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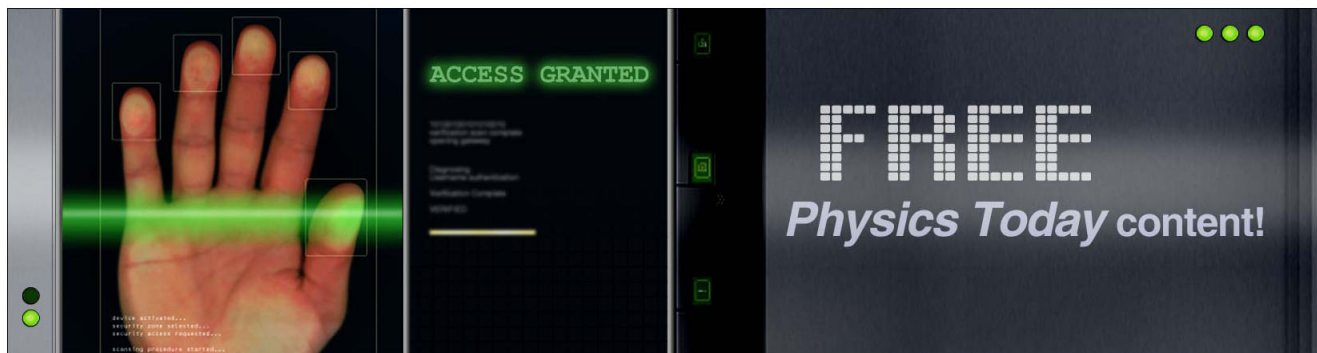
Time-of-flight analysis of charge mobility in a Cu-phthalocyanine-based discotic liquid crystal semiconductor

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We used a time-of-flight method to study the charge carrier mobility properties of a molecular-aligned discotic liquid crystal semiconductor based on Cu-phthalocyanine. The heated isotropic-phase semiconductor material was sandwiched between transparent electrodes coated onto glass substrates without conventional alignment layers. This was then cooled, and a discotic liquid crystal semiconductor cell was obtained, which we used to make mobility measurements. The material had a fixed molecular alignment due to the supercooling of the hexagonal columnar mesophase. It was clarified that the carrier mobility for electrons was as high as it was for holes at room temperature. The maximum value of negative charge mobility reached 2.60×10^{-3} cm^2/V s, although negative carrier mobility is often much lower than positive carrier mobility in other organic semiconductors, including conventional Cu-phthalocyanine vacuum-deposited films. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1805178]

The molecular-ordered self-assembly mechanism of liquid crystal (LC) materials is a very attractive feature of organic semiconductors for use in future plastic electronics, since the charge carrier mobility of organic materials depends heavily on the overlap of π^- electron orbitals in aligned organic molecules. The hole mobility of some kinds of organic semiconductors[1,2] (including a π^- electron-conjugated molecular system of pentacene) have recently achieved values of the same order as the inorganic semiconductor, amorphous silicon. Improvements in the vapor-phase deposition method for organic semiconductors (not soluble in organic solvent) have been extensively promoted[3–5] in order to obtain a highly ordered uniform molecular alignment, because microscopic crystal defects and interface traps generated in the film-formation process can reduce carrier mobility.

On the other hand, there have been several reports in which LC semiconductors with molecular alignment self-assembly have been shown to exhibit excellent mobility.[6] For example, LC materials with a rod-shaped molecular structure,[7] in which π^- electron conjugated rigid skeletons are aligned in one direction with a layered structure in the smectic phase. Another category of LC semiconductors[8] features large, two-dimensional, disk-shaped π^- electron conjugated molecular cores, which are stacked in close molecular alignment in the columnar phase. High mobility is expected from these discotic LC (DLC) semiconductors, and two main types of DLC materials have been investigated. These are triphenylene derivatives[8] and phthalocyanine derivatives.[9] Both of these DLC materials become fluid when heated (and soluble with respect to organic solvents) because they contain long alkyl chains, resulting in columnar alignment self-assembly without segregation (crystallization).

However, the second DLC group, which has larger solid molecular core and larger molecular weight, exhibits higher viscosity and experiences more difficulty in achieving molecular alignment, although metal-phthalocyanine systems are noted for having excellent chemical stability with respect to oxidization (which reduces electron mobility), photon energy, and heating processes for practical semiconductor device applications. To enhance the self-assembly properties of metal-phthalocyanine derivatives, the concept of steric exclusion has recently been applied to the disk-shaped molecular skeletons,[10] and homeotropic alignment has been achieved by casting a chloroform solution onto a glass substrate.[11] So far, although high mobility has been measured in powdered phthalocyanine derivatives by means of pulse-radiolysis time-resolved microwave conductivity,[12] the obtained values cannot be divided into the contributions of the positive (hole) and negative (electron) carriers. The time-of-flight (TOF) technique[13] is useful for evaluating the mobilities of both polarities individually, but a spatially uniform molecular-alignment DLC film with large thickness (several μm order) is essential to measure precisely the photocurrent decay time after light-illumination extinction.

In this letter, we clarify the positive and negative carrier mobility behavior of a Cu-phthalocyanine-based DLC semiconductor with molecular self-assembly, based on TOF measurement using a super-cooled columnar-alignment DLC film[14] sandwiched by transparent electrodes on glass substrates.

Figure 1 shows the synthesized molecular structure of the Cu-phthalocyanine derivative of 2-(12-hydroxydodecyloxy)-3-methoxy-9,10,16,17,23,24-hexakis(3,4-didecyloxyphenoxy)phthalocyaninato copper(II)[11] that was used in this experiment. In the molecular structure, 12 long dodecyloxy chains developed a starburst-like configuration with 6 phenoxy groups. The long flexible peripheral chains and the large rigid phthalocyanine core induce liquid crystal-line properties. Here, the existence of oxygen atoms between the benzene ring and the phthalocyanine ring engender molecular steric exclusion in the columnar phase because the two ring planes become significantly tilted to the phthalocyanine core. The molecular alignment structure and the phase
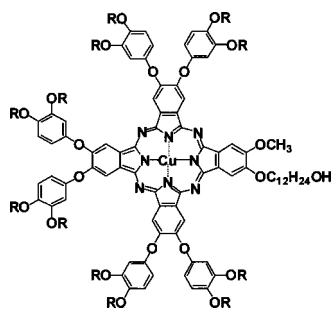
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FIG. 1. Molecular formula of the Cu-phthalocyanine-based DLC semiconductor that was used for the experiment. R represents $C_{10}H_{21}$ in this figure.

FIG. 3. Polarizing micrographs and molecular alignment models of the DLC cell for different temperatures.

transition temperature sequence have been examined in detail through x-ray diffraction measurements, differential scanning calorimetry, and polarizing microscope observations. The DLC semiconductor exhibits four different hexagonal columnar mesophases between 74.6 and 173.3 °C, a tetragonal columnar mesophase between 173.3 and 188.7 °C, and an isotropic phase above 188.7 °C.[11]

The DLC sample cell for the TOF measurement was fabricated by the following method. As shown in Fig. 2, the freshly synthesized powdered material was softened by heating at 120 °C. The DLC material was then sandwiched with rigid plastic spacer particles at the high temperature between 70-nm-thick transparent electrode films (ITO; In_2O_3:Sn) coated onto glass substrates. The thickness D of the DLC film between the substrates was controlled by the 5-μm-diameter spacer particles. The DLC film in the cell has an active area of 7 mm diameter, as shown in the photograph in Fig. 2. The cell contains no conventional alignment layers such as polyimide films.

The fabricated cell was heated at once to a temperature of 200 °C to exhibit the isotropic phase so that the tilted alignment[13] of the DLC columnar axis by the shearing substrates in the sandwiching process could not occur. It was then cooled to room temperature. During the thermal process, the phase transition was observed using a polarizing microscope, as shown in the upper photomicrographs in Fig. 3. The isotropic phase of the DLC film in the fabricated cell was transformed into the columnar phase. Namely, a tetragonal columnar mesophase without any domains (lower left model in Fig. 3) was observed first, and this mesophase was then transformed to the hexagonal columnar mesophase (lower right model in Fig. 3). In the hexagonal mesophase, large DLC domains of less than 1 mm were seen with different tilt angles slightly away from the direction normal to
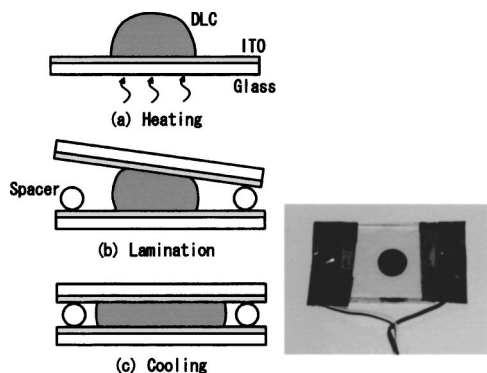
substrate surface plane. Subsequently, a semiconductor cell with molecular alignment could be fixed by supercooling of the hexagonal mesophase because of its extremely high viscosity. Consequently, the DLC molecules could be stacked and piled up approximately perpendicular to the substrate plane, even when sandwiched by ITO electrodes. The closely stacked phthalocyanine cores, which function as charge-hopping sites in the hexagonal mesophase, are useful for enhancing carrier mobility in the prepared cell.

The transmittance spectrum of the prepared cell is shown in Fig. 4(a). The DLC film strongly absorbs ultraviolet light. This wavelength of incident light is suitable for exciting the DLC and for generating photocarriers. Therefore, pulsed light (wavelength: 337 nm, pulse width: 5 ns) from an N_2-gas laser was used as the incident light onto the DLC cell in a TOF measurement system (TOF-301 from Optel), as shown in the middle schematic diagram of Fig. 4. The induced photocarriers were moved by the applied voltage between the ITO electrodes, and the decay time T of the electric current due to the photocarriers drifting through the DLC film was determined after the light illumination was extin-

FIG. 2. Fabrication process of the DLC cell for TOF measurement and the appearance of the prepared DLC cell.

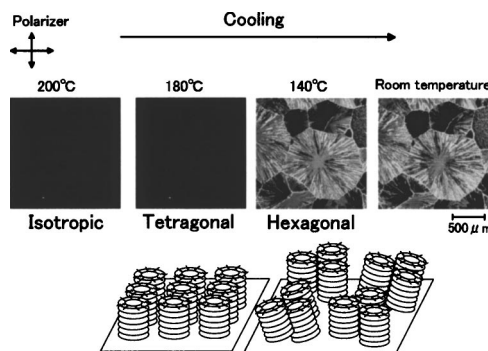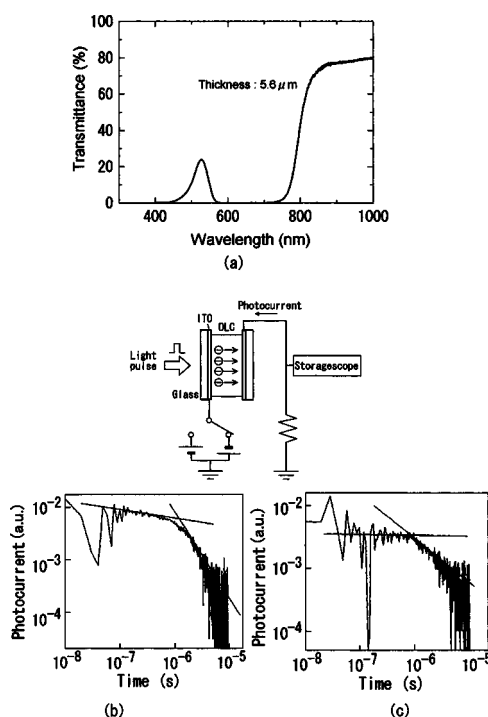FIG. 4. Transmission spectrum (a) of the fabricated cell, and photocurrent decay properties for negative (b) and positive (c) charge carriers.
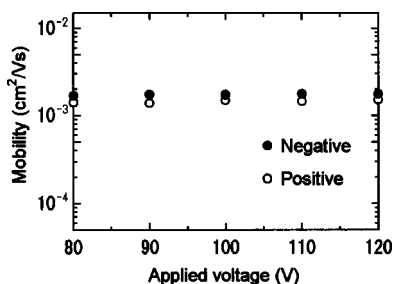
FIG. 5. Mobility property of negative and positive charges for various applied voltages.

guished. In this experiment, by changing the polarity of the applied voltage, the electron and hole carrier mobilities can be evaluated individually. Here, if the electric field intensity is expressed as E, the charge mobility can simply be evaluated as D/TE.

The lower left and right graphs in Fig. 4 show the intensities of the observed photocurrent for the electron and hole drift after light distinction, respectively. Here, a bias voltage of 100 V was applied to a 5.6-μm-thick DLC cell. The decay-starting times for the electrons and the holes are 1.21×10^{-6} and 1.05×10^{-6} s, respectively. From these values, it was found that the DLC semiconductor has a high electron charge mobility of 2.60×10^{-3} cm^2/V s and a hole mobility of 2.99×10^{-3} cm^2/V s at room temperature. It was clarified that both the negative and positive carrier mobilities are high, with values that are of the same order. We fabricated several DLC cells with different thickness from 5 to 6 μm in this experiment, and found that these electron and hole mobilities retained the values in the range of $1-3 \times 10^{-3}$ cm^2/V s. While the measurement of mobility was restricted by levels of dark current of DLC and discharge noise of the gas laser, we could evaluate the positive and negative mobility behavior in our experiment.

We then measured the influence of applied bias voltage on the mobilities using a DLC cell with a thickness of 5.0 μm. From the experimental result of Fig. 5, we confirmed that the mobility for negative charge carrier are similar to that of positive carrier for any voltage. Besides, the mobilities were almost constant for the voltage change, although a slight increase of mobility is recognized. Here, under applied voltages of 80 V, the photocurrent wave form was not observed precisely due to large electric noise, and the cell had dielectric breakdown over 130 V. When the measurement temperature was increased from room temperature, the mobility values of the cell used in Fig. 5 were slightly increased (applied voltage is constant at 100 V). The cell, heated at 110 °C, which is in the hexagonal phase, showed a negative charge mobility of 2.40×10^{-3} cm^2/V s and a positive mobility of 2.17×10^{-3} cm^2/V s, respectively. Over 120 °C, we did not confirm decay wave form because dark-current level increased, which is considered to be due to ion current in the DLC. As a result, we could not know the mobility behavior at the hexagonal-to-tetragonal phase transition in the experiment.

Generally, negative carrier mobilities are recognized as being much lower than positive carrier mobilities in many other organic semiconductors, including conventional vacuum-deposited films of non-liquid-crystalline Cu-phthalocyanine.[15] Although a vacuum-deposited film of a non-liquid-crystalline fluorinated phthalocyanine derivative has shown high electron mobility,[16] it cannot function as a p-type semiconductor because of its low hole mobility. Otherwise, similar behavior between the negative and positive carrier mobilities were found in smectic-phase LC semiconductors with the rod-shaped molecules of phenylnaphthalene derivatives.[17] We infer that the high negative/positive mobility of our DLC semiconductor is due to molecular fluidity and self-alignment, since microscopic alignment defects are suppressed, which would generate carrier traps, reducing electron mobility. Although it is thought that the high negative/positive mobility is mainly due to the high purity of this material without chemical contaminant species generating carrier traps, similar mobility behavior has not been obtained in any high purity non-liquid-crystalline Cu-phthalocyanine films so far. Detailed relationships between liquid crystalline nature and negative/positive mobility must be investigated in future works.

In conclusion, we measured the charge carrier mobility in a Cu-phthalocyanine-based DLC semiconductor using the TOF method. A DLC semiconductor cell with molecular alignment was obtained by supercooling of the columnar phase, even when sandwiched by ITO electrodes. It was clarified that the carrier mobility for both electrons and holes reached the high value of 10^{-3} cm^2/V s at room temperature.

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