

Nonlinear Photocurrent Spectroscopy

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[Abstract] The absorption spectra of as-deposited and annealed free base phthalocyanine (H₂Pc) thin films are derived from steady-state photocurrent measurements using a new method called Nonlinear Photocurrent Spectroscopy (NPS).

[Introduction] Photocurrent detection well-suited to *in situ* characterization of molecular semiconductor thin films and devices as the substrate need not be transparent and the sample dimensions can be smaller than the beam cross-section. A significant experimental challenge however is presented by the nonlinear dependence of the photocurrent frequently observed with respect to the incident light intensity[1]. In NPS the photocurrent is mapped to the incident photon flux using a photocurrent response function generalized to account for both linear and nonlinear dependencies.

[Methods] The photocurrent response function, I^* , is defined to be a continuous, monotonic function of photocurrent, I , chosen to be linear with the incident photon flux, F . Together with the sample transmittance, T , and a proportionality constant, Y , we can write, $I^* = eF(1 - T)Y$.

If an appropriate function I^* can be discovered for the measurement sample, the Napierian optical absorbance, neglecting the sample reflectance, is

$$A_e = -\ln\left(1 - \frac{1}{Y} \frac{I^*}{eF}\right)$$

An expression for I^* accounting for both linear and nonlinear dependencies was derived by modelling the photogeneration and recombination of charge carriers within an exponential density of gap states[2].

$$I^* = I \left(\frac{I}{I_{\text{ref}}} + 1 \right)^{\frac{1-\gamma}{\gamma}}$$

This photocurrent response function was found to give good agreement with the experimental data. In this formulation the scaling factor Y becomes the photocurrent gain in the linear response region and is proportional to the quantum yield. The parameters γ and I_{ref} are found by plotting the differential $(d \ln I / d \ln Y)$ against I .

The measurement device consisted of a 10 nm free base phthalocyanine (H₂Pc) thin film deposited on a sapphire test substrate patterned with aluminum electrodes. Film grown and measurements were made at 30 °C *in situ* under ultrahigh vacuum. After measuring the as-deposited film, the device was annealed at 240 °C to convert it to the β -form, cooled and re-measured. The light source was a single monochromator Bunkoukeiki SM-25 monolight. Current measurements were made with a Keithley 6487 picammeter. The Keithley unit also provided the applied bias of 10^5 V m⁻¹. The transmitted light through the sample was measured with a calibrated Si photodiode.

[Results and Discussion] Figure 1 compares the NPS spectrum of the as-grown H₂Pc film with the optical data. All results were obtained *in situ*. The structure of the Q-band is reproduced accurately by NPS.

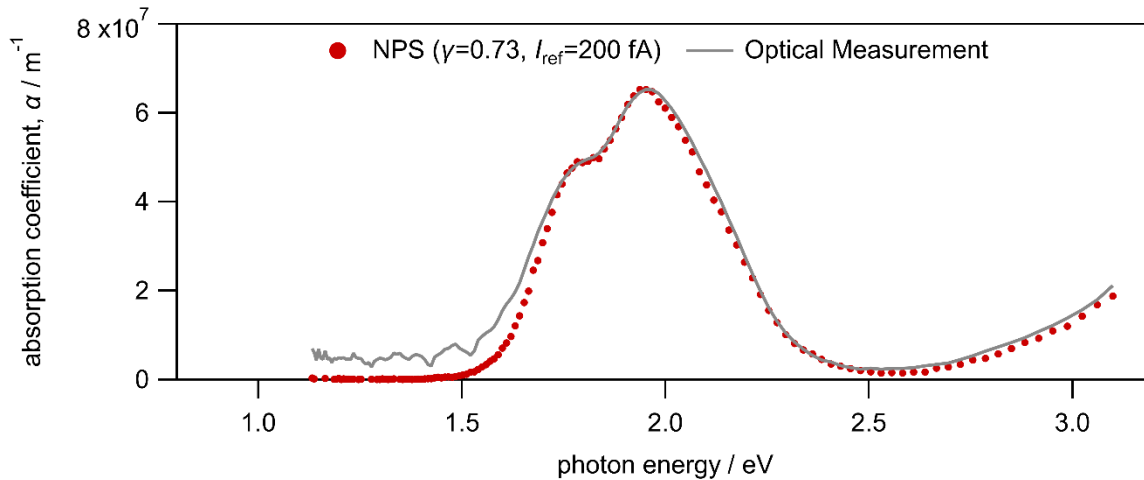


Figure 1. Absorption spectra of as-grown 10 nm H₂Pc thin film obtained by both photocurrent and optical detection methods.

In Figure 2 the NPS spectra for the as grown and annealed films is compared on a logarithmic intensity scale. The onset of the Q-band is linear, with characteristic Urbach energies of 51 meV and 31 meV respectively. While the smaller value for the annealed film indicates improved crystallinity, the electrical properties of the two films including the photocurrent gain do not change significantly. Explaining these results from the point of view of a de-trapping photogeneration mechanism, it appears the electrically relevant gap states are extrinsic in origin and lie at energies below those detected in the NPS experiment.

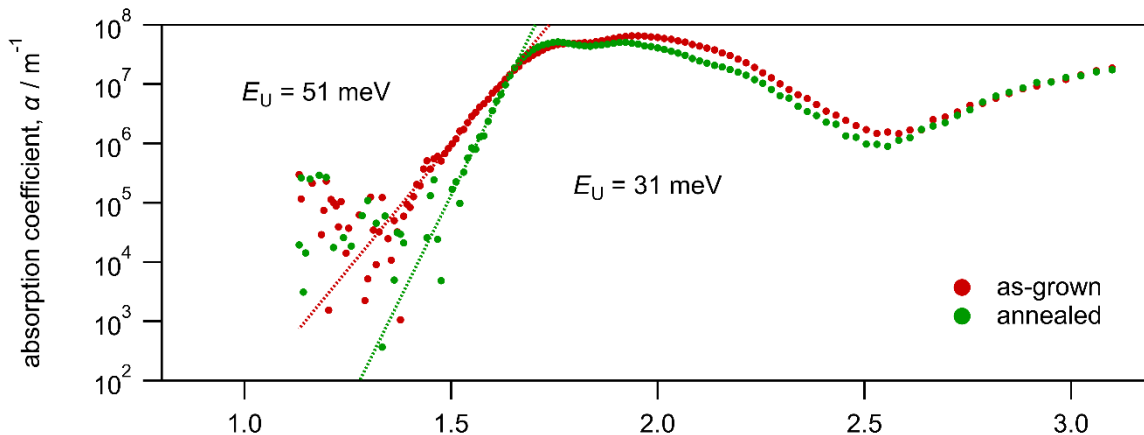


Figure 2. NPS spectra for as grown and annealed films, showing the difference in the Urbach energies E_U .

In summary, NPS is demonstrated to be an effective method to study the optical and electrical properties of molecular semiconductor thin films simultaneously. It is especially effective to observe the details of near-gap region.

[References]

- [1] G.H. Heilmeier, S.E. Harrison, Implications of the Intensity Dependence of Photoconductivity in Metal-Free Phthalocyanine Crystals, *Journal of Applied Physics* 34 (1963) 2732-2735.
- [2] A. Rose, *Concepts in photoconductivity and allied problems*, Interscience, New York, 1963.