## Pentacene Thin Film Photoconductivity : Influence of the Electrode.

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## Introduction

We have measured the photoconductivity action spectra for pentacene films on sapphire as a function of film thickness, using either gold or aluminum electrodes. The aim was to examine the influence of the electrode metal on the photo-generation of mobile charge carriers in organic semiconductor films.

## Experimental

The apparatus is shown schematically in Figure 1. Pentacene (TCI) was sublimed in vacuum three times and once under 30 Pa  $N_2$  gas flow before use. Single crystal sapphire [0001] substrates (Shinkosha) were first annealed at 1000 °C in air to expose atomically flat

terraces, after which metal electrodes spaced 0.1 mm apart were prepared by vacuum deposition through a metal mask. Gold electrodes were 100 nm thick, with a 5 nm titanium adhesion layer. Aluminum electrodes were 35 nm thick. The substrates were degassed at 150 °C under UHV before use. Leakage currents (dark or photoconductance) were below 10 fA. Pentacene films were prepared by stepwise thermal deposition from a resistively heated crucible to a maximum film thickness of 100 nm. The substrate temperature was kept at 30 °C, and the deposition rate was constant at  $2.0 \pm 0.3$  nm



**Figure 1.** Diagram of the experimental apparatus for *in situ* photoconductance measurements.

min<sup>-1</sup>. After each deposition step the photocurrent was evaluated for wavelengths from 400 nm – 1180 nm, using a Bunkokeiki SM-25 monochromatic light source and a Keithley 6487 picoammeter-sourcemeter. The incident photon flux was  $10^{19}$  photons m<sup>-2</sup> and the applied bias was  $10^5$  V m<sup>-1</sup>. Measurements were obtained at a repetition rate of approximately 0.1 Hz, with dark current subtraction performed for each data point.



**Figure 2.** Photoconductance of pentacene films of the indicated thickness. The optical absorbance of an 8 nm pentacene film is shown for comparison. The reported photoconductances are normalized against the incident photon flux and film thickness.

**Results and Discussion** 

The electrode metal influenced the dark conductivity of the film. The conductivity of the pentacene film with Au electrodes was  $6 \times 10^{-8}$  S m<sup>-1</sup> for films less than 20 nm thick, falling at higher thicknesses. The conductivity with Al electrodes was below the measurement threshold of  $10^{-9}$  S m<sup>-1</sup> for all thicknesses measured. The photoconductivity is also dependent on the electrode metal, as shown in Figure 2. The broad peak at around 2.7 eV is attributed to intrinsic photo-generation by excitation of electrons across the transport energy gap<sup>1</sup>. The cluster of peaks at lower energy correlates closely with the optical absorbance of the thin film and are assigned to a de-trapping mechanism where long lived triplet excitons excite trapped charges into mobile states. The de-trapping currents dominate for the thin pentacene films with Au electrodes, corresponding to the thicknesses where the dark conductivity is highest. The de-trapping photocurrent is an order of magnitude lower when Al electrodes were used, and the intrinsic photocurrents saturate only slightly at the lowest observed thicknesses. A 0.1 eV shift of the intrinsic photoconductivity peak to higher energy is also noted.