Self-Encapsulation of Organic Thin Film Transistors by means of ion implantation

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ABSTRACT

Long-term stability of devices based on organic materials is still impeding the diffusion of these structures in real applications. In this paper we have investigated the effects of low energy, combined, ion implantation (N and Ne) in the evolution of the electrical performances of pentacene-based Organic Thin Film Transistors (OTFTs) over time by means of current–voltage and photocurrent spectroscopy analyses. We have demonstrated that the selected combination of ions allows reducing the degradation of charge carriers mobility, and also stabilization of the devices threshold voltage over a long time (over 2000 h).

INTRODUCTION

One of the main open issues in the field of organic electronics is that, generally, the performances of organic semiconductors are severely affected by the exposure to ambient atmosphere [1-6]. In fact, it is well known that oxygen and moisture can interact with the organic semiconductor leading to its local doping or to the oxidation of the organic molecules and thus to a strong degradation of the charge transport properties of the active layer [7-11]. In particular, in the field of Organic Thin Film Transistors (OTFTs), the interaction of the organic active layer with oxygen and moisture is generally correlated with a pronounced increase of the threshold voltage of the devices and by a marked decrease of the carrier mobility. It is well known that the stability of organic semiconductors exposed to ambient oxygen and moisture is related to the distance of the Lowest Unoccupied Molecular Orbital (LUMO) of the semiconductor from the vacuum level [12, 13]. However, despite the continuous progress in the synthesis of new, high performing, organic semiconducting compounds, the stability of these molecules in ambient conditions is still a big issue.

A possible, alternative, approach consists in the employment of efficient encapsulating layers for protecting the active film from contamination and degradation. In this sense, several solutions have been proposed such as, the employment of hybrid multilayer barriers [14, 15]. However, the majority of proposed approaches have been reported only on devices fabricated on rigid substrates, and would not be suitable for the fabrication of flexible electronics. [16-23].

Recently, we have demonstrated on pentacene-based OTFTs, with a nominal pentacene thickness of 300 nm, that by locally changing the chemical/electrical properties of the organic semiconductor film by means of a selective ion implantation process, it is possible to dramatically reduce the mobility degradation and threshold voltage shift due to the exposure to ambient atmosphere [24]. The devices were implanted with two different kinds of ions, nitrogen or neon, and the implantation was made tuning the ion energy and dose in order to create a local damage only in the upper 250 nm of the pentacene film, so that, under this damaged layer, a pristine semiconductor layer (approx. 50 nm thick) is still preserved and acts as the active channel of the device. We found that the interaction of these two species with pentacene leads to a clear stabilization over time of the most meaningful electrical parameters, such as threshold voltage and carrier mobility. We demonstrated, in both cases, that the implantation induces a local permanent modification of the chemical and physical properties of the pentacene film: in fact, loss of hydrogen and carbonification effects have been observed in the top portion of the implanted layers, by means of Elastic Recoil Detection (ERD) and Fourier Transform Infrared (FTIR) analyses. However, when neon ions are implanted, a clear stabilization of the carrier mobility over time was noticed, whereas, when nitrogen ions were implanted, a dramatic reduction of the threshold voltage shift was observed. Moreover, nitrogen ions react with the organic hydrocarbon matrix inducing not only lattice damage (as happens for neon) but also the

formation of stable, positively charged, groups (not present in pristine pentacene nor in neon implanted films) which, inducing a permanent electrical field, leads to a pinning of the OTFT threshold voltage.

In the present work, we demonstrate that both effects, observed in the previous investigations, may be obtained at the same time, on the same device, in a controlled way, by performing a sequential ion implantation of these two different ions (Ne and N). To this aim, we have investigated the evolution over time of charge carrier mobility and threshold voltage in co-implanted pentacene-based OTFTs, realized with different implantation parameters. The potential of ion implantation as a novel method for effective self-encapsulation of organic devices has thus been assessed, offering a perspective for the elimination of additional barrier/coating layers.

All OTFTs have been fabricated on a heavily doped silicon substrate using a bottom gate, bottom contact configuration (Figure 1a). The highly doped silicon substrate acts as the bottom gate electrode, on which a 500 nm thick silicon dioxide film was thermally grown. Gold source and drain electrodes have been fabricated using a standard photolithographic process, with a channel width of 5 mm and a channel length of 50 μm . Finally, a 300 nm thick pentacene film was deposited by thermal evaporation.

All the electrical characterizations were carried out at room temperature in air and in dark with an Agilent HP 4155 Semiconductor Parameter Analyzer. For all devices, both mobility and threshold voltage were determined from the transfer characteristics in the saturation regime. After implantation all the devices have been stored in dark in ambient atmosphere, with a temperature ranging around 22-25°C and humidity around 60%.

Ion implantation was performed on a Varian CF-3000 ion implanter at Ion Beam Materials Laboratory in Los Alamos National Laboratory. The implantation was performed at room temperature with two different ion species (N and Ne) with various fluences. The beam flux was kept at a fixed value so that the flux effect is not a concern. Monte Carlo SRIM code was used to estimate ion beam parameters producing the required damage thickness and ion profile in the pentacene layer. The maximum ion energy was chosen so as not to completely damage the pentacene layer.

The thickness of the implanted samples has been measured by XRD analyses and with an Atomic Force Microscope and no significant modification has been observed after co-implantation.

Three different co-implantation combinations, labelled I, II and III (see Table I) have been carried out on several batches of samples to induce a controlled and different ion penetration and damage-depth distribution within the pentacene layer (Figure 1b, 1c, 1d, 1e). Considering the preliminary results obtained with single implantation [24], energy and fluence were varied in order to assess their role in the stabilization of the OTFT mobility and threshold voltage. In particular:

a) Combinations I and II are exactly the same, with opposite order of the implantation sequence. The goal is to understand if the order plays a role, i.e. if the co-implantation is simply a superposition of the effects of each single ion implantation. Energies and fluences were chosen so as to preserve the integrity of the active channel.

b) Combination III is, for both ions, at a significantly lower energy and higher fluence. The goal is to assess the relative effect of these two parameters.

It is well known [25] that the ion penetration range is larger than the damage depth profile. We have carried out Montecarlo SRIM simulations for our implant parameters to evaluate both. The results are shown in figures 1b, 1c for combination I and II (identical implantation parameters, only different sequence) and 1d, 1e for combination III. It can be noticed that the ion penetration depth and the damage profile reach much deeper into the pentacene layer for combination I and II (up to 170 nm approximately), while for combination III both are located within the first 120 nm. The amplitude of the peaks is proportional to the fluence that is higher in combination III.

All devices have been electrically characterized in order to determine their initial electronic parameters, in particular, mobility and threshold voltage; after that, ion implantation has been performed on all samples, always keeping some reference samples untouched. To minimize the sample exposure to the environment, all the samples (reference and implanted) have been sealed under vacuum in the periods of time going from the first electrical characterization and the ion implantation, and between ion implantation and the second electrical characterization. Therefore, all the devices have been affected, during the time interval between fabrication and measurement, by the same environmental effects. In this way, the evolution over time of the most meaningful parameters was monitored, and directly compared with the reference samples. Interestingly, as can be observed from the plots reported in Fig. 2, the reference devices, which were not implanted, are characterized by a pronounced reduction of the output current. On the contrary, devices co-implanted with N/Ne ions, showed a much less evident current reduction. In order to investigate the reasons for such reduction, we have extracted the charge mobility and the threshold voltage as a function of the aging time (Figs. 3a and 3b) for the OTFTs implanted with the three tested co-implantation combinations. Interestingly, it can be clearly observed that the

reference samples are characterized by a much more pronounced degradation of these two parameters. In particular, as also reported in table I, carrier mobility is reduced to almost half of its original value just after 15 days since their first exposure to ambient atmosphere. On the contrary, the implanted samples showed a much smaller reduction of carrier mobility, which is generally around 30% for samples of type I and II and almost close to 0% for type III samples (see Fig. 3a). We ascribe this improvement in ambient stability to the carbonification of the top pentacene layer induced by ion implantation, which acts a self-encapsulation for the active channel. Moreover, a clear stabilization effect on the threshold voltage can also be observed. Considering the data reported in Table I, it can be noticed that sample types I and II show a V_t variation ranging from -8 to -9 V, whereas the reference samples are characterized by an average V_t shift around -15V. In view of what already demonstrated with single ion implantations [24], it is interesting to note that for type III implantation, the ion energy is not enough to induce a stabilization effect on the threshold voltage.

It is likely that the charged species induced by N implantation are localized too far away from the device channel to affect its V_t . Therefore, in order to reduce the V_t shift, it is necessary to use a larger implantation energy for N ions, such as in combinations I and II. We think that this is also the reason why combination I and II are characterized by a more pronounced reduction of the mobility. In fact, when the charged species are too close to the channel, they also may induce scattering of charge carriers, thus reducing the device mobility. Therefore, they may have a double effect: stabilization of V_t and degradation of the charge carrier mobility. However, it is clear from Figure 3, that the latter effect is much less pronounced than the ageing effect observed in the reference samples. Obviously, if the charged species are far from the device channel, they

do not induce scattering of carriers, and only the effect of carbonification induced self-encapsulation is observed, and mobility stay stable over time.

In any case, it is noteworthy that the employment of a consecutive implantation of the two different kinds of ions has overall dramatically reduced the active layer degradation, and this effect is visible in all implanted devices, compared with the reference ones, demonstrating that the approach proposed in this paper can be used as a valuable method for mitigating the degradation of OTFTs.

In order to achieve a better understanding of the microscopic modifications induced in the organic semiconducting thin film by the ion implantation processes, photocurrent (PC) spectroscopy measurements were also carried out. As we can see in Fig. 4, the PC spectra give quite interesting information on the electrical density of states (DOS) distribution after the co-implantation. Samples implanted with combination III show PC spectra quite similar to the PC spectrum of the reference OTFTs, with a 300 nm thick pentacene active layer. This suggests that indeed the damage induced by the co-implantation process not only preserves the functionality of the OTFT but also induces a modification of a very limited portion of the organic semiconductor. The co-implant sequence of samples III is in fact characterized by a shallower N implant depth with a higher fluence, meaning that a thinner portion of the pentacene film has been damaged by implantation, although the damage is much denser than in the other cases.

On the contrary, the PC spectra of samples implanted with the combinations I and II, are rather similar to the PC spectrum of a reference sample with a 50 nm thick pentacene layer. This indicates that, in this case, after the co-implantation, a significant modification of the top portion

of the pentacene layer has occurred, leaving only about 50 nm of unaffected active pentacene at the bottom interface with the dielectric [26].

The results obtained from the PC measurements are thus in full agreement with what observed in the electrical characterization of the OTFTs. In summary we can conclude that:

- a. The employment of a consecutive implantation of two different kinds of ions has an effect that is the sum of the effects produced by each single implantation (superposition effect).
- b. Co-implanting Ne and N ions in configurations I and II does not induce different effects, i.e. the order of the implanted ions is not relevant, as long as the doses and energies are kept identical (no permutation effect).
- c. Co-implanting with combination III induces quite different effects since the implant energy is lower for both ions (12.5keV for N and 25keV for Ne), but the fluence is higher ($1 \cdot 10^{+15}$ for N and $2 \cdot 10^{+14}$ for Ne). This has a beneficial effect on the mobility, that is almost perfectly preserved over time but is not effective in the reduction of the threshold voltage shift.

In a few words, in agreement with what we have previously observed, neon ions induce a pure damage to the pentacene film without activating any charged species while on the contrary, nitrogen ions induce the formation of stable charges, thus leading, if these charges are close enough to the active channel (which is the case of type I and II implantations), to a pinning of device threshold voltage. Moreover: the higher the energy, the stronger is the effect (i.e. the positive threshold voltage pinning for N, the portion of damaged layer for Ne), the higher the fluence, the larger the density of the induced damage. As a consequence, when co-implanting with combination III, the formation of stable charges within the implanted semiconductor is too

superficial to induce an effective shift of the threshold voltage but the surface density of the damage induced by Ne is such to ensure a very substantial sealing effect of the active layer, whose mobility is fully preserved over time.

In conclusion, a novel and simple approach for increasing the lifetime and stability of OTFTs has been introduced. The approach is based on the implantation of two different species of ions in the upper portion of the organic semiconductor layer. By properly tuning the implantation parameters, it is possible to avoid or reduce the interaction of the device active layer with oxygen and moisture, and this leads not only to a clear stabilization of the threshold voltage, but also to a pronounced reduction of the mobility degradation. Further work is still required to fully understand the observed phenomena and possibly extend this approach to other ionic species.

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Figures Captions:

Figure 1: Schematic representation of the Organic Thin Film Transistor and of the implantation procedure (a) and Monte Carlo SRIM of the ion profile and damage thickness in the pentacene film induced by the implantation of N and Ne ions using the configurations I or II (b and c), and III (d and e)

Figure 2: Output characteristics in one reference device (a) and in the sample implanted using configuration III (c) (before performing ion implantation) and their evolution over time (b) and (d)

Figure 3: Relative mobility variation over time in all the different sets of measured devices (a) and threshold voltage shift (b) over time in all the different sets of measured devices

Figure 4: Photocurrent spectra recorded in the samples different implanted using the three different configurations (I, II and III) and their comparison with two different reference samples, one with a 300 nm and the second with a 50 nm thick Pentacene layer.

Figure 1

Figure 2

Figure 3

Figure 4

Table Caption

Table I: Implanting parameters and variation of the most meaningful electrical parameters over time

Table I

Sample type	Ion	Beam Energy (KeV)	Fluence (ions/cm ²)	$\Delta\mu/\mu_0$ After 300 hours	ΔV_t (V) After 300 hours
REFERENCE	Not implanted	NA	NA	-0.5 ± 0.1	$-15,4 \pm 3,7$
I	N ⁺	25	5 E+14	-0.3 ± 0.1	$-7.9 \pm 0,9$
	Ne ⁺	35	1 E+14		
II	Ne ⁺	35	1 E+14	-0.26 ± 0.02	$-8,7 \pm 1,9$
	N ⁺	25	5 E+14		
III	N ⁺	12.5	1 E+15	0,03	-12,48
	Ne ⁺	25	2 E+14		

ABSTRACT

Long-term stability of devices based on organic materials is still impeding the diffusion of these structures in real applications. In this paper we have investigated the effects of low energy, combined, ion implantation (N and Ne) in the evolution of the electrical performances of pentacene-based Organic Thin Film Transistors (OTFTs) over time by means of current–voltage and photocurrent spectroscopy analyses. We have demonstrated that the selected combination of

ions allows reducing the degradation of charge carriers mobility, and also stabilization of the devices threshold voltage over a long time (over 2000 h).

INTRODUCTION

One of the main open issues in the field of organic electronics is that, generally, the performances of organic semiconductors are severely affected by the exposure to ambient atmosphere [1-6]. In fact, it is well known that oxygen and moisture can interact with the organic semiconductor leading to its local doping or to the oxidation of the organic molecules and thus to a strong degradation of the charge transport properties of the active layer [7-11]. In particular, in the field of Organic Thin Film Transistors (OTFTs), the interaction of the organic active layer with oxygen and moisture is generally correlated with a pronounced increase of the threshold voltage of the devices and by a marked decrease of the carrier mobility. It is well known that the stability of organic semiconductors exposed to ambient oxygen and moisture is related to the distance of the Lowest Unoccupied Molecular Orbital (LUMO) of the semiconductor from the vacuum level [12, 13]. However, despite the continuous progress in the synthesis of new, high performing, organic semiconducting compounds, the stability of these molecules in ambient conditions is still a big issue.

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Three different co-implantation combinations, labelled I, II and III (see Table I) have been carried out on several batches of samples to induce a controlled and different ion penetration and damage-depth distribution within the pentacene layer (Figure 1b, 1c, 1d, 1e). Considering the preliminary results obtained with single implantation [24], energy and fluence were varied in order to assess their role in the stabilization of the OTFT mobility and threshold voltage. In particular:

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generally around 30% for samples of type I and II and almost close to 0% for type III samples (see Fig. 3a). We ascribe this improvement in ambient stability to the carbonification of the top pentacene layer induced by ion implantation, which acts a self-encapsulation for the active channel. Moreover, a clear stabilization effect on the threshold voltage can also be observed. Considering the data reported in Table I, it can be noticed that sample types I and II show a V_t variation ranging from -8 to -9 V, whereas the reference samples are characterized by an average V_t shift around -15V. In view of what already demonstrated with single ion implantations [24], it is interesting to note that for type III implantation, the ion energy is not enough to induce a stabilization effect on the threshold voltage.

It is likely that the charged species induced by N implantation are localized too far away from the device channel to affect its V_t . Therefore, in order to reduce the V_t shift, it is necessary to use a larger implantation energy for N ions, such as in combinations I and II. We think that this is also the reason why combination I and II are characterized by a more pronounced reduction of the mobility. In fact, when the charged species are too close to the channel, they also may induce scattering of charge carriers, thus reducing the device mobility. Therefore, they may have a double effect: stabilization of V_t and degradation of the charge carrier mobility. However, it is clear from Figure 3, that the latter effect is much less pronounced than the ageing effect observed in the reference samples. Obviously, if the charged species are far from the device channel, they do not induce scattering of carriers, and only the effect of carbonification induced self-encapsulation is observed, and mobility stay stable over time.

In any case, it is noteworthy that the employment of a consecutive implantation of the two different kinds of ions has overall dramatically reduced the active layer degradation, and this effect is visible in all implanted devices, compared with the reference ones, demonstrating that

the approach proposed in this paper can be used as a valuable method for mitigating the degradation of OTFTs.

In order to achieve a better understanding of the microscopic modifications induced in the organic semiconducting thin film by the ion implantation processes, photocurrent (PC) spectroscopy measurements were also carried out. As we can see in Fig. 4, the PC spectra give quite interesting information on the electrical density of states (DOS) distribution after the co-implantation. Samples implanted with combination III show PC spectra quite similar to the PC spectrum of the reference OTFTs, with a 300 nm thick pentacene active layer. This suggests that indeed the damage induced by the co-implantation process not only preserves the functionality of the OTFT but also induces a modification of a very limited portion of the organic semiconductor. The co-implant sequence of samples III is in fact characterized by a shallower N implant depth with a higher fluence, meaning that a thinner portion of the pentacene film has been damaged by implantation, although the damage is much denser than in the other cases.

On the contrary, the PC spectra of samples implanted with the combinations I and II, are rather similar to the PC spectrum of a reference sample with a 50 nm thick pentacene layer. This indicates that, in this case, after the co-implantation, a significant modification of the top portion of the pentacene layer has occurred, leaving only about 50 nm of unaffected active pentacene at the bottom interface with the dielectric [26].

The results obtained from the PC measurements are thus in full agreement with what observed in the electrical characterization of the OTFTs. In summary we can conclude that:

- a. The employment of a consecutive implantation of two different kinds of ions has an effect that is the sum of the effects produced by each single implantation (superposition effect).

- b. Co-implanting Ne and N ions in configurations I and II does not induce different effects, i.e. the order of the implanted ions is not relevant, as long as the doses and energies are kept identical (no permutation effect).
- c. Co-implanting with combination III induces quite different effects since the implant energy is lower for both ions (12.5keV for N and 25keV for Ne), but the fluence is higher (1×10^{15} for N and 2×10^{14} for Ne). This has a beneficial effect on the mobility, that is almost perfectly preserved over time but is not effective in the reduction of the threshold voltage shift.

In a few words, in agreement with what we have previously observed, neon ions induce a pure damage to the pentacene film without activating any charged species while on the contrary, nitrogen ions induce the formation of stable charges, thus leading, if these charges are close enough to the active channel (which is the case of type I and II implantations), to a pinning of device threshold voltage. Moreover: the higher the energy, the stronger is the effect (i.e. the positive threshold voltage pinning for N, the portion of damaged layer for Ne), the higher the fluence, the larger the density of the induced damage. As a consequence, when co-implanting with combination III, the formation of stable charges within the implanted semiconductor is too superficial to induce an effective shift of the threshold voltage but the surface density of the damage induced by Ne is such to ensure a very substantial sealing effect of the active layer, whose mobility is fully preserved over time.

In conclusion, a novel and simple approach for increasing the lifetime and stability of OTFTs has been introduced. The approach is based on the implantation of two different species of ions in the upper portion of the organic semiconductor layer. By properly tuning the implantation parameters, it is possible to avoid or reduce the interaction of the device active layer with oxygen

and moisture, and this leads not only to a clear stabilization of the threshold voltage, but also to a pronounced reduction of the mobility degradation. Further work is still required to fully understand the observed phenomena and possibly extend this approach to other ionic species.

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Figures Captions:

Figure 1: Schematic representation of the Organic Thin Film Transistor and of the implantation procedure (a) and Monte Carlo SRIM of the ion profile and damage thickness in the pentacene film induced by the implantation of N and Ne ions using the configurations I or II (b and c), and III (d and e)

Figure 2: Output characteristics in one reference device (a) and in the sample implanted using configuration III (c) (before performing ion implantation) and their evolution over time (b) and (d)

Figure 3: Relative mobility variation over time in all the different sets of measured devices (a) and threshold voltage shift (b) over time in all the different sets of measured devices

Figure 4: Photocurrent spectra recorded in the samples different implanted using the three different configurations (I, II and III) and their comparison with two different reference samples, one with a 300 nm and the second with a 50 nm thick Pentacene layer.

Figure 1