CHAPTER ONE

INTRODUCTION

1.1 Background

The preparation, characterization and applications of organic/inorganic hybrids materials have become a fast expanding area of research in materials science. The major driving forces behind the intense activities in this area are the new and different properties of the nanocomposite which the traditional macroscale composites and conventional materials do not have. For example, unlike the traditional composite materials which have macroscale domain size of millimeter and even micrometer scale, most of the organic/inorganic hybrid materials are nanoscopic, with the physical constraint of several nanometers, typically 1-100 nm, as the minimum size of the components or phases. Therefore, they are often still optically transparent materials although microphase separation may exist. Through the combinations of different inorganic and organic components in conjunction with appropriate processing methods, various types of primary and secondary bonding can be developed leading to materials with new properties for electrical, optical, structural, or related applications.

In the past two decades, organic/inorganic nanocomposites prepared by sol-gel process have attracted a great deal of attention, especially in the fields of ceramics, polymer chemistry, organic and inorganic chemistry and physics. The sol-gel process, which is mainly based on inorganic polymerization reactions, is a chemical synthesis method initially used for the preparation of inorganic materials such as glasses and ceramics. Its unique low temperature processing characteristic also provides unique opportunities to make well-controlled composite organic/inorganic hybrid materials through the incorporation of low molecular weight and oligomeric /polymeric organic molecules with appropriate inorganic moieties at temperatures under which the organics can survive. The organic/inorganic hybrid materials made in this way, which have been termed “ceramers” by Wilkes et al. [1] and “ormosils” or “ormocers” by Schmidt et al. [2], are normally nanocomposites and have the potential for providing unique combinations of properties which cannot be achieved by other materials.

Recent research work has been aimed to improve the properties of polymers with respect to better thermal stability and mechanical strength via sol-gel process. To date, polyimides have drawn the most attention since they have gained commercial importance in the aerospace and electronic industries (Figure 1.1) due to their reliable high-temperature stability, chemical resistance and good mechanical strength [3-5]. Unlike Kevlar or other aromatic, heterocyclic polymers, polyimides are synthesized form a precursor molecule (poly(amic) acid) which is soluble in some organic solvents such as *N,N*-dimethyl-acetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF). This opens the possibility of mixing this precursor molecule with metal alkoxides to produce homogeneously dispersed metal oxides in polyimide matrices through the usual hydrolysis and condensation reactions.

In addition, ultrafine particles have become a popular topic because of the novel properties they exhibit which greatly differ from the bulk properties. Due to the expected properties of TiO_2 (high-refractive-index, catalytic etc.), considerable attention has been devoted to the manufacture of high-content and well-dispersed TiO_2 in polyimide matrix used as interference filter, antireflective coating, and optical waveguides [6-8]. Numerous studies have been carried out on the preparation of polyimide/silica hybrid materials by sol-gel process. In contrast, titanium alkoxide has been less studied and polyimide/titania (PI/TiO_2) hybrid materials are less known, although they may find potential applications in many area.

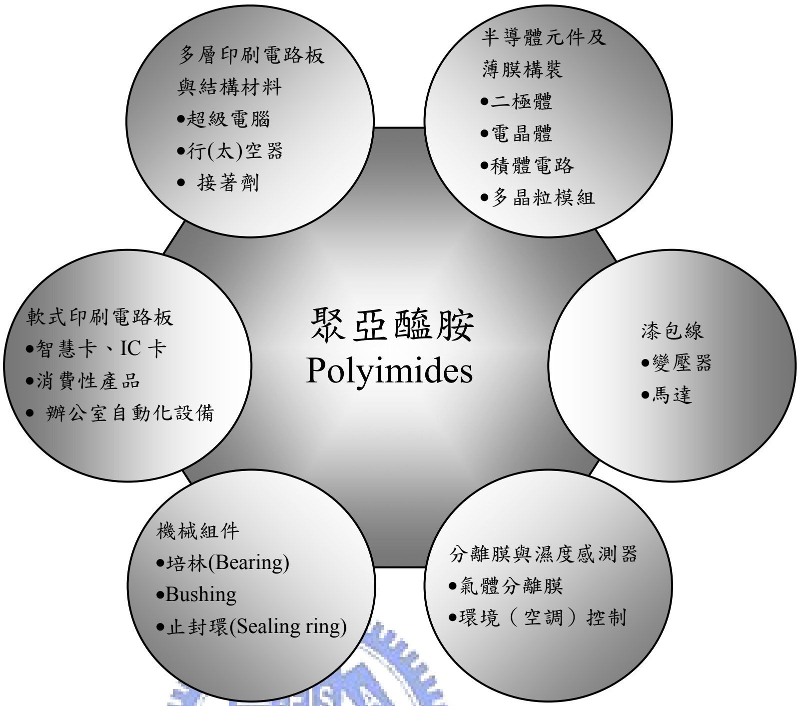

Figure 1.1 Applications of polyimides.

1.2 Aim and Objectives

Polyimides have been widely utilized for the microelectronic and aerospace applications because of their high thermal stability, mechanical strength, and chemical resistivity. In the view of the importance of polyimides, the present work focused on some new well-controlled nano hybrid film prepared by introducing titania (TiO_2) phase into polyimide matrix by using the sol-gel technique.

The objectives of this research are as follows:

- To study and review relevant literature on metal-containing polyimides.
- To develop a simpler way to prepare high content and well-dispersed PI/TiO_2 nano hybrid films.

- To investigate the effect of TiO_2 content upon microstructure and morphology.
- To characterize the obtained PI/TiO_2 nano hybrid films with regard to their physical, mechanical, electrical, optical, and thermal properties.
- To study the effect of TiO_2 content on adhesion strength and interfacial state between the PI/TiO_2 hybrid films and copper system.
- Surface modification of plasma treatment is also applied in this research to improve the adhesion strength between the PI/TiO_2 hybrid films and copper. To find out the difference on adhesion strength among the effects of Ar, Ar/N_2, and Ar/O_2 plasma treatments.
- To inspect the failure mode between the PI/TiO_2 hybrid films and copper system.
- To recommend how to improve the adhesion strength between the PI/TiO_2 hybrid films and copper system without compromising essential properties of polyimide.

1.3 Brief Structure of the Research

The research comprises eight chapters. Contents of each chapter are detailed as follows:

Chapter one provides the background of this study, stating the reason why the study is conducted. In addition, the objectives of the study are outlined in this chapter.

Chapter two is literature review of the research in the field of organic/inorganic hybrid materials by sol-gel process. Key area focuses on the basic understanding of sol-gel chemistry. Furthermore, the synthesis, structure-property response, potential applications of metal-containing polyimides, and motivation of this research are included.

Chapter three represents the theory quoted in this dissertation. On the one hand the viscoelastic behavior of solid polymer is described, and on the other hand the adhesion theories and adhesion measurement are illustrated.

Chapter four describes the experiment methodology used in the study. It contains the demonstration of synthesis procedures and sample preparation for analysis in this research. The equipments and experimental conditions of analyses are also detailed in this section.

Chapter five is the first part of results and discussion. It focuses on developing a method to prepare BAO-ODPA polyimide/TiO_2 nano hybrid films via sol-gel process and using acetylacetone as a chelating agent to reduce the hydrolysis rate of titanium alkoxide. The nano hybrid films obtained are further characterized by XRD, FT-IR, XPS, and TEM analyses.

Chapter six tries to get a better understanding of PI/TiO_2 nano hybrid films. Three kinds of polyimides matrices are chosen and incorporated with TiO_2 in the range of 1 wt% to 9 wt%. The resulting hybrid films are characterized with regard to their thermal, mechanical, and electrical properties.

Chapter seven attempts to gain an insight into the adhesion mechanism and the related microstructure at the interface between the PI/TiO_2 hybrid films and copper system. The influences of TiO_2 content and plasma treatment on adhesion improvement are investigated. The peeled-off failure mode between the hybrid films and copper is also proposed in this chapter.

Chapter eight draws conclusions from the results and discussion. In addition, some recommendations are made for future research.

1.4 References

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