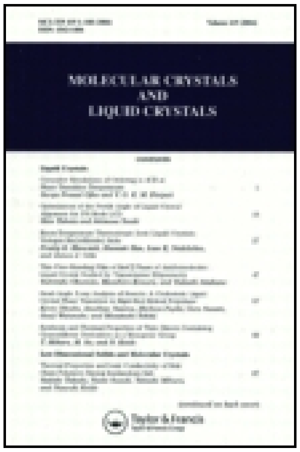

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Photovoltaic Effects in Tetracene Crystals

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Abstract—Studies on the photovoltaic effect in tetracene single crystals have shown that, in general, two photovoltaic mechanisms yielding signals of opposite sign can be observed. On illuminating the crystal, a fast photovoltage response is obtained which is eventually dominated by a more slowly rising photovoltage of the opposite sign. The action spectrum of the fast response is closely related to the absorption spectrum of the crystal. The slow response is more effectively induced by light in spectral regions where the crystal absorbs light weakly. Temperature higher than room temperature decrease the response time of the slow photovoltage. The results are discussed in terms of photovoltage mechanisms which involve singlet excitons and photoinduced detrapping of trapped charge.

Introduction

The photovoltaic effect i.e. the production of a voltage in response to illumination, has been reported in many organic systems.[1] In some cases the observed phenomena have been ascribed to the Dember effect.[2] In the majority of cases the effect is considered to arise from a potential difference developing at a contact barrier. The effect is usually charactrized by the sign of the charge which an illuminated electrode in contact with the organic substrate assumes when the electrode-substrate interface is illuminated.[1] In many measurements on the photovoltaic effect found in tetracene-semi-transparent electrode systems, however, it has been observed that the sign of the observed effect can vary from sample to sample with the same semi-transparent electrode. Moreover, the sign of the observed photovoltage varies with time in many samples, the ultimately achieved steady state photovoltage being of opposite sign to that observed initially. Similar phenomena in anthracene single crystals have been recently reported by Russian workers.[3] In order to achieve some understanding of these observations and clarify mechanisms whereby photovoltages are produced, the effect of time, temperature and wavelength of illumination on the photovoltaic effect in tetracene single crystals has been investigated. Single crystals are more suitable for such investigations since many of the problems of reproducibility and short-circuiting, associated with the ill-defined physical nature of evaporated polycrystalline samples are eliminated.

Experimental

In the experimental arrangement used two silver electrodes were deposited directly on the crystal, one being semi-transparent. Contact to the transparent electrode was made with 1-mil copper wire; contact to the back electrode was made with platinum foil. Other semi-transparent electrode assemblies such as a tin oxide coated slide in contact with the metallized or unmetallized crystal surface were also investigated. Similar results were obtained for all the electrode arrangements.

Photovoltages were measured with a Cary Model 31/31V Vibrating Reed Electrometer, operating in the 31V mode. Photovoltage measurement consisted of recording the potential induced on the illuminated electrode with respect to ground.

An Osram 900W Xenon lamp with Xetron CX–900 lamp housing and a Bausch and Lomb 150W Xenon lamp were used as sources of illumination. The light sources were used in conjunction with Bausch and Lomb monochromator gratings No. 33–86–02 or No. 33–86–07 to give monochromatic light. Light intensities were measured with an Eppley thermopile.

Tetracene was obtained from Henley and Co., Inc. After purification by Column Chromatography and vacuum sublimation, single crystals, 50–100μ in thickness, were obtained by sublimation at 255 °C in a stream of nitrogen (0.3 cu ft/hr).

Results

The photovoltage response as a function of time was qualitatively similar for all the electrode arrangements. Typical photovoltage-time data at room temperature are shown in Fig. 1. An initial fast response was observed which peaked within a few seconds. In some crystals the fast response was negative, in others positive. The crystals in Fig. 1 gave an initial negative

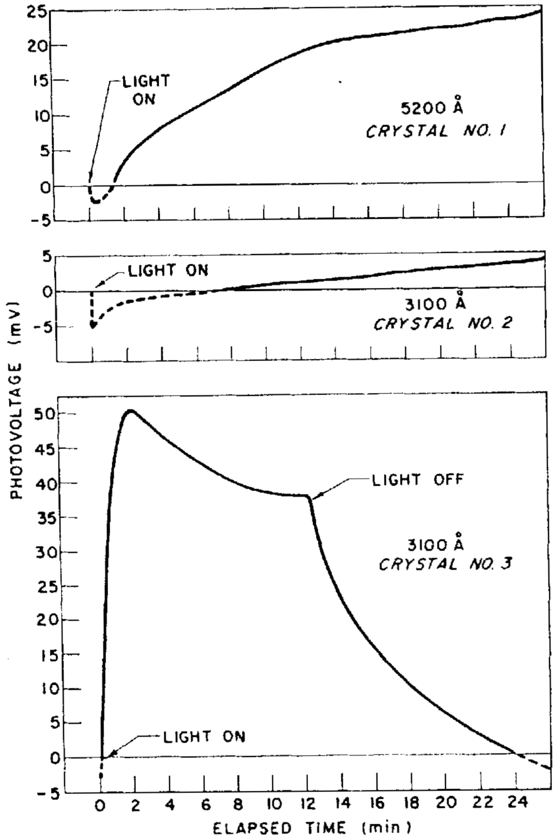

Figure 1. Photovoltage as a Function of Time for Tetracene Single Crystals.

fast response. After the initial photovoltage peak the photovoltage decreased in magnitude, eventually reversing in sign and building up to an equilibrium steady state photovoltage within 20–30 minutes. This signal remained fairly steady with steady illumination, a slight decrease with time being observable in some cases. When the illumination was removed the signal decayed to zero in most cases. In some cases a residual signal remained for some time after removal of the illumination. The spectral dependence of the initial fast signal and the ultimately achieved slow rising signal at constant illumination intensity is illustrated in Fig. 2. The spectral dependence of the fast signal was closely related to the absorption spectrum of the crystal. The arrows in Fig. 2 indicate the position of strong absorption bands in the crystal spectrum.[4] The slow signal showed maximum response in spectral regions where the crystal absorbs light weakly. The effect of temperature on photovoltage-time effects in tetracene single crystals is illustrated in Fig. 3 for a typical crystal. At 25 °C, in this case, a fast rising positive photovoltage reversed into

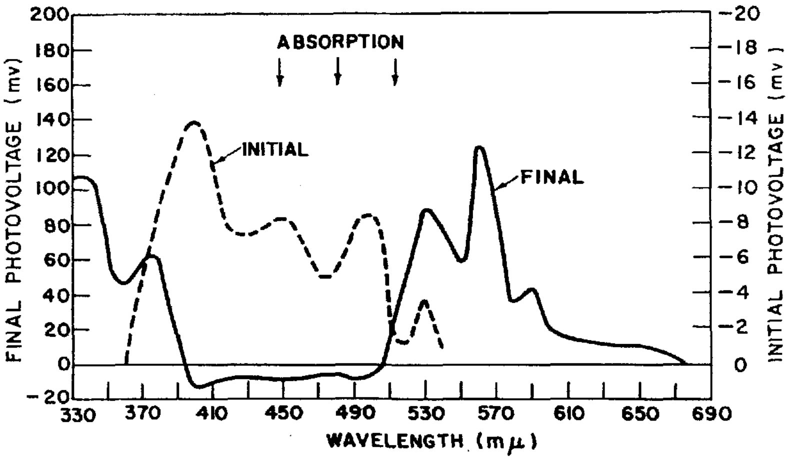

Figure 2. Spectral Dependence of the Initial and Final Photovoltage Magnitude for a Tetracene Single Crystal (Photovoltage Corrected to Uniform Illumination Intensity of 1.04 mw/cm^2).

a negative signal within two minutes. Twenty minutes was required to attain the maximum. At 75 °C the character of the response changed. The initial fast positive response was not observed. Instead a fast rising negative response was found which peaked within 15 seconds, reducing to a lower value within twenty minutes. Similar behavior was found at 125 °C, in this case a fast negative response peaked and then reduced to a lower value within five minutes. Raising the temperature thus had the effect of decreasing the response time of the photovoltaic signal that was slow rising at room temperature so that it became the dominant effect at all times after commencement of illumination.

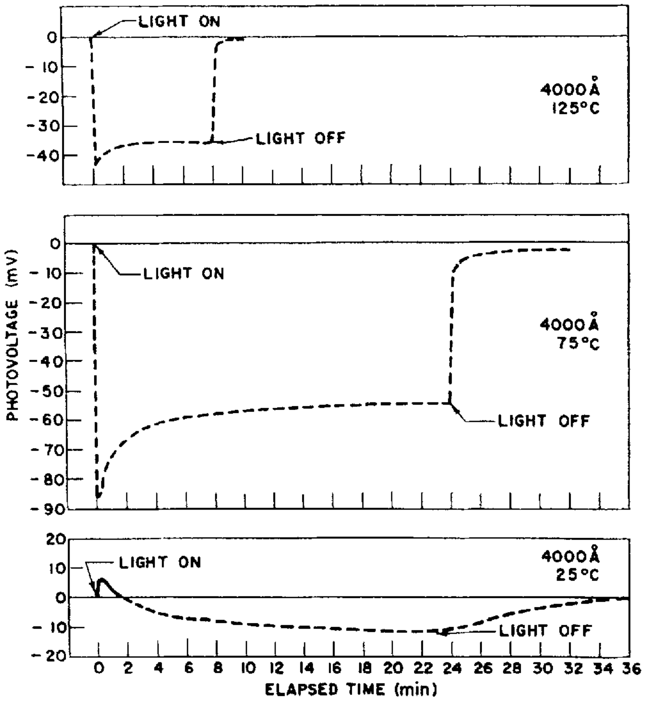

Figure 3. Photovoltage Time Plots at Different Temperatures for a Tetracene Single Crystal.

Discussion

The spectral dependence of the fast rising photovoltaic effect i.e. a close parallel between the photovoltage spectrum and the crystal absorption spectrum, suggests that excitation of the crystal singlet electronic energy levels is involved in this process. Photoconductivity in organic crystals is usually explained in terms of singlet excitons generated in surface layers of the crystal, dissociating at crystal defects and the crystal surface to give both positive and negative charge carriers.[5] The observed photovoltage can be explained in terms of the charge separation produced by carriers of one sign diffusing into the crystal bulk and carriers of the opposite sign remaining at the illuminated electrode. A fast response is expected for this type of effect since singlet states are usually excited and relax within 10^{-9} sec. If the net sign of trapped charge in the crystal can be positive or negative, the fast rising photovoltage may be negative in the former case, or positive in the latter.

The temperature and spectral dependence both point to photoinduced detrapping of charge in the bulk of the crystal as the most reasonable explanation of the slow rising photovoltage. Sign reversal of the photovoltage in anthracene single crystals has recently been attributed to the ionization of trapped electrons by weakly absorbed light.[3] At room temperature the detrapping process is slow and it is some time before the charge build-up can dominate the initial fast response arising from the generation of singlet excitons. At higher temperatures the detrapping process is accelerated and the photovoltage from this mechanism is immediately established. A maximum effect with weakly absorbed light is expected in the case of the slow-rising photovoltage since it will penetrate more deeply into the crystal, releasing more trapped charge and yielding a greater measured photovoltage. Since long time illumination will slowly release all the charge initially trapped in the crystal, photovoltages produced by the detrapping mechanism should slowly decrease with time. Evidence that this occurs can be seen in Figs. 1 and 3, where the photovoltage can be seen to slowly decrease with time.

The postulated mechanisms suggest that the slow rising photovoltage will be present to a greater or lesser extent depending upon the amount of trapped charge initially present. In studies on many crystals this has in fact been observed. The fast rising photovoltage was always present as expected since it depends upon the intrinsic electronic properties of the crystal. The slow rising photovoltage was present in a large number of samples demonstrating that most crystals have significant amounts of trapped charge.

The results on the photovoltaic effect in tetracene single crystals indicate that tabulations of the sign of the photovoltaic effect in organic solids should be treated with caution unless the conditions under which the measurements were obtained are specified.[1] It can also be noted that difficulties may arise in interpreting the measured photovoltages in terms of the Dember effect when effects due to trapped charge are operating. Considerations such as these may explain the lack of agreement between the sign of the majority carrier obtained from the Dember effect, the Hall effect and Seebeck coefficients.[6]

Acknowledgement

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