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A low-temperature-cross-linked poly(4-vinylphenol) gate-dielectric for organic thin film transistors

Peter Vicca^{a,*}, Soeren Steudel^a, Steve Smout^a, Arne Raats^b, Jan Genoe^a, Paul Heremans^{a,c}

^a Polymer & Molecular Electronics Group, IMEC, Kapeldreef 75 3001, Leuven, Belgium

^b Katholieke Hogeschool Leuven Gezondheid & Technologie, Herestraat 49 3000, Leuven, Belgium

^c KULeuven, Department ESAT, Kasteelpark Arenberg 10, B-3001, Leuven, Belgium

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ABSTRACT

We present experimental results using an alternative cross-linker for poly(4-vinylphenol) (PVP) that allows lowering of the thermal budget of the cross-linking reaction to 130 °C which compares very favorably to the 180 °C required by the commonly used cross-linking agent poly(melamine-co-formaldehyde). Furthermore, we characterize the dielectric properties of a 200 nm thick layer and realize high quality organic thin film transistors using this low-temperature PVP as a gate-dielectric.

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1. Introduction

Organic thin film transistors offer the potential of applications for electronics and active matrix back panels on foil [1,2]. The use of polymer foils limits the possible manufacturing temperature to below 130 °C for poly(ethylene terephthalate), and below 160 °C for Polyethylene naphthalate (PEN).

We prefer bottom-gate, bottom-contact transistor geometries, as with this geometry, connections between the gate metal layer and the source/drain metal layer only require via holes through the gate insulator, and furthermore the delicate organic semiconductor can be applied as last step in the transistor fabrication. In this geometry, the gate dielectric is the most challenging layer. When made of a polymer, it should be cross-linkable to withstand the impacts of solvents and bases from further process steps. The cross-linking reaction should not leave any mobile ions in the film, therefore excluding cross-linking reactions kin to the one used in photoresist. Further, the cross-linked polymer should have a very smooth surface (root mean square roughness < 1 nm) [3], a high electrical field strength, preferable a high dielectric constant, high purity, and preferably be hydrophobic while still permitting sufficient adhesion to adjacent layers – precluding a teflon-like chemical structure.

There are only a handful of polymers found in literature that fulfill those requirements [4,5]. One of the most widely used is cross-linked

PVP (Fig. 1.) which was for the first time reported by Drury [6] and later by Klauk [7]. Commonly, PVP [8] is dissolved in propylene glycol methyl ether acetate (PGMEA) and poly(melamine-co-formaldehyde) is used as a cross-linker. Subsequently the layer is spin-coated and baked on a hotplate at 180 °C or above [9].

At this process temperature even heat-stabilized PEN-foil [10] starts to shrink and causes misalignment. Furthermore, a noticeable hysteresis is present in the transistor curves, probably caused by incomplete cross-linking [11]. Recently several research groups published alternative routes how to lower the cross-linking temperature either by adding UV-light [12], incorporating silanes to the solution [13] or using a different cross-linker [14,15] or PVP derivatives [16]. We selected a series of commercially available (Sigma Aldrich) cross-linkers with secondary diamines, triazines and bis (trichlorosilanes). These have the potential to react with the alcohol group of the PVP. The cross-linkers were replacing 2 w% of the poly(melamine-co-formaldehyde) in a 10 w% PVP solution made in propylene glycol methyl ether acetate (PGMEA). The modus of preparing the experimental solutions was the same as used for the standard PVP solutions using poly(melamine-co-formaldehyde) as a cross-linker. For primary diamines, CAS 107-15-3, 462-94-2, 110-60-1 and 15520-10-2 and secondary types of diamines, CAS 112-21-0, 63737-71-3 and 74-31-7, an instant reaction at room temperature was noticed and therefore the diamines cannot be considered as a cross-linker anymore. The bis(trichlorosilanes), CAS 13083-94-8 and 2504-64-5, were too reactive with air or were not able to withstand the solvents used in organic thin film transistor (OTFT) processing. These solvent tests were done with common processing chemicals

* Corresponding author.

E-mail address: Peter.Vicca@imec.be (P. Vicca).

Fig. 1. Chemical structure of (a) Poly(4-vinylphenol) and (b) Poly(melamine-co-formaldehyde).

like acetone, isopropanol (IPA), deionized water, *n*-methyl-2-pyrrolidone, tetramonium hydroxide and 1-methoxy-2-propanol acetate. A selection of 1,3,5-Triazines, CAS 91-76-9, 542-02-9, 19338-12-6 and 29366-76-5, mostly failed to dissolve in PGMEA, with exception of (hydroxymethyl) benzoguanamine, HMBG (Sigma Aldrich product number 441945) shown in Fig. 2, which we choose to progress with further experiments. At first, we analyzed the film deposition by spin-coating of the PVP solution with HMBG cross-linker on a glass substrate.

Spin curves were established for various cross-linker and PVP concentrations. After bake-out of the films at 180 °C, the thickness of the resulting layer was measured by ellipsometry. The target thickness of 200 nm was reached by spin-coating a solution of a 10 w% PVP and 2 w% HMBG in PGMEA at 5000 rpm.

Next, the resistance of cured PVP to solvents was tested. After spin-coating, the samples were cured in a vacuum oven for 3 h at 110 °C, 130 °C, 150 °C and 180 °C. Subsequently, the samples were immersed for 1 minute in acetone, isopropyl alcohol (IPA) and toluene. For curing at 130 °C or higher, the solvent had no visible impact on the film. However, when cured at 110 °C, the film was removed by rinsing in any of the tested solvents.

The chemical proof of cross-linking was established by means of Fourier transform infrared spectroscopy (FTIR, Bruker IFS 66 u/S). Spectra were taken for non-cured and cured (130 °C) PVP, and compared to a blank sample that acts as reference (Fig. 3). In these spectra, the signature of the hydroxyl group of the PVP molecule is the peak in the range of 3200–3600 cm⁻¹. It can be observed in Fig. 3 that this peak is reduced after cross-linking PVP with HMBG at 130 °C, indicating that a certain concentration of hydroxyl groups have reacted with the cross-linker.

In a second test, we fabricated capacitor structures on glass to evaluate the leakage and breakdown of the cross-linked PVP. For this purpose, 30 nm Au was evaporated onto a glass substrate, defined by photolithography and wet etched with a commercial Iodine solution. Subsequently, a film of 200 nm cross-linked PVP was applied and baked at different temperatures. Via holes were defined in the PVP film by photolithography and dry-etched with O₂-plasma. Finally, a second 30-nm Au layer was applied by thermal evaporation, and structured by photolithography and wet etch.

Fig. 2. Chemical structure of (Hydroxymethyl)benzoguanamine.

Fig. 3. FTIR spectrum of a PVP/((hydroxymethyl)benzoguanamine) solution before and after curing at 130 °C.

The current–voltage (IV) characteristics of the capacitors are shown in Fig. 4. The breakdown voltage and leakage of the PVP with HMBG cross-linker baked out at 130 °C are similar to those of PVP cross-linked with poly(melamine-co-formaldehyde) at 180 °C. The capacitance value measured with quasi-static CV measurements corresponds to a dielectric constant of 4.5.

In a subsequent step, we made top-contact OTFTs using evaporated pentacene as a semiconductor to evaluate the compatibility of the low-temperature cross-linked PVP in a transistor process. We used a highly doped Si-wafer covered with 140 nm thermal grown SiO₂ as substrate. The PVP solution with HMBG cross-linker was spin-coated and baked at different temperatures. Afterwards, 30 nm of pentacene was deposited by organic molecular beam deposition on the samples as the organic semiconductor. Source-Drain contacts were realized by depositing 100 nm Au through a shadowmask. Electrical measurements were performed with a Keithley 4200 probe station in a nitrogen glovebox.

Fig. 5 shows that the transistor characteristics are similar at every temperature in excess of 130 °C and the mobility reaches 10⁻¹ cm²/Vs comparable to what has been shown before with the standard PVP cross-linker. The threshold voltage however is below -6 V, whereas for circuit applications a threshold voltage closer to 0 V would be preferred [17]. In an independent experiment, we varied the concentration of poly

Fig. 4. Leakage and breakdown test for 200 nm cross-linked PVP (standard = poly(melamine-co-formaldehyde); nX = HMBG); (inset) microscopic image.

Fig. 5. Electrical characteristics (I_{DS} vs. V_{GS}) of top-contact OTFTs for different PVP cross-linking temperatures ($\mu \sim 10^{-1} \text{ cm}^2/\text{Vs}$, $V_T \sim -6 \text{ V}$); (inset) schematic cross-section of device structure.

(melamine-co-formaldehyde) in PVP and observed that the threshold voltage is correlated with the amount of cross-linker, while the mobility is not much affected (Fig. 6). This result will be used as a starting point for optimizing the HMBG concentration in the PVP mixture.

Next, we investigated cross-linked PVP for transistor geometries where the source and drain contacts are defined by photolithography directly on top of the cross-linked gate insulator (so-called “bottom-contact” transistors). The bottom contact transistor structure is closer to the processflow of an integrated circuit [2] as compared to top contact test structures, because photolithography allows to define transistor channels down to $5 \mu\text{m}$ (see the inset of Fig. 7). The PVP was cross-linked with different amounts (0.5; 1; 1.5 and 2 w%) of (hydroxymethyl)benzoguamine and all were cured at a temperature of 130°C . Before the pentacene deposition a surface treatment [18] was performed. The electrical measurements of these OTFT are shown in Fig. 7. These transistors are well behaved with a mobility of around $0.55 \text{ cm}^2/\text{Vs}$. Using a cross-linker concentration of 1.25 w%, a V_T of 1.6 V was achieved.

In summary, we described the use of an alternative cross-linker for PVP that allows to decrease the cross-linking temperature to 130°C , while maintaining good electrical characteristics of the transistors. We demonstrated fully photolithographically patterned bottom-gate

Fig. 6. Effect of concentration of cross-linker in PVP on the threshold voltage in a pentacene top-contact OTFT.

Fig. 7. Electrical characteristics (V_{GS} vs. I_{DS}) of a bottom contact OTFT with PVP cross-linked at 130°C ; (inset) microscopic image.

bottom-contact transistors with this cross-linked PVP as gate dielectric, with charge carrier mobility of over $0.5 \text{ cm}^2/\text{Vs}$.

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