

Polyimide Based Nanohybrids; Characterization and Electro-optic Applications

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In this paper, our recent works on the microstructure and interfacial interaction of polyimide (PI) based hybrid nanocomposites were summarized. A series of PI-silica and PI-polysilsesquioxane hybrid nanocomposites were prepared via sol-gel reaction and thermal imidization. Poly(vinyl silsesquioxane), aminosilane, and titania played vital roles for the formation of nanocomposites for the PI/silica hybrid system. In addition, PI hybrid concepts to organic light-emitting devices (OLEDs) were introduced in order to enhance thermal stability and thus long-term lifetime property of the OLEDs. PIs and hybrid materials for microelectronic applications and OLED was further discussed. Finally, the transparent flexible substrate based on PI based nanohybrids were also briefly introduced.

Introduction

Polyimides (PIs) have been widely used in the aerospace, microelectronics devices, dielectric layers in multichip semiconductor packaging, and so on due to their high thermal stability and mechanical properties, low thermal expansion and dielectric constants, and good resistance to organic solvents. On the other hand, the dispersion of inorganic nanoparticles into a polymer matrix has been proved to be effective in the improvement of the performances of the organic polymers by yielding so-called organic-inorganic hybrid nanocomposites. These nanocomposites are one of the hottest issues among the today's materials scientists since its unique combinational properties from organic and inorganic materials could not be obtained by single component. The sol-gel reaction has been one of the most widely used approaches to obtain hybrid nanocomposites. In particular, an important advantage of the sol-gel synthesis route for polyimide/silica hybrid composites is that the poly(amic acid) organic matrix acts to prevent agglomeration of the silica, which can lead to nanometer scale silica clusters in the composites or, as often stated, "nanocomposites."

In this paper, our recent works on the microstructure and interfacial interaction of polyimide (PI) based hybrid nanocomposites were summarized[1]. A series of PI-silica and PI-polysilsesquioxane hybrid nanocomposites were prepared via sol-gel reaction and thermal imidization.

Organic light-emitting diodes(OLEDs) have attracted much attention because of their

potential application in full-color flat panel displays operated at low drive voltages[2-4]. A typical OLED consists of a hole-injecting contact, a hole-transporting layer(HTL), a light emitting layer, an electron-transporting layer, and an electron-injection contact in order. Sometimes a hole blocking layer is also introduced. High work function materials such as Al, Mg, and Li, etc. are used for cathode and indium-tin-oxide (ITO) coated glass is usually used for anode and substrate (see Figure 1). In figure 1, a typical thickness of each layer is also shown.

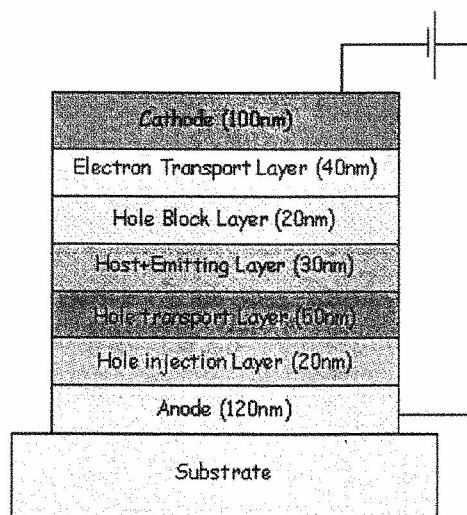


Figure 1. A typical multilayer OLED structure

Thermal stability is one of the most important requirements in OLEDs, because the joule-heat generated during the device operation may severely relax and damage organic materials with inherently lower thermal stability than inorganic materials or metals. Thermal stability is directly related to the device properties such as current density-voltage-EL intensity (J-V-L) characteristics, electroluminescent (EL) spectra, and lifetime. Another primary focus of this paper is, therefore, to review recent advances in utilizing polyimides in OLEDs which have been done in this laboratory[5].

Microstructure, Interfacial Interaction and Properties of Polyimide/Silica nanohybrids

It is utmost important to improve the compatibility between two phases to prepare polyimide-inorganic composites with good properties. There are several approaches to make compatibilized composites: (1) By adding coupling agent which makes bond with the growing inorganic oxides and PI chains, (2) functionalizing the PI chains at their end groups, (3) choosing a polymer with appropriate groups within the repeating units, (4) using

appropriate functional groups, (5) choosing judiciously the silsesquioxane, which can also make bond with the carbonyl groups of PI, (6) interestingly, introducing titania to be able to reduce particles of silica/silsesquioxane through Si-O-Ti bonding. A few methods employed for preparing compatibilized hybrid composites have been discussed in this presentation.

Ha et al. [6] introduced fluorescence spectroscopy to interpret the interfacial interaction between the inorganic particles and PI as shown in Figure 2. In this figure, silica was prepared by sol-gel reaction of tetraethoxysilane (TEOS) as a silica precursor. The peaks were obtained with the excitation wavelength of 350 nm. The results in Figure 2 can be summarized as follows: On increasing the amount of silica, the wavelength of emission peak for the 3, 3', 4,4'- biphenyltetracarboxylic anhydride (BPDA)-phenylenediamine (PDA) PI/silica composite films increases. A large red shift was observed for the BPDA-PDA PI/silica hybrid system (up to 50-70 nm) at high silica loadings (22 wt.%). The result suggests that the interaction between silica and polyimide is important and the interfacial interaction between BPDA-PDA PI and silica is strong. We found that in the BPDA-4,4'-oxydianiline (ODA) PI/silica composite there is no specific interaction or chemical bonding holding the silica to the polyimide matrix.

Highly compatibilized BPDA-ODA PI/silica films can be, however, successfully prepared if one use 3-aminopropyltriethoxysilane (3-APS) or polyvinylsilsesquioxane (PVSSQ). For instance, in Figure 3, 3-APS produced very compact and fine microstructure as well as improved optical transparencies in the hybrid composites of PI with silica from TEOS in comparison to the PI/silica hybrid composite without 3-APS, which exhibits gross phase separation. In this figure, the silica content is fixed at 30 wt. %. The enhancement of phase compatibility brought via PVSSQ was also clearly observed as for the case of 3-APS. The result was ascribed to the better interfacial interaction in the PI/PVSSQ hybrids in comparison to that of the PI/silica (from TEOS) hybrid system. The end hydrogen of PVSSQ and the hydrogen of Si-OH also provide hydrogen bonds in the carbonyl group of the PI matrix, leading to compatibilized morphology.

It was found that nanocomposites with BPDA-PDA PI can be obtained up to 30 wt% of PVSSQ, whereas ≤ 20 wt% of PVSSQ is the maximum composition to give nanocomposites for the BPDA-ODA PI. The mechanical properties of the nanocomposites were improved by the introduction of fine silica particles into a polymer matrix and better adhesion as well as strong interaction between PI and PVSSQ. It is noteworthy that the flexible organic phase of PVSSQ played a significant role in the interfacial adhesion between polyimide and the PVSSQ. It was also found that the addition of silica or PVSSQ affected on the dielectric constant of hybrid films, which was explained in terms of increasing free volume as well as domains sizes of PVSSQ and inherently higher dielectric value of silica.

Meanwhile, it is known that titania possess very fast hydrolysis and ultimately produces inhomogeneous and large agglomeration of domains, which can significantly impact on the polymer matrix. The introduction of titania into the PI/silica hybrid composites were, however, found to improve the interfacial interaction between silica and PI [1].

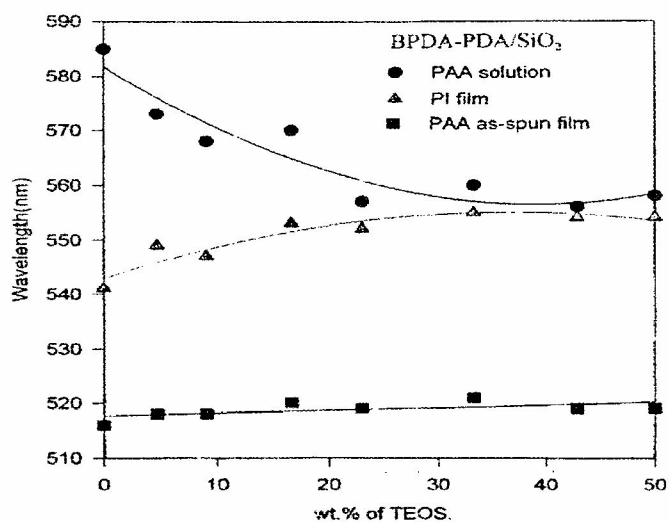


Figure 2. Emission wavelength change of BPDA-PDA PAA/TEOS hybrid solution in NMP, BPDA-PDA PAA/TEOS hybrid as-spun film and BPDA-PDA polyimide/silica composites.

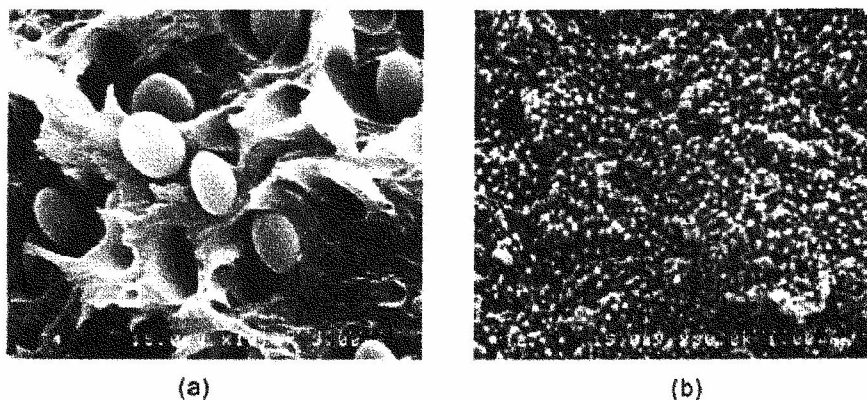


Figure 3. SEM images of the PI/silica hybrid composites containing 30 wt% of silica without (a) and with (b) 3APS.

Polyimides for Hybrid OLEDs

The first paper to utilize polyimides in OLEDs was reported by Kim, et al.[7], where they used poly(p-phenylene biphenyltetracarboximide)(BPDA-PDA PI) as a bind matrix

polymer for the green color emitter, tri(8-hydroxyquinolino)aluminium (Alq_3). Solution blends of the Alq_3 and poly(p-phenylene biphenyltetracarboxylic acid) (BPDA-PDA PAA) in N-methyl-2-pyrrolidinone (NMP) were prepared with the composition of 10/90, 30/30, and 50/50 by weight. The solid concentration was ca. 1 wt.%. The solutions were spin-coated at 300 rpm for 5 min onto a patterned indium tin oxide (ITO)-coated glass. The films were soft-baked at 80 °C for 60 min. The film thickness was 150-200 nm. The soft-baked films were thermally imidized into BPDA-PDA PI at 250 °C for 60 min at a heating rate of 2 °C/min.

It was found that the use of polyimide as a hole-transporting material is not efficient for its low photoluminescence. Therefore, polyimide has been used as a binder matrix polymer for low molecular weight hole-transporting material such as N,N'-diphenyl-N,N'-di(m-tolyl) benzidine (TPD). Various dyes were dispersed in polyimide matrix as a HTL. For instance, Choi, et al. used the 6FDA-3MPDA PI for a binder matrix polymer for TPD to optimize the design of blue OLED with a buffer layer of poly(styrene sulfonate) doped poly(3,4-ethylene dioxythiophene) (PEDOT/PSS)[8]. They also found that the soluble phthalocyanines were found to work as good hole-transporting materials with good thermal stabilities in the OLED using polyimide as a binder matrix polymer for TPD.

Kim, et al.[9] investigated the charge conduction and emission mechanisms in the PI-based OLED by the aid of conventional models. The theoretical analysis of the charge conduction and emission behavior of OLED is sometimes very important in the practical application of OLED in order to exactly understand the practical OLED characteristics such as current-voltage and luminance-voltage characteristics, etc. New non-linear models proposed by Kim, et al.[9] predicted the characteristics almost completely, even though the physical meaning of the included parameters was not clearly defined.

Polyimides as Plastic Substrate for the Flexible OLED

With the recent development of semiconductor techniques, it is feasible to fabricate semiconductor devices on organic flexible substrates. OLEDs can be also fabricated on flexible plastic substrates, creating the potential to reduce the weight of flat panel displays (FPDs). Flexible polymeric EL devices based on π -conjugated polymers have been demonstrated on polyaniline substrates and ITO-coated plastic substrates, which further spurred interest in FPDs. So far, the use of the flexible substrates for OLEDs has been restricted mainly to the polyester films due to their excellent transparent property. However, the plastic substrates till now can be severely damaged at high temperature (200 ~ 300 °C for sputtering method) during deposition process, mainly due to their intrinsic low thermal and mechanical properties compared with other inorganic or metal substrates. In this case,

therefore, it is impossible to use a common sputtering method at high temperature. Consequently, reduced electrical resistivity and long-term stability of the ITO surface cannot be achieved and maintained, which is directly related to the performance of applied devices.

Despite the excellent mechanical and thermal properties of polyimides, the applications of the aromatic PI films for optical application are very limited due to their yellowish nature due to the intra- and/or intermolecular charge transfer complex (CTC) formation. Recently, the syntheses of colorless transparent PIs have been achieved by the introduction of non-aromatic, fluorine, or sulfone groups into the polymer main chain, which systems minimize the formation of the intra- and/or intermolecular CTC in the molecules. It leads aromatic PIs to be applied in optical components. Aliphatic cyclic polyimide (alicyclic polyimide) was synthesized from alicyclic dianhydride and was used as flexible transparent substrate for the deposition of ITO thin films by Lim, et al.[10] ITO thin films were prepared at typical high substrate deposition temperature with a r.f. planar magnetron sputtering system.

The plastic substrates with transparent ITO thin films have been successfully prepared with aliphatic bicyclic polyimide (PI) synthesized from bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCOEDA) and 4,4'-oxydianiline (ODA) monomers[10]. It was summarized that the BCOEDA-ODA PI substrates with ITO thin film has a good electrical conductivity, in spite of its relatively lower optical transmission property. The substrate can be applicable to display devices with from yellow to red emission property, except for blue or green emission devices.

Another colorless polyimide substrates with ITO thin films have been also prepared by Lim, et al.[11] with a novel fluorine-containing colorless aromatic PI derived from 2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2'-bis (trifluoromethyl)-4,4'-diaminobiphenyl (TFDB), which has been used as a transparent flexible substrate for OLED. The PI substrate has high glass transition and decomposition temperature, low water absorption, good transmission, and low optical loss. Figure 4 shows current density-voltage-luminance ($J-V-L$) characteristic of the flexible OLED (PI/ITO/TPD/Alq₃/Al) prepared onto the PI substrate. The inset shows the luminous efficiency with the current density. It was also found that the electrical sheet resistance, optical transmission, grain size, and structural orientation significantly depend on the substrate temperatures. Most of all, the sheet resistance value was the lowest value of the ITO films coated onto polymer substrates have been reported in the previous literatures. From the dependence of the sheet resistance on the grain size, it can be considered that the predominant scattering mechanism limiting the mobility is the grain boundary scattering mechanism for the ITO films deposited onto the PI substrates.

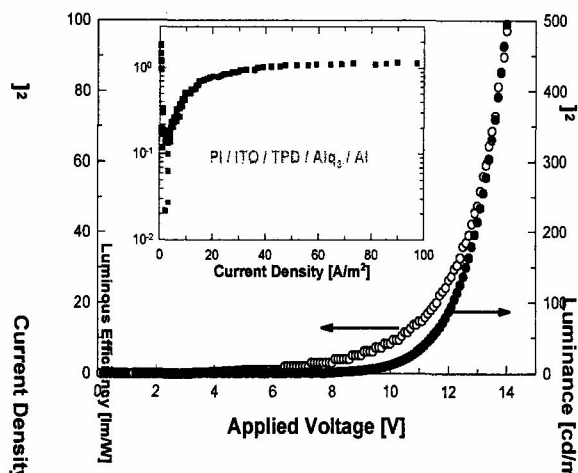


Figure 4. Current density-voltage-luminance (J - V - L) characteristic of the flexible OLED (PI/ITO/TPD/Alq₃/Al) prepared onto the PI substrate. The inset shows the luminous efficiency with the current density[11].

Conclusions

Our recent works on the microstructure and interfacial interaction of PI based hybrid nanocomposites were introduced in this paper. A series of PI-silica and PI-polysilsesquioxane hybrid nanocomposites were prepared via sol-gel reaction and thermal imidization. It was found that PVSSQ, aminosilane, and titania can effectively play vital roles to produce better environment by reducing fast hydrolysis for the homogeneous nanoscale distribution and by avoiding agglomeration of large domains, which helps the formation of nanocomposites for the PI/silica hybrid system. In addition, the utilization of polyimides for OLEDs is a fascinating challenging problem but the interest in polyimides is also rooted in their wide array of potentially usable applications. Polyimides have been extensively studied for the application of a dielectric or insulating layer in micro-electronic devices because of various outstanding properties such as low thermal expansion and high mechanical strength. These excellent characteristics of polyimides, especially high T_g of above 200 °C in general lead to their application of OLED. According to the motivation, we have previously reported the successful fabrication of OLED with a polyimide thin films containing hole-transporting small molecules or a conducting polymer as an HTL.

Acknowledgements

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