CHAPTER EIGHT

CONCLUSION AND RECOMMENDATIONS

8.1 Conclusion

A simpler method of preparing the polyimide/titania (PI/TiO_2) nano hybrid films has been developed by sol-gel process. The titanium ethoxide ($Ti(OEt)_4$), used as a source of TiO_2, is incorporated into the poly(amic acid) (PAA) and followed by thermal conversion. During the final curing process, imidization occurs, leading to ring closure which releases water that can hydrolyze the titanium ethoxide to eventually generate the TiO_2. By using catalyst-free polymerization, acetylacetone (acac) is used as a chelating agent to stabilize the titanium alkoxide through the formation of an acetylacetate complex.

The nano hybrid films of TiO_2 within the polyimide from 2,5-bis(4-amino-phenyl) 1,3,4-oxadiazole (BAO) and 4,4′-oxydiphthalic anhydride (ODPA) show a broad and strong absorption in the visible region as TiO_2 content is more than 10 wt%. The increase of absorption is due to the formation of an acetylacetate complex. The incorporation of TiO_2 also disrupts the intermolecular regularity of the polyimide chains because no sharp peak is observed in the XRD spectra. The composition-depth profile shows that the topmost surface of the hybrid films is consisted of fewer TiO_2 content as compared with the bulk of the hybrid films. It is suggested that the rigidity of the polyimide backbone and the cross-linked structure of the TiO_2 impede the migration of titanium to the hybrid film surface. The TEM observation indicates the formation of a homogeneous dispersion of TiO_2 nanoclusters within the polyimide matrix. Furthermore, the size of TiO_2 domain increases from 10 to 40 nm as TiO_2 content increases from 5 wt% to 30 wt%. Although the thermal stability of the hybrid films is decreased by introducing

TiO_2, the hybrid films still reveal pretty good thermal resistance for practical application.

Three series of PI/TiO_2 hybrid films, based on diamine of 4,4'-diaminodiphenyl-ether (ODA) and three kinds of dianhydrides, are synthesized. All the hybrid films show less transparent than host polyimides. By comparing the three series of hybrid films, the most flexible hybrid films are based on BTDA/DAO and the least flexible ones are based on PMDA/ODA. In the study of thermal expansion, a tendency of decreasing thermal expansion with increasing TiO_2 content is observed for the hybrid films. This remarkable decrease is due to TiO_2 moiety having lower coefficient of thermal expansion (CTE) values. The cross-linked structure of the hybrid films also leads to decrease the expansion at elevated temperature.

These PI/TiO_2 hybrid films exhibit higher glass transition temperature (T_g), an increase of storage modulus, and a decrease in loss modulus at their T_gs as compared with the pure polyimides. All these results are associated with the TiO_2 content and the cross-linked structure of the hybrid films. The results of DMA studies also indicate there are two obvious transitions at T_g, implying the existence of another partially miscible inorganic/organic phase. We suppose this phase represents the interfacial region between the TiO_2 domains and the polyimide matrix. In the PMDA/ODA series, there is only one broad transition peak noted in the entire range due to the PMDA/ODA with higher T_g than the other two series. The observed changes in tan δ magnitude and breadth suggest that the introduction of TiO_2 moiety restricts the motions of the polymer chains.

Results presented also demonstrate that by incorporating small amounts of TiO_2 (1-3 wt%) into the polyimide enhances the mechanical properties of the hybrid films and maintains the good thermal stability. The investigation of electrical properties shows that the lowered surface and volume resistivities appear to be correlative with the presence of TiO_2 in the hybrid film. The more amount of TiO_2 is contained, the lower resistivity is measured. The dielectric constant and dissipation factor are also varied by TiO_2 content. A trend of increasing dielectric constant and dissipation factor with increasing TiO_2 content is observed.

The BTDA/ODA based hybrid films are further investigated to elucidate the adhesion strength between the PI/TiO_2 hybrid films and copper. It is found that the hybrid films exhibit enhanced adhesion strength at low TiO_2 content, usually inferior to 5 wt%. The improvement of adhesion strength could be attributed to the higher conductivity resulted by TiO_2 existed on the hybrid films surface. However, the additional introduction of TiO_2 causes the hybrid films too brittle to afford larger load without fracture during the peel test.

The hybrid films modified by plasma treatment also greatly improve the adhesion strength. A correlation between the enhancement of the peel strength and the content of oxygen-containing groups at the hybrid films surface is observed. Besides, an increase of surface roughness and surface energy as a result of plasma treatment is noticed. In the process of plasma treatment, the hybrid films treated with Ar/N_2 plasma displays stronger adhesion strength than the results of the other plasma treatments. The maximum adhesion value of 9.53 N/cm is measured for the PI/TiO_2-1 wt% hybrid film with Ar/N_2 plasma treatment. Based on the results of XPS and EDS, the formation of copper oxide at the interface between the hybrid film and copper during the copper sputtering is responsible for the lower adhesion strength obtained by Ar/O_2 plasma treatment. Furthermore, the cohesive failure occurs for the hybrid films treated with Ar/N_2 plasma treatment. However, the failure locus is shifted to the interphase between the hybrid film and copper by Ar/O_2 plasma treatment. To compare the both effects of TiO_2 content and plasma treatment on the adhesion strength, incorporating TiO_2 into the polyimide matrix results in a smaller adhesion promotion than plasma treatment does.

8.2 Recommendations for Future Research

Owing to the time limitation, the research cannot cover every aspect relating to the PI/TiO_2 hybrid films. If there were a need to extend the research in the future, the author would like to recommend exploring how the additive of TiO_2 affects the adhesion mechanism between the PI/TiO_2 hybrid films and copper. Moreover, it also would be worthy to investigate how to increase the driving force for metal oxides to migrate from the bulk to the hybrid films surface, since the metal oxides on the hybrid films surface can be served as active sites.

LIST OF PUBLICATIONS

■ Journal Publications

1. Pei-Chun Chiang, Wha-Tzong Whang, "The Synthesis and Morphology Characteristic Study of BAO-ODPA Polyimide/TiO_2 Nano Hybrid Films", ***Polymer*** vol. 44, pp. 2249-2254, 2003.

2. Pei-Chun Chiang, Wha-Tzong Whang, Mei-Hui Tsai, Sheng-Chang Wu, "Physical and Mechanical Properties of Polyimide/Titania Hybrid Films", ***Thin Solid Films*** vol. 447-448, pp. 359-364, 2003.

3. Pei-Chun Chiang, Wha-Tzong Whang, Sheng-Chang Wu, Kuen-Ru Chuang, "Effects of Titania Content and Plasma Treatment on the Interfacial Adhesion Mechanism of Nano Titania-Hybridized Polyimide and Copper System", ***Polymer*** vol.45(13), pp. 4465-4472, 2004.

■ Conference Papers

1. Pei-Chun Chiang, Wha-Tzong Whang, "Preparation of Polyimide/ $LiMn_2O_4$ Nano Hybrid films and its Characterization, Morphology, and Conductivity Properties", The International Conference on Metallurgical Coatings and Thin Films 2002.

2. Pei-Chun Chiang, Wha-Tzong Whang, Mei-Hui Tsai, Sheng-Chang Wu, "Physical and Mechanical Properties of Polyimide/Titania Hybrid Films", The International Conference on Metallurgical Coatings and Thin Films 2003.

3. Pei-Chun Chiang, Wha-Tzong Whang, Mei-Hui Tsai, "Adhesion Strength and Interface Analysis of Polyimide/Titania Hybrid Films and Copper System", The International Conference on Metallurgical Coatings and Thin Films 2003.

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