Self-Alignment Method for Solution-Processable Dielectric Structures via Joule Heating

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ABSTRACT

We present a versatile method to create self-aligned patterns of polymer dielectric on metal by the use of Joule heating. In contrast to global thermal or light based curing, the method self-aligns the dielectric to a metal pattern on the substrate. A current-induced temperature rise along a metal line cures the insulator locally; uncured material is then removed by rinsing with solvent. We have obtained very promising results for aligning thermally cross-linkable and selectively baked dielectrics. Alignment of cross-linkable polymers is less sensitive to the rinsing step than selectively baked dielectrics. Finite-element simulations were used to determine the range of suitable curing current. After optimization of the curing parameters high yield and low leakage dielectrics were obtained.

Keywords: Cross-linking, Polymer, Dielectric, Joule heating

1. Introduction

Printed electronics is being studied intensively as a promising alternative to conventional electronics, especially for inherently large-area applications or integration of multiple functionalities. Whereas conventional electronics has minimized the cost of devices by miniaturization, printed electronics can produce large area patterns at very low cost. [1]

A variety of semiconducting, conducting and insulating materials is needed to print an electronic circuit; in this paper we focus on insulators, though the same concepts may be extendable to semiconductors. High quality dielectric materials are essential for electronics applications: in particular high capacitance and low leakage current are required from the transistor gate dielectric. To fulfill the needs of printed electronics, insulators should be compatible with flexible substrates and low-cost manufacturing methods. Insulating polymers can be processed as solvent based inks which enable their use in printing and coating processes. To guarantee pinhole free insulator layers, polymer films usually need to be relatively thick (a few hundred nanometers). If multiple process stages are used to manufacture a circuit, the insulator should be insoluble in solvents used in the subsequent processing steps.

Inorganic insulators usually have higher dielectric constants than organic dielectrics [2] and are insoluble in organic solvents. However, they usually require vacuum or vapour phase processes such as Physical Vapor Deposition, sputtering, Chemical Vapor Deposition or Atomic Layer Deposition. In addition, the patterning of inorganic layers by low-cost methods is also frequently challenging. Furthermore, there is some evidence that high-k dielectrics are not always the preferred choice for applications in printed electronics [3]. Therefore, there is a need for both high and low k dielectrics in printed electronics.

One approach to fabrication of inorganic insulators is electrochemical anodization of metal. Anodization is compatible with the demands of printed electronics. It is a cheap, solution based technique, and compatible with plastic substrates. Anodization has been used to create thin high quality metal oxides from aluminum, titanium, and tantalum. These metal oxides tend to have high dielectric constant and they have been used in thin-film transistor gate dielectrics, where the gate dielectric and gate electrode are automatically self-aligned [4, 5, 6].

We report here an approach that allows self-aligned patterning of solvent based, low dielectric constant organic dielectrics on metal lines. Metal lines patterned onto a substrate are heated with electric current. Localized heating cures the insulator surrounding the heated part of the line. If the insulator is cross-linkable, it is resistant to organic solvents and uncured dielectric can be rinsed away. This method has high potential in printable electronics. Whereas in electrochemical anodization process the whole metal is covered with the oxide film, here the electrode can be selectively covered with polymer dielectric layer using appropriate electrode design. For instance, it provides insulator-free areas for electrical contacts while allowing bridges for signal lines – no vias are needed. Previously, use of Joule heating was reported

for selective ablation of polymer layer on a silicon nanowire [7]. In contrast to this work, we use Joule heating for the stabilization and patterning of the polymer.

We have demonstrated self-aligned patterning of insulating polymers by selective baking in the case of poly(methyl methacrylate) (PMMA) and by thermal cross-linking in the case of poly(4-vinylphenol) (PVP) using suberoyl chloride (SC) as a cross-linking agent. Thermal modeling has been used to estimate the effect of current density on the temperature increase at the conductor.

2. Materials and methods

All the materials were purchased from Sigma-Aldrich unless otherwise noted. PMMA (weight-average molecular weight M_w = 120,000 g/mol) was dissolved in a 1:1 by weight mixture of toluene and ethyl acetate. Three different PMMA solutions where the PMMA weight percentage was 5 wt%, 9 wt% and 15 wt% were formulated. The baking time of PMMA was varied between 40 to 70 minutes and current density was 7.8-8.5×10^9 A/m^2.

The solution of PVP/SC was formulated in propylene glycol monomethyl ether acetate (PGMEA). The PVP (weight-average molecular weight M_w = 25,000 g/mol) to cross-linker molar ratio was 10 and the PVP concentration was 50 mg/ml. Joule heating was applied with current density from 7.3 - 9.2×10^9 A/m^2, and curing time was 5 minutes.

A 125 μm thick heat stabilized poly(ethylene terephthalate) (PET, Melinex® ST506 from DuPont Teijin Films) film, was used as the substrate. Copper conductors of a thickness of 100 nm, width of 390 μm, and length of 5 mm were deposited onto the substrate using electron beam evaporation and a shadow mask. The polymer layer was applied to the substrate by spin coating with rate of 2000 rpm or 500 rpm. An electrical current was passed through the conductor causing heating of the narrow parts of the conductor. Due to the temperature rise at the conductor, the dielectric is cured locally above the conductor. The noncured soluble insulator can be rinsed away with the solvent as shown in Fig. 1. In the case of multiple dielectric layers, insulators were cleaned after each spin coating and curing steps.

The Joule heating was carried out with 390 μm wide copper traces. To control the heating process, a steel plate was placed under the PET substrate. Effects of the curing time and current density on cross-linking

of PVP were studied. Capacitances, leakage currents, and surface roughness of the insulators were measured from devices consisting of a sandwich electrode structure.

The top electrode was evaporated on cured insulator film forming a capacitor with an area of 0.15 mm^2. Capacitances were measured with a network analyzer (Hewlett Packard 8752 A) and leakage current with a semiconductor parameter analyzer (Agilent 4155B). Breakdown voltages were investigates with a source meter (Keithley 2425 100W SourceMeter). Films were imaged with optical microscope (Olympus BX51) using brightfield setting, a reflected illuminator, objective lens (Olympus MPLAN 10×/ 0.25), and a digital camera (ARTRAY ARTCAM). The roughness of the insulator film was measured using atomic force microscopy (AFM) (Veeco Dimension 3100) operated in tapping mode (~260 kHz frequency, Nanosensors PPP-NCH-50 silicon probes).

3. **Modeling**

The PET substrate is stable at temperatures up to 150°C; therefore the curing temperature should be kept below that. To estimate the influence of current density on the temperature rise at the conductor, Joule heating was modeled using a finite element method (Comsol Multiphysics® , version 3.5a from Comsol, Inc.) The simulation combined heat transfer model of the Heat Transfer Module and electrical conductivity model of the AC/DC Module.

Heat transfer in bulk material was modeled with the Fourier law of heat conduction [8]. The modeled domain is described in the inset of Fig. 2. The surface of the insulator was described with the heat-flux condition [9]. No inward heat flux was applied. The temperature of the bottom face of the PET substrate was forced to room temperature which corresponds to having a heat sink under the substrate during heating. The conductivity model was connected to the heat transfer model via heat source generated by the current.

The modeling results are illustrated in Fig. 2. They indicate that the substrate thickness has a strong effect on the temperature rise due to the relatively low thermal conductivity of PET. For a 125 μm thick substrate the temperature rise from 60°C to 120°C is achieved with current densities of 6.7- 8.8×10^9 A/m^2. The thermal conductivity of PVP was considered to be constant in the model.

The model corresponds well to the observations; the insulator was heated in an oven and by Joule heating to temperatures near the boiling point of the PGMEA solvent (145-146°C) in order to observe the formation of bubbles in the insulator due to boiling of the solvent. Comparison of temperatures in the oven and simulated temperatures corresponding to Joule heating currents showed that the error limit in the model is ca. 10°C.

4.   Results and discussion

Heating of PMMA causes solely evaporation of the solvent; no chemical reactions are taking place. In order to evaporate the solvent, heating current densities between 7.8 and 8.5×10^9 mA/m^2 were used. According to the modeling results these correspond to temperature between 100 °C and 130°C. The curing time was long, 40 to 70 minutes, and the result was dependent on the rinsing step. The baked PMMA dissolves into the solvent, but significantly more slowly than non-baked PMMA. Due to this residual solubility, films made from the 5 wt% PMMA formulation were too thin, and the insulator dissolved completely during the rinsing step. In the case of 15 wt% PMMA a few ca. 2 μm thick insulating films were obtained, but the yield was low due to pinholes formed during the baking. The leakage current was 10^{-6} A/cm^2 at 20 V bias voltage.

The cross-linking of PVP and SC takes place through esterification of (4-vinylphenol) with acyl chlorides [10]. A cross-linking test for PVP was made by varying the Joule heating current. The dependence of capacitance on current with different parameters is illustrated in Fig. 3. Capacitances were measured at 40 MHz for which the measurement error was 2 pF. Thicknesses of the insulator layers are calculated from capacitance data using 4.2 as a material dielectric constant of cross-linked PVP [10].

Thicknesses of the single layer insulators deposited using a spin coating rate of 2000 rpm were between 150 nm and 200 nm. Insulators having thicknesses from 270 nm to 510 nm can be constructed with lower spin coating rate or by depositing multiple insulator layers. Microscope images of single and three layer insulators deposited with speed of 2000 rpm and cured with 8.2×10^9 A/m^2 current density are shown in Fig. 3A and 3B. The thickness of the multiple layer film is approximately the number of layers multiplied by the film thickness of one layer. With a speed of 500 rpm the film thickness is approximately 400 nm. Using a slower spin-coating rate enables the use of lower Joule heating current.

A slightly negative slope can be observed in the capacitance curve, which indicates increased film thickness as a function of current density. In the case of thicker insulator layers, a broadening of the temperature distribution causes widening of the cross-linked insulator over the wire edges. This can be prevented by minimizing the current and curing time.

Surface analysis with AFM revealed that insulator films cross-linked and patterned by Joule heating and washing with PGMEA are highly uniform and pinhole free layers with the RMS roughness values as low as 1.3-2.1 nm, slightly depending on the amount of insulator layers or applied current. In comparison, the RMS roughness of spin-coated PVP film was 0.9 nm after baking in the oven and 1.7 nm after PGMEA wash, which indicate that use of Joule heating and subsequent solvent wash very smooth dielectric surfaces can be obtained.

Leakage currents for the single layer insulator spin coating with 2000 rpm and 3 layer insulator are presented in Fig. 4. Measured leakage currents for multiple layer insulators did not differ significantly from the data of single layer insulators spin coated with 500 rpm. Breakdown voltages were investigated applying DC bias voltages. We observed that 3 layer dielectrics could withstand voltages up to 60 V (field strength 140 MV/m) and single layer dielectrics up to 50 V (field strength 250 MV/m).

5. Conclusion

In this study, we have demonstrated a method for selective, self-aligned curing of polymeric insulators. A copper conductor is selectively heated by Joule heating creating a temperature rise at the conductor that cures the insulator and makes it insoluble. Curing is followed by a rinsing step that washes away uncured insulator. The method has been demonstrated for PMMA and cross-linkable PVP. Patterning of PMMA is dependent on control of the rinsing step, because curing of PMMA only slows down the dissolving of insulator. Heating of thermally cross-linkable dielectrics such as PVP/SC creates an insoluble insulator film. Optimization of curing parameters minimizes the widening of the insulator.

To conclude, we have demonstrated Joule heating as a way to perform self-aligned patterning of polymer dielectrics on metals. The patterned 3 layer film can withstand voltages up to 60V without breakdown (field strength 140 MV/m) and if thermal cross-linking is used they are also highly resistant to solvent.

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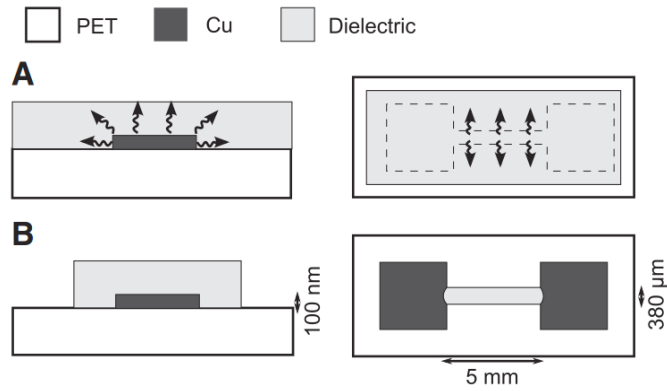
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Fig. 1. Selective curing by Joule heating: A temperature rise at the conductor is caused by the electric current. (A) Insulator surrounding the conductor is cured and (B) residues can be rinsed away.
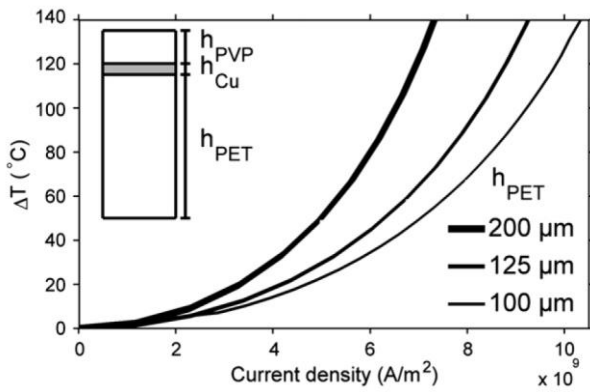

Fig. 2. Heat modeling was done for 100 nm thick copper conductor evaporated on PET substrate. Copper conductor is coated with 1 μm thick PVP-insulator. The curing temperature was estimated from modeling results. The substrate thickness has a strong effect on Joule Heating efficiency.
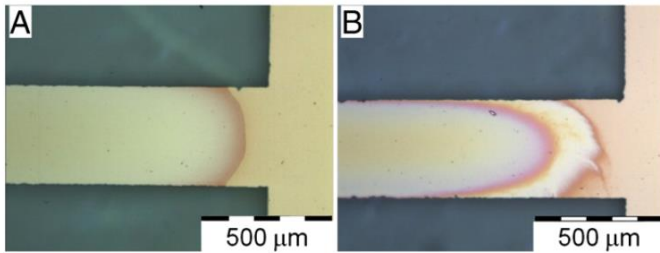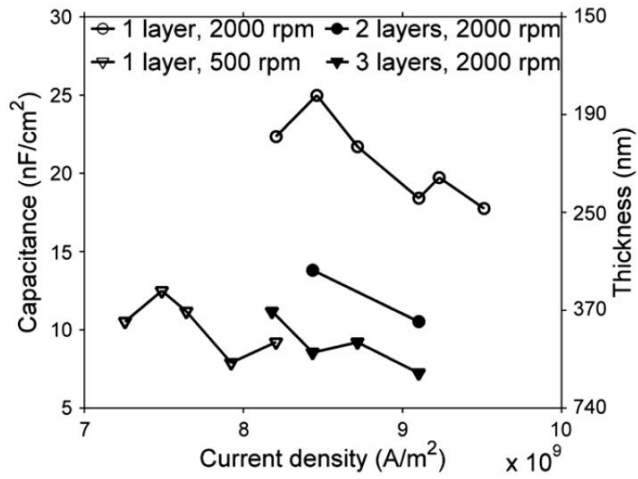
Fig. 3. Measured capacitances and calculated thicknesses as a function of heating current. Measurements were done for 1 to 3 layer PVP insulators cured 5 minutes. Optical microscopy images of (A) a single insulator and (B) a three layer insulator coated with speed of 2000 rpm and cured with current density of 8.2×10^9 A/m^2.
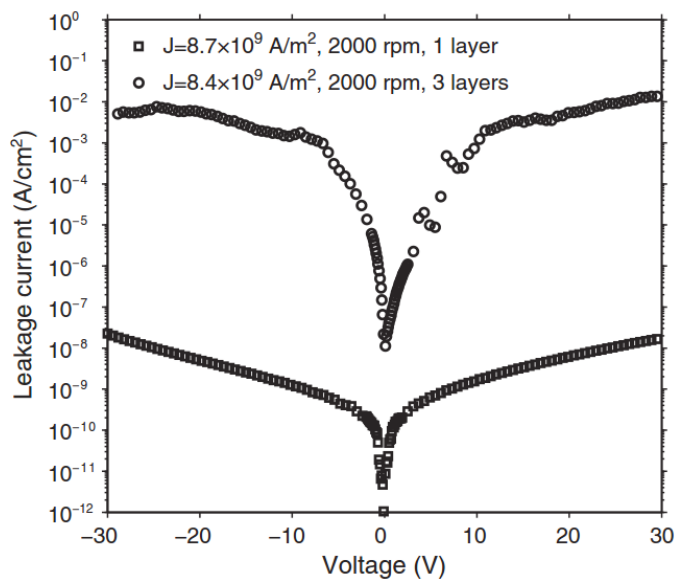

Fig. 4. Leakage current measurement for single and three layer PVP insulators with spin coating rate of 2000 rpm.