figure 1.2



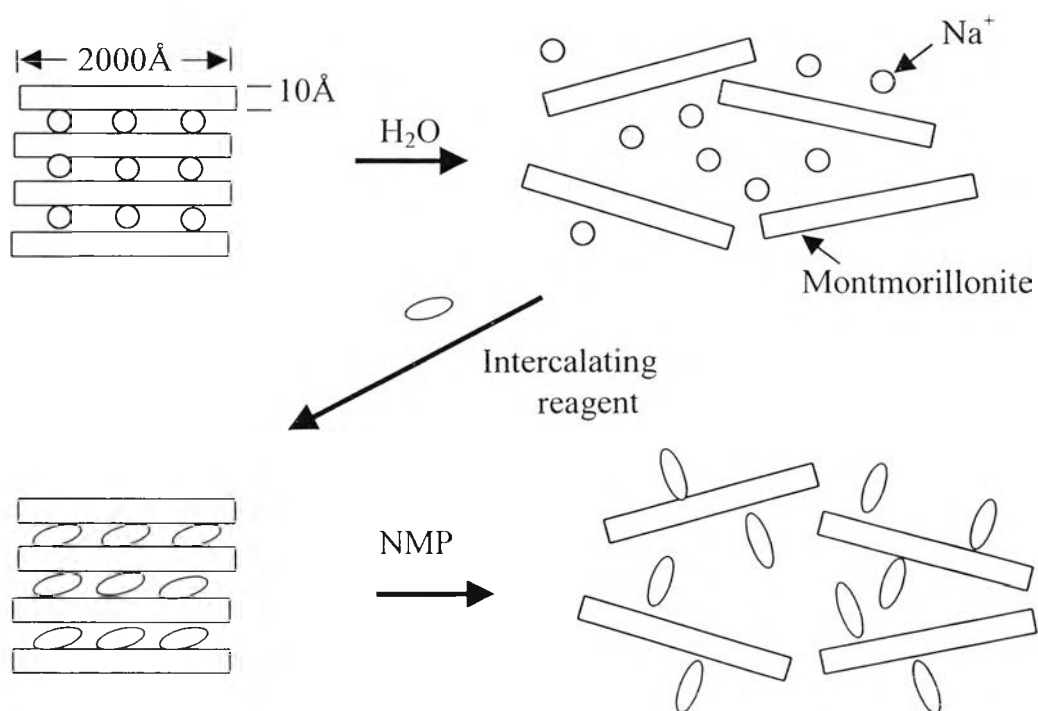
**Figure 1.2** The two-dimensional model illustrating the arrangement of each component in a unit of clay mineral.

There are many species of clays in a group of smectite clay minerals which consist of many layers of octahedral aluminate sheets sandwiched between tetrahedral silicate layers as list in Table 1.1.

**Table 1.1** The species in smectite clay group.

Subgroup	Species	Ideal Formula
Saponites	Saponite	$\text{Na}_{0.6}[\text{Mg}_6(\text{Al}_{0.6}\text{Si}_{7.4})\text{O}_{20}(\text{OH})_4]$
	Hectorite	$\text{Li}_{0.6}[\text{Li}_{1.6}\text{Mg}_{4.4}\text{Si}_8\text{O}_{20}(\text{OH})_4]$
	Fluorohectorite	$\text{Li}_{0.6}[\text{Li}_{1.6}\text{Mg}_{4.4}\text{Si}_8\text{O}_{20}\text{F}_4]$
Montmorillonites	Montmorillonite	$\text{Na}_{0.6}[(\text{Mg}_{0.6}\text{Al}_{3.4})\text{Si}_8\text{O}_{20}(\text{OH})_4]$
	Beidellite	$\text{Na}_{0.9}[\text{Al}_4(\text{Al}_{0.9}\text{Si}_{7.4})\text{O}_{20}(\text{OH})_4]$

Montmorillonite is one in smectite group which has a low thermal expansion coefficient and a high gas barrier property. Stacking of this structure leads to a regular weak dipolar or van der Waals interaction between the layer. Isomorphous substitution in each layer generates negative charges that are counterbalanced by hydrated sodium or potassium ions residing in the interlayer spaces. Due to this special characteristic, montmorillonite can be easily dispersed in water resulting in a stable colloid. Typically, the natural montmorillonite is too hydrophilic to disperse in an organic matrix. Its dispersibility can be improved to make it useful by ion exchanges with an organic cation molecule, such as cationic surfactant, onto the filler's surface. The arrangement of smectite-clay structure by cation exchanges with cationic surfactant is shown in Figure 1.3.



**Figure 1.3** Dispersion behavior of montmorillonite.

The functions of organic cation molecules in organophilic-clay are to lower the surface free energy of the silicate layers and to improve

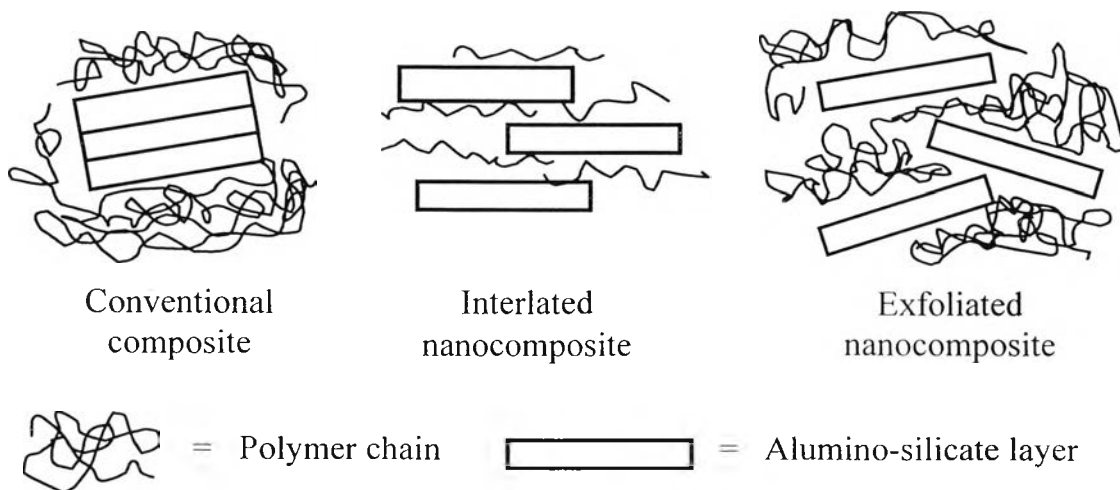
the wettability behavior of hydrophobic polymer matrix. In addition, the organic cation may contain various functional groups that can react with the polymer molecule to improve the adhesion strength between the inorganic phase and the matrix as reported by Giannelis (1996).

### 1.2.3 Nanocomposite

Composites that exhibit a change in composition and structure over a nanometer length, nanocomposites, have been shown over the last 10 years to afford remarkable property enhancements relative to conventionally-scaled composites. Layered silicates dispersed as a reinforcing phase in an engineering polymer matrix are one of the most important forms of such “hybrid organic-inorganic nanocomposites”.

Dispersion of clay minerals in a polymer matrix was recently described by Pinnavaia *et al.* (1996). A ***conventional composite*** contains the existing clay tactoids in their original aggregated state with an unintercalated polymer chain along the silicate layers. The clay tactoids are simply dispersed as a segregated phase. An ***intercalated nanocomposite*** is formed by the insertion of one or more polymer chains into the clay galleries resulting in a well ordered multilayer with alternating polymer chains and nanoscale inorganic layers. Owing to the spatial confinement of the polymer between the densely packed clay layers, intercalated polymer-clay nanocomposites can exhibit improved conductivity. An ***exfoliated nanocomposite*** can be obtained by separation of a single silicate layer in the polymer matrix with the average distance of each layer depending on the clay content. The clay contents of an exfoliated nanocomposite are usually much lower than in intercalated nanocomposites. In addition, the undispersed hybrid corresponds to a conventional composite whereas the fine dispersed hybrid corresponds to either an intercalated or an exfoliated nanocomposite. The

schematic illustrations of the three possible types of polymer-clay composites are shown in Figure 1.4.



**Figure 1.4** The schematic illustration of the three possible types of polymer-clay composites.

Although the high aspect ratio of silicate nanolayers is ideal for reinforcement, the nanolayers are not easily dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids. Dispersion of the tactoids into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophilic layered silicates and hydrophobic engineering plastics. However, as was first demonstrated by the Toyota group more than 10 years ago, the replacement of the inorganic exchange cations in the galleries of the native clay by alkylammonium surfactants can compatibilize the surface chemistry of the clay and the hydrophobic polymer matrix.

### 1.3 Objectives

This thesis wants to use polyimide as an appropriate protective coating for gas sensor application by improving the film properties by



polymer-clay nanotechnology. From previous work (Lilayuthalert, 1998), polyimide-clay film at 3 wt% clay was the optimum content of clay which was determined from TGA and TEM results, as well as CTE, water absorption, and dielectric strength properties. The main purposes of this study are gas permeability, adhesion, and electrical resistivity. Moreover, coating thickness effect on gas permeability and adhesion property of polyimide-clay nanocomposite films is provided. The film requires low gas permeability, good adhesion to silicon substrate, and electrical insulation (electrical resistivity  $10^5$ - $10^{18}$   $\Omega$ .cm).