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High Temperature Organic Electronics

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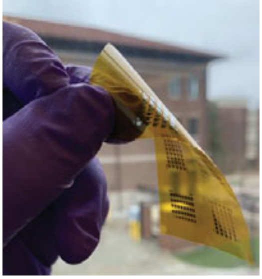
ABSTRACT



The emerging breakthroughs in space exploration, smart textiles, and novel automobile designs have increased technological demand for high temperature electronics. In this snapshot review we first discuss the fundamental challenges in achieving electronic operation at elevated temperatures, briefly review current efforts in finding materials that can sustain extreme heat, and then highlight the emergence of organic semiconductors as a new class of materials with potential for high temperature electronics applications. Through an overview of the state-of-the art materials designs and processing methods, we will layout molecular design principles and fabrication strategies towards achieving thermally stable operation in organic electronics.

INTRODUCTION

From daily appliances (ovens, cellphones, computers, etc), to vehicles, space shuttles, and oil drilling devices, electronics that must operate in harsh thermal conditions are needed.[1, 2] Unfortunately, the functional component in the building units i.e. semiconductors, are sensitive to temperature.[3, 4] For the ubiquitous silicon technology, the optimal operation temperature cannot exceed 80 °C. Beyond these conditions, the electronics begin to malfunction. For these reasons, most of the devices come with a cooling system and a large amount of insulating materials to maintain the temperature within the optimal operation range. Cooling and insulation, though efficient for devices such as cellphones and computers, become ineffective approaches for space shuttles and downhole drilling devices where weight is a crucial and costly parameter. Intrinsically thermally stable materials are ideal for these applications. This snapshot will first briefly discuss the limitations of existing semiconducting materials for high temperature operation, introduce the potential recently discovered in organic semiconductors, and highlight recent efforts towards stable operation in semiconducting polymers. We will layout key aspects towards achieving stability at high temperature in organic semiconductors by detailing materials design principles, processing routes, and device architectures suitable for thermally stable electronics.

BACKGROUND AND CURRENT TECHNOLOGY

Fundamentally, charge transport is a combination of temperature dependent processes: i) temperature-dependent charge carriers concentration; ii) the activation energy required to excite carriers into higher energy levels; iii) temperature-dependent delocalization of carriers; and the detrimental iv) temperature-induced lattice expansion and charge scattering.[2] As shown in figure 1 a), regardless of the starting doping level, the intrinsic carrier concentration will increase with increasing temperature. In terms of stability, this increase in carrier concentration is not necessarily detrimental with moderate temperatures. In fact, this is the main reason why most electronics operate optimally between room temperature and 80 °C. In highly crystalline materials, as it is the case for inorganic semiconductors (e.g. silicon), charge carriers scattering becomes problematic once the concentrations become too high; charge carrier mobility becomes slower. As shown in figure 1 b), charge carrier mobility gradually decreases as the temperature increases as a result of carrier concentration increases and scattering. This behavior is quasi linear in high performance materials (mostly inorganics) where band transport is the main carrier pathway. As the lattice expands and scattering arises, the performance drops. For lower performance, mainly lower crystallinity and “impure” materials, temperature is initially beneficial. This is because in these lightly doped and lower mobility materials, charge transport mechanism begins to involve hoping. Carriers need activation energy to hop between domains. However, this thermally-promoted behavior is only observed with moderate heating. Beyond the optimal temperature range, lattice scattering takes over again, and charge mobilities begin to decline once more (figure 1 b).

In real device applications, the increase in temperature typically translates to i) increasing intrinsic carrier density (doping becomes ineffective); ii) exponentially increasing junction leakage current (which degrades performance, increases power consumption); iii) increased electromigration in conductors (lower reliability, shorter lifetime); iv) decreased dielectric breakdown strengths; v) mechanical stress due to coefficient of thermal expansion (CTE) mismatch; and vi) variation in device parameters. These changes are mirrored by the changing transfer characteristics as shown in figure 1 c).[5] Consequently, a lot of efforts are put into insulating the functional component in integrated circuits to ensure the surrounding temperatures do not elevate. Figure 1 d) illustrates the typical mounting approach in circuits to isolate the functional units. Up to 8 additional components are commonly required to maintain silicon-based chips within the optimal range.

The ideal case to obviate the need for insulation and cooling would be the use of semiconducting materials that are intrinsically thermally resistant. Wide band gap (WBG) materials have been proposed and studied for their thermal stability. With more energy levels to be populated upon temperature increase, materials such as carbides (e.g. 6H-SiC) and nitrides (2H-GaN) show to maintain much lower carrier concentrations than the ubiquitous silicon (figure 1 a).[5-7] In fact, the starting (i.e. room temperature) intrinsic carrier concentration of Si is nearly equivalent to that of 6H-SiC when the latter is studied at 225 °C. This thermal tolerance of WBGs has kindled the exploration of carbides and nitrides for high temperature applications.[5] At elevated temperatures, as high as 500 °C, doping remains relatively effective in WBGs and signal modulation can still be realized in thermal regimes where the traditional electronics begin to malfunction (figure 1 e). However, these materials are still rare, and their crystal growth remains challenging to realize. In addition, these materials tend to be expensive, not to mention heavy. This heavy and brittleness nature makes WBG materials less attractive candidates for technologies such as aerospace engineering. Besides, the use of these highly crystalline would not overcome the bottleneck that is the lattice expansion which leads to decrease in charge carrier mobilities due to scattering.

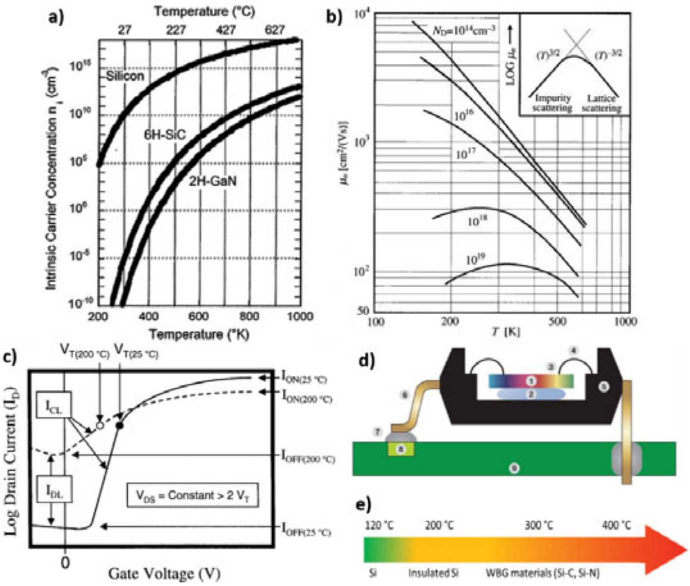


Figure 1. Illustration of temperature dependence of electronic properties in existing technologies.

a) Temperature-dependence of carrier concentration in commonly studied inorganic semiconductors. Adopted from ref.[2] b) Impact of temperature on charge carrier mobility as a function of doping level. For high mobility materials where band transport is predominant the mobility drops with increasing temperature. The opposite is true with moderate heating for materials with impurities where carriers need to hop between sites. Beyond an optimal temperature, mobility also begins to drop due to lattice scattering. Adapted from ref.[4] c) Typical behavior of transfer characteristics with changing temperature. The amplification power begins to decline with excess thermal activation. From ref.[5] d) A representation of the commonly used insulation strategy to maintain silicon-based semiconductors (component 1) functional at high temperature in integrated circuits. e) Temperature functionality limitations for current inorganic semiconducting materials. Wide bandgap materials have shown to be more promising for extreme temperature operation. Adapted from ref.[2]

ORGANIC SEMICONDUCTORS AND HOPING BEHAVIOR

Organic semiconductors present a special case in the design of high temperature operating electronics. Most organic semiconductors are not highly crystalline in nature, which renders their charge mobility thermally favored mostly through the hoping mechanism.[8] However, the realization of a thermally insensitive charge transport remains equally challenging in organic systems.[9] This is mainly because with increasing temperature, though the hoping is favored, other factors including lattice expansion and unstable morphologies begin to impede charge carrier transport. For instance, recent efforts mainly by Someya et. al. using organic small molecule semiconductors in thermally-sterilizable medical devices have revealed the following in the quest for thermal stable operation: [10-15] i) the thermally promoted transport in organic materials is mainly hampered by unstable morphologies and defects formation at elevated temperature. ii) Improved ordering achievable through molecular design strategies, leading to retained close packing at elevated temperature leads to improved thermally-stability. And iii) large pendant groups which help prohibit molecular rearrangements upon heating can improve the semiconductor's thermal stability. By extending the conjugation while improving the stacking in crystal-based films, the phenyl-substituted bis[1]benzothieno[2,3-d;2,3-d]naphtho[2,3-b;6,7-b]dithiophene (DPh- BBTNDT) showed excellent thermal stability in comparison to the parent dinaphtho[2,3-b:2,3-f]thieno[3,2-b]thiophene (DNTT) (figure 2).[14, 16] Though the use of these small molecule semiconductors has promised relatively excellent stability, their difficult processability into thin films, complicated device architectures, and limited scope have limited the emergence of these materials as potential candidates for applications. Besides, most of the studies on such devices have merely focused on the effects of annealing and unstable performances remain an issue when in-situ thermal stressing is in effect.[10, 17]

Alternative material candidates are organic semiconducting polymers. Though polymers –mainly insulating polymers such as polyimides, have been studied for decades owing to their excellent mechanical, thermal, and environmental robustness, such properties are not as readily attainable in high performing semiconducting polymers. Principally, to design thermally robust polymers, the following strategies are normally utilized: i) increasing the polymer backbone rigidity and planarity commonly achieved by introducing para-substituted rings, ii) excluding any flexible linkages and incorporating bulky side groups to decrease rotational freedom, iii) incorporating high energy bonds and resonance stable functional groups, iv) increasing the molecular weight of the polymer, and v) crosslinking the polymer matrix.[18] Unfortunately, most of these strategies are concomitant with poor electronic performances and impoverished processability making the thin films formation for high performance electronic devices a major challenge.

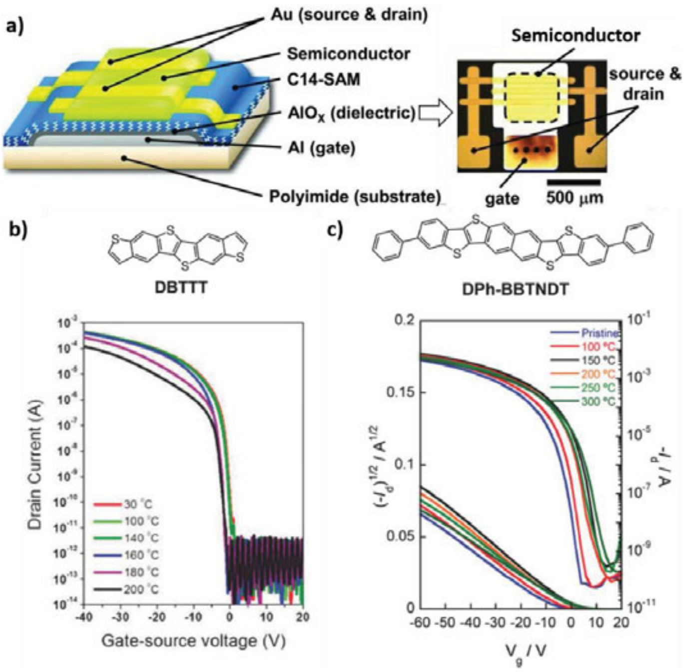


Figure 2. Thermally resistant organic semiconducting small molecules.

a) Architecture of a flexible sterilizable transistor device using organic small molecules as the semiconductor. After ref.[16] b) Example of using fused benzo-and thiophene-rings to afford highly planar semiconductors operational at high temperatures. c) Extended conjugation and improved close packing as a strategy to improve thermal stability. Resulting transfer curve can remain ideal even after the device is sterilized above 200 °C. After ref.[9]

BEATING THE HEAT BY BLENDING

Thermal stability in conjugated polymers gets a new meaning since, unlike the case for small molecules, polymer thin films are less crystalline, and their charge transport behavior relies heavily on the hoping between ordered domains.[19] This behavior implies that the semiconducting properties in polymer thin films improve with moderate heating. The instabilities commonly begin to arise once the temperatures become high enough to affect the morphology in the functional layer.[20-22] With microscopic morphological changes, polymer backbone twisting and rearrangements, increasing inter-chain packing distances, and increased carrier densities, the electronic performances typically begin to decline above 150 °C. Polymers, however, offer structural tunability as backbone and sidechain engineering have been widely studied to afford novel mechano-, opto-electronic properties. In fact, some of the most thermally stable materials are polymers, though insulating polymers. The lightweight nature of polymers has made materials such as Kapton and nylon to be excellent candidates for aerospace applications.

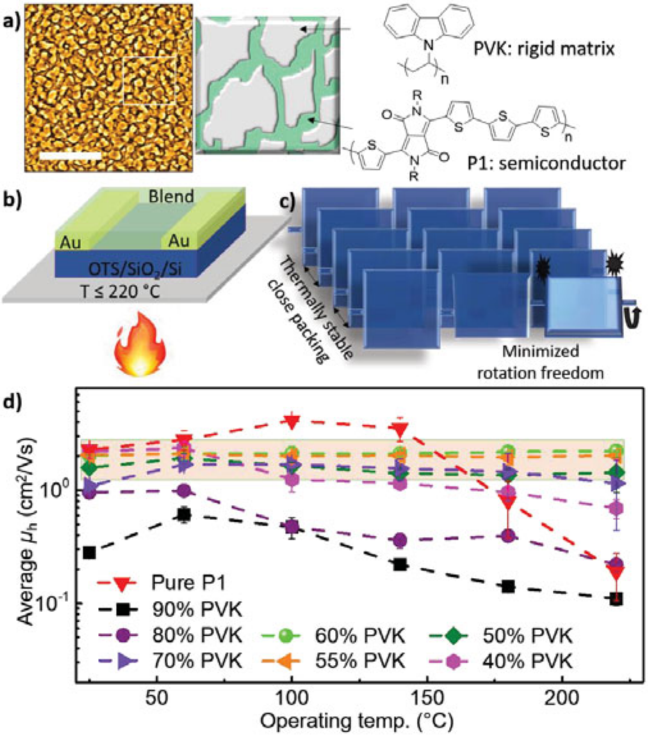


Figure 3. Semiconducting polymer blends that exhibit thermally stable charge transport.

a) Formation of spinodal morphology in binary polymer blends for high temperature operation. Semiconducting polymer domains are confined by the rigid host matrix for a stable morphology, improved ordering, and more efficient charge transport at elevated temperature. The scalebar for the atomic force microscopy (AFM) image is 4µm. b) Device architecture of a thermally stable organic field effect transistor where a semiconductor/insulator blend is used as the functional layer. c) Illustration of stabilized packing behavior in blend films where the induced close packing minimizes the rotation freedom of the semiconducting chains and leads to maintained effective charge carrier mobility at elevated temperatures. d) Comparative in-situ temperature dependent hole mobility illustrating the impact of blending on thermal stability. In comparison to the pristine films, the blend films that form interpenetrating network between the semiconductor and the host matrix exhibit improved thermal stability even when operating at 220 °C. Adapted after ref.[22]

The tradeoff between thermal robustness and electronic performance was recently lifted through a blending approach by Gumyusenge et. al.[22] With this approach, a semiconducting polymer is blended with a thermally robust insulating matrix to form nanocomposites that are both semiconducting and thermally stable. This blending approach has serendipitously been used to improve environmental stability and boost the semiconducting properties in other reports.[23-26] The novelty in thermally robust blends is rooted in selecting matrix polymers with extremely high glass-transition temperatures (Tg) and in ensuring intimate confinement of the semiconducting polymer chains within the matrix. Figure 3 a) shows the bi-continuous spinodal-like morphology obtained when a diketopolypyrrolopyrrole (DPP, P1) semiconducting polymer is blended with poly(9-vinylcarbazole) (PVK) as the high Tg host matrix in optimized ratio. This type of morphology where the semiconductor is closely housed by the rigid matrix showed to offer: i) microscale morphology stability; ii) shortened π-π stacking distances of the semiconducting polymer chains even at high temperatures; and iii) minimized rearrangement and disentanglement freedom of the polymer chains. In comparison to the pristine P1 films, the PVK blend films showed to retain excellent charge transport properties even when heated up to 220 °C as a result of minimized distortions along the semiconducting backbones. Figure 3 d) shows the comparison in charge carrier mobilities at different temperatures when different fractions of the insulating host matrix were used in the blend. With the optimal ratio (near 60% of PVK) and optimized confinement of the semiconductor, stable electronic performance can be attained. This blending strategy has thus kindled a new direction for semiconducting polymers and organic electronics: the search and design for high-temperature operation stability in semiconducting polymers and polymer blends.

Since the blending shows to improve ordering, induce closer packing, and stabilize the film morphology, further investigation on these properties in pristine semiconducting polymers has recently become a field of great interest to investigate whether the thermal transition behaviors could be enhanced without impacting the effective charge transport along the conjugated backbone. In that regard, sought after is using sidechains engineering, as well as backbone planarization to achieve the confinement effect that is currently afforded by blending. With the blending approach, the selection of the appropriate host matrix also constitutes another intriguing field of study. Given the wide library of high Tg insulating polymers, the puzzle becomes the prediction and selection of the insulator that will best interact, confine, and stabilize the semiconductor. Potential is found in the selection of functional groups that are beneficial for thermal stability without impeding charge transport in corresponding blends. Our previous reports have thus selected fused ring-based olefins (e.g. polyvinylcarbazole, polyacenaphthalene) as matrices that offer rigidity but are readily processable and contain no charge-trapping functional groups.[22] However, the library of such polymers remains limited and further molecular designs investigations are warranted.

Polyimides, a class of thermally robust insulating polymers have been studied for various applications owing to their ability to be solution processable into thermally resistant films.[27, 28] For instance, Matrimid a polymer with a glass transition temperature exceeding 320 °C is easily solution processable and can be blended with conjugated polymers to form films functional in transistor devices. [22, 29] Not only does this enable high temperature operation in organic transistors, but it also opens a new venue for organic transistors: all-plastic thermally stable electronics. This is important because instead of simply serving as insulating components, now organic materials find a role in electronics especially for aerospace engineering. As we recently celebrated the 50th anniversary of the moon landing, we were not only reminded that space exploration is on the verge of taking even large leaps than before, but also that thermally robust plastic materials were at the core of the equipment and attire that made the historic trip a success. As excellent thermal shields, polyimides are thus excellent substrates for an all-plastic electronic assembly. Gumyusenge et. al. recently demonstrated that by using Kapton as the substrates, a polyimide-based thin dielectric layer, and a Matrimid semiconducting blend, all-polyimide lightweight and flexible transistor devices that are functional even when heated up to 250 °C can be readily fabricated.[29] Figure 4 a) shows the concept of all-plastic device arrays achieved by sequential layering of polyimide layers. With this approach, the compatibility between transistor device layers is improved in terms of functional groups, surface energies, and most importantly, thermal expansion coefficients. The assembly is highly flexible and can sustain prolonged heat exposures (figure 4 b, c, d, and e). Such lightweight electronics, able to operate under harsh thermal environments would play a huge role in the sensing on spacecrafts and astronauts and could soon transform space exploration by expanding the current limitations while lowering the cost and weight.

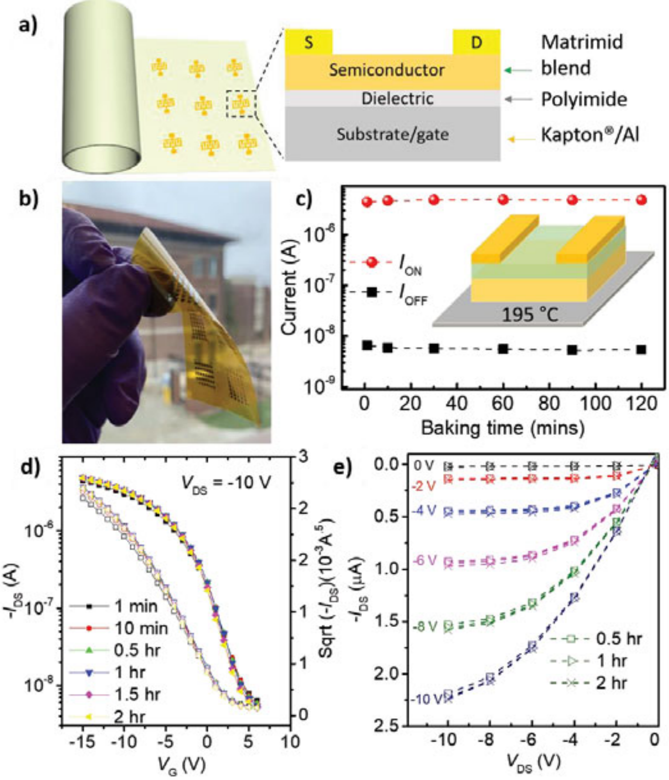


Figure 4. All-plastic electronics a new venue for thermally-robust lightweight circuitries.

a) Device architecture of transistors using polyimide as substrates, dielectrics, and semiconducting blends. b) Micrograph of a flexible device array fabricated on Kapton. c) Temperature-dependent current measured from a device subjected to prolonged baking at ambient. Stable currents can be retained even when the plastic devices were placed in oven-like conditions for two hours. The characteristic transfer (d) and output (e) properties could also be retained in such conditions. After ref.[29]

CLOSING REMARKS

The need for electronics that can function in harsh thermal environments keeps rising as humankind strives to revolutionize modes of transportation, navigate the outer space, and upgrade ways of energy harvesting. This is no easy task because electronic performances tend to decline with increasing temperature. This review gave a glimpse of recent potential found in organic materials, specifically semiconducting polymer blends. The marriage of robustness found in insulating polymers and the electronic performance of conjugated polymers has demonstrated the ability to yield blend composites that can effectively transport charge in extremely harsh thermal conditions. In principle, organic materials are not afraid of heat. Their structural changes at high temperatures are the key challenge. Once mitigated via molecular rigidification, polymers hold promising potential as they offer thin film processability, lightweight electronics, tunable molecular structures, as well as a wide scope of applications.

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