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Polyimide-Based High-Temperature Plastic Electronics

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Supporting Information

ABSTRACT: **All-plastic transistor devices with thermal stability up to 220 °C are demonstrated. We employ polyimide substrates, polyimide dielectrics, and a polyimide-based semiconducting blend to achieve flexible and thermally-robust transistors. An in situ temperature-dependent charge transport study was used to demonstrate that these devices can operate in extremely high temperatures and can sustain prolonged baking. Our devices maintained stable charge-transport characteristics with charge mobilities of 0.20 cm^2/(V s), I_{ON}/I_{OFF} of 10^4, threshold voltage of 3 V, and operational voltage of 10 V when baked at 195 °C for 2 h.**

Organic-based electronics that are conformable, flexible, low-cost, and lightweight have been studied for the past two decades as alternatives for silicon-based technologies.[1,2] Today, flexible electronics are on the verge of becoming a commodity in daily life applications, such as flexible displays and wearables. One class of application that is yet to benefit from these lightweight and cost-effective electronics is for high-temperature applications, especially in aerospace engineering and the automobile industry, as well as in gas and oil drilling industries.[3,4] These applications require lightweight materials that can sustain harsh thermal conditions for prolonged operation times without requiring additional insulation or cooling. Currently, active or passive cooling and insulation are needed for such applications, resulting in a weight and cost burden especially in aerospace engineering.[5] Carbides and wide-band gap inorganics have been studied as thermally-robust alternatives, but their cost and complicated processing limit their wide adoption.[3] With such requirements, plastic electronics based on thermally-stable plastic substrates, dielectrics, as well as semiconductors potentially become excellent candidates.

Polyimides have been used as heat-resistant materials for high-temperature applications and have been investigated as substrates for fabricating thermally stable, flexible electronics.[6−8] For instance Kuribara et. al. utilized polyimide substrates and fabricated transistor devices for sterilizable medical devices.[6,9] By using thermally-resistant organic small-molecule semiconductors, the fabricated flexible devices showed to remain functional after annealing at temperatures up to 250 °C. The use of polyimide substrates thus enables the fabrication of flexible electronics able to sustain thermal environments in which the commonly used plastic substrates such as polyethylene terephthalate (PET) would not survive.[10] In separate reports, polyimides also constitute a class of excellent dielectric materials as they exhibit excellent capacitive response to electric field, as well as high capacitive breakdown ability with low power consumption in transistor devices.[11−15] For instance, the polymerization of pyromellitic dianhydride (PMDA, $C_{10}H_2O_6$) with 4,4′-oxydianiline (ODA, $C_{12}H_{12}N_2O$), followed by a thermal curing step, has been used to process highly uniform and smooth films of polyimide dielectrics used in transistor devices.[16,17]

The long-standing challenge towards achieving thermal stability has been the design of thermally-stable semiconductors as electronic properties are temperature-dependent and degrade especially at extremely high temperatures.[18,19] Organic semiconductors, a class of materials that exhibit a thermally activated electronic behavior, were recently demonstrated by our research group to be rendered thermally-stable through strategical blending and composites formation.[20] High glass-transition temperature (T_g) matrix polymers were used as hosts in thin films to increase the thermal stability of the semiconducting blends up to 220 °C. With this approach, we demonstrated excellent high-temperature operation stability as opposed to other works that mostly investigated the effect of annealing temperatures.[6,9,21−23] The blending strategy allows for common semiconducting polymers to be processed into thermally robust thin films to fabricate transistor devices that can function under thermal stress. This strategy thus offers the

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opportunity for facile fabrication of large-scale plastic electronics functional under extreme temperatures.

In this Letter, we demonstrate all-plastic, thermally stable transistor devices fabricated through a facile sequential layering of polyimide films. We utilized Kapton substrates as the support, solution-processed polyimide as the dielectric layer, and a thermally stable Matrimid-based blend as the functional semiconducting layer. With this fabrication strategy, we aim to not only facilitate and generalize the device fabrication process but also to reduce the mismatch in thermal expansions between different layers and, therefore, improve the overall thermal stability in all-plastic device assemblies. Figure 1a shows the transistor device architecture using all-polyimide components. Also shown are the molecular structures of (b) the semiconducting polymer (PII-2T), (c) Matrimid used as the host matrix in the channel layer, and (d) polyamic acid (PAA) used as the precursor solution to process polyimide (PI) as the dielectric layer (e). We selected Kapton as the plastic substrate because of its thermal durability, its flexibility, and most importantly, its compatibility with the dielectric layer. Kapton substrates were also available in different thickness gauges (25 μm for Kapton HN 100 and 125 μm for Kapton HN 500), which allows to tune the flexibility and the overall weight of the devices. We then chose polyimide as the dielectric component not only because it can be solution-processed from a readily available PAA precursor but also because it has previously demonstrated excellent thermal stability, excellent capacitive properties, and low power consumption in transistor devices.[12] We selected isoindigo, PII-2T, as the semiconducting polymer which was recently found to have heat resistant semiconducting properties on its own.[20] Finally, to improve the thermal stability of the semiconducting layer, while increasing its compatibility with the consecutive layers, we used Matrimid 5218 as the high-T_g host matrix and processed semiconducting blend films with PII-2T as demonstrated in our previous studies.[20]

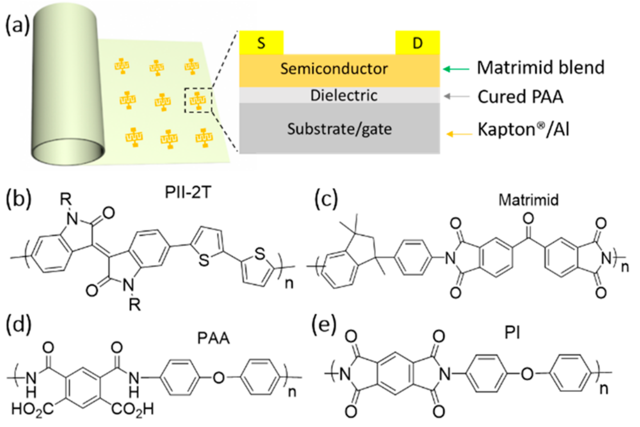

Figure 1. (a) Device architecture of an all-plastic transistor using polyimides. Molecular structure of (b) PII-2T, the conjugated polymer used in the semiconducting blends, (c) Matrimid, the high-T_g matrix, and (d) PAA used as the precursor for processing (e) the PI dielectric layer.

We fabricated the transistor devices by, first, patterning and depositing Al gate contacts on cleaned Kapton substrates, followed by spin coating a PAA solution onto the device (Figure 2a). A smooth film (root-mean-square = 0.22 nm) of PI dielectric layer (Figure 2b) could be readily obtained after full imidization by thermal curing with a thickness of 200 nm (Figure S1) and a capacitance of 4.5 nF/cm^2 (Figure S2). The solvent resistance and robustness of the formed dielectric layer allowed to process the semiconducting layer on top. The Matrimid/PII-2T blend solution could be processed by spin coating from chloroform mixture yielding a ~150 nm thin film (Figure S4). The blend formed a bicontinuous network in which the semiconducting polymer is surrounded by the high-T_g host (Figure 2c), a feature that has been shown to be beneficial for improving the thermal stability in thin films. After annealing the semiconducting layer, the device structure could be completed by depositing Au source/drain contacts. The fabricated transistor devices are flexible, light-weight with charge carrier mobilities as high as 0.20 cm^2/(V s), ON to OFF current ratios around 10^4, and threshold voltages of 3 V could be attained, while requiring operation voltages as low as 10 V (Figure 2d and e). Other properties, such as low hysteresis and low leakage currents, are also achieved (Figures S7 and S8).

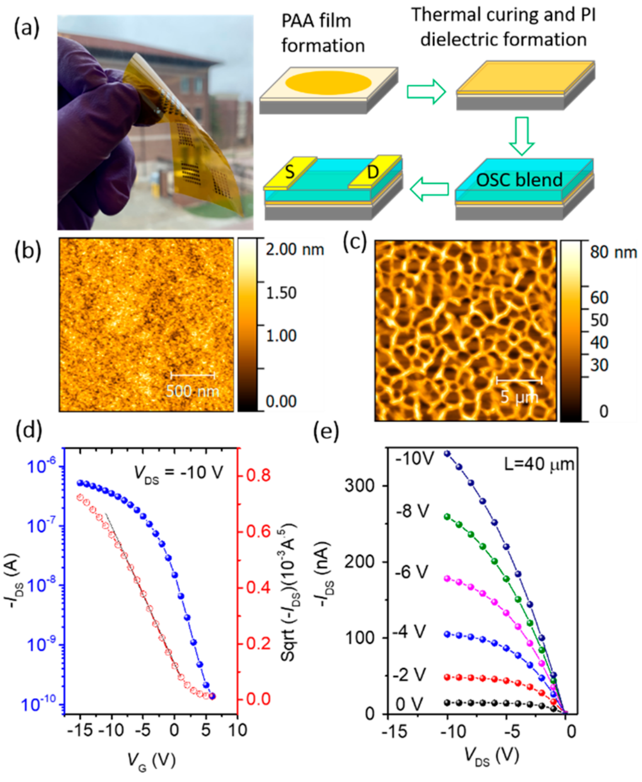

Figure 2. Proposed device fabrication route for all-plastic, polyimide-based transistor devices. (a) Micrograph of Kapton 100 substrates with patterned Al gates and the sequential layering device fabrication. AFM height image of (b) the very smooth thermally-cured dielectric layers and (c) the interpenetrating film of PII-2T/Matrimid blend processed on top of the PI dielectric. Characteristic (d) transfer curve and (e) output curve of the measured transistor devices showing ideal behavior, as well as low power consumption (V_{DS} of −10 V).

To test the thermal stability of the fabricated plastic devices, we measured their electronic properties from room temperature up to 220 °C in ambient air. In typical electronics, such thermal stress will lead to uncontrolled increase in charge carrier density leading to excessive doping levels and carriers scattering resulting into the loss of the amplifying power of the transistor devices. Especially for conventional organic semiconductors, in this temperature regime, morphological fluctuations and thermal expansion normally will lead to significant decline in device performances.[8,23−25] Figure 3a shows the source/drain current with increasing temperature from our plastic transistor devices. Upon heating, the thermally-activated increase in the charge carrier density leads to increased ON and OFF currents, but our devices retain the ideal behavior and stable currents at all temperatures. These plastic devices can retain their I_{ON}/I_{OFF} even when operating at 220 °C in the open air (Figure 3c). The extracted threshold voltage also shows minimal variation as the operating temperature increases (Figure 3d). The in situ temperature-dependent capacitance study also revealed that the PI dielectric layer can retain its excellent capacitive behavior even when under baking conditions (Figure S2) in agreement with previous reports.[12] We attribute this excellent thermal stability of our plastic devices, first, to the compatibility in thermal expansion between all polyimide-based components of the transistor devices and, second, to the blending strategy, which enables the semiconducting polymer chains to remain confined by the polyimide host. This confinement in bicontinuous morphologies minimizes morphological variations and reduces carriers scattering.

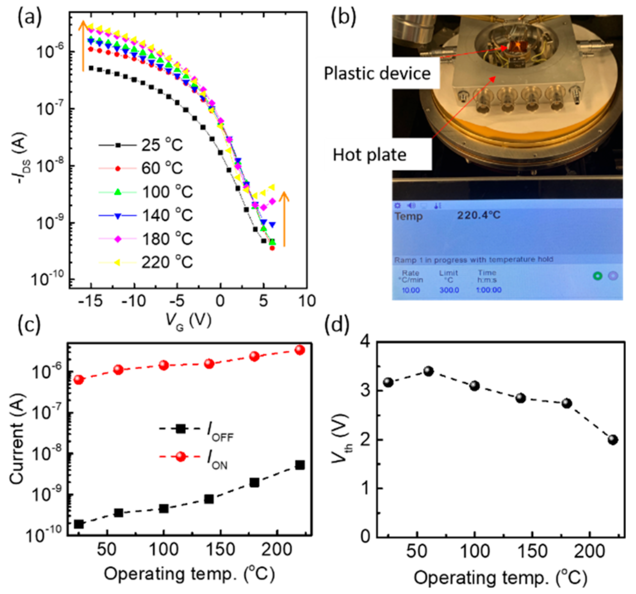

Figure 3. (a) Characteristic transfer current of the plastic device under different heating temperatures. Upon heating, the current increases indicative of a thermally activated behavior that remains stable even when the operating temperature reaches 220 °C. (b) In situ temperature-dependent device characterization set up with precise temperature control. Temperature-dependent (c) ON and OF currents and (d) threshold voltage of the transistor device measured in open air. Similar stable behavior could be observed on 10 other different devices.

To further test the thermal durability of our plastic devices, we tested the transistor properties under continuous heating at 195 °C equivalent to a baking oven environment. Upon baking, our transistors devices can retain ideal transfer and output characteristics as shown in Figure 4a and b. More importantly, these characteristics are retained after 2 h of heating in the open air. Figure 4c shows minimal to no change in the ON and OFF currents with increasing baking time. Similarly, the threshold voltage shows to remain around 3 V even after 2 h of heating (Figure 4d). In conventional transistors, prolonged heating normally leads to increased charge carriers scattering and uncontrolled changes in threshold voltages resulting into increased power consumption. In our devices, the required operational voltage (V_{DS}) was kept at −10 V and the transistor devices could still exhibit excellent electronic properties. This ideality renders our approach an excellent candidate for high temperature sensing in which functional device components can sustain long-term heating with minimal power consumption.

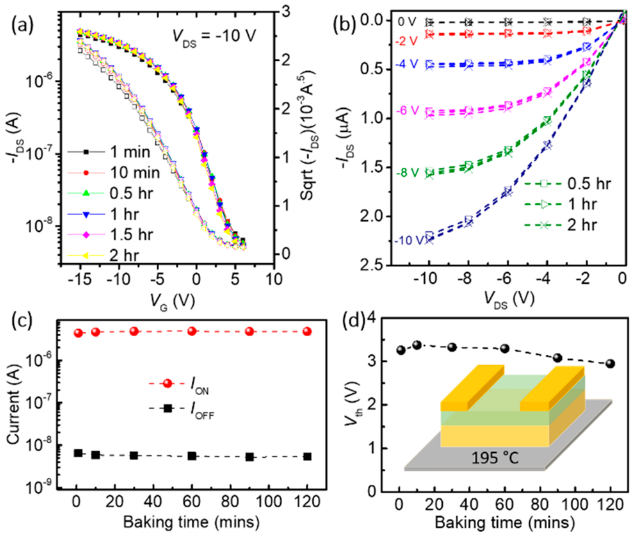

Figure 4. Characteristic (a) transfer and (b) output curves of a typical plastic transistor device measured with increasing heating time at 195 °C. The transistor devices exhibit minimal change in (c) current ratio and (d) the threshold voltage even after 2 h of constant baking. The same behavior was observed for 10 other different devices.

To summarize, we have demonstrated a general, robust, and facile fabrication of all-plastic transistor devices that are thermally stable. We used polyimide components in all transistor layers and demonstrated a sequential stacking route enabling the facile fabrication of lightweight and flexible all-plastic electronics. Our devices exhibit electronic performance stable up to 220 °C and can sustain prolonged heating. We demonstrated that by utilizing semiconducting polymer blends and form thermally-robust blend composites, the amplifying power in transistor devices can be retained even under very harsh thermal conditions while requiring minimal power consumption.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmaterialslett.9b00120.

Experimental details and supplemental figures showing thickness evaluation of the thermally-cured PI film using AFM, temperature-dependent capacitance measurements, morphology optimization in PII-2T/Matrimid blend films, thickness extraction of PII-2T film, optical micrographs of the steel shadow masks used for metal deposition and the plastic devices, statistical distribution of extracted mobility values, characteristic transfer curves, temperature-dependent source to drain and source to gate currents from the plastic device, characteristic transfer curves of devices measured at different operation temperatures in the open air, and characteristic output curves of devices measured at different operation temperatures in the open air (PDF)

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Notes

The authors declare no competing financial interest.

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