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Significant enhancement in dielectric constant of polyimide thin films by doping zirconia nanocrystals

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ABSTRACT

Polyimide thin film has a low dielectric constant of 3.2. In this paper, we fabricated polyimide/ZrO_2-nanocrystals hybrid thin films with a high dielectric constant of 6.1. The polyimide/ZrO_2-nanocrystals hybrid thin films were formed by a spin-coating and a sintering process. The organic/inorganic hybrid thin films were characterized by X-ray powder diffraction, transmission electron microscopy, scanning electron microscopy, and LCR meter. Our experimental results confirmed that ZrO_2 nanocrystals were well dispersed and embedded in the hybrid thin films. Compared with pristine polyimide thin film, the dielectric constant of polyimide/ZrO_2-nanocrystal hybrid thin film significantly increased due to the incorporation of inorganic component.

1. Introduction

The polyimide (PI) thin films with high dielectric constant have an important potential application in thin film transistors (TFT) owing to its light weight, low-cost processability and high mechanical flexibility [1–3]. However, pure PI thin films only have a low dielectric constant of 2.8–3.2. Therefore, various high dielectric constant ceramic components, such as TiO_2, Al_2O_3, ZrO_2, and $BaTiO_3$, have been successfully incorporated in PI thin films, forming PI/ceramic hybrid thin films in order to enhance the dielectric constant of PI thin films [4–12]. However, amorphous ceramic particles will form in the matrix of PI thin films due to a low sintering temperature, which cannot remarkably enhance the dielectric constant of hybrid thin films [5–8]. In most cases, the micro- or submicro-ceramic particles are used as the dopant, so it is hard to fabricate ultra-thin PI/ceramic hybrid thin films. More importantly, these large sized and unfunctionalized ceramic particles will lead to the agglomeration of ceramic particles [10–12]. Thus, it is great significance to prepare well-dispersed PI/ceramic hybrid thin films with a high dielectric constant by using extremely small ceramic nanoparticles as the inorganic components. Oleic acid (OA)-capped ZrO_2 nanocrystals were synthesized according to a previously reported two-phase approach [13]. Note that many types of extremely small metal oxides and metal chalcogenides nanoparticles, such as TiO_2, CdS, CdSe and Mn_3O_4, have been successfully synthesized by this approach [14–19]. In this paper, we prepared the polyimide/ZrO_2-nanocrystals hybrid thin film by a spin-coating and a sintering process. The dielectric constant of polyimide/ZrO_2-nanocrystals hybrid thin film was significantly increased to 6.1 from initial 3.2 due to the incorporation of high dielectric constant ZrO_2 nanocrystals.

2. Experimental

Preparation of polyamic acid: In a glass vial, 200 mg of 4, 4′-diaminodiphenylmethane were dissolved in 8.0 mL of *N*,*N*-dimethylacetamide under magnetic stirring. Next, equimolar Pyromellitic dianhydride was loaded into the vial. A clear polyamic acid solution was obtained after 24 h.

Synthesis of oleic acid-capped ZrO_2 nanocrystals: First, 10 mL of water and 0.2 mL of *tert*-butylamine were loaded into a 30-mL teflon-lined stainless steel autoclave. Afterward, a 10 mL toluene solution containing zirconium *n*-butoxide (0.3 mL) and OA (1.0 mL) was transferred into the autoclave to form a two-phase reaction system. Next, the autoclave was sealed and maintained at 180 °C for 18 h in an oven. Finally, the crude solution of ZrO_2 nanocrystals was precipitated with methanol and further isolated by centrifugation and decantation.

Modification of oleic acid-capped ZrO_2 nanocrystals and preparation of polyimide/ZrO_2-nanocrystaals hybrid thin films: 0.1 g of

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as-prepared ZrO_2 nanocrystals, 0.2 g of 3-chloroperoxybenzoic acid, and 5.0 mL of toluene were mixed under magnetic stirring for 5.0 h. Subsequently, a certain amount of polyamic acid solution was added to modified ZrO_2 nanocrystals solution. After 2 h, the mixed PAA/ZrO_2 nanocrystals solution was used to deposited polyimide/ZrO_2-nanocrystals hybrid thin films by a spin-coating approach, following by a sintering process on a pre-heated hotplate on a ITO substrate for 1 min.

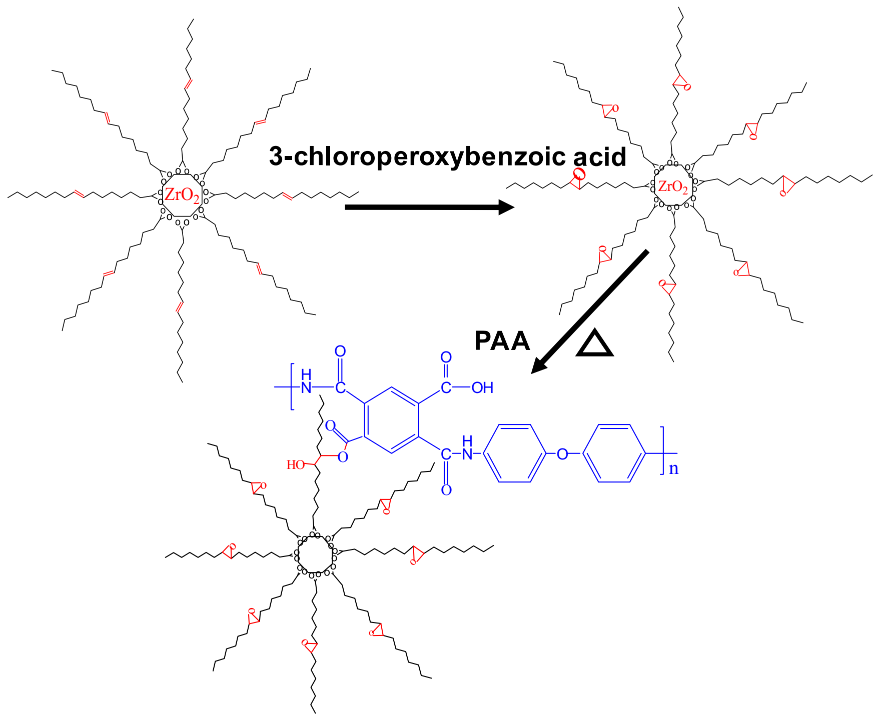

Fig. 1. Mechanism of modified ZrO_2 nanocrystals and the formation of polyimide/ZrO_2-nanocrystals hybrid thin films.

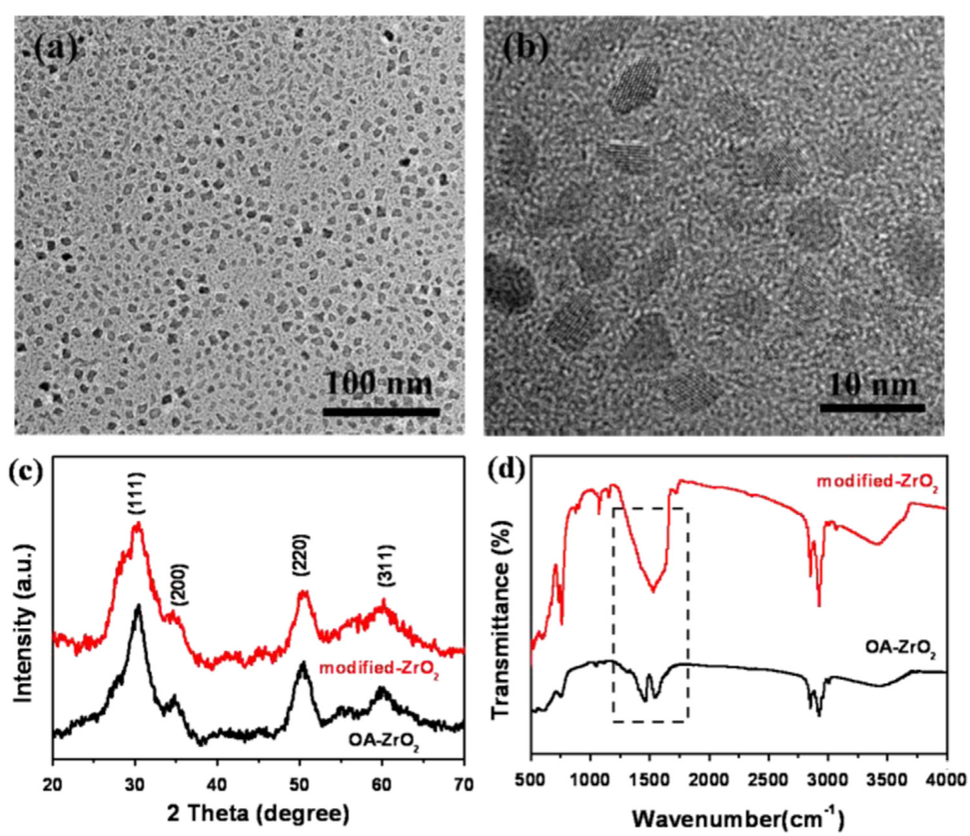

Fig. 2. LR-TEM (a) and HR-TEM (b) images of ZrO_2 nanocrystals; XRD patterns (c) and FT-IR spectra (d) of OA-capped ZrO_2 nanocrystals and modified ZrO_2 nanocrystals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)