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A new nanocomposite dielectric ink and its application in printed thin-film transistors

Xinzhou Wu [a,b], Fei Fei [a], Zheng Chen [a,*], Wenming Su [a], Zheng Cui [a,*]

[a] Printable Electronics Research Centre, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

A new nanocomposite dielectric ink has been developed by dispersing $Ca_2Nb_3O_{10}$ nanosheets in acetone diluted PMMA solution. Dielectric films were formed by printing the ink with an aerosol jet printer. SEM images showed that the 2D nanosheets were homogeneously distributed in the printed films which exhibited higher dielectric constants than PMMA, low dielectric loss and good dielectric stability over a wide range of frequencies. The effect of nanosheet content in the ink has been investigated. Thin-film transistors based on indium gallium zinc oxide semiconductor material were fabricated with the printed nanocomposite insulator. The feasibility of printing dielectrics based on the new nanocomposite ink for thin-film transistors has been demonstrated.

1. Introduction

In recent years, printed electronics have gained great interest due to its potential applications in large size, flexible, and most importantly, low cost electronics [1–5]. Many efforts have been devoted to printed thin film transistors (TFTs) since they are the core devices of electronics [1,6,7]. Considerable progress has been made in printable semiconductor and electrode materials within the last few years [7]. However, as one of the most important constituents of TFTs, the dielectric layers are rarely printed because of the lack of printable dielectric materials and the difficulty of printing a high-quality dielectric layer [8]. In general, the dielectric films in printed TFTs must be thick enough (usually hundreds nanometers or even a few micrometers) to prevent leakage current. On the other hand, large capacitance per unit area of the printed dielectric layer is required in order to reduce the gate voltage of the transistors. The large capacitance, which is directly proportional to the dielectric permittivity and inversely proportional to the film thickness, implies that the printed dielectric material must have high-permittivity (high-k) so that a thick layer can be tolerated.

Many solution processable dielectric materials have been developed as gate dielectrics, including polymer [8], inorganic oxide [9], ion-gel [10] and solid-state electrolyte [11]. Ion gel [6,7,12,13] and solid state electrolytes have high dielectric constant but high conductivity at high frequency, which limits the switching speed of a transistor. Solution processable inorganic materials such as ZrO_2 [9] have higher permittivity and high frequency stability, but it is difficult to prevent the printed ceramic film from pinholes and crack which can cause deadly short circuits in devices. In contrast, polymer dielectric materials are easy to print but of low permittivity. Composites combining high-k inorganic nanoparticles with printable polymer may generate new type of dielectric materials which would have high dielectric constant and high frequency stability as well as good printability.

For such a composite material, its dielectric constant generally increases with the loading of high-k inorganic nanoparticles. However, the leakage current also increases with increased loading of nanoparticles due to the insufficient filling of polymer among nanoparticles and electromigration of metallic atoms through the gaps from electrode material. In this case, two dimensional (2D) dielectric materials are more suitable comparing to the spherical nanoparticles, because of their lamellar geometry. Similar principle has been done to prevent oxygen permeation by introducing exfoliated sodium montmorillonite clay, and the resulted film has an oxygen transmission rate much below the detection limit of commercial instrumentation [14].

In the present work, a new nanocomposite combining 2D dielectric nanosheets with polymer has been investigated as a printable dielectric material. The nanocomposite dielectric ink was formed by dispersing $Ca_2Nb_3O_{10}$ (2D nanosheets) into acetone diluted PMMA solution. Thin films of $Ca_2Nb_3O_{10}$–PMMA were formed by printing the ink with an aerosol jet printer and their

* Corresponding authors. Tel.: +86 (0)512 62872730; fax: +86 (0)512 62603079.
E-mail addresses: zchen2007@sinano.ac.cn (Z. Chen), zcui2009@sinano.ac.cn (Z. Cui).

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dielectric properties were studied as a function of frequency and inorganic material loading. Indium gallium zinc oxide (IGZO) TFTs were fabricated and characterized using the printed nanocomposite film as the gate dielectric layer.

2. Experimental

2.1. Materials

Niobium pentaoxide (Nb_2O_5), tetrabutylammonium hydroxide (TBA^+OH^-) K_2CO_3, and $CaCO_3$ were purchased from Aladdin-Reagent. Poly(methyl methacrylate) (PMMA, average M.W. 35,000), $In(NO_3)\cdot 6H_2O$, $Ga(NO_3)_3\cdot 9H_2O$ and $Zn(NO_3)_2\cdot 6H_2O$ was purchased from Acros. All solvents were analytical grade and used without further purification.

Layered (TBA^+) $Ca_2Nb_3O_{10}$ (denoted as CNO) was prepared according to the literatures [15,16]. The starting material $KCa_2Nb_3O_{10}$ (KCNO) was prepared by a solid-state reaction at 1200 °C. The protonated form $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ (HCNO) was obtained by stirring the $KCa_2Nb_3O_{10}$ powder in dilute HNO_3 solution. A white colloidal suspension of CNO nanosheets was obtained by delaminating HCNO with TBA^+OH^-. Finally, the water-wetted white CNO solid, obtained by centrifugation, was dispersed into PMMA acetone solution to form the CNO–PMMA dielectric nanocomposite ink.

2.2. Formation and characterization of films

ITO glass slides were ultrasonic cleaned in acetone, isopropyl alcohol and deionized water in turn. CNO–PMMA nanocomposite films were deposited on the ITO glass substrates by printing the CNO–PMMA dielectric nanocomposite ink with an aerosol jet printer (M3D-103, Optomec), followed by drying on a hot-plate at 140 °C for 10 min. The loadings of CNO in the nanocomposite were ranged from 7 wt% to 82 wt%. The printed composite films with 1–3 μm were obtained by adjusting the pressure of aerosol flow or the printing speed. For dielectric analysis, aluminum electrodes were fabricated on the top surface of films by thermal evaporation. Frequency-dependent capacitance and loss tangent (dissipation factor) were measured by Keithley 4200 Capacitance Voltage Unit (from 10 kHz to 1 MHz at 5 V). A step profiler (Veeco, Dektak 150) was used to measure the thicknesses of the composite films. The dielectric constants were calculated from the measured capacitances, thicknesses and areas of top electrode. At least seven individual measurements were made to determine the dielectric parameters of printed films. The cross-sectional morphology of CNO–PMMA films was observed with scanning electron microscopy (SEM, Hitachi S-4800). Surface morphology was characterized using an atomic force microscope (AFM, Veeco, CA, USA).

2.3. Fabrication and characterization of TFTs

IGZO-based TFTs were fabricated on heavily doped Si wafer with 300 nm-thick thermally grown SiO_2. The IGZO precursor solution was prepared by dissolving $In(NO_3)\cdot 6H_2O$, $Ga(NO_3)_3\cdot 9H_2O$ and $Zn(NO_3)_2\cdot 6H_2O$ (molar ratio In:Ga:Zn = 3:1.5:2) with ethanolamine in 5 mL 2-methoxyethanol. The total concentration of metal salts was 0.05 mol/L. The IGZO film was prepared by spin coating (4000 rpm, 30 s) the precursor solution and annealing at 350 °C in air for 60 min. The thickness of IGZO film was ca. 25 nm, according to the SEM cross-sectional image. Al source/drain electrodes (ca. 120 nm thick) were thermally evaporated onto the IGZO film via a shadow mask (W/L = 20, L = 50 μm) to form an n-type transistor. Then the CNO–PMMA nanocomposite layer was deposited by aerosol jet printing on top of IGZO film. Finally, the top Al electrode was thermally evaporated onto the CNO–PMMA dielectric layer to complete device stacks. All the TFTs were characterized by Keithley Instruments Model 4200-SCS in atmospheric condition. The saturation mobility (μ_{sat}) is calculated from the formula [17] as follows:

$$\mu_{sat} = \left(\frac{\partial\sqrt{I_D}}{\partial V_{GS}}\right)^2 \frac{2L}{WC_i} \quad (1)$$

where C_i is the capacitance of the gate dielectrics per unit area.

3. Results and discussion

CNO nanosheets were prepared by exfoliation of layered bulk $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ using TBA^+ ion [18]. Fig. 1a shows the TEM image of thin CNO nanosheets whose lateral dimension is in the range from several nanometers to several micrometers. CNO–PMMA nanocomposite inks are prepared by dispersing these CNO nanosheets into acetone diluted PMMA solution. CNO nanosheets are usually dispersed in water to form a stable suspension [18,19]. The present experiment exhibited that the CNO nanosheets could be dispersed in acetone as well. Fig. 1b indicates the stability of the dispersed composite dielectric ink. The ink maintains stable up to 6 h.

CNO–PMMA nanocomposite films formed by printing the CNO–PMMA nanocomposite inks with different CNO loadings were characterized by AFM and the results are shown in Fig. 2. The surface roughness of the films is lower for low loading than for high loading of CNO. Their corresponding cross-sections were inspected by SEM and shown in Fig. 3. It is interesting to notice that with CNO

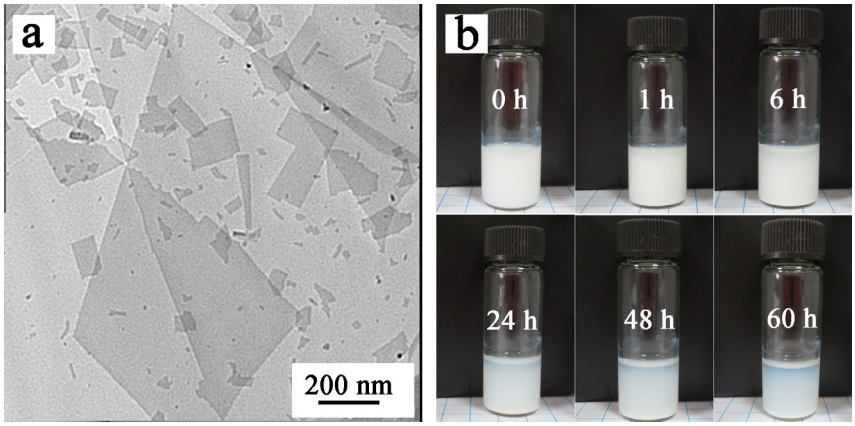

Fig. 1. (a) TEM image of $Ca_2Nb_3O_{10}$ nanosheets, (b) suspensions of CNO nanosheets at different hours after preparation.