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Synthesis and characterization of a novel polyimide/TiO_2 nanocomposite for solution processable high k dielectric

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The polyimide/TiO_2 nanocomposite thin films have been successfully synthesized. The surfaces of TiO_2 particles were chemically modified with a γ-glycidyloxypropyltrimethoxysilane (GPTS) functional group to enhance the compatibility with polymeric matrix and to avoid the aggregation of particles. The dispersion of surface modified TiO_2 in polyimide film was greatly improved and it was confirmed by the scanning electron microscope (SEM) analysis showing that well dispersed nanosized TiO_2 particles. Compare to thepolyimide/unmodified TiO_2 (T5) nanocomposite film, the size of the TiO_2 particles in the polyimide/surface modified TiO_2 (T5-GPTS) film was substantially reduced due to the increased solubility of surface modified TiO_2 (T5-GPTS). The mechanical properties, thermal stabilities and dielectric properties of polyimide/surface modified TiO_2 (T5-GPTS) nanocomposite films were also systematically investigated.

Key words: Polyimide, TiO_2, Nanocomposite, Surface modification.

Introduction

Organic/inorganic nanocomposites have become an effective source of advanced materials as they usually exhibit unique properties that traditional composites and conventional materials do not have. They combine the advantages of the inorganic material (rigidity, high thermal stability) and the organic polymer (flexibility, dielectric, ductility, and processibility) [1, 2]. High-performance polymers of the polyimide (PI) type are already widely used in microelectronic industries because of their outstanding characteristics such as excellent tensile strength and modulus, low thermal expansivity and good resistance to organic solvents. Very recent specific examples of their application are their uses as gate insulator layers in thin-film transistor technologies [3, 4].

Among the different compounds largely used as inorganic fractions in hybrids with PI, titanium dioxide (TiO_2) has received particular attention in recent years. Several reports on the synthesis and characterization of PI/TiO_2 hybrids have been described, aiming to obtain materials that find application in electrochromic devices, nonlinear optical systems, thin-film transistors, and so forth. The TiO_2 is viewed as an important inorganic component in nanocomposites for the improvement of thermal stability, mechanical properties, and dielectric constant [5, 6]. Therefore, polyimide-titanium dioxide (PI/TiO_2) nanocomposites have attracted particular interest. Many researchers have been focusing on developing PI-TiO_2 hybrid nanocomposites such as the use of dianhydride and diamine for synthesis of PI matrix and the use of metal alkoxide to provide the inorganic network. However, increasing the content of metal alkoxide (TiO_2) causes the films the agglomerations of the TiO_2 into large particles are usually happened.

In this work, we have investigated polyimide-TiO_2 nanocomposite system to reduce the agglomeration and to achieve the mono-dispersity of the nano-sized TiO_2 in polyamic acid (PAA) through a surface modification of TiO_2 using a silane coupling agent. γ-Glycidyloxypropyltrimethoxysilane (GPTS) was chosen as the silane coupling agent for the modification of TiO_2 surface to enhance the compatibility between the PI and TiO_2. The Fourier transformed infrared spectroscopy (FT-IR) studies showed that successful surface modification of TiO_2. The dispersion of nano-sized TiO_2 particles in PI matrix was studied by a scanning electron microscope (SEM). The mechanical properties of PI-TiO_2 nanocomposite films were affected by the amount of TiO_2 particles. In addition, the capacitances (dielectric constants) of nanocomposite films were also systematically studied through the metal-insulator-metal devices.

Experimental

Modification of TiO_2 particles (T5-GPTS)

A solution of 5 g of deionized (DI) water, 95 g of *N*-methyl-2-pyrrolidone (NMP) and 5 g of TiO_2 particles

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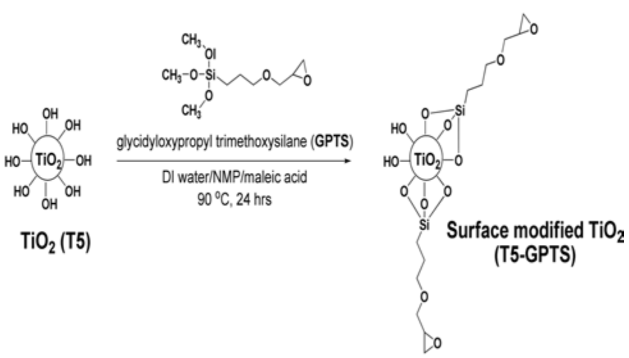

Fig. 1. A schematic synthetic route of surface modified TiO_2 (T5-GPTS).

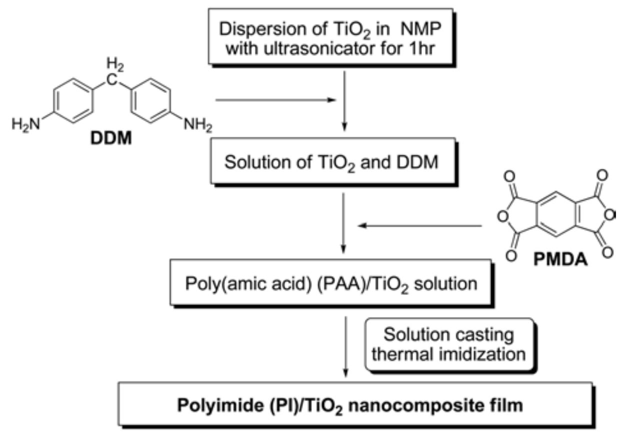

Fig. 2. The process flow diagram for the preparation of polyimide/ TiO_2 nanocomposite films.

(T5, anatase 99%, average particle size = 5 nm) were mixed in a reaction system with anultrasonicator for about 1 h. A specific amount of the coupling agent (γ-glycidyloxypropyltrimethoxysilane, GPTS) was then added into the mixture. And then maleic acid (0.075 g of maleic anhydride and 0.5 ml of DI water) was added as a catalyst. The mixture was refluxed for 24 hours at 90 °C under nitrogen atmosphere. After cooling down, a white precipitate from the mixture was centrifuged and washed with acetone. Then obtained modified TiO_2 particles (T5-GPTS) were dried under vacuum for 24 hours at 100 °C. The synthetic scheme for the surface modification of TiO_2 is shown in Fig. 1.

Preparation of the polyimide/TiO_2nanocomposite films

The process flows of the PI/TiO_2nanocomposite films fabrication are displayed in Fig. 2. A specific amount of T5 (or T5-GPTS) dispersed in NMP with ultrasonicator for about 1 hour. 3-neck round bottom flask (with N_2 purge and ice-bath) prepared and 4, 4'-diaminodiphenylmethane (DDM) was dissolved in T5 (or T5-GPTS)/NMP mixture. After dissolving of DDM, pyromelloticdianhydride (PMDA) added into the reactor and stirred for 24 hrs. We obtained a viscous polyamic acid (PAA)/T5 (T5-GPTS) solution and fabricated thin films on a dust free glass substrate by spin-coating method. The film was pre-cured at 90 °C for 2 minutes on a hot plate and then the film was finally imidized at 250 °C for 2 minutes on a hot plate. The thickness of the imidized films was about 2 μm.

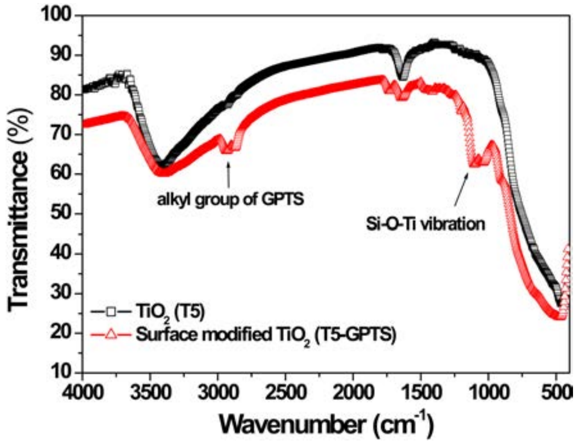

Fig. 3. The FT-IR spectra of the TiO_2 (T5) and surface modified TiO_2 (T5-GPTS).

Results and discussion

The surface modification of TiO_2 by a γ-glycidyloxypropyltrimethoxysilane (GPTS) was confirmed by the Fourier transformed infrared spectroscopy (FT-IR). FT-IR spectra of surface modified TiO_2 (T5-GPTS) and nonmodified TiO_2 (T5) were measured using KBr pellets. As shown in Fig. 3, the band at 3200 ~ 3400 cm^{-1} is a result of the Ti-OH group and new peaks at 2840 ~ 2930 cm^{-1} are appeared after the surface modification of TiO_2 using GPTS. These bands correspond to the alkyl group of GPTS. In addition, the band at 1020 ~ 1250 cm^{-1} is the Si-O-Ti vibration and this clearly proves the attachment of GPTS group into the surface of TiO_2 by chemical reaction. To investigate the effect of GPTS on PI/TiO_2nanocomposite films, we compared PI/T5-GPTS films with PI/T5 (unmodified TiO_2) films through the SEM anaysis. Fig. 4 shows SEM images of PI/T5 and PI/T5-GPTS nanocomposite films. Both films were fabricated in NMP solvent and TiO_2 particle as 5 wt% to PI monomers. By comparison of these two samples, it was observed that the TiO_2 particle size in the composites decreases with the addition of GPTS. We also found that the dispersion of the TiO_2 particles in the composite films becomes more even, narrower in size distribution, and less aggregated with the addition of GPTS. In the case of PI/T5-GPTS, average particle sizes are in the range of between 50 ~ 70 nm, which are smaller than the particle sizes (100 ~ 200 nm) of PI/T5 film.

The thermal stability of pure PI, PI/T5 and PI/T5-GPTS films were investigated by thermal gravimetric analysis (TGA) under nitrogen atmosphere. The thermal decomposition temperatures (T_d) (temperature at 5 wt.-

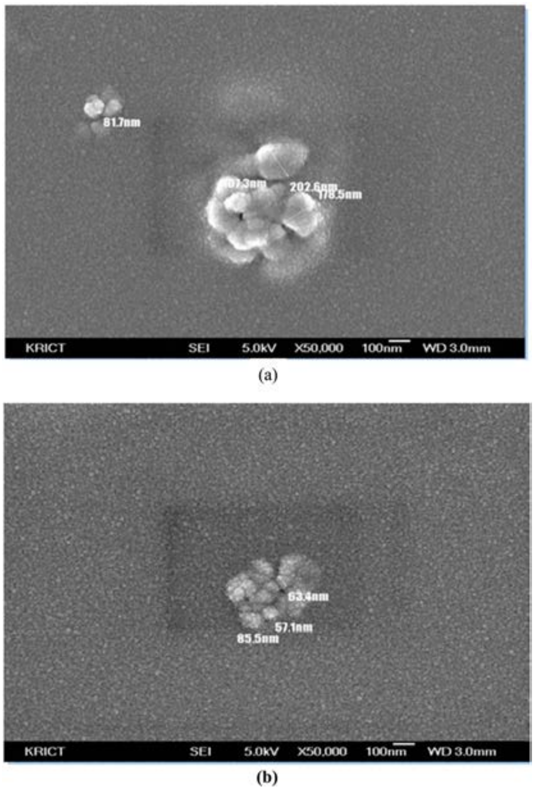

Fig. 4. SEM micrographs of (a) PI/TiO_2 (T5) and (b) PI/surface modified TiO_2 (T5-GPTS) nanocomposite films.

% weight loss of sample) of PI/T5-GPTS was measured at 540 °C which is higher value than pure PI (514 °C) or PI/T5 (530 °C). The effect of the surface modification of TiO_2 for nanocomposite with PI is apparent in the measurement of the coefficients of thermal expansion (CTE) of pure PI, PI/T5, and PI/T5-GPTS as shown in Fig. 5. Large reductions in CTE were observed in a PI/T5-GPTS nanocomposite film. The effect became even more pronounced at temperatures above T_g of the PI. Clearly, this was attributed to the enhanced compatibility of the PI and TiO_2 phase because the surface of TiO_2 were reacted with functional GPTS groups, resulting in good interface formations between PI and TiO_2 (T5-GPTS). To investigate and compare the mechanical properties of PI, PI/T5, and PI/T5-GPTS, the tensile tests were also carried out on these samples. The mechanical strength of PI/T5-GPTS nanocomposite film was enhanced by the introduction of the surface modified TiO_2 in PI matrix. The tensile strength of a PI/T5-GPTS film was measured to be 101.2 MPa, which is an improved result compared to that of pure PI (33.5 MPa) or PI/T5 film (66.4 MPa). This was attributed to the development of co-continuous phase morphologies leading to efficient stress-transfer mechanisms.

Recently, organic thin-film transistors (OTFTs) have been recognized as promising technology for next generation electronics due to their unique advantages, such as light-weight, flexibility, and low-cost fabrication.

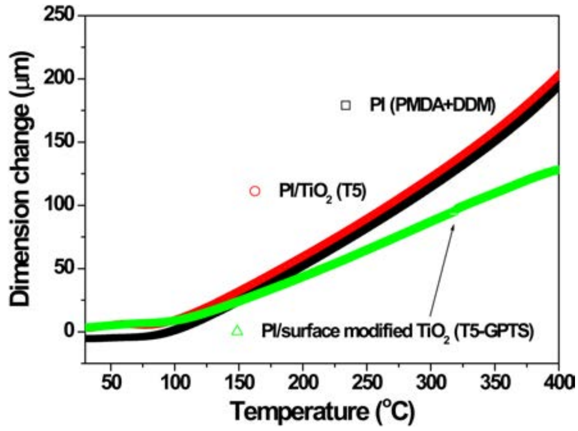

Fig. 5. Effects of compatibilization on the coefficients of thermal expansion of pure PI (PMDA + DDM), PI/TiO_2 (T5) and PI/surface modified TiO_2 (T5-GPTS) nanocomposite films.

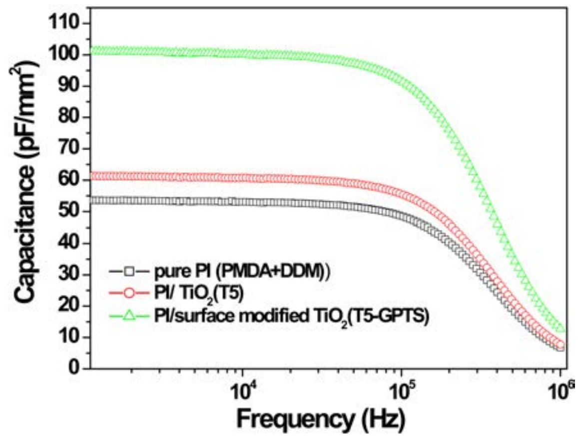

Fig. 6. The capacitance as a function of the frequency for the metal-insulator-metal (MIM) structure of pure PI (PMDA + DDM), PI/TiO_2 (T5) and PI/surface modified TiO_2 (T5-GPTS) nanocomposite films.

The major challenge to realize the commercialization of organic electronics products based on OTFT comes from their high threshold and operating voltages, due to the intrinsic low charge mobilities of organic semiconductors. One feasible approach to achieve low-voltage operation in OTFTs is to use high dielectric constant (high-k) materials as the gate insulators, which can afford greater surface charge density at the semiconductor-dielectric interface. Several groups already have tried the nanocomposite films between TiO_2particles and polymers such as polystyrene (PS) and poly 4-vinylphenol (PVP) to obtain high k gate insulator materials [7-9]. Our PI/surface modified TiO_2nanocompostie system could be a promising candidate for solution processable high k dielectrics. Excellent thermal stability of PI and good compatibility of surface modified TiO_2 with PI can provide good gate dielectric films. To measure the dielectric properties of the PI/TiO_2nanocomposite films, we prepared metal-insulator-metal (MIM) capacitor structures on the precleaned glass substrates by sandwiching the composite layer between ITO as bottom and gold as top electrode. For

MIM devices, the final thicknesses of dielectric layers (pure PI, PI/T5, or PI-T5-GPTSnanocomposite films) were controlled to about 0.5 μm andthe active area of MIM device was 50.24 mm^2. The capacitance of the film was measured with HP 4924 LCR meter. Fig. 6 shows the capacitance values of pure PI, PI/T5, and PI/T5-GPTS samples. Pure PI film (DDM + PMDA) showed the capacitance as 53.7 pF/mm^2 (calculated dielectric constant is 3.04) at 10 kHz, but as increasing the T5-GPTS content, dielectric constant also considerably increased. It was found that 5 wt% T5-GPTS containing PI nanocomposite films show the highest the capacitance as 100.9 pF/mm^2 (dielectric constant is 5.70) at 10 kHz. Interestingly, PI/T5 nanocomposite film from unmodified TiO_2 particle exhibited no significant increase in capacitance (61.3 pF/mm^2, dielectric constant, 3.46) as increasing the content of TiO_2. Clearly, the compatibilities between TiO_2 particles and PI polymer matrix were improved through the surface modification of TiO_2 with organic functional GPTS group, which influences the dielectric properties of nanocomposite films. We propose that the PI/T5-GPTS (surface modified TiO_2) nanocomposite systems could be good candidates as solution processable high k dielectrics in thin-film transistor applications. Further studies of the PI/T5-GPTS nanocomposite film as gate insulators for the low-operating-voltage OTFTs are in progress.

Conclusions

Polyimide/TiO_2nanocomposite films were successfully prepared from a polyamic acid (PAA) and modified TiO_2 particles. We have confirmed that the silane functional group (g-glycidyloxypropyltrimethoxysilane, GPTS) was well grafted to the TiO_2 surface by FT-IR study. PI/T5-GPTS (surface modified TiO_2) nanocomposite films exhibited the highest thermal stability than pure PI and PI/T5 (TiO_2) film. The mechanical properties (tensile strength and CTE) were markedly improved in the PI/T5-GPTS nanocomposite system, especially greater reductions in CTE values of PI/T5-GPTS film resulted from the enhanced compatibility between PI and surface modified TiO_2 (T5-GPTS). In addition, dielectric constant of the composite film was increased up to 5.7 by the incorporation of surface modified TiO_2 particles in PI polymer. The prepared PI/TiO_2 nanocomposite film have excellent thermal stability, enhanced mechanical properties and increased dielectric constant, thus providing the potentials application as gate insulators in the preparation of low-operating-voltage thin-film transistors.

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