

Dielectric Properties of Poly(vinyl phenol)/Titanium Oxide Nanocomposite Thin Films formed by Sol-gel Process

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Abstract.

Poly(vinyl phenol)(PVP)/TiO₂ nanocomposite the films have been prepared incorporating metal alkoxide with vinyl polymer to obtain high dielectric constant gate insulating material for a organic thin film transistor. The surface composition, the morphology, and the thermal and electrical properties of the hybrid nanocomposite films were observed by ESCA, scanning electron microscopy (SEM), atomic force microscopy (AFM), and thermogravimetric analysis (TGA). Thin hybrid films exhibit much higher dielectric constants (7.79 at 40wt% metal alkoxide).

1. Introduction

In order to develop the flexible display systems flexible driving devices must be available. An organic thin film transistor (OTFT) on the flexible substrates (ie., plastic films, papers, etc) is one of the most promising potential flexible driving devices. Because the development of the OTFT devices is still in its infancy, there has been an extensive research efforts in "organic electronics" to improve the semiconducting, conducting, and gate insulating properties of organics (polymer and oligomers) and hybrids (organic-inorganic composites) through novel synthesis and self-assembly techniques.

In the organic electronics, the polymeric insulator has been an essential component to provide performance and reliability of the semiconductor devices. Capacitance and breakdown voltage are two important parameters for the organic insulators. A mobility of $0.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on/off current ratio of 3×10^5 have been reported for OTFT devices

comprising pentacene film and barium strontium titanate (BST) gate insulator deposited by chemical solution processing [1]. BST insulator had a high dielectric constant ($\epsilon = 16$), but showed a relatively low dielectric strength. Liang and Cui were able to fabricate an OTFT using poly(styrene sulfonate)-doped poly(3,4-ethylenedioxythiophene) as semiconductor prepared by spin coating technique [2]. Their device showed the field effect mobility of $0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and on/off current ratio larger than 10^5 . Poly(4-vinyl phenol) (PVP) as the gate dielectric insulator layer was spun on the wafer substrate.

Recently the demand of high performance OTFT has led to the reduction in the channel length and the gate oxide thickness. For this reason, the materials with a high dielectric constant are now considered as an alternative gate dielectric to silicon dioxide. However, it is difficult to obtain a high dielectric constant in a one-component material. Conventional polymeric materials are flexible, easy to fabricate and have a high dielectric strength, but their low dielectric constant limits their dielectric application. Metal oxide materials usually possess high dielectric constant but have inferior processing performance. Hybrids of the polymers and inorganic materials can be a pathway to design the dielectric materials with desired properties.

Sol-gel process, which can synthesize ceramic particles at room temperature, can effectively be used to prepare novel organic/inorganic nanocomposites [3,4]. Synthesis of ceramic nanoparticles by this procedure may result in new materials having merits of both the organic materials and the inorganic materials.

In this study, we prepared nanocomposites of

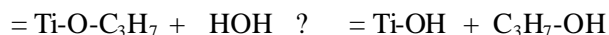
poly(vinyl phenol)/titanium oxide by sol-gel process and examined the physical and electrical properties of thin films, which were fabricated through spin coating. The surface composition, the morphology, and the thermal and electrical properties of the hybrid nanocomposite films were observed by ESCA, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The effects of the polymer matrix and the titanium oxide content on the dielectric properties of the sol-gel hybrid thin films were also investigated.

2. Experimental details

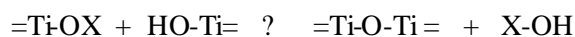
Poly(vinyl phenol) (PVP: Mw 20,000) was obtained from Aldrich Co., and used without any purification. Titanium tetra-isopropoxide (TTIP) $[\text{Ti}(\text{OC}_3\text{H}_7)_4]$ (Wako Chemical Ind., Ltd) was used as the precursor to the inorganic material.

In general, TiO_2 nanoparticles can be synthesized by the hydrolysis and condensation of metal alkoxide $\text{M}(\text{OR})_n$, where M is a metal, O is oxygen, and R is the organic group. We used TTIP as the metal alkoxide.

1) Hydrolysis reaction



2) Condensation reaction



(X = H or C_3H_7)

Since the TTIP and water are not soluble in each other, they must be dissolved in an alcoholic solvent. We diluted the TTIP to 0.1 M in 1-methoxy-2-propanol acetate to carry out the reaction, and rigorously stirred under N_2 atmosphere for one hour. 0.5 N hydrochloric acid was dropped and stirred into the TTIP solution, to promote hydrolysis of the transparent solution.

Once particles begin to grow in the 1-methoxy-2-propanol acetate, they are likely to collide with each other because of the Brownian motion. Hence, forming a stable colloidal suspension of titanium oxide nanoparticles is essential to produce mono-disperse oxide powders.

To provide an effective barrier against the particle

agglomeration, a polymeric layer can be used to cover the oxide particles. As the polymeric stabilizer, PVP was dissolved in 1-methoxy-2-propanol acetate (15 wt%), respectively, and a amount of TiO_2 sol was added to 10wt% and 40wt% each PVP solution. These mixed solutions were stirred at room temperature under N_2 for 20 hours, resulting TiO_2 sols that are ready to be used for the coating. The PVP/ TiO_2 sol-gel films was spun on the silicon wafer by single spin-coating at room temperature. The spinning speed varied from 2000 to 3000 rpm, and the deposition time was fixed at 60 sec. After the film was deposited, the substrates were baked for about 15 min at 150 and then annealed at room temperature. The film thickness was measured by an alpha step (AS-IQ), Electrical measurements were performed using a parameter analyzer (HP4145B, Hewlett Packard). Dielectric constants of the polymers were obtained from capacitance frequency (C-F) and impedance measurements carried out with the HP4194A impedance analyzer.

3. Results and Discussion

Chemical compositions of the hybrid film surface were determined by ESCA (PHI 1600, Physical Electronics; USA) with a magnesium anode ($\text{MgK}_\alpha = 1253.6 \text{ eV}$).

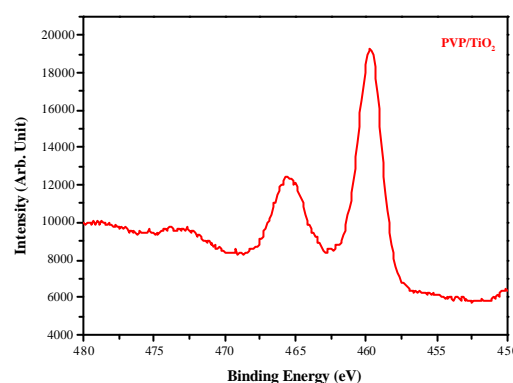


Figure 1. ESCA spectra of TiO_2 nanocomposite films deposited on Si wafer.

Figure 1 shows the Ti 2p peaks of each nanocomposite film. Two characteristic peaks were observed; one at 465.5 eV ($\text{Ti}(2p_{1/2})$) and the other at 459.5 eV ($\text{Ti}(2p_{3/2})$). The binding energy difference, $\Delta E_b = E_b(\text{Ti}2p_{1/2}) - E_b(\text{Ti}2p_{3/2})$ is 6.0 eV, which

agrees well with the value reported in the literature. In Figure 2 SEM micrographs of the top surface and of the fractured cross-section of both hybrid films are shown. SEM micrographs of film reveal a relatively dense microstructure with smooth surface. From the cross-section of the PVP/TiO₂ nanocomposite film, the thickness was approximately 200 nm.

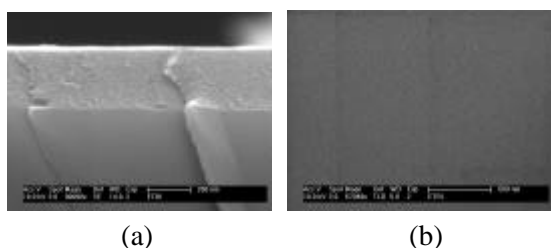


Figure 2. SEM micrographs of the sol-gel processed TiO₂/PVP nanocomposite films; (a) cross-section of the nanocomposite film, (b) surface of the nanocomposite film.

The thermal stabilities of pure PVP, and their hybrids with titanium oxide are listed in Table 1. It is clearly seen that the initial degradation temperature (T^i) (at 3 wt% weight loss) of the hybrid films decreased with an increase in the titanium oxide amount. It is generally believed that the introduction of the inorganic component such as titanium oxide into the organic matrix can improve the thermal stability of the matrix. This increase in the thermal stability can be attributed to the high thermal stability of titanium oxide and also to the interaction between the titanium oxide particles and the polymer matrix. However, our results indicated that the titanium oxide particles somehow promoted the thermal deformation of the hybrid nanocomposites. In fact, Ogata et al. observed in their PLA/clay nanocomposites that the clays seemed to hinder deformation of the crystalline structure of the hybrids at low temperatures, but that the clays acted as deformation accelerators at higher temperature [5]. The thermal deformation rate of the PVP/TiO₂ hybrids depended strongly on the titanium oxide content.

TiO ₂ wt%	PVP/TiO ₂ hybrid T^i (°C)
0	196
10	140
20	120
40	92

Table 1. Thermogravimetric analysis of the Polymer/TiO₂ hybrid films

The electrical characteristics of these nanocomposite films were studied by fabricating a sample with the metal-insulator-metal (MIM) structure. Glass-based capacitor structures of Au/polymer/Au were fabricated using Au electrodes deposited in a high vacuum. Electrode structures were defined using a shadow mask during vapor deposition of Au. In order to form the polymeric insulating layer, the solution where the crosslinker is added was spin-coated onto Au/glass and then irradiated to form the cured insulator.

The dielectric constant () of each gate insulator was calculated from the capacitance (C_0) measurements at 100KHz. The device area of MIM was 1 x 1mm².

To investigate the TiO₂ effect, the current-voltage(I-V) characteristics of the PVP film and PVP/TiO₂ nanocomposite films were examined, as show in Fig. 3. The I-V measurements were recorded in accumulation region while a positive/negative voltage was applied across the device. It was observed that current flowing through the increases by 5 orders of magnitude with TiO₂ contents. The Increase of leakage current with TiO₂ content would came from the poor interfacial contact between TiO₂ particles and polymer molecules.

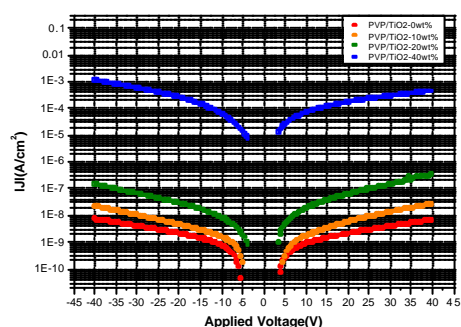


Figure 3. Structure of MIM capacitor to evaluate the electrical characteristic of cross-linked PVP insulator and PVP/TiO₂ dielectric

TTIP (wt%)	Dielectric loss(%) at 100KHz	Thickness (nm)	Capacitance (pF) at 100KHz	Dielectric constant
0	0.05	550	71.83	4.46
10	0.06	700	65.27	5.16
20	0.04	700	79.38	6.28
40	0.04	800	86.18	7.79

Table 2. Electrical parameters of the PVP/TiO₂ nanocomposites in this study

Table 2 lists the measured dielectric constant, film thickness, dielectric loss, and capacitance to illustrate the effect of TiO₂ content.

Dielectric constant values increase with TiO₂ content.

4. Conclusions

In this paper we investigated the preparation of organic-inorganic hybrid films by sol-gel technique.

The SEM photograph shows that TiO₂ particles were dispersed well in the polymer matrix.

The current-voltage characteristics for the hybrids shows their leakage current level is relatively good enough to apply to the devices. But the thermal stability results of nanocomposite decrease with the amount of the inorganic particle. Because of the deformation rate of PVP/TiO₂ hybrids are retarded with the amount of the inorganic particle.

5. Acknowledgements

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6. References

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