

Photocurrent studies of stress and aging in pentacene thin film transistors

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In this work the authors report on photocurrent spectroscopy analyses on pentacene thin film transistors that have been bias stressed and exposed to atmosphere over a long period of time (up to 80 days). They have studied the charge transport properties and the electronic excited state energy and distribution of these organic thin film devices. They also have identified the major excitonic and band gap transition energies and have investigated their quite different behavior following exposure to atmosphere or to bias stress. Different charge carrier distributions and trapping phenomena are proposed to describe the observed effects. © 2006 American Institute of Physics.

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Organic thin film devices based on conjugated molecules are receiving quite a large attention due to their potential in optoelectronic, photovoltaic, and sensor applications.¹

The determination of the charge transport properties of the material and of the electronic excited state energy and distribution is still an open and controversial issue, even if it plays a crucial role in the applicability of the material under study. Since most of the applications of organic semiconductors rely on the conductive and photoconductive properties of the material, it is necessary to achieve a deeper understanding of the physical mechanism of charge carrier photo-generation, transport, trapping, and recombination. Pentacene is one of the materials that has been intensively studied over the last years thanks to its large field effect mobility and good environmental stability. Yet, despite the large number of reports, the energy, number, and nature of its excited electronic states, as well as the material energy gap, are still under discussion.²⁻⁵

In this work we report on the charge transport of pentacene thin film transistors (TFTs) that have been stressed either by repetitively biasing the device between $V = +100$ V and $V = -100$ V or by testing their electrical parameters at room temperature and in atmosphere over a long period of time (up to 80 days).

The mechanism of photocarrier generation is still an open question and no theoretical model has been appropriately developed to account for the whole process occurring in polycrystalline thin films.^{6,7} Most studies suggest that primary step of photocurrent generation in organic thin film devices is the creation of excitons even if recent reports indicate that free carriers can also be directly photoexcited.⁸⁻¹¹ The charge transport process is then controlled by the diffusion of excitons and by their trapping and dissociation at the grain boundaries and metal/organic interface. Since an organic active layer exposed to atmosphere or to bias stress can modify its structure and affect the electronic transport process, the focus of this work is to investigate to what extent such alterations influence the charge carrier trapping and transport mechanisms.

Two-terminal devices have been obtained by patterning on a thin film of polyethylene terephthalate (Mylar, Du Pont) gold contacts separated by a channel 30 μm long and 5 mm wide. Then a pentacene layer (average thickness 50 nm) was thermally evaporated through a shadow mask in order to cover the channel and, partially, the gold contacts. The gate layer was then formed on the opposite side of the Mylar film by thermal evaporation of either gold or aluminum. In this way, identical bottom contact organic thin film transistor (TFT) structures were formed. Aside each OFET structure, an identical two-terminal structure without any gate was fabricated (source and drain gold contacts covered by the pentacene layer with the same geometry of channel and contact coverage), in order to compare performances of three-terminal devices with those of two-terminal devices. The current-voltage characteristics of the fabricated devices were measured with a semiconductor parameter analyzer. The photocurrent spectroscopy analyses were carried out in air at room temperature by biasing the drain of the sample (with the source at ground) with a low bias (>7 V, leaving the gate unbiased) and by measuring the current through a load resistance of 200 k Ω . As a light source we used a 150 W Xe arc lamp and a quartz-tungsten-halogen lamp coupled to a Jarrel monochromator and mechanically chopped at low frequency (<20 Hz). The photocurrent was then measured as a function of wavelength (varied in the range $\lambda = 400\text{--}750$ nm) using a current amplifier connected to a digital lock-in amplifier (Stanford Research 850). The photon flux was measured with a calibrated Si photodiode to normalize the photocurrent (PC) spectra.

Figure 1 reports the photocurrent spectra obtained for pentacene TFTs that only differ in the presence or in the type of metal gate contact evaporated on the back of the polyethylene terephthalate thin film that acts both as the dielectric and the device support layer. Several peaks can be identified and the main ones are located at 1.86, 1.98, and 2.13 eV. Absorption spectra reported in the literature on pentacene³⁻⁵ indicate the presence of intense peaks located at similar energy values, even if there is no general consensus on the nature, energy location, and physical origin of these transitions. The peaks around 1.85 and 2.1 eV have been recently attributed to Frenkel excitons, but still there is no reliable

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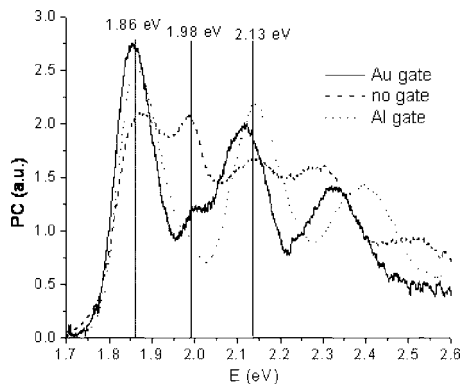


FIG. 1. PC spectra taken under identical experimental conditions of different TFTs with Al, Au, and no gate, fabricated with pentacene deposited at the same time on the same Mylar substrate.

information on the exact energy gap of pentacene.

One noteworthy observation is that spectra obtained from devices that have been prepared by evaporating pentacene at the same time on the same substrate, and that only differ in the presence of the metal gate or in the metal used to fabricate it (Au or Al), are significantly different. In particular, the devices with Al or Au gate show similar spectra while the spectrum of the device without gate is characterized by a markedly lower 1.86 eV peak.

Two possible explanations could account for this observation:

- (1) The presence of a metal contact at the back of the thin film structure may affect the reflection and the following interference effects of the impinging light beam. Light generation in the bulk pentacene layer exposed to multiple reflections could, in fact, be stronger in the gated devices and selective interference could take place and enhance the response at certain wavelengths.^{8,11} To test for such effects we have carried out the measurements at different tilting angles, varying from -45° to $+45^\circ$ (with respect to the normal direction of incidence), but we could not observe significant variations.

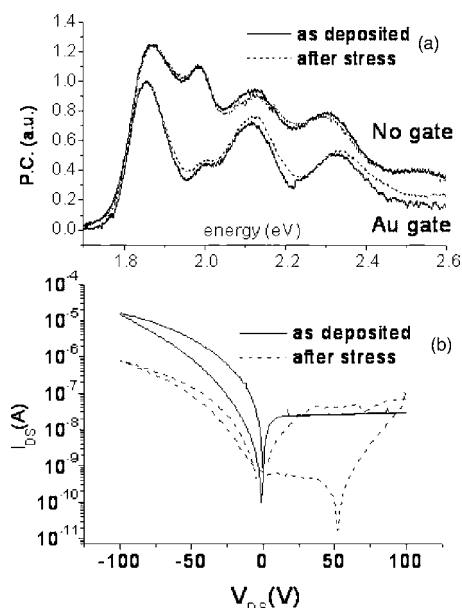


FIG. 2. Effects of repetitive I_{DS} - V_{DS} scans: (a) PC spectra and (b) I - V curves.

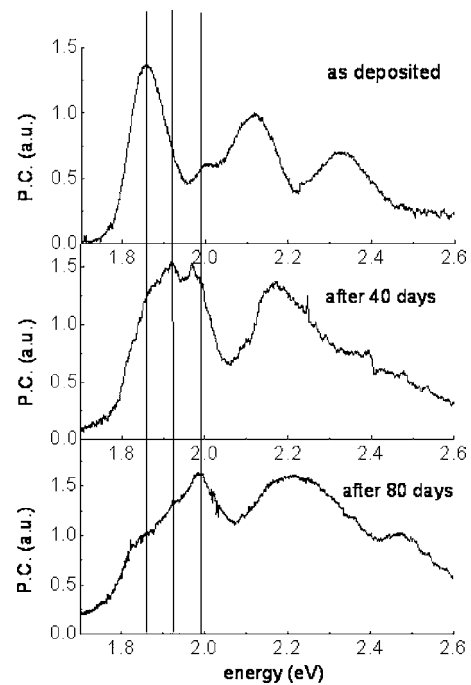


FIG. 3. Evolution with time of PC spectra of the same pentacene TFT with a Au gate taken under identical experimental conditions after exposure to light and air while tested with I_{DS} - V_{DS} measurements.

- (2) The presence of a metal gate can also affect the charge distribution of a metal-dielectric-semiconductor structure by altering the concentration of charge carriers at the dielectric-semiconductor interface. In fact, even if the metal contact is floating (i.e., not intentionally connected to an external voltage source) its equipotential surface may be assumed to have a nonzero value. This could induce the presence of a higher density of charge carriers at the dielectric-semiconductor interface that, following the absorption of the incident light, result in the formation of a larger number of excitons.⁶ By applying a positive gate bias ($V_G = +20$ V) the peak intensity decreases, thus confirming that the channel carrier density has a role in determining the photocurrent intensity (data not shown). Therefore, this explanation seems at the moment to be the most plausible one.

The effect of bias stress on these devices has been studied by repetitively measuring the current-voltage curves I_{DS} - V_{DS} with V_{DS} varying between $+100$ and -100 V. The I_{DS} - V_{DS} measurements have been carried out in air but in the dark, at room temperature over a whole day. Figure 2 shows how no variations are induced in the PC spectra of both gated and ungated devices after prolonged bias stress, while the I_{DS} - V_{DS} characteristics indicate a strong decrease in the current values. These results suggest that the observed degradation of the macroscopic transport properties cannot be ascribed to alterations of the structure and of the electrical properties of the excited states, rather it could be associated with polarization effects that locally redistribute the density of trapped charge.

We have also studied the effects of aging, i.e., of a combination of prolonged bias stress and exposure to air and room light and temperature, on similar devices. We tested the devices up to 80 days after fabrication. The results of PC analyses are reported in Fig. 3 and indicate a marked evolu-

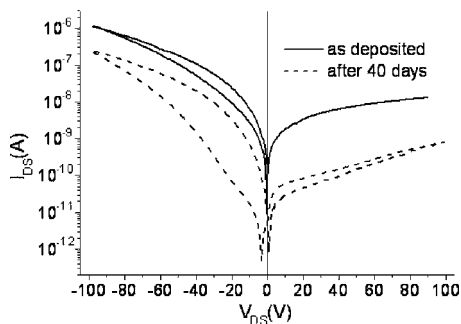


FIG. 4. I_{DS} - V_{DS} measurements on the same pentacene TFT with a Au gate whose PC spectra are reported in Fig. 3. The reported measurements have been carried out immediately after fabrication of the devices and after 40 days of exposure to atmosphere.

tion of the relative intensities of the peaks with elapsed time. The presence of a peak at about 1.91 eV is highlighted by the redistribution of the amplitudes of the other peaks. The most evident variation is observed for the lowest lying excited state, the one at 1.85 eV that gradually decreases in intensity leaving the dominant role to the transition at 1.98 eV.

These observations indicate that the exposure to air and light has a significant effect on the excited state structure and energy distribution, on the contrary to what we have observed in the case of pure bias stress (Fig. 2).

The effect of aging on the I_{DS} - V_{DS} characteristics is reported in Fig. 4 for the same Au gated devices whose PC spectra are shown in Fig. 3. After 40 days the current intensity has decreased while the hysteresis observed between the 0 to -100 V curve and the -100 to 0 V curve has increased. These effects could be understood in terms of an increased charge carrier trapping efficiency possibly caused by the formation of trapping sites. The hysteresis, in particular, could be associated with a quite long charge carrier emission time constant peculiar to the trapping sites.

Again, as highlighted by PC analyses, I_{DS} - V_{DS} characteristics show how the effects of aging are quite different from those observed after long bias stress.

A variation in the relative strength of the various bands located around the energy gap has been observed with optical spectroscopy on pentacene thin films as a function of temperature and it has been attributed to molecular reorientations that cause changes in mutual molecular overlap within the unit cell.⁹

It has been recently suggested that the influence of air on the charge carrier transport properties of pentacene consists of at least two separate contributions.¹²⁻¹⁴ The first one is due to the adsorption and diffusion of oxygen, enhanced by the presence of light, that is reported to produce a reversible effect of the material transport properties. The other is related to the presence of water that may easily diffuse through the gaps between the pentacene grains and be incorporated into the film changing its morphology. This could induce the formation of trapping sites for the injected charges and, due to the polar nature of H₂O, a greater interaction with the charge carriers, resulting in an increase of the energetic disorder through charge-dipole interactions.¹⁵

The morphology of pentacene films has been reported to vary after exposure to atmosphere and the changes have been correlated to adsorption on the film of the hydroxyl radical, caused by the presence of H₂O, that induces a structural alteration of the pentacene film.¹⁴ Variations observed in the saturation current of a pentacene TFT have been reported as

a function of the ambient humidity and have been attributed to induced changes in the hole mobility.¹⁴

Our results suggest that the prolonged exposure to atmosphere during operation of pentacene TFT induces significant alteration in the structure and in the electrical properties of the excited states that permanently alter the macroscopic electronic transport characteristics of the TFT, differently from what we have observed for TFT only exposed to bias stress during operation. The I_{DS} - V_{DS} characteristics show both a decrease in the current values and an increase in the hysteresis effect, suggesting a larger contribution from charge trapping sites, possibly characterized by a long emission time constant. We believe O and H adsorbed from the atmosphere play a major role in the observed alteration of the semiconductor structure and in the formation of permanent trapping sites.

The correlation of our PC spectra with the I_{DS} - V_{DS} characteristics supports the attribution of the peaks at 1.85 and 2.13 eV to excitons since they decrease with aging, a process that enhances the formation of charge carrier trapping sites. The increase in number and strength of carrier traps indeed could hinder the formation and affect the transport of excitons in the pentacene film. The peak at 1.98 eV, on the other hand, seems to be a good candidate for the energy gap of pentacene since it is not markedly affected by aging and since it has an energy larger than the lowest lying excitation (here the 1.85 eV excitonic transition).⁵

In conclusion, we have analyzed by current-voltage analyses and by photocurrent spectroscopy the effects on pentacene thin films of a prolonged bias stress and of exposure to atmosphere. We have identified the major excitonic and energy gap transition energies. We have observed a quite different electrical behavior and structure and energy distribution of the excited states. By repetitively biasing the device, even for long periods of time, only a local redistribution of charges takes place, possibly due to reversible polarization and short term trapping effects. On the contrary, exposure to atmosphere induces significant alterations on the structure and energy distribution of the excited states, associated with the formation of permanent trapping sites.

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