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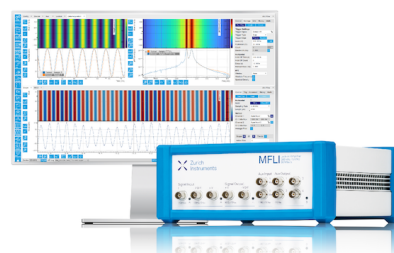
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High electron mobility in bathophenanthroline

Shigeki Naka,^{a)} Hiroyuki Okada, and Hiroyoshi Onnagawa

Department of Electric and Electronic Engineering, Toyama University, Toyama 930-8555, Japan

Tetsuo Tsutsui

Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816-8580, Japan

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We have measured electron mobility in vacuum-deposited films of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline, or BPhen) using a time-of-flight technique. Electron transport was highly dispersive for BPhen with a dispersion parameter of a value 0.30. The electron mobility in excess of 10^{-4} cm²/V s has been observed at electric fields of the order of 10^5 V/cm with weakly dependent on the electric field. The characteristic energy of the distribution is obtained a value 0.09 eV. It is directly confirmed that the BPhen has superior electron-transport capability. © 2000 American Institute of Physics. [S0003-6951(00)04102-4]

Organic charge transporting materials have found a number of technological applications. One of the interesting applications is an organic electroluminescent (EL) device that shows excellent properties of realizing low driving voltage and bright emission.^{1–5} In general, the device structures have organic hole- and electron-transport layers sandwiched between two electrodes. Tris (8-quinolinolato) aluminum (III) (Alq₃) is frequently used as an electron transport layer and an emission layer. Electron mobility of Alq₃ was reported to be of the order of 10^{-6} – 10^{-5} cm²/V s.^{4–7} This value is lower than hole mobility of a typical hole transport material (HTM). For example, hole mobility of *N,N'*-(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) is of the order of 10^{-3} cm²/V s.⁸ In double layered device fabricated with Alq₃ and TPD, an electrical property of the devices is dominated by the lower electron mobility of Alq₃ rather than hole mobility of TPD.⁷ Therefore, new organic materials with high electron mobility need to reduce the operation voltage of the devices.

Phenanthroline derivatives are well known organic materials and are used as a ligand in metal complex,^{9–11} an electron transport layer,¹² a hole blocking layer,^{13,14} and a host material of a metal-doped electron-injecting layer¹⁵ in organic EL devices. However, electrical properties of the phenanthroline derivatives are still unknown. In this study, we measured the electron mobility of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline, or BPhen) in vacuum-deposited films using the time-of-flight (TOF) technique.

The as-produced compound was purified by vacuum sublimation. BPhen films were prepared by vacuum vapor deposition onto a glass substrate precoated with semitransparent aluminum (15 nm). Typical evaporation source–substrate distance was 35 mm. During this deposition process, the background pressure was approximately 10^{-6} Torr and the deposition rate was 5–10 nm/s. The upper aluminum electrode was deposited on the BPhen film to the thickness of 15 nm. Thickness of the BPhen film was 9.9 μm,

measured by a surface profiler (Sloan Dektak 3). The sample area was 2×2 mm².

The mobility measurements were carried out using conventional TOF techniques. Charge carriers were generated in a thin BPhen layer close to an illuminated electrode by exposure to a N₂ laser with a pulse width of 3 ns at a wavelength of 337 nm. A resistor with the value between 1 and 100 kΩ was connected in series to the samples. The current response time was longer than $10RC$, where R was the series resistance and C the sample capacitance (typically 15 pF). The photocurrent was measured with a digitizing storage oscilloscope. All measurements were carried out at 298 K. The forward bias corresponds to a positive voltage on an illuminated electrode.

Measurements were performed with the reversed bias polarity in order to study the transport of electrons. Figure 1(a) shows a transient photocurrent profile for electron in BPhen. The transient photocurrent shows highly dispersive behavior and transit time could not be determined from double linear plot of photocurrent versus time characteristics. The observation of nondispersive transient photocurrent of electron is difficult because impurities act as carrier traps.¹⁶ Figure 1 (b) shows a logarithmic representation of the previously mentioned photocurrent. Clear change of two slopes was obtained in the double-logarithmic plot. The transit time t_T is determined from the intersection of the two slopes in the transient photocurrent profile. The mobility μ is determined as

$$\mu = \frac{d}{t_T E}, \quad (1)$$

where E is the electric field and d is the film thickness. The electron mobility of BPhen was 4.2×10^{-4} cm²/V s at $E = 3 \times 10^5$ V/cm. Measurements were performed with the forward bias in order to study the transport of holes. However, transient photocurrent of hole was not observed. This indicates that the BPhen shows poor hole transport properties.

For the dispersive transport mode, the time-dependent transient photocurrent and the transit time is given by

^{a)}Electronic mail: nak@eng.toyama-u.ac.jp

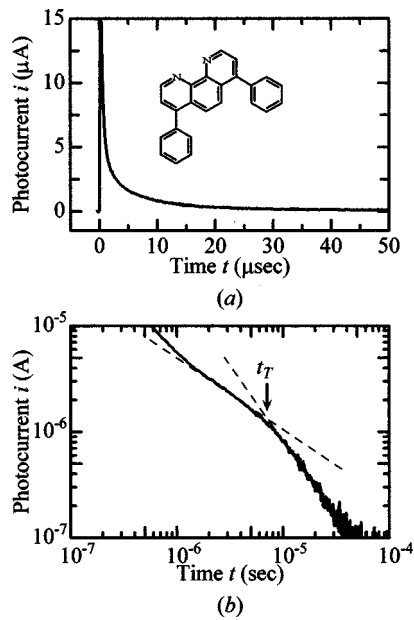


FIG. 1. Typical transient photocurrent profiles measured at 298 K and for an electric field of 3×10^5 V/cm. Sample thickness of BPhen was $9.9 \mu\text{m}$. Data are plotted in both (a) double-linear and (b) double-logarithmic representations. Inset in (a) shows the chemical structure of BPhen.

$$i(t) \propto \begin{cases} t^{-(1-\alpha)}, & (t < t_T) \\ t^{-(1+\alpha)}, & (t > t_T) \end{cases} \quad (2)$$

where α is the dispersion parameter with $0 < \alpha < 1$ and decrease with increasing dispersion.¹⁷ In the case of dispersive transport photocurrent controlled by multiple trapping in localized states with an exponential trap energy distribution:¹⁸

$$N(\varepsilon) = N_0 \exp\left(-\frac{\varepsilon}{\varepsilon_0}\right), \quad (3)$$

where ε and ε_0 are the trap energy and the characteristic energy of the distribution, respectively, the dispersion parameter α is expressed by¹⁸

$$\alpha = \frac{kT}{\varepsilon_0}, \quad (4)$$

where k and T are the Boltzmann's constant and temperature, respectively. Figure 2 shows the superposition master plot in double logarithm of the transient photocurrent of

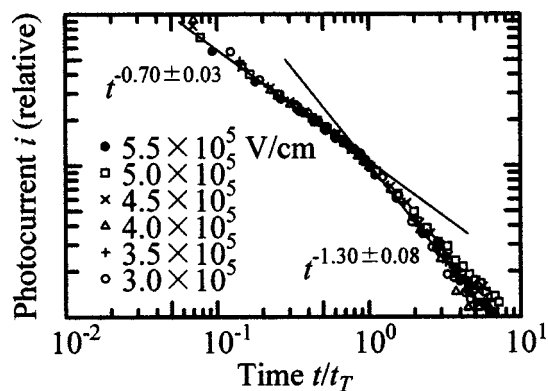


FIG. 2. Double-logarithmic plots of the transient photocurrents of BPhen in several electric fields. Time was normalized to t_T and photocurrent was shifted to vertical direction. Slopes of the solid lines are -0.70 and -1.30 , respectively. The value of the exponent α is 0.30 .

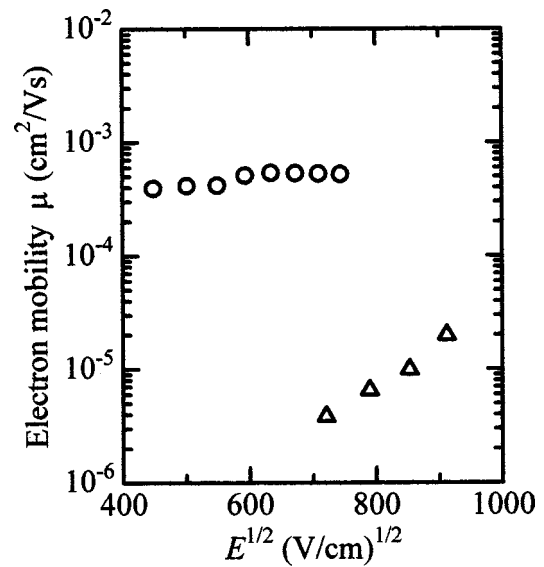


FIG. 3. Logarithmic electron mobilities of BPhen (circles) compared with that of Alq₃ (triangles) represent the results reported by Naka *et al.* (See Ref. 7) vs square root of electric field. The data points were determined from the intersection of the asymptotes to the corresponding double-logarithmic plots of transient photocurrents (Fig. 2).

BPhen obtained at a number of electric fields. The value of α is independent of electric field. The first and the second slopes are -0.70 ± 0.03 and -1.30 ± 0.08 , respectively, and α is about 0.30 . This α value is smaller than the value of other amorphous materials.¹⁷ The reasons of smaller α value may be originated from the effect of disordered molecular film and/or oxygen traps¹⁹ by exposure to air. We obtained for ε_0 a value 0.09 eV from Eq. (4).

The mobility can be described as $\mu \propto \exp(\beta E^{1/2})$, where β is a constant.²⁰ Figure 3 shows the logarithmic mobility versus $E^{1/2}$ plot for electron mobilities of BPhen (circles) compared with that of Alq₃ (triangles).⁷ The electron mobility for BPhen approaches on the range $3.9 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (2×10^5 V/cm) to $5.2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (5.5×10^5 V/cm) with a weakly dependent on the electric field. It was found that the electrons in BPhen are about two orders of magnitude more mobile than in Alq₃. In comparison with other electron-transport materials, for example, oxadiazole derivatives,^{21,22} bipolar molecular composites,²³ and starburst phenylquinoxalines,²⁴ BPhen has the highest electron mobility. The intermolecular packing affects the electron transport in BPhen film. BPhen films will keep amorphous states because of attached phenyl groups. Phenanthroline is also a small, rigid and planar molecule with extended π -electron. Therefore, the high electron mobility of BPhen may be originated from short hopping length for electron transport.

In the dispersive transport mode, the mobility is an effective parameter that depends on time, because the carrier thermal equilibration time is comparatively longer than the transit time and the average velocity of the carriers decreases with time throughout the transit time.¹⁷ We note that the electron mobility of BPhen may be affected by the film thickness. Further investigations on this point are in progress.

In conclusion, the electron mobility of BPhen was measured in vacuum-deposited films using the TOF technique.

room temperature. The transient photocurrent showed highly dispersive shape. The electron mobility of BPhen was of the order of 10^{-4} cm²/V s and was weakly dependent of the electric field. This material with high electron mobility might offer the possibility for low driving voltage in organic EL devices.

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