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Photopatternable ultrathin gate dielectrics for low-voltage-operating organic circuits

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We report here a photopatternable ultrathin gate dielectric for the fabrication of low-voltage-operating organic field-effect transistors (OFETs) and inverters. The gate dielectric material is composed of a photocrosslinkable polymer, poly(vinyl cinnamate), and a thermally crosslinkable silane crosslinking reagent, 1,6-bis(trichlorosilyl)hexane. The spin-coated dielectric is photocured with ultraviolet light, which enables fine film patterning via regular photolithography. After thermal curing (at 110 °C), the dielectric showed excellent insulating properties (a leakage current density of $\approx 10^{-7}$ A/cm² at 2.0 MV/cm) for an ultrathin film thickness of 70 nm, thus reducing the operating voltage of the OFETs and inverters to -5 V. © 2009 American Institute of Physics. [DOI: 10.1063/1.3206665]

Organic semiconductor and dielectric materials that can be obtained using simple solution-based processes have gained considerable interest in recent years because of the widely increased demand for low-cost and flexible electronic devices.^{1,2} The potential applications of organic semiconductor and dielectric materials have led to intense research in the field of organic electronics, including organic field-effect transistors (OFETs).²⁻⁷ Since gate dielectrics should be patterned to form vertical interconnections (i.e., via holes) between the gate electrodes and the underlying bus lines in backplane circuits, photocrosslinkable polymer gate dielectrics have been promising candidates as they can be prepared via simple and low-temperature curing processes and allow easy patterning.^{3,4} Conventional polymer dielectrics require a complex lithography process that includes photoresist deposition and chemical/plasma etching. These complicated and time-consuming processes increase the production costs, distort plastic substrates, and may cause dielectric surface contamination.⁵ On the other hand, a photocrosslinkable polymer can be simply patterned by means of photoirradiation through a photomask followed by developing in a solvent.³

Generally, it is difficult to fully crosslink a photocrosslinkable polymer by simple photoirradiation because the molecular motion of the polymer chains decreases due to the increased molecular weight upon crosslinking.⁸ Therefore, to enhance the electrical strength of the polymer film by reducing the free volume, further thermal curing is required.^{3,8-10} However, high-temperature curing processes (above 120 °C) are not compatible with the organic materials contained in OFET devices, for example, with the plastic substrates.⁶ Photocrosslinkable polymer dielectrics with low curing temperatures have been reported recently in OFET applications.^{3,4} Nevertheless, these dielectrics require a high operating voltage due to their substantial thickness (>500 nm), which implies extremely high power consumption if they are operated in integrated circuits. Thus, achieving photopatternable gate dielectrics that are electrically

strong at ultrathin thicknesses (<100 nm), thus enabling the operation of organic circuits at low voltages, has been a research priority in this field.

Here, with a view to achieving the above-mentioned characteristics, we introduce a two-step curing process (photocuring followed by thermal curing) that uses a photocrosslinkable polymer/silane crosslinking reagent blend as the dielectric for the organic circuits. Poly(vinyl cinnamate) (PVCN) is used as photocrosslinkable polymer, providing the blend dielectric with photopatternable properties. The compound 1,6-bis(trichlorosilyl)hexane (TCSH) is blended with PVCN (as silane crosslinking reagent), and it remarkably improves the electrical strength of the dielectric through a 40 min thermal curing process (at 110 °C) for an ultrathin film thickness of about 70 nm. The silane reagent, which was introduced recently by Yoon *et al.*⁷ to enhance the electrical strength of polymer dielectrics, produces dense siloxane networks via crosslinking at temperatures below 100 °C. The structures of PVCN and TCSH as well as their corresponding crosslinking reactions are shown in Figs. 1(a)–1(c), respectively.^{4,7}

The dielectric was prepared from a blend solution of PVCN (Polysciences, Inc.) and TCSH (Aldrich) in chloroform (Aldrich). TCSH (4–5 μ l) was added to the PVCN solution (7.4 mg/ml) and then spin coated onto a 20 nm thick titanium gate-patterned glass substrate. This film was then exposed (for 7 min) to ultraviolet (UV) light ($\lambda = 255$ nm, power = 50 W) (G15T8, Sankyo Denki) to induce photocrosslinking. Subsequently, the film was placed for 40 min on a 110 °C hot plate (in air) for solvent evaporation and curing of TCSH. The thickness of the resulting films was found to be between 70 and 74 nm (Alpha-step[®] 500, KLA Tencor). A 50 nm thick pentacene (Aldrich, without purification) active layer was deposited on the dielectric (at a rate of 0.2 Å/s) using an organic molecular beam deposition system. Finally, we deposited the source/drain electrodes by thermally evaporating a 100 nm thick gold layer through a shadow mask on the active layers, as shown in the full structure of the OFET in Fig. 1(d). The channel length (L) and width (W) of the OFETs were 50 and 2000 μ m,

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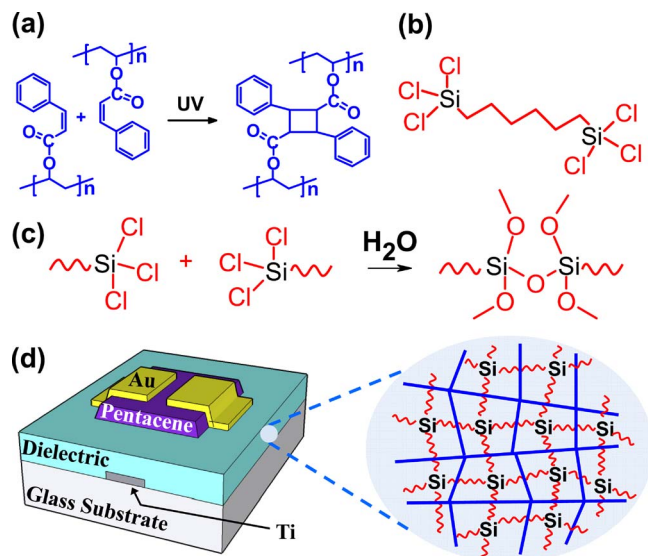


FIG. 1. (Color online) (a) Chemical structures of PVCN (left) and photocrosslinked PVCN (right). (b) Chemical structure of TCSH and (c) corresponding crosslinking reaction. (d) Transistor structure used in this experiment. The picture on the right illustrates the photochemically and thermally crosslinked PVCN/TCSH blend dielectric.

respectively. All electrical measurements were performed using Keithley 2400 and 236 source/measure units, but those of the inverters were carried out with an Agilent E5270A instrument. The dielectric solution was prepared in an N_2 -rich glove box (with H_2O and O_2 concentrations below 0.1 ppm) whereas all the other fabrication and measurement steps were performed in ambient air.

Figure 2 shows optical microscopy images of photopatterned PVCN/TCSH blend films with various shapes achieved via 7 min UV curing through a conventional quartz photomask followed by developing [dipping in a developing solvent, dimethylformamide (DMF)]. High-resolution patterning is achieved without the need for photoresist deposition and chemical/plasma etching on the film. During UV irradiation, the cinnamate moieties in the PVCN are crosslinked via (2+2) cycloaddition and therefore the dielectric film shows a high chemical resistance toward the developing solvent.⁴ Note that in the developing step, a proper choice of developing solvent is very important because the developing solvent dissolves the uncrosslinked PVCN parts without significant loss of TCSH in the residual crosslinked PVCN parts in the dielectric film. Table I shows the solubility parameters (δ) of the solvents used herein as well as the experimental solubilities of PVCN and TCSH in these

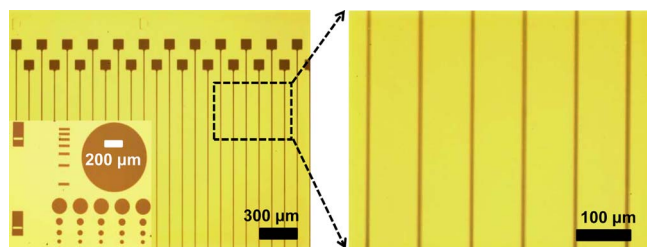


FIG. 2. (Color online) Optical microscopy images of a photopatterned PVCN/TCSH blend film coated on a Si/SiO₂ substrate. The images illustrate the photopatternability of the film using the patterns of a conventional quartz photomask. The yellow area is the residual film and its thickness is 72 nm.

TABLE I. Solubility parameters of the solvents and experimental solubilities of the materials used in this study.

Solvent	Solubility parameter [(MPa) ^{1/2}]	PVCN solubility (wt %)	TCSH solubility (wt %)
Hexane	14.9	<0.01	>100
Chloroform	19.0	>30	>100
DMF	24.8	>30	<0.2

solvents.¹¹ Chloroform ($\delta=19.0$) dissolves both PVCN and TCSH very well and was therefore chosen as the solvent for our system. On the other hand, DMF ($\delta=24.8$) dissolves large amounts of PVCN but very little amounts of TCSH, which indicates that DMF is a good developing solvent for our blend dielectric system. In hexane, which has the lowest δ value among all three solvents (14.9), PVCN is not dissolved at all but TCSH is dissolved quite well. All the experimental results imply that the solubility parameter of PVCN is somewhat higher than that of TCSH. From the differences in the solubility parameters of PVCN and TCSH, DMF is able to selectively remove uncrosslinked PVCN parts without any serious loss of TCSH in the crosslinked PVCN parts during the developing step. To confirm the remaining TCSH in the developed dielectrics, measurements of the current-density-versus-electric-field characteristics of the dielectrics were carried out using Au/dielectric/Ti structures. Three kinds of dielectrics were tested, all of which had been UV cured for 7 min and subsequently thermally cured at 110 °C for 40 min. As shown in Fig. 3(a), both the developed (i.e., developed in DMF between the UV and the thermal curing steps—photopatterned) and the undeveloped (i.e., without developing between the two steps) PVCN/TCSH dielectrics showed good electrical strength compared to the simple PVCN dielectrics. This implies that TCSH does not

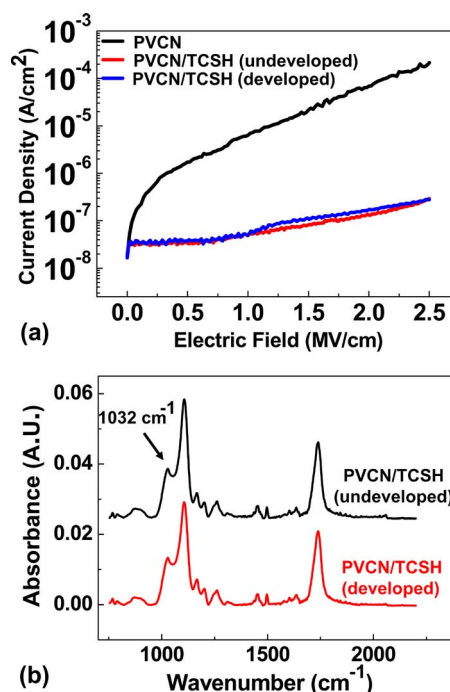


FIG. 3. (Color online) (a) Current density–electric field characteristics of “PVCN,” “undeveloped PVCN/TCSH,” and “developed PVCN/TCSH” dielectrics. (b) FTIR spectra of the undeveloped PVCN/TCSH and developed PVCN/TCSH dielectrics (Nicolet 6700, Thermo Electron).

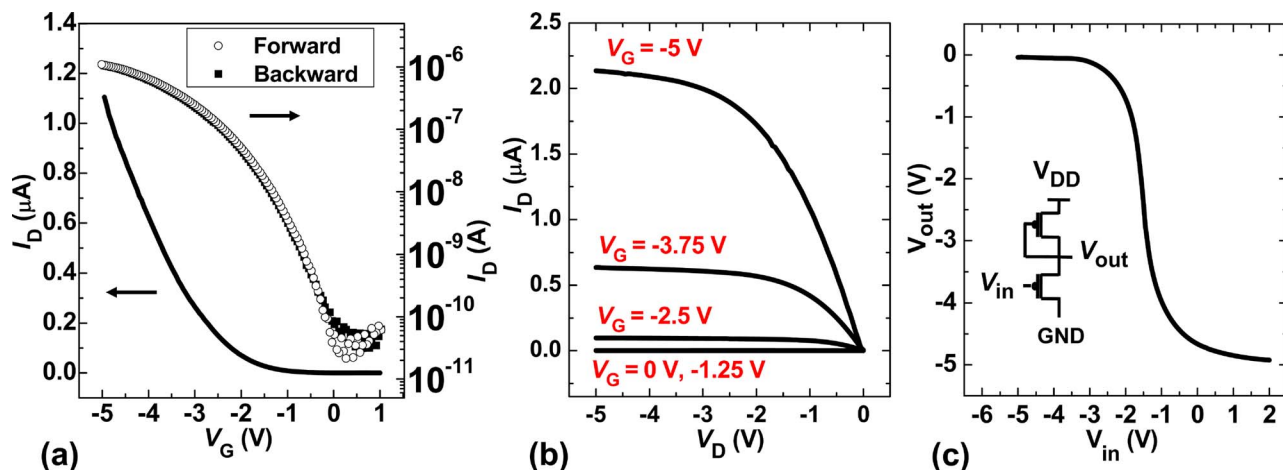


FIG. 4. (Color online) (a) Transfer and (b) output characteristics of an OFET containing a blend dielectric. (c) VTCs of an inverter composed of two OFETs containing blend dielectrics ($V_{DD} = -5$ V). The inset illustrates the schematic structure of the inverter based on the zero drive load logic: with the load transistor ($W/L = 1600/50$ μm) and the drive transistor ($W/L = 200/50$ μm).

wash out after developing and produces dense siloxane networks via a 40 min thermal curing process in both the developed and undeveloped dielectrics, as illustrated on the right-hand side of Fig. 1(d). The Fourier transform infrared spectroscopy (FTIR) spectra shown in the Fig. 3(b) also provide a definite verification of the presence of siloxane networks in both developed and undeveloped PVCN/TCSH dielectrics. The band due to Si–O–Si stretching (1032 cm^{-1}) vibrations was still observed, and the intensity of this band was not significantly reduced in the developed dielectric as compared with the undeveloped one.¹²

Figure 4(a) shows the transfer characteristics in the linear regime (drain voltage, $V_D = -1.5$ V) for OFETs fabricated using the blend dielectrics. The field-effect mobility (μ) was calculated by fitting the experimental data to the equation $\mu = (L/W C_i V_D)(\partial I_D / \partial V_G)$, where I_D is the drain current, V_G is the gate voltage, and C_i is the capacitance per unit area. The OFETs exhibited a μ of $0.25 \pm 0.03\text{ cm}^2/\text{V s}$, an on/off ratio of about 10^5 , and a subthreshold swing of $320 \pm 14\text{ mV/decade}$ with a measured C_i of 58 nF/cm^2 at 10 kHz (4284A Precision LCR meter, Agilent Tech.). In the transfer curves, no hysteresis behavior was observed in the forward (from 1 to -5 V) and subsequent backward (from -5 to 1 V) gate voltage sweeps. The hysteresis-free properties of the OFETs originate from the hydroxyl-free nature of PVCN, which is the polymer backbone of our blend dielectric system.⁴ The OFETs exhibited a good linear/saturation behavior within the operating voltage range of -5 V, with no apparent leakage current at zero V_D , as shown in Fig. 4(b). To verify the potential application of our blend dielectric to a gate dielectric of organic integrated circuits, we fabricated organic inverters composed of two OFETs. Zero-drive-load logic was employed as the frame of the inverter structure, as illustrated in the inset of Fig. 4(c).¹³ Figure 4(c) shows the voltage transfer characteristics (VTCs) of the inverter. The inverter gain, defined as the absolute value of dV_{out}/dV_{in} (where V_{out} and V_{in} are the output and input voltages of the inverter, respectively), reached a value as high as 13.5. Moreover, the inverter was capable of properly performing the voltage inversion within -5 V: the logic high (V_{in} : -5 to

-2.5 V) and low (V_{in} : -1 to 2 V) states of V_{out} were clearly distinguished in the VTCs.

In summary, we have realized photopatternable ultrathin gate dielectrics composed of a blend of PVCN/TCSH, which can be used to fabricate low-voltage-operating OFETs and inverters. The photo-crosslinkability of PVCN enables the dielectrics to be finely patternable by using a process that is much simpler than the conventional photolithography process. TCSH is crosslinked at a temperature of 110°C , which significantly enhances the electrical strength of the dielectric for an ultrathin film thickness of 70 nm . This enables low-voltage operation of OFETs and inverters that incorporate these dielectric films.

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