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Optimization of nanocomposite gate insulators for organic thin film transistors

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ABSTRACT

Nanocomposite gate insulators consisting of (Ba, Sr)TiO_3 (barium strontium titanate; BST) nanoparticles and crosslinked poly(4-vinyl phenol) (PVP) polymers were fabricated. Well-dispersed nanocomposite films were prepared by optimizing the BST nanoparticle size sorting process (ultrasound crushing and centrifuge method). The size-sorted BST nanoparticles (~30 nm in size) were homogeneously mixed in the PVP host polymer in various BST contents, from 0 to 70 wt%, to tune the dielectric constant (κ) of the resulting nanocomposite films. The composite films exhibit three-fold increase in the κ value from 3.9 to 11.3. The physical properties including leakage current and surface roughness of the composites were also measured as a function of the BST loading content and particle dispersion. The relationship between these properties and the electrical performance of the corresponding organic thin film transistor were explored.

1. Introduction

Organic thin film transistors (OTFTs) have received significant research attention due to the emergence of flexible displays, radio-frequency identification tags, and sensor applications [1–5]. The solution processability of organic electronic materials facilitates their use in low-cost large-area manufacturing techniques such as inkjet printing, conventional film coating, and roll-to-roll techniques, for the mass production of flexible electronic goods [6–8]. In this research area, most studies have been devoted to synthesize new functional materials (semiconductors, gate insulators, and conductors) and to improve the electrical performances of solution-processed OTFT devices. These efforts may position OTFTs as viable alternatives to amorphous Si-based devices [9–11].

Traditional OTFTs frequently suffer from high operating voltages due to the low charge carrier mobilities of organic semiconductors. As a result, OTFTs are generally not suitable in electronic applications that require a high current output such as switching in organic light emitting diodes. The field-induced current in an OTFT is proportional to accumulated charge density and the charge carrier mobility; therefore, such problems can be tackled by using gate insulators with high dielectric constants (κ) that can enhance the field-induced charge carrier density in the semiconductor channel. To this end, various high κ ceramics have been incorporated in OTFTs as gate insulators. However, these inorganic ceramics are typically brittle and expensive vacuum evaporation process needs to be applied [12,13]. To overcome these issues several research groups have reported OTFT devices operated with nanocomposite gate insulators composed of high κ inorganic nanoparticles dispersing within a polymer matrix [14–

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16]. Nanocomposite strategies generally yield films with outstanding electronic properties derived from the synergy between the two constituents [17,18]. For example, gate insulators based on organic–inorganic hybrid nanocomposites commonly exhibit higher κ values than those of pure polymer hosts. In addition, these composites can be mechanically flexible and solution processable [14–16]. To use the nanocomposites as high-κ gate insulators for OTFTs, they must satisfy several requirements; e.g. avoiding leakage current through the film and providing surface properties that are compatible with the semiconductor growth conditions. Therefore, development of nanocomposite gate insulators with surface and bulk properties that are suitable for various organic semiconductors is necessary to realize effective electronic switches.

This study describes the preparation of nanocomposite films composed of (Ba, Sr)TiO_3 (barium strontium titanate; BST) nanoparticles within a crosslinked poly(4-vinyl phenol) (PVP) polymer. Poly(melamine-co-formaldehyde) (PMFA) was used as a crosslinking agent. BST is a common high-κ material. OTFTs prepared using ceramic BST thin films exhibit high field-effect mobilities (μ_{FET}s) and transistor output currents (I_Ds) [16,19]. PVP can be used to fabricate thin films from a solution state, and it provides surface characteristics suitable for semiconductors (a low surface roughness and appropriate surface energy) and high dielectric strengths that minimize the leakage current through the gate insulator. The combination of the two materials in a nanocomposite film can generate solution processable gate insulators that produce OTFTs with high μ_{FET} and I_D. To this end, we fabricate and optimize high-quality BST/PVP nanocomposites for gate insulators in pentacene transistors. BST nanoparticles synthesized by flame spray pyrolysis were treated using a simple ultrasonication and centrifugation process. The resulting size-sorted BST nanoparticles dispersed in the n-methyl-2-pyrrolydinone were very stable and did not precipitate even after 1 month at room temperature. With a 70 wt% BST loading the nanocomposite showed a high κ value of 11.3, much higher than the value obtained from a PVP (κ = 3.9) host polymer. The effects of the BST content on the insulator properties and electrical characteristics of the corresponding OTFTs are also discussed.

2. Experimental

Nano-sized BST particles were purchased from MCT and the Br, Sr, Ti, and O atomic contents in the BST particles were 0.65:0.35:1:1, as reported by the manufacturer. The PVP polymer, PMFA crosslinking agent, and n-methyl-2-pyrrolydinone (NMP) solvent were obtained from Aldrich, and used as received.

A stable size-sorted BST dispersion was prepared by the procedure explained below. First, BST nanoparticles were dissolved in NMP. The solution was then ultrasonicated for 2 h and centrifuged at 10,000 rpm for 30 min to obtain non-aggregated individual particles suspended in the solution. PVP and the crosslinking agent were added to the BST dispersion to prepare a BST–polymer solution. The BST particle content was varied from 0 to 70 wt% relative to the amount of total solids (BST, PVP and crosslinking agent). The amount of crosslinking agent was 25 wt% relative to the amount of PVP and crosslinking agent.

The crosslinkable BST/PVP solutions were spun onto pre-cleaned heavily doped (ρ = 0.002 Ω cm) Si wafers. The nanocomposite films coated on the wafer were pre-baked at 80 °C for 20 min, followed by curing at 180 °C for 1 h in a furnace under a N_2 atmosphere. The thicknesses of the resulting films measured by ellipsometry were ~300 nm. A 40 nm thick pentacene films were deposited onto the PVP/BST nanocomposites by organic molecular beam deposition with a deposition rate of 0.1–0.2 Å/s and a substrate temperature of 30 °C. The 100 nm thick gold electrodes were thermally evaporated onto the pentacene semiconductor layer through a shadow mask. The channel length and channel width of the devices were 100 μm and 1500 μm, respectively. The electrical characteristics of the BST/PVP insulator-gated OTFTs were measured in air using Keithley 2400 and 236 source/measure units.

Transmission electron microscope (TEM) experiments were carried out to characterize the size and the degree of dispersion of BST nanoparticles (Tecnai G2 F20 S-TWIN). The root-mean-square (RMS) roughness values of the nanocomposite layers were characterized by a tapping-mode AFM (Digital Instrument Multimode SPM). The capacitance measurements were performed using an Agilent 4284 precision LCR meter at 1 MHz to determine the κ of the BST/PVP nanocomposites. X-ray diffraction (XRD) experiments were performed at the 10C1 beam line (wavelength 1.54 Å) of the Pohang Accelerator Laboratory (PAL).

3. Results and discussion

The BST nanoparticles obtained from MCT were prepared by a flame spray pyrolysis known to produce high-purity nano-sized powders of metal oxides [20]. Fig. 1a and c shows that as-received BST nanoparticles were not stable in a solution and agglomerated to form large clusters in the size range ~few hundreds nanometers. In general, scaling down a material to the nanometer size increases the surface tension due to the increased surface area-to-volume ratio. Agglomeration among these nanoscopic particles is often spontaneous because this process offers thermodynamically favorable pathway to reduce the surface tension of the materials. In the assembly point of view, however, large agglomerates usually impede the homogeneous distribution of the inorganic fillers in the polymer matrix and thereby leading to a macrophase separation of the clusters from the nanocomposites. This is because taking the large particles within a polymer matrix is entropically costly. To prevent the macrophase separation of the inorganic phase, it is desirable to avoid agglomeration of the oxide and to maintain stable small nanoparticles in the assembly. BST clusters can be pulverized into individual particles by physically crushing the clusters using an ultrasonic treatment, followed by sorting the stable supernatant particles by centrifugation. In the process, ultrasonication separates individual particles from weakly bound clusters and the sequential centrifugation removes aggregated particles remaining in the solution.