

# CHAPTER I

## INTRODUCTION



### 1.1 Problem Statements

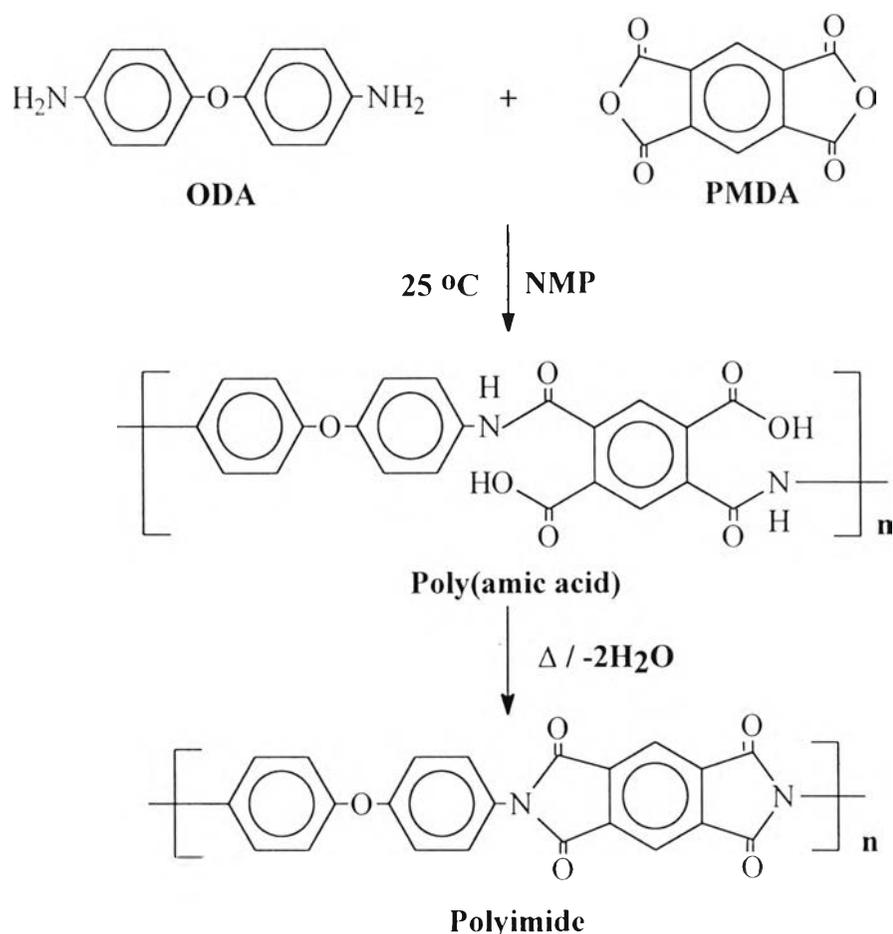
In the past decade, the development of micromachined silicon-based devices such as a solid state gas sensor have been rapidly growing because of their lower manufacturing cost, lower energy consumption and faster response. The sensor can be used to monitor the purity of microelectronic processing gases, environmental and automotive exhaust gases. The active sensing area contains a temperature-programmable ultra thin film fabricated onto a single silicon crystal wafer using a chemical vapor deposition (CVD) technique. This CVD process utilizes the boron-doped silicon heater built into each sensor unit to initiate the thermal decomposition of the metal precursor molecules. The backside of the sensor was getting hot causing metal films to be shorted out during the CVD process. A suitable material is needed to protect the backside of the sensor with thermal stability, good adhesion, good conformal coverage, electrical insulation, and a thermal expansion coefficient (CTE) is close to that of the substrate. Polyimide is an appropriate protective material because it can fulfill almost all of the specific requirements. However, all of polyimide properties may be improved by adding an inorganic filler to produce a composite material.

## 1.2 Background

### 1.2.1 Polyimides-Synthesis and Properties

Polyimides have played an important role as coating materials in the microelectronics industry due to their outstanding thermal stability, electrical resistance, inertness to solvents, and excellent durability. 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.

The one-step synthesis is another method that can be used to prepare a polyimide. In particular, the diamine and dianhydride are mixed together and stirred with a high-boiling point of organic solvent at 180 to 220 °C. Under these conditions, chain growth and imidization essentially occur spontaneously. 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 sterically 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 pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA).

During the past decade, polyimides have been prepared with various types of structures. 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 imparting 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

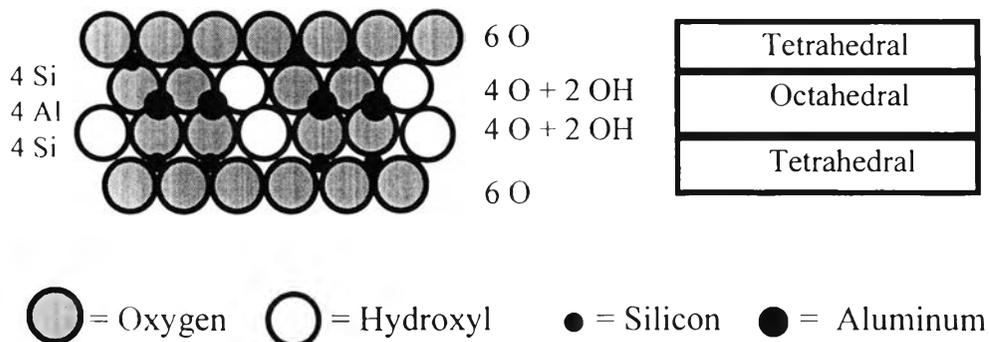
polyimides can be related to the oxidation state of the constituent diamine and dianhydride moieties, with the diamine being more important than the dianhydride. Preferred units in the diamine would be bridging groups such as carbonyls, sulphones or highly fluorinated alkyls. The solubility of polyimides is related to their chemical structure. 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 should be the stress development during thermal processes which arises from the mismatch between coating material and the substrate. It was found 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 The Organophilic-Clay Filler

Clay mineral is a specific material in soil which consists of many kinds of minerals. Most of the clay minerals are crystalline and composed of many repeating planes of oxygen anion holding together with the specific cations, such as aluminum and silicon ions as described by Miller and

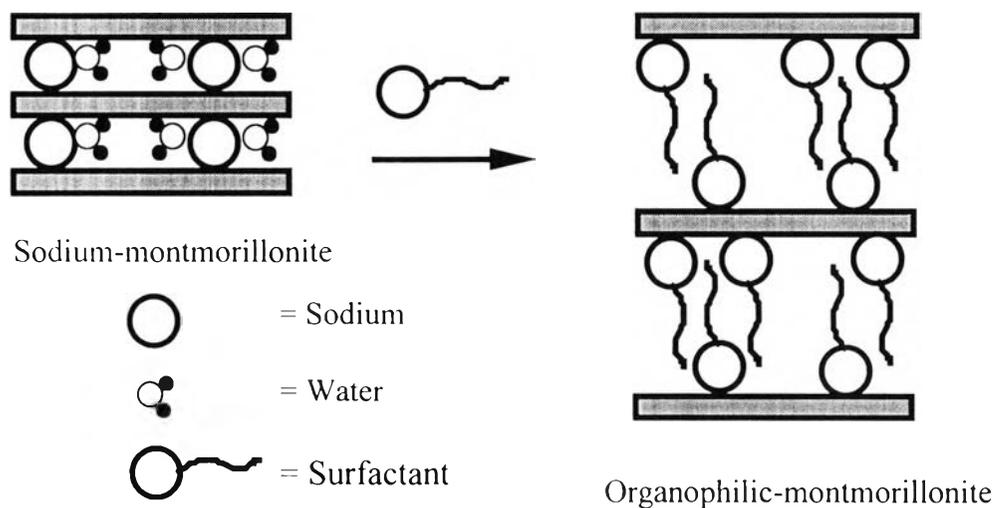
Donahue (1990). The structure of a particular clay mineral is shown in Figure 1.2.



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

Montmorillonite is a group of smectic-clay minerals which consists of many layers of octahedral aluminate sheets sandwiched between tetrahedral silicate layers. Stacking of this structure leads to a regular weak dipolar or van der Waals interaction between the layers. Isomorphic 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 smectic-clay structure by cation exchanges with cationic surfactant is shown in Figure 1.3.



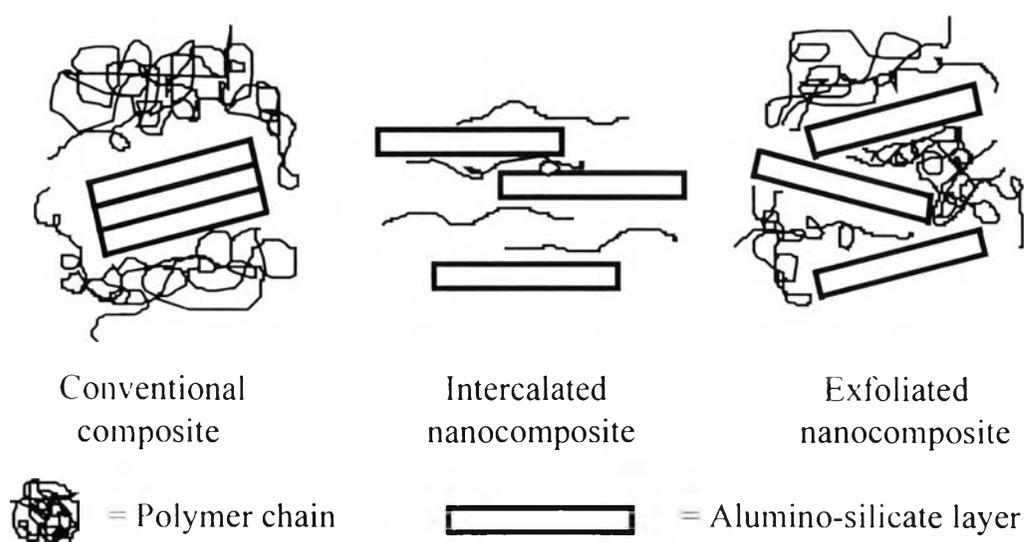
**Figure 1.3 The arrangement of smectic-clay structure by cation exchanges with cationic surfactant.**

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

Nanocomposite is a type of composites containing filler that has at least one dimension in range of nanometer, i.e. a billionth of a meter, as defined by Morrell (1994). Most of nanocomposites can be produced by using metal particles, colloids, and smectic-clay minerals. Nanotechnology has gained wide interest in the development of a novel polymeric composite, such as nylon 6-clay nanocomposites which were produced by Usuki et al. (1993). The polyimide-silica hybrid prepared by Mascia and Kioul (1995) is another example of polymer nanocomposites.

Recently, Pinnavaia et al. (1996) described the three general types of composites which are produced by dispersion of clay minerals in a polymer matrix. A *conventional composite* contains the existing clay tactoids in their original aggregated state with an unintercalated polymer chain along the silicate layers. 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. 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 illustration of the three possible types of polymer-clay hybrids are shown in Figure 1.4.



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

In this research, the organophilicity of nanoscale filler will be improved by cation exchanges with a surfactant compound prior to preparing polyimide hybrid materials. This modification technique will increase the dispersion of filler into the polymer matrix. Both physical and thermomechanical properties of the nanocomposite will also be expected to improve by using this method.

### **1.3 Objectives**

The goal of this work is to find out an appropriate protective polymer coating for microelectronics devices using polymer-clay nanotechnology concept. The material requires a high thermal stability of more than 400 °C, good electrical insulation and conformal coverage together with a thermal expansion behavior is close to that of the silicon crystal wafer substrate (CTE average between 50 and 300 °C is 2-4 ppm/°C).