Electronic Effects of O₂ on Organic Semiconductors

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<u>Background:</u>

Organic semiconducting materials are fascinating for use in (opto)electronic devices like photovoltaic (PV) cells. These organic materials possess numerous advantages due to their ease of processing, low cost, availability, and non-toxicity in comparison to traditional inorganic counterparts. While most organic semiconductors are used as poly-crystalline, nano-crystalline or amorphous materials, even crystalline organic semiconductors are less ordered than their crystalline inorganic counterparts, because of the weak forces between the molecules. The issue of (dis)order is important, because the less ordered a material is, the higher the density of electronic states within the bandgap, known as gap or tail states. These states decrease the performance of solar cells by trapping the carriers. This disorder serves to penalize all aspects of PV performance, through reduced free carrier mobilities, enhanced recombination, and reduction in photovoltage [1].

One possible way to negate the effect of gap states is to fill them by doping. However, doping has to be done in a controlled way as otherwise more gap states can be produced due to excess presence of foreign materials.

Oxygen is well known to dope a large group of inorganic semiconductors p-type (or n for unipolar n-semiconductors). This effects stems from the high electron affinity of oxygen, which, upon adsorbing (initially as O₂) on the solid surface, extracts/localizes (previously free) electrons, thus decreasing free electron concentration [n] / increasing the free hole concentration [p]. The effect depends on the area of the exposed surfaces and is, thus, strongest for polycrystalline material. It can be reversible, unless strong covalent bonds form. We set out to see if a similar *general* effect exists for organic semiconductors and if interaction of the organic material with oxygen will affect its gap states.

Materials and Experimental Methods.

We chose organic semiconductors that are studied in organic electronics or are relevant to organic electronic applications, e.g. metal phthalocyanines (MPc), Pentacene and Poly-3-Hexylthiophene (P3HT). Thin films of these materials were prepared by spincoating or thermal evaporation methods. O₂ exposure to these films was done in a controlled manner in the dark. Contact Potential Difference (CPD) measurements were done using a Kelvin probe in an inert atmosphere. Conductivity measurements at different temperatures (in lateral direction) were done using inter-digitated Au fingers in an evacuated probe station. Hybrid solar cells were also fabricated using 6-H SiC and ZnPc.

Findings

Contact Potential Difference (CPD) measurements showed that oxygen causes effective p-type doping (with work functions increasing 0.1-0.3 eV). The extent of

doping, as deduced from change in CPD values, roughly follows the relative ionization potential (IP) of the materials, i.e., $P3HT > MPc > Pentacene > PTCDA \approx PTCDI$. It is seen that materials with a deep IP level are least affected by O_2 exposure. The doping effect, which is found to be (nearly) completely reversible for the organic materials that we studied, is explained by formation of a weak charge transfer complex between oxygen and the organic molecule/polymer. In the solid state, broadening of the density of states (DOS) around the mean IP level can happen due to static disorder of the organic materials. Tail states spill into the bandgap, with the density of tail states dependent on the degree of disorder. A higher degree of charge transfer is expected if oxygen interacts with molecules, contributing towards tail states, than if it interacts with other molecules in the matrix. Molecules contributing toward tail states mostly are present at the surfaces and grain boundaries (GBs). In polycrystalline material the surface area/volume is larger than for a single crystal, i.e., a larger area is available for adsorption. That effect is further increased if also the GBs are accessible for adsorption. Such effects are known from work on polycrystalline inorganic materials, such as CuInSe₂, ZnO and SnO₂. By analogy, oxygen adsorption at GBs of polycrystalline organic material can increase the hole concentration, which brings the Fermi level closer to the mean IP level.

The conductivity (at room temperature) of an undoped organic semiconductor (here ZnPc) is $< 10^{-10}$ S/cm, while for oxygen-doped samples $\sim 10^{-7}$ S/cm is found, i.e., a change in conductivity of three orders magnitude is obtained by oxygen doping. Further conductivity measurements (of p-phthalocyanine thin films) were done as function of temperature to extract the activation energy for hole transport, which was found to decrease with O-doping. The tail states, which are inert in doped condition, become active to trap holes upon de-doping and as a result the activation energy increases. This finding corroborates the above-described tail state-assisted doping model

To illustrate electronic effects of oxygen on organic thin films in a device, a model hybrid solar cell was made with SiC and an MPc. An increase in open circuit voltage (V_{OC}) occurred upon exposure to O_2 . The increase in V_{OC} can be attributed to filling of tail states in the organic material, which allows a larger photo-induced separation of the quasi-Fermi levels as tail state assisted recombination is suppressed.

In addition to experimental data, theoretical modeling of the gap states was conducted, approximating a Gaussian density of states centered around a mean ionization potential. Assuming a zeroth order O-doping reaction, experimental CPD data were fitted to simulated hole concentration changes that correspond to the measured changes in Fermi level. A good fit was obtained between experimental data and simulations. All the experimentally observed facts and simulations suggest that O₂ p-dopes organic materials and that tail states are in fact those that are filled upon O-doping. *Conclusion*

A wide range of organic materials can be p-doped with O_2 and it is likely that there exists a common mechanism for this doping process. The effect of oxygen doping is consistent with the formation of "weakly bound CT states". The magnitude of the effect mainly depends on the difference between the IP of the to-be doped material and on the effective electron affinity of O_2 . The extra holes created, due to O-doping, fill the gap states of the material and can, thus, improve the conductivity by reducing carrier loss due to trapping and recombination. As the doping is mostly reversible, the extent of doping may be tuned. Moreover, understanding this principle of O_2 doping provides an additional lever to control organic semiconducting behavior.

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- work done with Ron Rosenberg, Lee Barnea, David Cahen