

行政院國家科學委員會補助專題研究計畫成果報告

有機半導體之光學及電子性質研究

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計畫編號：NSC 89-2112-M-009-008

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計畫主持人：孟心飛

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一、中文摘要

研究旨在探討在共軛高分子能隙中具有結構性以及碳氧鍵缺陷能階之局域深層電子的性質。我們以鏈扭曲來模擬結構性缺陷，鏈末端就成了一個特殊情況。我們以清晰直觀的圖像對深層能階和遊走能階的能量以及波函數給出了解析表示式。碳氧鍵則是以緊束縛模型來求得數值解。我們還計算了，透過深層能階經由多聲子放射，自由載子的捕捉率與激子解離率。結果發現，缺陷解離比經由熱激發而致之本徵解離效率更好，是光電導載子生成主要機制。本研究結果解決了氧化光電導增強的疑惑，以及最近在外掃區域觀察到的與溫度無關光電流現象。成果已發表於文獻一。

關鍵詞：共軛高分子、光電導專題計畫

Abstract

We study the localized deep electronic level within the bandgap of conjugated polymers in the presence of structure or oxygen (carbonyl group) defects. The structure defect is modeled as a chain twist, including the chain end as a special case. Analytic expressions for both the energy and the wavefunction of the deep levels and the itinerant levels are obtained and supplemented by clear intuitive pictures. Carbonyl group is treated numerically within the tight-binding model. The rates of free carrier capture and exciton dissociation through the defect level via multi-phonon emission are calculated. We conclude that the defect dissociation dominates the intrinsic dissociation through thermal activation, and is the primary carrier generation mechanism in photoconductivity. Our results explain the

photoconductivity enhancement due to oxidation, as well as the recent observation on the temperature-independent photocurrent in the sweep-out regime. The results are published in reference 1.

Keywords: conjugated polymer, photoconductivity

二、緣由與目的

One of the major differences between conjugated polymers and inorganic semiconductors is the possibility of a large exciton binding energy. There have been controversies on how the tightly-bound excitons dissociate into free carriers. The carbonyl group introduced by oxidation is found to enhance the photoconductivity (PC) efficiency of poly(*p*-phenylene vinylene) (PPV) by a factor of forty, suggesting that the excitons are dissociated by the carbonyl group through its defect levels. Besides, excitons can also dissociate through the surface levels at the polymer/metal junction. Barth and Bassler measured the intrinsic PC by eliminating the oxidation and junction exciton quenching, and concluded that in such conditions the excitons have to overcome a binding energy of 0.34 eV through thermal activation or electric field tunneling in order to dissociate into free carriers. The temperature and field dependence of the PC quantum yield was shown to be consistent with the Onsager model. This picture is, however, inconsistent with the PC measurement in the sweep-out regime by Moses *et al.*, which shows that the effective activation energy decreases with the film thickness, contrary to the constant value (exciton binding energy) as the Onsager model would predict. Moses *et al.*, thus propose that the temperature dependence of PC is mainly due to thermal activation out of the deep levels (traps) into which the carriers fall along their passage to the electrode, and

the carrier generation process itself is temperature-independent. This behavior is interpreted as the evidence of a small exciton binding energy, similar to the situation of inorganic semiconductors. Such a small binding energy is, however, difficult to reconcile with the absorption spectrum, as well as the recent work on the electron injection by the STM. The fundamental question is then how the carriers are generated through exciton dissociation in the absence of oxidation, and why it has only a weak temperature dependence. It is well-known that exciton dissociation can be mediated by the deep levels, which can be caused by not only the carbonyl group but also the unavoidable structure defects. It is generally believed that the perfect δ -conjugation lasts for no more than 10 monomers in conjugated polymers, while the polymer chain is as long as 1000 monomers. The δ -bonding must be weakened in the conjugation interruption some way or the other, e.g. twist, by the structure defect. In addition, the chain end should also be considered as a kind of defect. Large binding energy and weak temperature dependence can be reconciled if the predominant carrier generation channel for photoconductivity is not intrinsic but mediated by such defects. The purpose of this work is to confirm this possibility by theoretical studies.

In this project we study the properties of the electronic states in the presence of the defects, including the chain twist and the carbonyl group, as well as the exciton dissociation process through the defect levels via multi-phonon emission. We found that the defects do introduce deep localized levels within the energy gap. For the twist case, analytical expressions are obtained for both the energy and wavefunction of the deep levels. The scattering of the itinerant states by the defect is also considered. In practice, whether the defect is actually a rotation or other fault is not critical because such bonding weakening is the sole assumption in our calculation on the deep level. Such deep level is strongly coupled to the local phonon mode centered around the defect because of the large wavefunction overlap. The local

phonon mode is displaced to a new equilibrium position once the electron drops into the deep level from the conduction band. When the level is initially empty, the electron of the exciton can be captured by the deep level while releasing the hole into a free carrier, assuming the defect binding energy is larger than the exciton binding energy. The reversed process happens when the level is initially empty. This is a relaxation instead of activation process. Carriers can therefore be generated almost independent of the temperature.

The dissociation through structure defects is found to be the predominant carrier generation process at a typical density level of the structure defects. The temperature-independence of the photocurrent is not due to the smallness of exciton binding energy, but the high quenching efficiency of the deep levels. From the exciton capture rate we calculate the steady state PC quantum yield, i.e. the number of carriers per absorbed photon. As expected, the quantum yield decreases with the light intensity because the carrier generation process is blocked when the defect levels are saturated by high photoexcitation. Similar behavior has been, in fact, suggested by the two-pump experiments. These results provide a unifying picture for the PC experiments and clarify the controversy on the origin of the photocarrier generation process.

三、結果與討論

Our results was published in reference 1. They predict that the photoluminescence quantum yield is reduced to about one half when there is one oxygen defect per 400 unit cells. Moreover, the PC quantum yield α caused by the structure defects (chain ends) is predicted to be 8.9×10^{-4} when the average number of unit cells N_c in a chain is at a typical value of 5×10^3 . Our predictions on the relation between the PC quantum yields with the oxygen density (for oxidized samples) and with the chain length (for pristine samples) have been quantitatively compared with experiments, and the results are reasonable. The interpretation of the temperature T and electric field (\mathcal{E})

dependence of the steady state photocurrent density $j(T, E)$ is now clear. Assuming that singlet excitons are generated with quantum yield close to one, j can be expressed as $j(E, T) = I_p \gamma_p d' \epsilon_i(T, E) / (E, T)$. ϵ_i is the total carrier generation quantum yield, including activation and the defect dissociation. $\hat{\epsilon}$ is the collection efficiency by the electrode, and d is the film thickness. ϵ_i can be written as $\epsilon_i + b e^{-sE_b}$, where ϵ_i is the defect part and $b e^{-sE_b}$ is the activated dissociation part. The T -dependence of ϵ_i comes mainly from the activation part, while the T -dependence of $\hat{\epsilon}$ comes from the activation from the traps along the passage to the electrodes. For thin films in the sweep-out region, the collection efficiency $\hat{\epsilon}$ is close to one, so we have $j = I_p \gamma_p \epsilon_i$ and j should be proportional to $\epsilon_i + b e^{-sE_b}$. The weak T -dependence in this situation implies that $b e^{-sE_b} \gg \epsilon_i$. This is no surprise because ϵ_i has been estimated to be about 10^{-3} even without oxygen, while the factor $b e^{-sE_b}$ is only 1.24×10^{-6} at 300 K. The "intrinsic" photocurrent of pure samples is therefore not mainly determined by the intrinsic properties of a perfect chain like exciton binding energy, but by extrinsic factors including the defect density and the strength of the coupling between the lattice and the deep level. In thicker films the T -dependence of j is dominated by the transport factor $\hat{\epsilon}$ instead of the generation factor ϵ_i , as suggested by Moses *et al*

四、計畫成果自評

Our results agree with the experiments on the PC enhancement and PL quenching by oxidation. Moreover, even without oxygen the mid-gap level at the chain end causes a carrier generation rate larger than the thermal dissociation rate. The "intrinsic" photocurrent is therefore disorder-sensitive and not primarily determined by the intrinsic properties of a perfect chain. Our study clarifies the controversy on the origin of photoconductivity in conjugated polymers. It is important to the understanding of many

related phenomena.

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