Facile and low-cost mechanical techniques for the fabrication of solution-processed polymer and perovskite thin film transistors

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Abstract
Low-temperature solution-processed polymer and perovskite thin film field effect transistors (FETs) are attractive, as they are compatible with flexible and printed electronics. Given that chemical treatment of the FET channel is expensive and tedious, and sometimes damages the underneath (dielectric) solution-processed layers, in this work, two facile and scalable mechanical treatment techniques are proposed. In the case of polymer FET, the wet spun film was excited by ultrasonic vibration imposed on the substrate. It is demonstrated that the micromixing effect induced by the ultrasonic radiation results in disentanglement, reorganization, and recrystallization of the polymer chains in the wet film. Ultrasonic vibration also improves the film leveling and uniformity and enhances the charge mobility of the channel of the polymer FET. In the case of the perovskite FET, we found that nitrogen blowing over the spun sample of the perovskite solution is a facile, yet effective substitution for the conventional anti-solvent treatment, commonly used to control the solvent evaporation rate. By nitrogen blowing, we achieved a uniform film of perovskite deposited on a solution-processed dielectric layer with domain sizes up to several hundreds of nanometers. By applying these techniques, the linear charge mobility of 0.041 cm²Vs⁻¹ and 0.055 cm²Vs⁻¹ were obtained for polymer and perovskite FETs under illumination, respectively. It is shown that while the performance of the polymer FET is only slightly sensitive to illumination, the perovskite FET performs well only under illumination.

1. Introduction

Organic light emitting diodes (OLED) and organic field effect transistors (OFET) have been already commercialized and used in TV and cellular phones. However, currently such devices are manufactured using thermal evaporation process. To reduce the cost and versatility of the products, it is desirable to manufacture such devices at low temperature and from solution, using printing and coating methods [1]. Thus, in this work, except for the electrodes, all-solution-processed polymer and perovskite FETs, in a bottom contact/bottom gate (BC/BG) configuration, are adopted, where the dielectric layer (poly(4-vinylphenol) (PVP)) separates the gate (indium-doped thin oxide (ITO)) from the source/drain (gold electrodes) and the semiconductor layer (polymer or perovskite). Poly(3-hexylthiophene) (P3HT) and methylammonium lead iodide (CH₃NH₃PbI₃) perovskite are employed as the solution-processed semiconducting channels. P3HT has been used extensively in organic photovoltaics (OPV) [2] and OFETs [1, 3–8]. Perovskites, which have been extensively used in perovskite solar cells [9, 10], have been recently employed in the area of thin film FETs to develop high performance devices. Morphology and nanostructure of the semiconductor channel in a thin film FET has an important role on its performance [1]. Currently, various chemical and thermal post treatment methods are used for this purpose, e.g. [11–13]. These methods are successful to some extent, but are sometimes tedious, energy-intensive, or environmentally disfavored and overall are not in line with high volume printing of such
devices. Therefore, in this work, to enhance the quality of the solution-processed polymer and perovskite channels, two room-temperature mechanical treatments are proposed and employed which are potentially capable of being extended to large scale production of flexible and printed FETs by scalable coating and printing methods.

In the case of the polymer FET, we show that imposing ultrasonic vibration on the substrate and the wet spun polymer film improves the device performance, because it enhances the polymer crystallinity and charge mobility (charge velocity per unit electric field), and reduces the film roughness. Application of acoustic (sound or ultrasound) vibration in transistor fabrication has been reported in the literature [14–18], Diemer et al [14] used a low frequency loudspeaker (100 Hz) to transmit acoustic waves to the sample via air so as to improve the crystallinity and increase the mobility. From a fundamental point of view, the application of acoustic vibration on wet films or liquid films results in creation of microstreaming and micromixing within the film [19], due to the destabilizing effect of the imposed vibration [20], increased evaporation rate and in situ heat treatment [21], and increased alignment of the polymer chains and improved uniformity and leveling of the film [22]. Using a different approach, Aiyar et al [15], through applying a low intensity ultrasound on the bulk solution of a high molecular weight (MW) P3HT solution, managed to prepare ordered supramolecular regioregular P3HT solutions, which resulted in increased crystallinity and mobility in the ensuing spun thin solid films. Using another approach but similar concept, Kondo et al [18] prepared and accommodated wet drop-cast P3HT FETs in a closed beaker and placed the beaker in an ultrasonic bath filled with water, where the ultrasonication for 30 min resulted in ordering of the polymer molecules. In the present work, the concept developed for the fabrication of polymer FETs is similar to the aforementioned works [14–18], but the approach is faster, facile and in line with commercialization purposes. In addition, we reexamined the method used in [15–17] and obtained similar promising results, but we also noticed that the ultrasonicated solution returns to its original state within a short time, whilst direct imposing of the ultrasonic vibration on the wet film of P3HT (method of this work) shortens the time of vibration, and with less effort shows the same effect as that of the ultrasonication of the solution.

Polymer semiconductors, discussed above, are only partially crystalline. In contrast, perovskite semiconductors are highly crystalline, although their film is polycrystalline. While we have exploited ultrasonic excitation of wet perovskite films deposited atop porous substrates with impressive results in perovskite solar cells [23], we found that to prepare small channels, ultrasonic vibration does not work effectively, and therefore, an alternative strategy was adopted to be elaborated on in the following. A high performance perovskite FET should have a fully-covered perovskite channel with low density of grain boundaries (large grains) and effective contacts between the grains, to minimize trap sites and to enhance the charge carrier mobility and lifetime [11, 24]. The aforementioned characteristics of a perovskite film is directly affected by the deposition method [25]. Application of spin coating commonly results in a dewetted film with poor coverage. The as-spun FET device, fabricated using such method, exhibited leakage-dominant characteristics with poor performance [11]. In order to control the solvent evaporation rate and crystal growth, and achieve a smooth, high performance and dense perovskite film, several treatments have been employed, such as anti-solvent dripping during the single-step deposition [26, 27] and gas blowing over PbI2 or optimization of precursors concentration in the sequential approach [25, 28, 29]. Although the reported techniques have shown satisfactory outcome [25, 26, 28, 30], all of them were performed on perovskites deposited on SiO2 dielectric substrates, which is an inorganic material. We observed that employing these techniques to fabricate perovskite atop organic PVP:HDA dielectric substrates results in unsatisfactory device performances. In this paper, and in an attempt to develop fully solution-processed FETs, PVP is used, which is dissolved in polar solvents. Therefore, to fabricate a fully-covered and smooth thin film of CH3NH3PbI3 in a single step, we optimized the process with the help of nitrogen blowing over the mixed perovskite film during spin coating. This method was found to be capable of yielding a functional perovskite film.

It is noted that although high charge mobility has been reported via using different perovskites (e.g. triple cation perovskite) [27] or systematic control of grain size and contact interface engineering [11], in the case of single halide CH3NH3PbI3 perovskite, the fabricated devices show low performance at room temperature [31], due to the migration of cations within the perovskite crystal, which induces a partial screen of the applied gate field, decreasing the mobility [26]. Thus, to investigate this effect, we tested the perovskite and polymer devices under illumination, as well as in dark. We will show that while the performance of the polymer FET is only slightly sensitive to illumination, the perovskite FET performs well only under illumination.
2. Experimental

2.1. Materials

Lead iodide (PbI₂, 98.5%), dimethyl sulfoxide (DMSO, 99.5%), γ-butyrolactone (GBL), and poly(4-vinylphenol) (PVP, MW = 11 000 g mol⁻¹) were purchased from Sigma-Aldrich. Methylvanionium iodide (MAI, 99.5%) and poly(3-hexylthiophene) (P3HT) were supplied from Xi’an Polymer Light Technology Co, China. Propylene glycol monomethyl ether acetate (PGMEA), triethylamine (TEA) and 1, 2-dichlorobenzene were purchased from Macklin, and 4, 4-(hexafluoroisopropylidene) diphthalic anhydride (HDA) was purchased from Aladdin, China.

2.2. Device fabrication

The polymer and perovskite FETs were fabricated based on the following procedure: Indium tin oxide (ITO)-coated glass substrates (1.5 cm × 2.5 cm or 1 cm × 1 cm) with average roughness of about 1 nm were cleaned by ultrasonication in solution of deionized water and soap, acetone and then isopropyl alcohol, sequentially. Then the substrates were treated with UV/Ozone irradiation for 15 min, to remove the moisture and increase the surface energy and wettability of the substrates. To prepare the dielectric layer, 150 mg of PVP mixed with a small amount of HDA cross-linker (10:1 wt. ratio, respectively) was dissolved in 1 ml of PGMEA, and the solution was filtered with a 0.2 μm filter and then spun onto ITO-coated glass patterned substrates at 1500 rpm, for 30 s. Then the films were cured at 100 °C, for 3 h in a glovebox, in order to initiate crosslinking. Dried films had an average thickness of 500 nm with average roughness of 10 ± 3 nm. Then the gold electrodes were thermally evaporated on the dielectric films through a shadow mask with a channel width (W) of 2000 μm and length (L) of 110 μm. The solution of P3HT was prepared through dissolving P3HT (MW of 10 000 to10 0000 g mol⁻¹) in 1, 2-dichlorobenzene (10 mg ml⁻¹), which was stirred for 3 h at 50 °C, and then filtered with a 0.2 μm filter. The solution was spun at 1000 rpm, for 12 s. Some of the wet films were immediately subjected to vertical ultrasonic vibration for 2 min, by placing the substrates on an ultrasonic transducer, mounted inside of the top surface of a steel box. The transducer was operated by a signal generator at 50 W and 40 kHz (Yuhuan Clangsonic Ultrasonic Co., Ltd, Yuhuan County, Zhejiang, China). At this power and frequency, the amplitude of vibration is about 60 nm [19]. After the formation of a wet film (with or without imposed ultrasonic vibration), the films were immediately annealed at 130 °C, for 20 min. The average film thickness was 70 nm. In another series of experiments, and in order to evaluate the method of sonication of the solution and compare the results with those of our ultrasonic SVPT method, the P3HT solution was ultrasonicated in a glass vial for 2 min, in an ultrasonic bath, and then the solution was returned to the glovebox for spin coating.

In the case of the perovskite FET, CH₃NH₃PbI₃ solution was prepared by dissolving CH₃NH₃I and PbI₂ powders in GBL and DMSO solvents, with volume ratio of 7:3, respectively, to obtain a solution with a mass concentration of 20%. The solution was preheated to 60 °C and stirred overnight. Perovskite films were spun at 4000 rpm, for 20 s in a glovebox, where nitrogen was blown over the wet film by a spray nozzle for 7 s starting from the third second of the spin coating process. The nozzle was installed 10 cm above the sample with the air pressure of 1 bar. The spun films were immediately annealed on a hotplate at 100 °C, for 10 min. The nitrogen-treated spun films had an average thickness of 160 nm.

2.3. Characterization

The surface topography of the perovskite films was examined by scanning electron microscopy (SEM, Hitachi, Model S-3400N, Tokyo, Japan). The profile roughness (Ra: arithmetic average of peaks to valleys) of P3HT films and their phase images were obtained by atomic force microscopy (AFM, Bruker, Model FastScan Bio, Japan). UV–vis absorption spectrophotometry (UV/Vis spectrometer, PerkinElmer Inc., Lambda35, Model LS 50B, USA) was used to measure the absorption spectra. Thicknesses of the dielectric and channel films were determined by a stylus profiler (KLA-Tencor P7, Milpitas, CA, USA). The crystal structures of the films were characterized by x-ray diffraction (XRD, Ultima IV, H-12, KYOWAGLAS-XA, Japan). All electrical characteristics of the devices and also the leakage current of the PVP film were taken under ambient conditions, using a Keysight source meter (Model B2902A, Japan). Although the perovskite FETs have an ambipolar behavior, here to have an unbiased comparison with the P3HT FETs, all measurements were performed in the p-type mode. The capacitance of the FETs were measured using an LCR meter (Jinko Model JK2817U, China) operated at 150 kHz, by sandwiching the PVP layer between ITO and Au electrodes (area = 0.015 cm²). The dielectric constant was obtained from capacitance data in the range of 100 Hz to 150 kHz. Conductivity of the P3HT films was measured by the van der Pauw method (Hall, van der Pauw controller, Model H-50, MMR Technologies Inc., USA).
3. Results and discussions

Figures 1(a) and (b) show the architecture and layout of the bottom-contact/bottom-gate geometry in this work based on ITO (gate)/PVP:HDA (dielectric)/polymer or perovskite (conducting channel)/gold drain and source. PVP was cross-linked with HDA \[32, 33\] for improving its performance. The cross-liked PVP leakage current and dielectric constant are shown in figures 1(c) and (d). The low current density below $3.5 \times 10^{-7}$ A cm$^{-2}$ at 40 V for a 500 nm film shows that the dielectric film can withstand biases up to 40 V without breakdown. The relative dielectric constant of the PVP layer was estimated by measuring the capacitance ($C_i$), thickness ($d = 500$ nm) and area of the capacitor ($A = 1.5$ mm$^2$). The relative dielectric constant at 150 kHz was estimated to be 3.5 (dielectric constant is equal to $C_i \varepsilon_0 A$, where $\varepsilon_0 = 8.854 \times 10^{-12}$ F m$^{-1}$). Figure 1(c) shows the dielectric constant versus frequency and also the cross-sectional image of the PVP layer on ITO substrate, where it is observed that the PVP layer is uniform and fully-covered.

3.1. Polymer FET

It has been reported that P3HT films with higher crystallinity have higher mobility, when used in FETs \[1\], and ultrasonication of the precursor solution can promote the charge transfer in the ensuing thin films \[16\]. To fabricate highly crystalline films, normally methods that apply low shear stress on the solution, such as drop casting or low-speed spin coating using solvents with high boiling points, have been suggested \[1\]. Therefore, here we used 1,2-dichlorobenzene solvent with the high boiling point of 174 $^\circ$C, at a low spinning speed of 1000 rpm. After spin coating, one sample was subjected to substrate vibration post treatment (SVPT) (vibrated sample). Figure 2 illustrates the schematic of preparation procedure of the P3HT films: pristine films, the films subjected to the SVPT and the films prepared by ultrasonication of the precursor solution.

Figure 3(a) shows the XRD patterns of four P3HT samples fabricated based on the strategies depicted in figure 2. In an additional case, a sample was prepared using an ultrasonicated solution that was kept still for 30 min before spinning.

One of the most interesting features of P3HT is its configuration in creation of ordered $\pi$-stacks and side-chain lamella stacks in the thin film \[1\]. According to figure 3(a), for the vibrated sample as well as the sample fabricated by vibrated solution, crystalline diffraction peaks are observed at $2\theta = 5.3^\circ$, associated with the (100) plane. This is ascribed to the ordered lamellar packing of polymer chains along the crystallographic direction,
perpendicular to the polymer backbone \[15, 16\]. The peak intensities have the same magnitude, which implies that the influence of imposing the ultrasonic vibration on the substrate of the wet film during drying has a similar effect as ultrasonication of the solution prior to casting. Absence of the (100) peak in the pristine sample reveals that this sample is amorphous. This peak is absent also in the sample that was produced from the ultrasonicated solution that was kept still for a prolonged time of 30 min, which indicates that ultrasonication of the solution has a temporary effect, and after a short time, the polymer solution returns to its initial condition, i.e. the polymer chain entanglement is reestablished over time.

Figure 3(b) shows the Ra roughness data of each sample, where the error bars denote the standard deviation of three measurements performed on different spots of the same sample. Samples prepared by vibration of the wet film and ultrasonication of the solution yield a film with lower roughness in comparison with the pristine film. It has been argued that polymer chains are gradually disentangled by ultrasonication of solution \[17\]. Here, the roughness of the vibrated sample is somewhat close to that of the ‘vibrated solution’ sample, suggesting that the SVPT of the wet film also results in gradual disentangling of the polymer chains, and the formation of a smoother film, compared to the pristine film. Conductivity of the films is shown in figure 3(c). The error bars are the standard deviation of the data obtained from three samples in each case. Noticeably, application of ultrasonic vibration on both the wet spun film and the solution of P3HT results in comparable enhancement of the film conductivity, simply because of enhanced crystallinity, as a result of ultrasonic vibration, which in turn causes an increase in the charge mobility \[1, 15–17\].

Figures 4(a) to (c) show the AFM phase images of three spun P3HT films: pristine or no vibration, vibrated sample, and vibrated solution. Ordered structures in the form of nanowires are observed in the films treated with
Where \( C_i \) is the capacitance per unit area of the gate insulator (500 nm thickness), \( L \) and \( W \) are the channel length and width, respectively, and \( V_{TH} \) is the threshold voltage. \( C_i \) was measured to be 9.35 nF/cm² (at 150 kHz), and \( V_{TH} \) derived from the transfer graph, is equal to −7 V. According to equation (1), \( \mu_{lin} \) is 0.016 cm²/Vs⁻¹ for the pristine sample, which rises to 0.038 cm²/Vs⁻¹ for the vibrated sample. In the case of the vibrated sample, increasing the gate voltage \( V_{GS} \) from 0 to −40 V (at \( V_{DS} = -40 \) V) resulted in an increase in the drain current \( (I_{DS}) \) from 2.58 nA to 4.7 µA (figure 5(a)). In other words, the on to off current ratio \( (I_{ON}/I_{OFF}) \) is equal to vibration (figures 4(b), (c)), which are absent in the no-vibrated sample (figure 4(a)). The appearance of ordered and aligned structures are in agreement with the XRD patterns in figure 3(a). Therefore, a higher crystalline P3HT thin film corresponds also to well-formed and well-aligned polymer chains distributed in the film [15], which stems from energy impartment to the film and micromixing, due to the ultrasonic vibration of the substrate or solution (acoustic radiation).

To further substantiate the positive effect of vibrational excitation, the three aforementioned strategies were repeated on drop-cast films as a low-shearing and slow process (figures 4(d) to (f)). In slow casting methods, due to slower drying process, the polymer has more time to self-align itself into an edge-on orientation. The ordered structures are clearer in AFM images of drop-cast samples with the vibrated substrate (figure 4(e)), and ultrasonicated solution (figure 4(f)). Again in the absence of vibration, no significant structural order is observed (figure 4(d)). Although drop-cast films show better ordered structures and it was reported that drop-cast FETs have better mobility than spin-coated samples [28], we found that drop-cast films tend to form non-uniform films compared to spin-coated films, and therefore, were not used toward device fabrication.

In the previous sections, it was substantiated that the crystallinity, conductivity and uniformity of the films prepared by ultrasonic vibration of the substrate or the solution are higher than those of the pristine film. In the next step, using the proposed technique (SVPT), FETs were fabricated. According to the principles of OFETs, applying a negative voltage to the gate with respect to the source \( V_{GS} \) leads to the accumulation of positive charges in the channel, adjacent to the dielectric layer. Raising the \( V_{GS} \) to the threshold level \( V_{TH} \) fills the existing trapping sites, due to impurities in the semiconductor (unintentional doping [34]). Then, further increasing of \( V_{GS} \) causes higher charge accumulation in the channel, resulting in charge injection from the source to the drain and establishment of a current \( (I_{DS}) \) in the channel. In this work, within the range of the voltages applied, the IV curves were not saturated, therefore, the field effect mobility \( (\mu_{lin}) \) is calculated in the linear region (at \( V_{DS} = -4 \) V) from the plot of the \( I_{DS} \) versus \( V_{GS} \) (figure 5(a)) by fitting the data in the following equation [16]:

\[
I_{DS} = \mu_{lin} W C_i \frac{(V_{GS} - V_{TH}) V_{DS}}{L}
\]

Figure 4. Tapping mode AFM phase images of P3HT films obtained by spin-coating (top) and drop casting (bottom) panels, in the case of no vibration (a), (d), vibrated substrate (b), (e), and ultrasonicated solution (c), (f).
For the pristine device, the $I_{\text{ON/OFF}}$ is $9.20 \times 10^2$, which is half of the $I_{\text{ON/OFF}}$ of the vibrated sample. Figure 5(b) also shows the output characteristics of the FETs at $V_{\text{GS}} = -40$ V with and without applying ultrasonic vibration.

### 3.2. Perovskite FET

In the case of the perovskite FET, we found that fabrication of the perovskite channel using nitrogen blowing over the wet perovskite film during spin coating is an effective mechanical treatment method (figure 6).

Fabrication of a perovskite film without using any treatments leads to the formation of a defective film (figure 7(a)). On the other hand, the film treated with nitrogen blowing, shown in figure 7(b), is fully-covered with large grains and low roughness of 18 ± 5 nm (measured by profilometry of three different lines on the sample). The corresponding XRD spectra of this film deposited atop a PVP layer is depicted in figure 7(c). The (110) and (220) diffraction planes, corresponding to 14.2° and 28.5° XRD peaks, respectively, reveal a standard and acceptable perovskite film [9, 10]. The positive effect of nitrogen blowing is interpreted as follows: nitrogen
blowing over the wet perovskite film during the spin coating process increases the evaporation rate, expedites supersaturation and nucleation rate. This results in a controlled and accelerated crystallization with fully-covered film with low roughness, without any need for performing expensive and tedious chemical treatments.

Literature results on the performance of perovskite FETs are controversial and inconclusive. While in some studies, e.g. [24, 25], high mobility higher than 1 cm² V⁻¹ s⁻¹ has been reported, in some other studies the mobility was found to be weak, when the device was tested at room temperature [26, 28], no field-induced transport was observed [11], or the source-drain current was low and the output characteristics were independent of the gate voltage [24]. Table 1 summarizes the electronic characteristics of some perovskite FETs obtained from recent works. These data show the dependence of the mobility and device performance on processing and operating conditions, such as the working temperature [11, 26], materials or fabrication method [11, 24, 27, 28], and operation with or without illumination [28].

In this study, the CH₃NH₃PbI₃ perovskite FETs showed weak performance when tested in dark and at room temperature (figure 8(a)). The obtained |I_DS| is smaller than 2 nA in different gate voltages (0 to −40 V), which is an indicative of a weak field effect in the channel. Because of the low performance of the CH₃NH₃PbI₃ FETs at room temperature and in dark, most of the recent studies have used perovskite FETs as phototransistors (photodetectors) [28, 30] or in hybrid structures [29, 35]. As shown in figure 8(b), compared to the dark condition, the transistor performance under standard one sun illumination is boosted, and |I_DS| reaches 8.73 μA at V_DS = V_GS = −40 V (near four orders of magnitude increase), while other conditions are kept the same. According to the transfer characteristic graph in figure 8(c), when V_DS = −40 V and V_GS changes from 0 V to −40 V, |I_DS| increases from 1.9 nA to 8.73 μA (|I_ON/OFF| = 4.61 × 10³). This value is significantly higher than the |I_ON/OFF| in dark condition (6.88). Using equation (1), the field effect photo-induced carrier mobility for the perovskite FET in the linear regime (at V_DS = −4V) is equal to 0.055 cm² V⁻¹ s⁻¹.

The electrical parameters extracted from I_DS–V_GS graphs of polymer and perovskite FETs (p-type) are summarized in table 2. Similar to the perovskite FETs, we have also listed the parameters of polymer FETs under illumination and in dark. Table 2 shows that the pristine perovskite FET tested in dark has no detectable output, but nitrogen blowing treatment improves the performance. Furthermore, illumination leads to a significant increase in the |I_ON/OFF| ratio and field effect mobility of the nitrogen treated perovskite FETs. In the case of polymer FETs, the proposed method of the ultrasonic vibration treatment brings about a very significant increase in the linear mobility and the |I_ON/OFF| ratio. To evaluate the numbers of table 2 and compare them to

### Table 1. Performance parameters, in dark or under illumination, obtained from p-type graphs of perovskite FETs in some recent works. RT denotes room temperature. The data associated with FETs of this work are listed in table 2.

| References | Channel | Temperature | |I_ON/OFF| (μA) | μ(cm⁻² V⁻¹ s⁻¹) | Fabrication method |
|------------|---------|-------------|-------------|-------------|------------------|------------------|
| [26]       | CH₃NH₃PbI₃ (dark) | 198 K | | | 0.01 < μ < 0.1 | Spin coating + anti-solvent |
| [11]       | CH₃NH₃PbI₃ (dark) | 270 K | | | 0.01 < μ < 0.1 | Spin coating |
| [28]       | CH₃NH₃PbI₃ (illumination) | RT | 3.32 × 10⁴ | 0.18 | Spin coating |
|            | CH₃NH₃PbI₃,Cl (illumination) | RT | 4.38 × 10⁵ | 1.24 | Spin coating |
| [24]       | CH₃NH₃PbI₃,Cl (dark) | RT | 10² | 1.3 | Spin coating |
| [27]       | Csₓ(MAₓFₓ,Aₓ)−ₓPb(Brₓ,3Iₓ)₃ (dark) | RT | 10⁴ | 2 | Spin coating + anti-solvent |

Figure 8. Electronic characteristics of the perovskite FET fabricated by spin coating plus nitrogen blowing: (a) output characteristics at various V_GS in dark, (b) output characteristics at various V_GS under illumination, and (c) |I_ON| and |I_DS| |I_ON/OFF| versus V_GS at V_DS of −40 V under illumination.
due to increasing the charge carrier scattering the perovskite layer is not the only factor that affects the charge transfer in the channel. Charge trap sites in the longer diffusion length dielectric layer underneath the perovskite or polymer channel.

Those of the literature listed in table 1, one should note that in this work, both the dielectric and conducting channels are solution-processed/printable and the employed treatment methods are facile, mechanical, and compatible with the components of the device. Chemical treatment would deteriorate the solution-processed dielectric layer underneath the perovskite or polymer channel.

Although by nitrogen blowing we prepared a smooth perovskite film, it has been reported that the quality of the perovskite layer is not the only factor that affects the charge transfer in the channel. Charge trap sites in perovskite grain boundaries and a rough dielectric under-layer may deteriorate the conductivity of the channel, due to increasing the charge carrier scattering [24]. But these are not the main reasons for low performance of the perovskite FET at room temperature and in dark condition with respect to the P3HT FET. Although, carriers in methylammonium lead iodide perovskite have a long lifespan [35] and charge carriers in perovskite have a longer diffusion length (100 nm) [10], compared to that of P3HT (9 nm) [36], perovskite FETs have shown high performance only at low temperatures, e.g. 200 K [26], 220 K [31] and 250 K [11]. This may be explained as follows.

Generally, in a crystalline semiconductor, charge carrier transport is due to band-transport, and phonon scattering results in an inverse relationship between mobility and temperature [37]. In contrast, in a molecular semiconductor, like a polymer, the hopping mechanism is dominant and it increases with temperature [38]. It has been reported that in methylammonium perovskites, fabricated in a one-step method, the band-transport mechanism is dominant and mobility decreases with temperature, although the possibility of hopping mechanism in perovskite semiconductors cannot be ruled out, because the perovskite film is not a perfect crystalline semiconductor [39]. This argument is consistent with our results and those of the literature showing that, in dark, the perovskite FETs only work well at low temperatures, whereas the polymer FET performs normally at room temperature. Specific to polycrystalline perovskite film, diffusion of ions and charged point defects have been argued to be responsible for low perovskite FET performance at high temperatures [11, 31]. Chin et al [26] reported that methylammonium cations are temperature-activated and their migration within the methylammonium lead iodide perovskite crystal induces a partial screen of the applied gate field, which results in a significant reduction in the mobility at temperatures higher than 198 K. In other words, in high temperatures, due to the low activation energies for perovskite ions (mostly iodide ion), the probability of their diffusion increases. Therefore, after applying a gate voltage (here negative), ions (here positive) and charged point defects move toward the interface and reduce the concentration of the accumulated positive charges in the channel, which partially screen the gate voltage [11].

Under the illumination condition, the performance of the perovskite channel is different from that of the dark condition. Figure 9(a) shows the absorbance spectra of the perovskite and P3HT polymer films subjected to the SVPT. It is evident that the perovskite film has a much higher absorbance in a broad range (~400 nm to ~780 nm). In the case of the P3HT polymer film, a weaker absorption is observed in a shorter range of wavelengths (~400 nm to ~650 nm). The optical bandgap in these two cases were extracted from the absorbance graphs (figure 9(b)), based on the Tauc plot method [40]. According to figure 9(b), the intersection points of the tangent lines on the curves and horizontal axis shows the band gap of the perovskite (~1.6 eV) and P3HT (~1.95 eV). Thus, compared to the P3HT polymer, methylammonium lead halide perovskite has a higher potential to generate photo-induced charge carries, due to its large absorption in a wide range and its direct and shorter band gap around 1.6 eV. Therefore, the photo-generated carriers dominate the carrier transport in the channel leading to an increase in the current. The corresponding current can be defined by

\[ I_{ph} = I_{illuminated} - I_{dark} \]

where \( I_{illuminated} \) refers to the field effect current after light exposure and \( I_{dark} \) is the dark field effect current [35]. According to our measurements, \( I_{ph} \) for the perovskite FET after treatment is 8.73 \( \mu \)A (\( I_{illuminated} - I_{dark} = 8.73 \mu \text{A} \) – 0.84 nA). In the case of the vibration treated P3HT FET, \( I_{ph} \) is 0.4 \( \mu \)A (=5.1 \( \mu \)A – 4.7 \( \mu \)A). Low density of photo-induced carriers in P3HT stems from its higher band gap (~1.95 eV) (figure 9(b)), and its lower absorption with respect to the perovskite film (figure 9(a)). This leads to a low variation in the mobility of P3HT and insensitivity of the P3HT FET against illumination.

| Table 2. Parameters obtained from p-type graphs of solution-processed FETs in this work, treated with mechanical methods only. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Active layer** | **\( I_{ON}/I_{OFF} \)** | **\( \mu_{in} \)(cm\(^2\) V\(^{-1}\) S\(^{-1}\))** | **Fabrication method** | **Test condition** |
| CH\(_3\)NH\(_2\)PbI\(_3\) | \( 4.61 \times 10^3 \) | 0.055 | Spin coating + nitrogen blowing treatment | under illumination |
| | 6.88 | \( \sim 0 \) | Spin coating + nitrogen blowing treatment | In dark |
| | " | " | Spin coating | In dark |
| P3HT | \( 1.89 \times 10^3 \) | 0.041 | Spin coating + SVPT | under illumination |
| | \( 1.82 \times 10^2 \) | 0.038 | Spin coating + SVPT | In dark |
| | \( 9.2 \times 10^2 \) | 0.016 | Spin coating | In dark |

* No measurable output.
Finally, it is noted that in this study, we focused on developing effective strategies to prepare polymer and perovskite channels used in solution-processed FETs. System or device optimization is also important and will be the subject of future works. In addition to having high quality components, a high performance and stable thin film device should possess good alignment of electronic energies at the interface as well as robust mechanical contacts (epitaxial matching) between all layers, to facilitate effective charge transport and reduce or eliminate carrier recombination sites, respectively [41]. Another important topic in emerging FETs is the stability of the solution-processed layers and the device hysteresis when subjected to a pulsed gate voltage over multiple cycles [11]. While the topic was not studied in this work, in [2] and [42] we have demonstrated that the application of the ultrasonic vibration on the active layers has a remarkable effect on the stability of the films used in polymer and perovskite solar cells, respectively.

4. Conclusions

Solution-processed/printable polymer (P3HT) and perovskite (CH$_3$NH$_3$PbI$_3$) FETs were fabricated on solution-processed PVP dielectric films, using two proposed mechanical treatments as low-cost and facile methods to enhance the quality of the channels in FETs. In the case of the P3HT film preparation, we enhanced the performance of the device by imposing ultrasonic vibration directly on the substrate of the wet spun P3HT film, which brought about structural order and crystallinity to the ensuing solid film, due to the micromixing and in situ heating effects of the ultrasonic vibration. XRD, UV–vis, AFM, and conductivity data revealed that the effect of the proposed method is similar to a reported method in which the ultrasonic vibration was applied on the solution of P3HT, prior to deposition. However, the proposed method in this work is in situ and reduces the processing time, substantially. Moreover in the literature reported method, the ultrasonicated solution returns to its initial condition (absence of crystallinity), if it remains still for several minutes, whereas this weakness is circumvented in our proposed technique. The results also showed that the performance of the polymer FET is insensitive to illumination.

In an attempt to eliminate the anti-solvent treatment, commonly used in the fabrication of perovskite semiconductors, the perovskite FET was fabricated by blowing nitrogen gas over the perovskite film during spin coating. This was performed due to the disruptive effect of conventional anti-solvent treatment of perovskite on the underneath solution-processed PVP layer. This proposed method as a simple mechanical treatment of mixed perovskite wet films, resulted in a fully-covered and smooth film with large crystal sizes. It is found that in room temperature, the perovskite FET works best under illumination, whereas the polymer FET works in dark, as well.

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