Bias-Dependent Generation and Quenching of Defects in Pentacene

Authors: D. V. Lang ,X. Chi ,A. M. Sergent ,A. P. Ramirez

Commentary by Peter Littlewood, Cambridge University

Crystals of small organic molecules such as pentacene are often referred to as organic semiconductors, but there has been little systematic work to determine whether there are true parallels with the familiar inorganic semiconductors. As we all learn, one of the characteristics of semi conducting materials is that the electrical properties are determined by doping and the transport by charge traps. Over the years, a menagerie of these centers has been analyzed in the familiar semi conducting materials.

A recent paper by Dave Lang and collaborators analyses current-voltage curves on pentacene in a space-charge-limited regime - a classic semiconductor experiment to look for traps. In such an experiment, when the Fermi level moves through the trap level (by varying the bias voltage) there is a rapid increase in current as the traps are emptied. They indeed find the classic signature of traps, *though only if the sample had been previously polarized.* The memory of the bias polarization can be long, even at room temperature, but is rapidly erased by illumination. This indicates metastable trap states that are induced by a large bias voltage.

They produce a detailed analysis of the trap activation behavior to support this view, but there is then room for speculation about the physical origin. Metastable traps involving local atomic displacements are known in III-V semiconductors (giving rise to persistent photoconductivity), but recent calculations by Northrop and Chabinyc led Lang et al to a different scenario. They suggest the characteristics of their trap are consistent with defects involving excess hydrogen - a C-H_2 defect involving an additional H and therefore a fourfold-coordinated C atom - or hydroxylation. Molecules with two excess H are more stable than single H, so this provides a kind of "negative-U center" for H atoms – one expects to see excess H incorporated into the system in pairs (and chemically neutral, not trapping charge). However, the stability can be reversed by a bias, which favors a singly occupied H (and at the same time a hole trap) the metastability of trap formation then occurs because the motion of protons is slow.

This is a novel and unexpected origin for metastable trap formation that is probably peculiar to organic materials. However, also experiments such as these will eventually lead to a serious evaluation of these materials for practical devices.