Fabrication of Thin Films Using a Soluble Metal Phthalocyanine Salt and Their Photoconductive Properties

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We fabricated thin films from an acetone solution containing $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$ (Pc = phthalocyanine). The quality of films was improved by the pretreatment of the substrate with 3-trimethoxysilylpropyl chloride. The fabricated films exhibit the photoswitching phenomenon for ultraviolet (UV) irradiation.

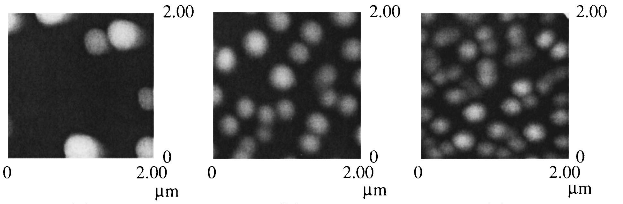
The study of molecular electronic devices using thin films has become of interest both for basic research and applications. Up to now, the best-studied films are polymer films prepared from solution and molecular films fabricated by the vacuum-evaporation technique. There are few reports for the device fabrication using thin films of molecular anion (cation) salts.[1–4]

In this letter, we report the fabrication of thin films from an acetone solution containing $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$. The molecular anions, $[Fe^{II}(Pc)(CN)_2]^{2-}$ and $[Fe^{III}(Pc)(CN)_2]^{-}$ have unique features. First, these phthalocyanine anions form various simple salts soluble to organic solvents, while the solubilities of planar metal phthalocyanines (Ni(Pc), Cu(Pc), etc.) to ordinary organic solvents are quite low at room temperature. Secondly, $[Fe^{III}(Pc)(CN)_2]$ has an $S = 1/2$ magnetic moment, and the g-factor of the magnetic moment is highly anisotropic for the field orientation. By oxidizing the $[Fe^{III}(Pc)(CN)_2]$ unit electrochemically, conducting charge-transfer salts such as $TPP[Fe^{III}(Pc)(CN)_2]_2$ (TPP = tetraphenylphosphonium) are obtained. The crystals of these salts exhibit giant-negative magnetoresistance at low temperatures below 50 K.[5] In contrast to $[Fe^{III}(Pc)(CN)_2]$ salts, the transport properties of $[Fe^{II}(Pc)(CN)_2]$ salts have not been reported yet. However, the solubilities of $[Fe^{II}(Pc)(CN)_2]$ salts to organic solvents are generally higher than those of $[Fe^{III}(Pc)(CN)_2]$ salts, when both salts contain the same cation. Therefore, $[Fe^{II}(Pc)(CN)_2]$ salts are more suitable than $[Fe^{III}(Pc)(CN)_2]$ salts as for the film fabrication from a solution.

The thin films of $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$ were fabricated on glass substrates from an acetone solution saturated with $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$ by the spin-coating technique. In order to measure the electrical resistivity, two gold electrodes were in advance prepared on a glass substrate by the vacuum evaporation. The width and gap of the two electrodes are 30 mm and 80 μm, respectively. Some of the glass substrates were pretreated by 3-trimethoxysilylpropyl chloride before the gold evaporation.

The observation of the thin films was done by use of AFM. The photocurrent was measured using an electrometer and a Hg–Xe lamp for a UV light source. The characterization of the fabricated films was done using a micro-Raman spectrometer. The size of the light spot focused under the microscope was less than 1 μm in this apparatus.

Figure 1 shows AFM images of the films fabricated on the glass substrates pretreated in different conditions. The grains of $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$ are clearly seen. The sizes of the grains on the untreated substrate are 200–300 nm in diameter. The size becomes small by the pretreatment of the substrate using 3-trimethoxysilylpropyl chloride. By heating the fabricated film on the pretreated substrate (100 °C, 3 min), the grain size becomes further small. In the following, we will simply refer to the film fabricated on the untreated substrate as "untreated" film, to the film fabricated on the pretreated substrate but not heated up as "pretreated" film, and to the film heated up after the fabrication on the pretreated substrate as "heated" film.



(a) (b) (c)

Figure 1. AFM images of $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$. (a) untreated film, (b) pretreated film and (c) heated film (see the definitions in the text).

Figure 2 shows Raman spectra of a bulk crystal and an untreated film of the $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$. We have measured the Raman spectra on a grain and on a gap region between grains for the untreated film. Since the Raman spectrum on the grain completely coincides with that of the bulk, we concluded that films of $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$ are surely formed on the substrate. The Raman spectrum on the gap region is also very similar to the other two spectra, although the spectral

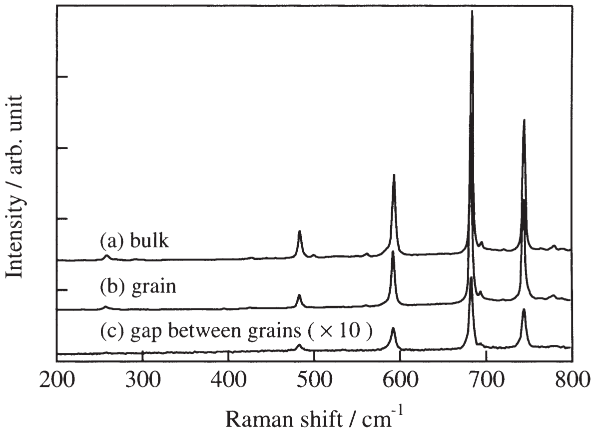


Figure 2. Raman spectra of $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$. (a) a bulk crystal, (b) a grain in the untreated film and (c) a gap region between grains in the untreated film.

intensity is seriously decreased. This suggests that a very thin film of $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$ is formed even in the gap regions.

In metal coordinate complexes such as $[Fe^{II}(Pc)(CN)_2]$, LMCT (ligand-to-metal charge transfer) or MLCT (metal-to-ligand charge transfer) is expected to occur through photoexcitation. If it occurs, excess electrons or holes are produced in the π-orbital, and photocurrent generation is expected. In this respect, we measured the photoconductivity for the fabricated thin films in the air. Figure 3a shows the photocurrent responses of the pretreated film at the applied voltage of 10 V. The photocurrent changes are due to opening and closing a shutter attached to the UV light source. Since the changes occur immediately, we concluded that they are not due to the sample heating accompanying the irradiation. This phenomenon was not observed for visible irradiation. Figure 3b shows the *I–V* characteristics of the pretreated film under the UV irradiation. The dark current was less than 10 pA at all the applied voltages between −10 V and 10 V. Under the UV irradiation, the current drastically increases and reaches up to 1.7 nA at the applied voltage of 10 V. Interestingly, the *I–V* curve under the UV irradiation is not linear and similar to that of phototransistor. The nonlinear behavior is observed also in the untreated and heated films. The photocurrent of the heated film was almost the same as that of the pretreated film. However, the photocurrent of the untreated film was approximately half of the pretreated film, and was seriously affected by experimental conditions especially by the humidity, although the dark current of the untreated film was almost the same as that of the pretreated film. This may be due to the poor quality of the untreated film. Figure 3c shows the decay of the photocurrent during the successive *I–V* sweep. For simplicity, only the photocurrent at the applied voltages of 10 V and −10 V is plotted versus time. The figure shows that the photocurrent decreases with the lapse of time. We suspected that the decrease in the photocurrent is due to the chemical reaction of $[Fe(Pc)(CN)_2]$ with oxygen in the air. Then, we investigated the effect of the sample-space atmosphere on the photocurrent decay. Figure 4 shows the results. As can be seen from this figure, the decrease in the photocurrent is suppressed by the nitrogen-gas flow around the sample space. This strongly suggests that the photocurrent decay is due to the chemical reaction.

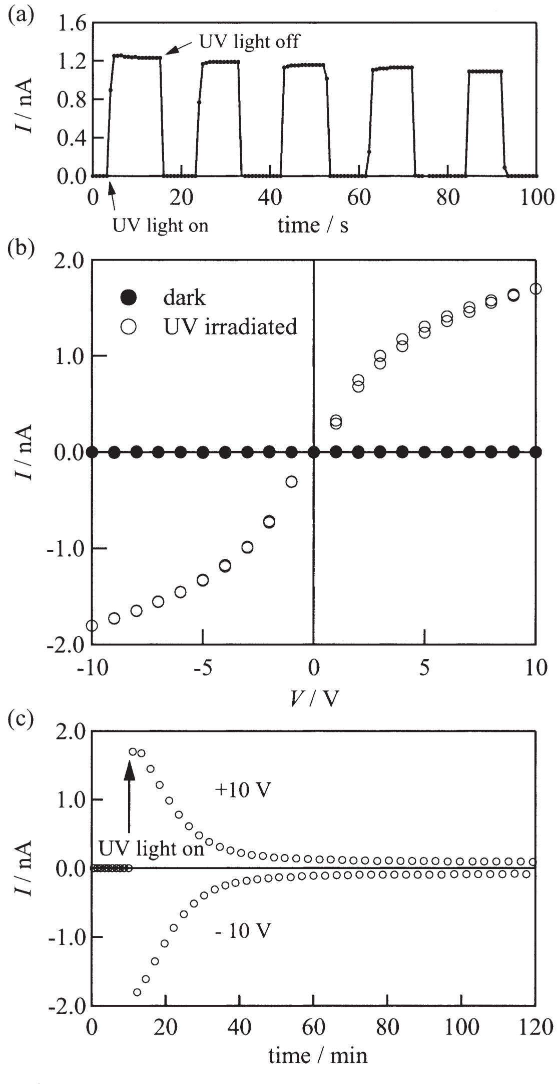


Figure 3. Photocurrent of the pretreated film in the air. (a) Photocurrent response. (b) *I–V* characterisitic. (c) Photocurrent-decay during the successive *I–V* sweep.

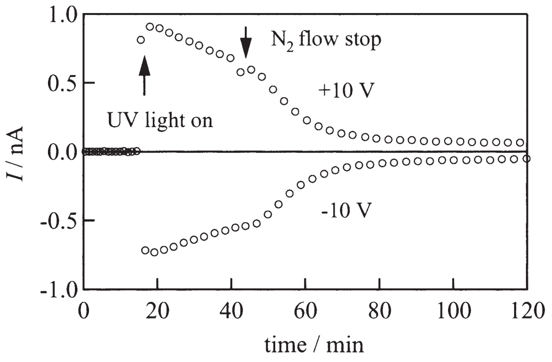


Figure 4. The effect of the sample-space atmosphere on the photocurrent decay for the untreated film.

In conclusion, we have fabricated the films of $[(n\text{-}C_7H_{15})_4N]_2[Fe^{II}(Pc)(CN)_2]$ from an acetone solution. The quality of the films was improved by the pretreatment of the substrates with 3-trimethoxysilylpropyl chloride. The fabricated films exhibit large photocurrent response for the UV irradiation. The thin films of soluble phthalocyanine are useful for the fabrication of electric devices. The FET fabrication using a soluble phthalocyanine film will be published elsewhere.

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