Gate dielectric based on organic-inorganic hybrid polymer in organic thin-film transistors

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Keywords : Sol-gel, Hybrid Materials, Dielectric

Abstract

Inorganic-organic hybrid polymer provides various advantages including low-temperature process, high dielectric constant and direct photo-patterning. The hybrid dielectric was synthesized by the sol-gel process in which an acid-catalyzed solution of Si alkoxide and Zr alkoxide was used as a precursor. The electrical performance of transistors with hybrid dielectric was investigated.

1. Introduction

Inorganic dielectric is widely used as a gate insulator to fabricate electrical devices because it provides high dielectric constant, high dielectric strength and stability. Inorganic dielectric is generally produced by vacuum-deposition at high temperature and etching. High temperature process makes inorganic dielectric incompatible with plastic substrate which is requisite for flexibility. On the other hand, organic dielectrics have lots of advantages including low temperature process, flexibility, solution process. However, it suffers from low dielectric constant and sensitivity to ambient condition.[1-2] In this regard, inorganic-organic hybrid dielectric can be an alternative material to overcome each weakness of inorganic dielectric and organic materials. Hybrid dielectric by means of sol-gel reaction is produced to be a gate insulator having a high dielectric constant, high dielectric strength as well as flexibility and solution process. In the present study, hybrid dielectric based on organically modified Si-alkoxide and Zr-alkoxide is prepared.

2. Experimental

The organic-inorganic hybrid gate dielectric solution was synthesized by sol-gel reactions between 3-methacryloxypropyltrimethoxysilane (MEMO, Sigma-Aldrich), zirconium isopropoxide ($Zr(OPr^i)_4$, 70% in 1-propanol, Sigma-Aldrich), and methacrylic acid (MAA, 97%, Sigma-Aldrich). In the first step, a MEMO solution was mixed with HCl as a catalyst, which was followed by vigorous stirring for 30 min. A mixture of $Zr(OPr^i)_4$, MAA and 1-propanol was also prepared in a molar ratio of 1:1:1. The amount of $Zr(OPr^i)_4$ with respect to the MEMO solution was varied to control the dielectric constant of the resulting gate dielectric. Four different compositions were synthesized, as follows: MEMO : $Zr(OPr^i)_4$ = 8.5 : 1.5, 8 : 2, 7.5 : 2.5, 7 : 3, and 6.5 : 3.5 in a molar ratio, respectively. When $Zr(OPr^i)_4$ was mixed with MEMO, the alkoxy groups present in both precursors were partially hydrolyzed. DI-water was then added to facilitate the hydrolysis and condensation reactions. The synthesized sol-gel solution was diluted to control the thickness of the gate dielectric.

The hybrid dielectric films were obtained by spin coating the precursor solution at 4000 rpm for 30s on an n-type heavily doped silicon wafer substrate. After spin coating, the films were immediately prebaked at 110℃ on a hot plate in air for 30min to evaporate the solvent and improve adhesion to the substrate. A final thermal treatment was carried out at 170℃ for 3 hrs.

To study the electrical performance of gate dielectrics as a function of the ZrO_2 composition, capacitance-voltage (C-V) at a frequency of 1 MHz and leakage current-voltage (I-V) characteristics were measured using an Agilent 4284A precision LCR meter and an Agilent 5263A source-measure unit, respectively.

3. Results and discussion

A gate dielectric for OTFTs is required to be smooth and uniform in order to prevent the degradation of mobility. The carrier mobility could be lowered by interfacial charge trapping and by poor molecular ordering of the semiconductor, both of which are greatly affected by the surface structure of gate dielectrics.[3-4] The surface morphology of the synthesized films was analyzed using an atomic force microscope (AFM).

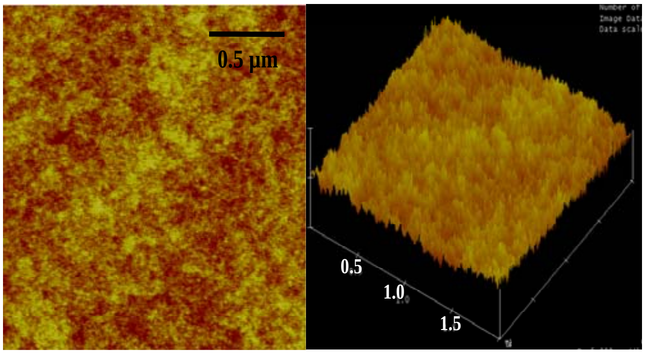

Fig. 1. AFM images showing the surface morphologies of the hybrid dielectrics: height mode image and 3D image for the dielectrics with 20 mol% $Zr(OPr^i)_4$ addition

All of the sol-gel-derived hybrid gate dielectrics exhibit a very smooth surface morphology with no apparent pinholes, regardless of the Zr alkoxide content. No significant microstructural variation was observed as a function of the zirconium propoxide concentration, as observed by both two-dimensional and three-dimensional surface topographs. The average surface roughness RMS values for the hybrid dielectrics at 20 mol%, 25 mol% and 30 mol% were 0.242 nm, 0.217 nm, and 0.263 nm, respectively, with a scan area of 2 µm × 2 µm. These values are comparable or superior to reported surface roughness values of poly(vinylphenol) or polyimide gate dielectrics.

Another important property associated with gate dielectric material is the leakage current. Fig. 2 shows the leakage current density through the dielectric layer vs. an electric field for the hybrid films as a function of differing molar ratios of $Zr(OPr^i)_4$ to MEMO. The dielectric strength of the films changed slightly from 1.2 to 1.5 MV/cm as a function of the zirconium alkoxide molar ratio. The dielectric strength was defined as the electric field at a current density of 10^{-6} A/cm^2. The gate dielectric leakage for the hybrid gate dielectric films was less than -50 pA/cm^2 at a bias of -10V and less than -200 nA/cm^2 at a bias of -30V. This indicates that the proposed gate dielectrics can allow an OTFT to be operated stably without excess current leakage through the gate dielectric.

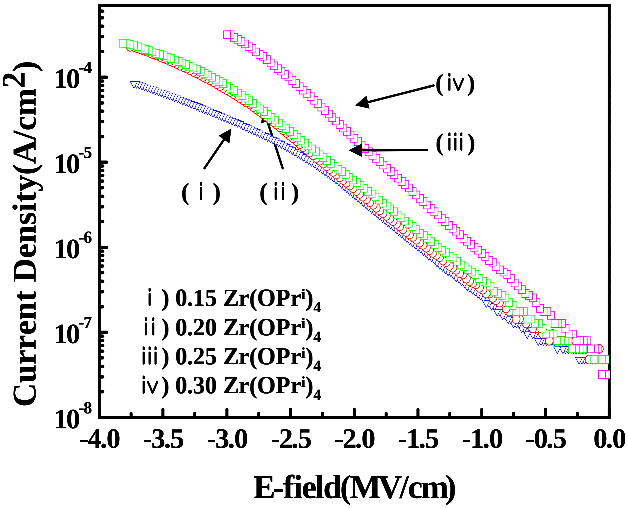

Fig. 2. Current density vs. electric field characteristics of hybrid dielectric films as a function of the $Zr(OPr^i)_4$ molar concentration with respect to MEMO.

In order to evaluate the dielectric constant (*k*) of the gate dielectrics, the C-V characteristics as a function of the zirconium alkoxide molar ratio as were measured, shown in Fig. 3(a). The thickness of the hybrid films with varying $Zr(OPr^i)_4$ contents was determined to be 140 nm at 15 mol%, 125 nm at 20 mol%, 110 nm at 25 mol%, 105 nm at 30 mol% and 98 nm at 35 mol%. An addition of zirconium alkoxide effectively increases the capacitance of the hybrid films. The capacitance values were 33 nF/cm^2, 40 nF/cm^2, 47 nF/cm^2, 53 nF/cm^2, and 61 nF/cm^2, respectively. Using the C-V result, the dielectric constants were calculated using the following equation:

$$C = \frac{k\varepsilon_o A}{t}$$

where C is the measured capacitance, ε_o is the permittivity of free space, A is the area of the capacitor, and t is the thickness of the dielectric. Fig. 3(b) shows the variation of the dielectric constants of the hybrid dielectrics. The observed values of the dielectric constants for the hybrid materials were in the range 5.3~6.6, depending on the concentrations. It is believed that $Zr(OPr^i)_4$ added to the precursor solution undergoes hydrolysis and condensation to form continuous -Si-O-Zr- networks, resulting in the incorporation of ZrO_2 nanoparticles uniformly distributed within the organosiloxane matrix phase. Such a microstructural feature of the hybrid dielectrics gives a rise to a smooth surface morphology, as shown in Fig. 1, with a relatively high dielectric constant, compared to the values (k ~ 3.5- 3.9) of most of organic dielectrics.[5]

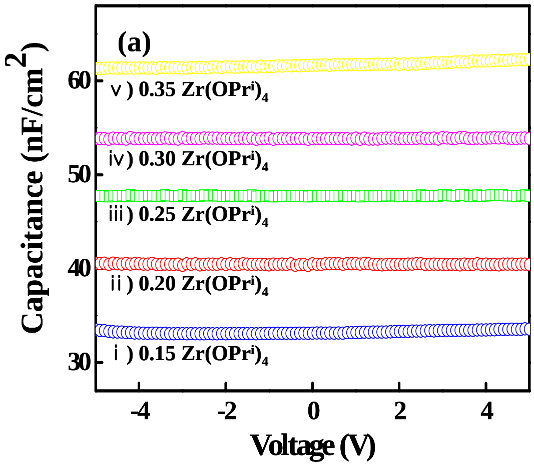

Fig. 3. (a) Capacitance vs. voltage characteristics of hybrid dielectric films

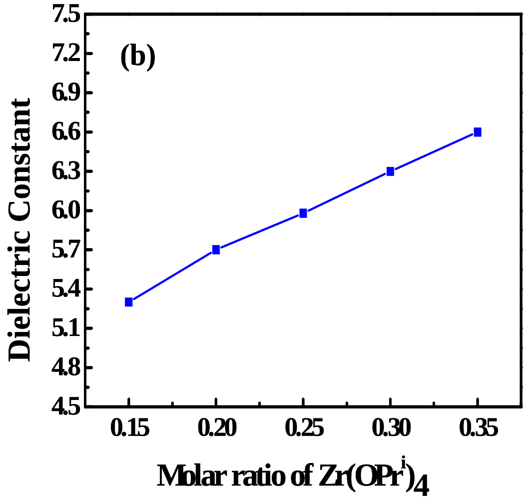

Fig. 3. (b) the dielectric constant of the film as a function of the $Zr(OPr^i)_4$ molar concentration with respect to MEMO.

4. Summary

The synthesis of organic-inorganic hybrid gate dielectric materials with a high dielectric constant was demonstrated. An acid-catalyzed solution of Si alkoxide and Zr alkoxide was utilized to prepare a hybrid precursor solution. The amount of Zr alkoxide added to a MEMO solution was varied to increase the dielectric constant of the hybrid gate dielectrics. High quality, crack-free patterns with a very smooth surface were obtained, as confirmed by confocal laser scanning microscope (not shown here). The hybrid films for the gate dielectric exhibit a dielectric strength in the range of 1.2~1.5 MV/cm and dielectric constants of 5.3~6.6 as the concentration of $Zr(OPr^i)_4$ to MEMO increases. The use of the sol-gel hybrid dielectrics with a relatively high dielectric constant is shown to be beneficial to reduce the threshold voltage significantly, lowering it close to ~ 0 V, which makes it viable for use as an organic transistor operated at a low voltage.

5. Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the National Research Lab Program funded by the Ministry of Science and Technology (No. R0A-2005-000-10011-0). It was also partially supported by Samsung Electronics and the Second Stage of Brain Korea 21 Project in 2007.

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