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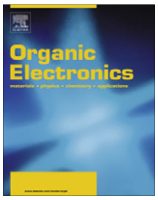

Letter

Free radical fast photo-cured gate dielectric for top-gate polymer field effect transistors

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ABSTRACT

We demonstrated top-gate organic field effect transistors (OFETs) made with free radical photo-cured polymer gate dielectrics and poly(3-hexylthiophene). We introduced a new approach of cross linking dielectric polymers in OFETs by using acrylate monomers cured with UV irradiation directly on the semiconductor. Three different blends were formulated: one self-initiating acrylate oligomer and two epoxy acrylate monomers mixed with 4-phenylbenzophenone as photo initiator and N-methyldiethanolamine as amine synergist. Thin films of these blends were cured in air within one minute. The curing process was monitored with FT-IR spectroscopy and the effect of a wetting agent was studied by measuring the CV characteristics of metal–insulator-semiconductor (MIS) structures made with these formulations. OFETs made with the demonstrated formulations showed high on/off ratios (10^5–10^6) and low sub-threshold slopes (0.44–1.42 V/dec).

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1. Introduction

One of the most important advantages of using organic materials in electronics instead of inorganic materials is the possibility of using low-cost, low-temperature, and solution-based processes. These features are necessary to produce printable electronic circuits on flexible substrates [1–3]. Different soluble insulating materials were investigated including poly(methylmethacrylate), poly(4-vinylphenol), polystyrenes, and poly(vinylalcohol) [4]. Many reports showed that cross linking of the dielectric material enhances its dielectric and chemical properties. Polymers with a functional group were used and cross linked thermally or using UV-irradiation [5–9]. We show here a new approach of cross linking dielectric polymers by using free radical cured systems. These systems have high potential in the application of organic electronics since they cure very fast (compared with thermally cured systems), produce no ions (compared with the cationic systems) and could be patterned directly without use of photoresist for example to form vertical interconnections (vias). Also the use of low viscosity monomers enables the production of low/no volatile organic component (VOC) formulations. Some issues should be considered in the choice of the right raw materials:

- *O_2 inhibition:* Similar to all radical reactions the free radical UV curing is inhibited by oxygen [10,11]. This effect is more pronounced in thin films [12,13]. Different methods used to overcome the oxygen inhibition include increasing the reactivity of the monomers and the initiators and the use of synergists like tertiary amines [14,15].
- *Substrate wetting:* To form a pinhole-free film on P3HT, used as the organic semiconductor here, the formulation should have a low surface tension. This is achieved through the use of hydrophobic monomers or the use of a wetting agent.
- *Shrinkage:* This is one of the concerns for curing acrylates and affects the adhesion to the substrate [16–18]. The use of oligomers or flexible monomers can reduce the volume shrinkage during polymerization.

We chose three formulations which fulfil these conditions. The monomers were chosen because of their high

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reactivity, flexibility and low irritancy. 4-Phenylbenzophenone (PBZ) was used because of its good surface curing properties. Since it is a Norrish Type II initiator a hydrogen donor is needed. One efficient hydrogen donor is N-methyldiethanolamine (MDEA) which can also act as an oxygen scavenger [19–20]. We used also one wetting agent which contains an acrylate group to enhance the substrate wetting and to be part of the cross-linked system. The combination of these materials makes it possible to cure thin films (<1 μm) in air on a time scale of one minute. After characterizing the curing process with FT-IR spectroscopy, the leakage currents and the dielectric constants of the photo-cured films were characterized by preparing metal–insulator-metal (MIM) structures. Furthermore, we showed the influence of the wetting agent on the flat-band voltage of metal–insulator-semiconductor (MIS) structures prepared with the photo-cured insulators. Then the electrical properties of organic field-effect-transistors (OFETs) produced with these formulations were investigated.

2. Experimental

Poly(3-hexylthiophene) (P3HT) was supplied by BASF. Bisphenol A diglycidylether diacrylate (BDGDA) and PBZ were supplied by Rahn GmbH. PolyQ 9300 which is a self-initiating acrylic oligomer and Doublemer 9136 (wt) which is a silicon acrylate were supplied by Double Bond Chemical Ltd. Ethoxylated (3) bisphenol A diacrylate (BEODA) was supplied by Sartomer. MDEA and toluene were purchased from Sigma–Aldrich, and xylene, *n*-Butylacetate (BuAc), ammonia (aq.) and hexamethyldisilazan (HMDS) from Carl-Roth. All chemicals were used without further purification. The chemical structures of the materials used in this work are presented in Fig. 1.

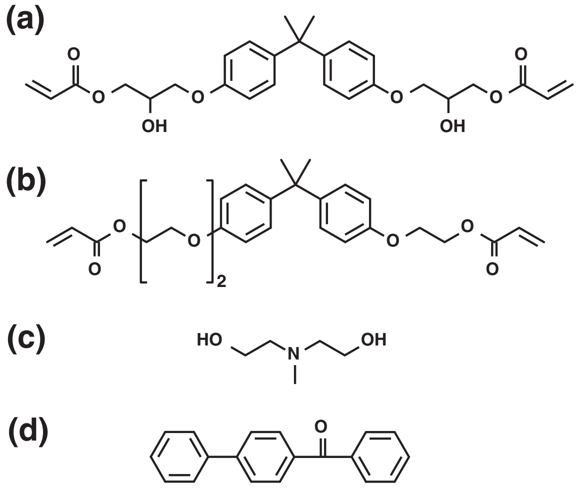

Fig. 1. Chemical structure of (a) bisphenol A diglycidylether diacrylate (BDGDA) (b) ethoxylated (3) bisphenol A diacrylate (BEODA) (c) N-methyldiethanolamine (d) 4-phenylbenzophenone.

The monomers BDGDA and BEODA were blended with the photoinitiator PBZ, the amine synergist MDEA and Doublemer 9136 to get four different formulations in the ratios shown in Table 1. The formulation were optimized to use a minimum concentration of PBZ and MDEA and to get tack-free films within one minute. PolyQ 9300 was also mixed with the wetting agent in the ratio 100:1. These formulations were diluted in BuAc to get 25 wt.% solutions for MIS and MIM structures and 12.5 wt.% solutions for transistors. P3HT was dissolved in toluene (1.5 wt.%) for MIS structures and in xylene (0.7 wt.%) for transistors.

For MIS and MIM structures Cr and Au were evaporated on a glass substrate. For the transistors silicon wafers with 300 nm silicon oxide were used as substrates. First they were immersed for 30 min in a 25% aqueous solution of ammonia and then cleaned with water and immersed for 6 h in 250 ml of toluene with two drops of HMDS. After cleaning the wafer with acetone in an ultrasonic bath, source and drain electrodes were prepared using a lithography/Cr-Au deposition/lift-off process. After spin coating of P3HT (2000 rpm, 15 s) and the dielectric (2000 rpm, 15 s) on the substrate, the devices were exposed to UV-C irradiation using the eprom eraser “Dienies LG 18” (16 mW/cm^2) for 90 s for formulations done with BEODA and 60 s for all the other formulations. Then gold was evaporated through a shadow mask to get the gate electrode.

FT-IR spectra of the solid films spin-coated onto a double-side polished silicon wafer before and after the curing were recorded in a transmission mode using a Bruker Tensor 37 FT-IR Spectrometer. The CV characteristics of the MIS structures were measured using HP 4284A Precision LCR meter at 1 kHz and the electrical characteristics of the MIM structures and of OFETs were measured using an Agilent 4156C Precision Semiconductor Parameter Analyzer.

3. Result and discussion

Fig. 2(a) shows the disappearance of the peak at 1408 cm^{-1} when formulations made with the three acrylates are exposed to UV. From the spectra we can estimate that at least 70% of acrylate groups in the formulations PolyQ9300, BDGDA-2 and BEODA-3 have been converted. The conversion of the acrylate group in the formulations was calculated by measuring the rate of disappearance of the

Table 1
Composition of the formulations, dielectric properties of them and the electrical properties of the OFETs made with them.

Sample	Monomer:PBZ:MDEA:wt	ρ@1 MV/cm [Ω cm]	ε_r	μ [cm^2 V^{-1} s^{-1}]	On/off ratio	SS [V/dec]	V_{th} [V]
BDGDA-2wt	100:2:2:1	1.2×10^{15}	3.9	1.5×10^{-2}	2.6×10^{6}	0.44	−14.3
BDGDA-2	100:2:2:0	–	–	–	–	–	–
BEODA-3wt	100:3:3:1	4.1×10^{14}	5.1	1.2×10^{-2}	2.4×10^{5}	1.42	−6
BEODA-3	100:3:3:0	–	–	–	–	–	–
PolyQ-wt	100:0:0:1	2.4×10^{15}	3.8	2.3×10^{-2}	1.9×10^{5}	0.85	−6.8

$=CH_2$ twisting mode at 810 cm^{-1} or the deformation mode of $=CH_2$ at 1408 cm^{-1} [21]. The absorption peak of the carbonyl group at 1727 cm^{-1} and the absorption peak of the aromatic ring at 1510 cm^{-1} could be used as reference for the calculation of the relative disappearance of the acrylate group for respectively PolyQ 9300 and the two other monomers containing Bisphenol A in the structure. The leakage currents of these films according to Fig. 2 (b) are lower than 3×10^{-9} A/cm^2 at 1 MV/cm. PolyQ-wt sample has the lowest leakage current and was equal to 4.2×10^{-10} A/cm^2 at 1 MV/cm. The high viscosity of PolyQ 9300 and of BDGDA allowed the formation of thin films on the P3HT without wetting agent. However it wasn't possible to get films of BEODA-3 on P3HT. The CV-curves in Fig. 3(a) show that the flat-band voltage (V_{fb}) of the MIS-structures made with formulations without wetting agent has a shift of at least 20 V. This shift was expected based on many reports about the effect of an UV treatment on organic transistors or MIS-capacitors [22–23]. In these studies it was shown that UV light increases the density of the negative charged traps at the interface semiconductor/gate insulator. This optically induced shift could be reduced when a wetting agent is used. That means that the density of the generated traps at the wetting agent/semiconductor

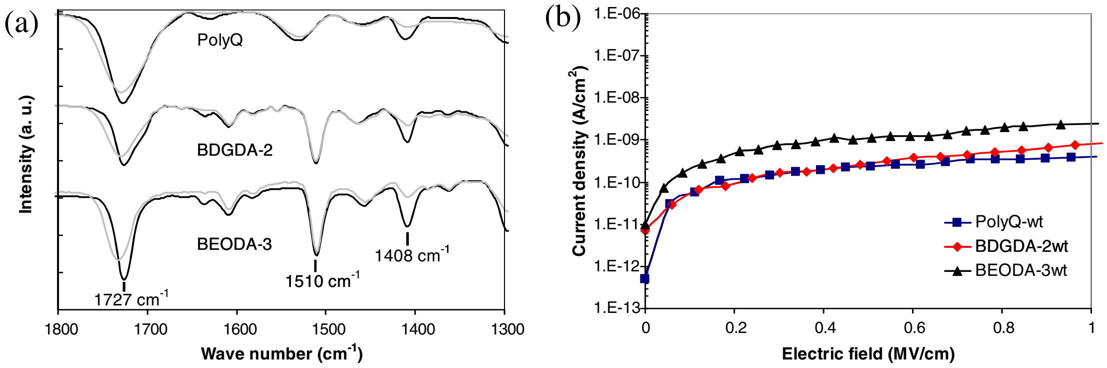

Fig. 2. (a) FTIR spectra of three acrylate systems before (black) and after (grey) exposure to UV-irradiation. (b) Leakage current density versus applied voltage for films made with blends containing PolyQ 9300, BDGDA and BEODA.

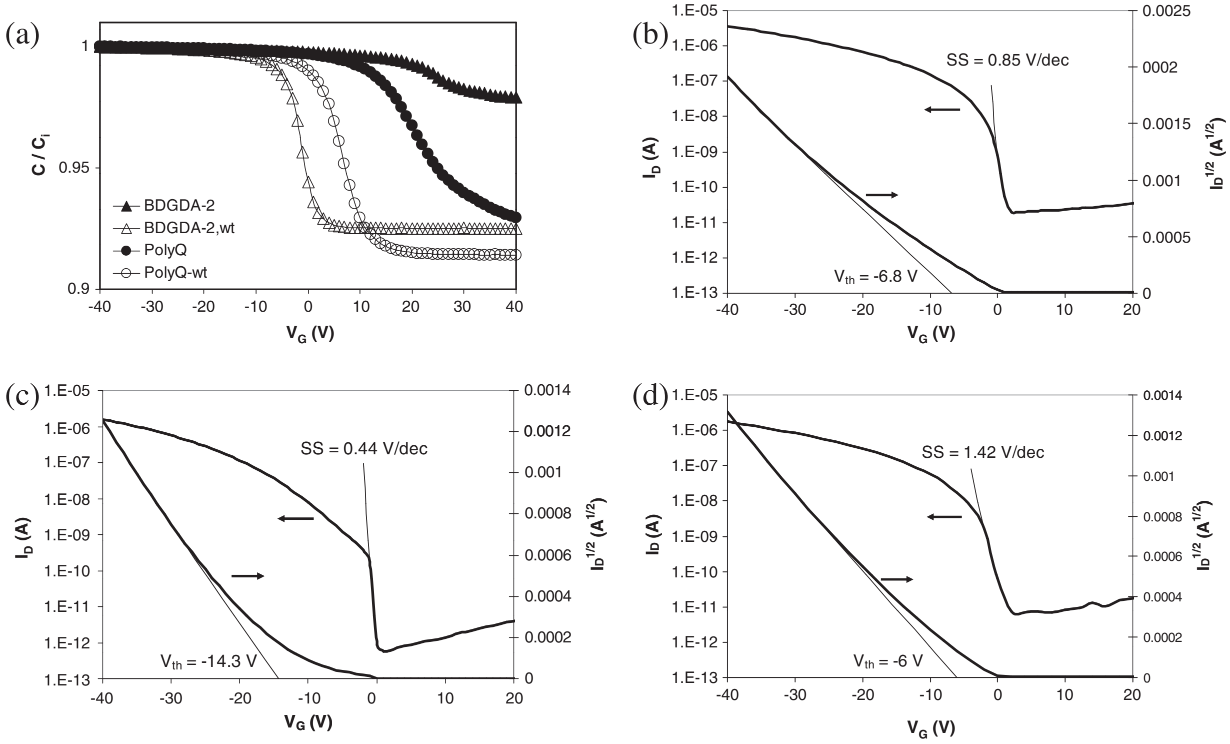

Fig. 3. (a) CV curves (1 kHz) measured on Au/P3HT/polymer/Au MIS-structures using different blends as dielectric material. The effect of the wetting agent on the flat-band voltage V_{fb} of the device can be seen. Transfer characteristic of top gate OFETs made with P3HT and (b) PolyQ-wt, (c) BDGDA-2wt and (d) BEODA-3wt. The drain-source voltage VDS = −40 V and W/L = 6260 μm/20 μm.

interface is lower than at the acrylates/semiconductor interface, since the wetting agent would adsorb at semiconductor interface [24].

Top-gate OFETs were fabricated using the blends PolyQ-wt, BDGDA-2wt and BEODA-3wt, and annealed for 30 min at 90 °C in nitrogen to remove water. Their transfer characteristics are shown in Fig. 3(b–d). The field effect mobility and the threshold voltage V_{th} were calculated in the saturation regime from the plot of the square root of the drain current versus the gate voltage which could be described with this equation:

$$\sqrt{I_{D,sat}} = \sqrt{\frac{W}{2L} \cdot \mu \cdot C_i} \cdot (V_g - V_{th}) \qquad (1)$$

where $I_{D,sat}$ is the drain current in the saturation regime, W and L are the channel width and length, μ is the mobility, V_{th} is the threshold voltage and V_g is the applied gate voltage. The field effect mobility values determined from the saturation region were 2.3×10^{-2}, 1.5×10^{-2} and $1.2 \times 10^{-2}\ cm^2\ V^{-1}\ s^{-1}$ for transistors with PolyQ-wt, BDGDA-2wt and BEODA-3wt respectively at $V_{DS} = V_{GS} = -40$ V. Top gate transistors made with the same charge of P3HT and polystyrene as gate material exhibit field effect mobility values between 1×10^{-2} and $3 \times 10^{-2}\ cm^2\ V^{-1}\ s^{-1}$. This means that the UV-irradiation exposure and the curing process don't deteriorate the mobility of holes in the semiconductor. The sub-threshold slopes of the transistors were 0.85, 0.44 and 1.42 V/dec when PolyQ-wt, BDGDA-2wt and BEODA-3wt respectively were used. The sharpness of the field effect onset of the transistors is a sign for the quality of the insulator/semiconductor interface [25]. Transistors made with BDGDA-2wt have lower off current than transistors made with the two other formulations, and have therefore higher on/off ratio. Although all the transistors have an onset-voltage approximately equal to zero volts, BDGDA-2wt produce a lower V_{th} than the other two formulations. Table 1 summarizes the electrical data of the transistors made with the three formulations. These results show that free radical photo cross linking makes possible to have high performance transistors with simple, fast and low cost processes.

4. Conclusion

In conclusion, we presented new free radical photo-cured top-gate dielectric materials. The new materials are cured in air within minutes, which simplifies the fabrication of high-performance printed electronics. These materials enable also the development of low/no VOC formulations which are environmentally friendly. Using a wetting agent was beneficial to get thin films on the hydrophobic semiconductor and to improve the dielectric/semiconductor interface. It was shown that the curing process does not deteriorate the mobility of the semiconductor. OFETs with on/off ratios between 10^5 and 10^6 and sub-threshold slope between 0.44 and 1.42 V/dec could be achieved.

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