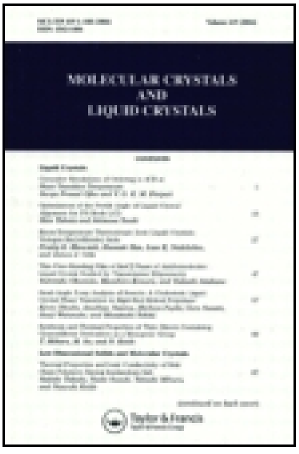

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Doping Effect in Merocyanine Evaporated Films

S. Kuniyoshi [a] , K. Kudo [a] & K. Tanaka [a]
[a] Department of Electrical and Electronics Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba, Japan
Version of record first published: 24 Sep 2006.

Mol. Cryst. Liq. Cryst. 1993, Vol. 227, pp. 199–205
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

DOPING EFFECT IN MEROCYANINE EVAPORATED FILMS

S. KUNIYOSHI, K. KUDO, and K. TANAKA
Department of Electrical and Electronics Engineering,
Chiba University, 1-33, Yayoi-cho, Inage-ku,
Chiba, Japan

ABSTRACT Doping effect of organic molecules in merocyanine evaporated films are investigated. As organic dopant, tetracyanoquinodimethane and tetrathiafulvalene were employed and the merocyanine films containing organic dopant were fabricated by using a co-evaporation technique. The electrical properties of Al/MC/Ag Schottky cell were examined by current-voltage, thermally stimulated current and capacitance-temperature measurement. Forward current in TCNQ-doped-MC sample was increased with increasing concentration of TCNQ. On the contrary, forward current in TTF-doped-MC sample was decreased with increasing TTF concentration.

INTRODUCTION

The evaporated merocyanine (MC) films have a property of p-type organic semiconductor[1-5] and a optical absorption band in the visible range, and were applied to photo-voltaic cell. The power conversion efficiency in Schottky type solor cells using MC film is relatively high. There are several reports on these high photo-voltaic effect and mechanism of photo-carrier generation in MC evaprated film.[3-5] It may be expected that higer efficiency of the MC solar cell can be obtained by increasing bulk conductivity of MC. In this study, we have investigated the electrical properties of evaporated MC films doped with tetracyanoquinodimethane (TCNQ) and tetrathiafulvalene (TTF) which are electron acceptor and donor, respectively. The doping of TCNQ and TTF was accomplished by co-evaporation technique. The electrical properties were examined by current-voltage (I-V), thermally stimulated current (TSC) and capacitance-temperature (C-T) measurements.

EXPERIMENTAL

The chemical structures of MC,TCNQ and TTF used in this study are shown in figure 1. The MC,TCNQ and TTF were purchased from the Japanese Research Institute for Photosensitizing Deys Co., Wako Pure Chemical Industries,Ltd. and Aldrich Chemical Co., respectively. These materials were used without further purification.

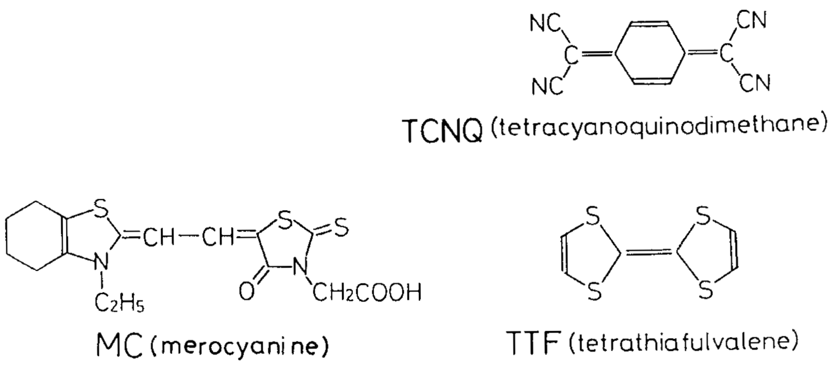

FIGURE 1 Chemical structure of MC, TCNQ and TTF molecules used in this study.

The samples used in this experiment are Schottky type cell of Al/MC/Ag structure (see fig.2). The diameter of upper Ag electrode is 5 mm.

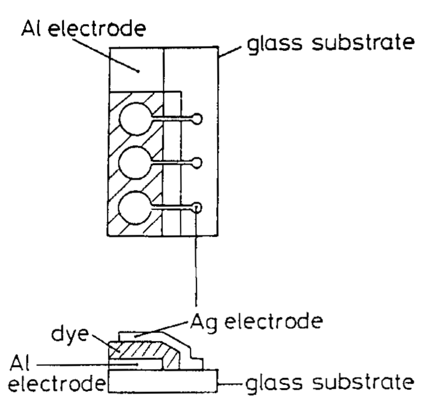

FIGURE 2 Schematic diagram of the Al/MC layer/Ag Schottky type cell used in this study.

A schematic view of the evaporation system is shown in figure 3. For the preparation of undoped MC sample, the powder source of MC was loaded into a crucible. At a base pressure of $1x10^{-5}$ Torr, the crucible was heated to 285±15°C. This temperature was chosen to avoid the molecular decomposition and to achieve a proper deposition rate. The thickness of evaporated MC film is 1500 Å. In optical absorption spectra for evaporated MC, there are two peaks at 515 nm and 545 nm, which are due to MC dimer and monomer respectively. In preparing the doped sample, doping of TCNQ and TTF was accomplished by co-evaporation with MC. Temperature of crucible was kept at 200±5°C for doping of TCNQ and TTF respectively.

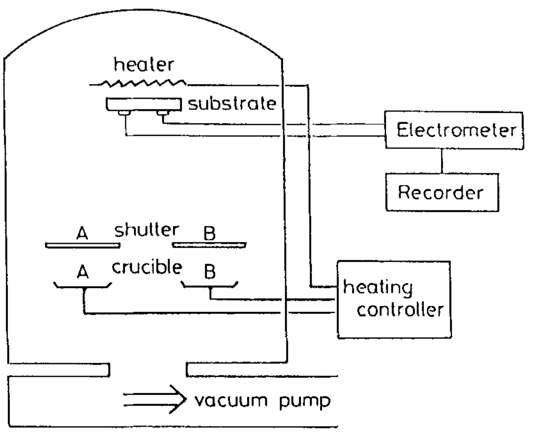

FIGURE 3 Schematic view of the co-evaporation system.

The I-V characteristics were measured by applying voltages between -2 and 2 V in nitrogen atmosphere at room temperature using YHP 4140B electrometer. At forward bias condition the upper Ag electrode was positively biased with respect to the lower Al electrode.

In TSC and C-T measurements, the samples were placed in a shielded cryostat which could be cooled from room temperature to 100 K and heated at a constant rate of approximately 0.05 K/s. The temperature was measured with a thermocouple placed near the sample. The TSCs were measured by using a KEITHLEY mode 617 programable electrometer. C-T curves were obtained by using the linear voltage ramp technique.

RESULTS AND DISCUSSION

Figure 4 shows I-V characteristics of undoped sample, TCNQ-doped and TTF-doped samples. Rectifying characteristics were obserbed for all samples. At forward bias condition the current rises at the applied voltage of 1 V, and increases rapidly with increasing applied voltage. In this voltage region, the current for the TCNQ-doped sample became greater than that for undoped sample, but for the TTF-doped sample became smaller. This result sugests that the resistance of MC film could be controlled by doping of TCNQ and TTF which are electron accepter and donor respectively, because the magnitude of current in this region is mainly dominated by bulk resistance of Schottky cell. The dependence of capacitance,C, on applied voltage,V, was measured for each sample at room temperature.

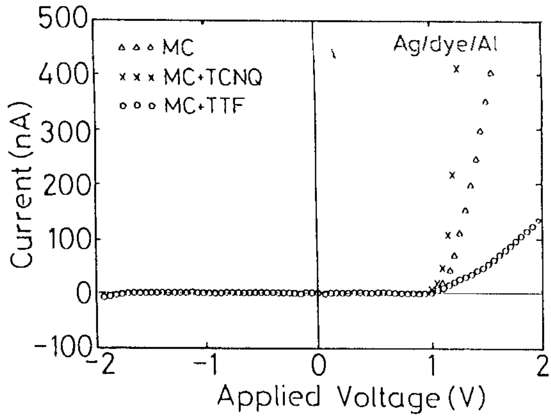

FIGURE 4 I-V characteristics for Al/MC/Ag Schottky cell in dark. X, TCNQ-doped ; Δ, undoped ; O ,TTF-doped sample.

The data, $1/C^2$, was plotted as a function of V ,and the good linearity was obtained. The carrier concentration calculated from the slope of this data are $1.6\times10^{18}/cm^3$ and $3.5\times10^{18}/cm^3$ for undoped and TCNQ-doped sample respectively. For beter understanding of this change in resistivity of doped MC, TSC and C-T spectra were measured. Figure 5(a) shows the dependence of TSC for undoped-sample on carrier-injection-voltages and figure 5(b) for TCNQ-doped-sample. In figure 5(a), the peaks are broad and a probably made up of several overlapping peaks.

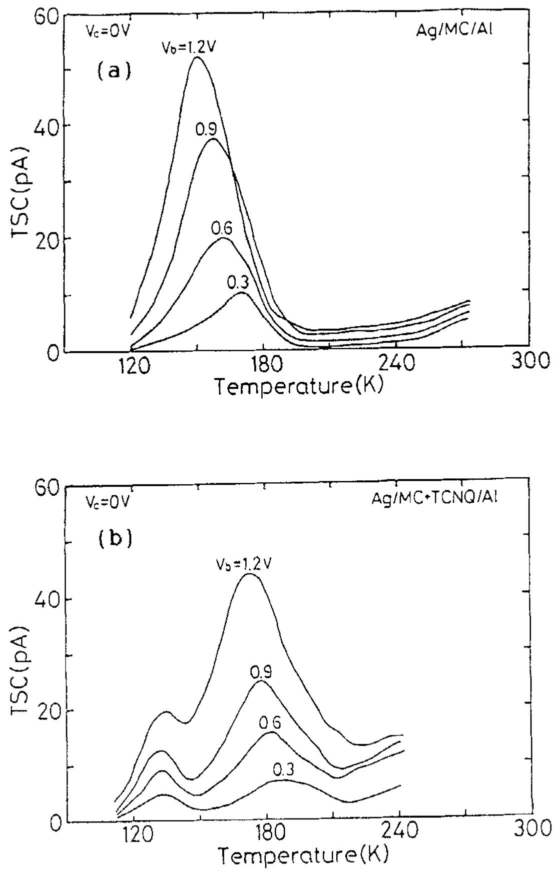

FIGURE 5 Plot of the TSC curves of current versus temperature for different injecting voltages at a injecting temperature of 273 K. (a), undoped-MC sample; (b), TCNQ-doped-MC sample.

The peaks generally occur at approximately 170 K, although at high applied voltages ther is a downward shift and at low appliedvoltages an upward shift in the peak position. This dependence of peak position on applied voltages is also shown in figure 5(b). To check this behaviour of peak positions we measured the dependence of TSC on collecting voltages which are applied to the sample while the sample is heating. At high collecting voltages ther is a downward shift of peak position. This result suggests that Pool-Frenkel effect occurs in the sample. In the TSC spectra for TCNQ-doped-sample (figure 5(b)), a new peak occurs at approximately 130 K, but no new peak occurs in the TSC spectra for TTF-doped-sample. The activation energies of these peaks are 0.13 and 0.23 eV for peaks at 130 K and 170 K respectively.

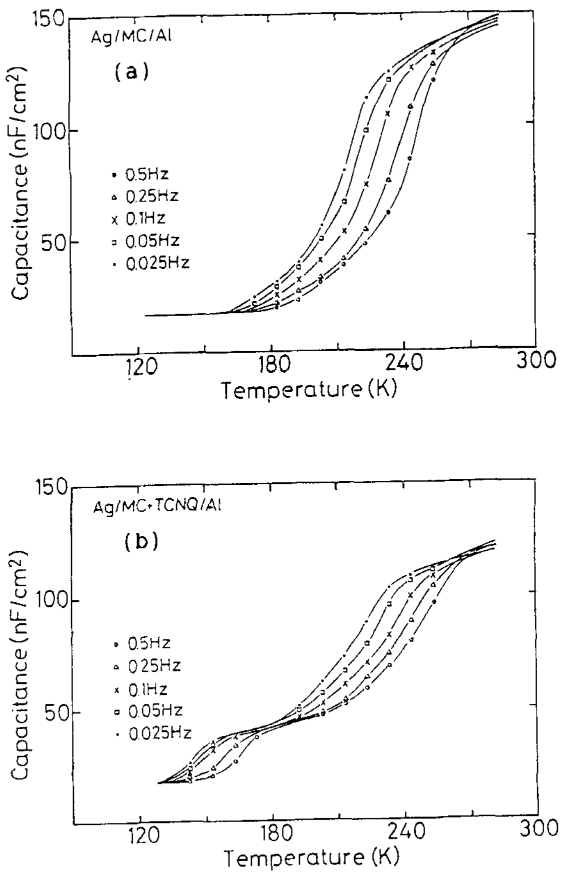

FIGURE 6 Plot of the C-T curves of capacitance versus temperature for different frequency of triangular wave voltage with an amplitude of 0.15 V. (a), undoped-MC sample; (b), TCNQ-doped-MC sample.

The measurement procedure for obtainingthe C-T curve consisted of applying a triangular wave voltage to the Schottky cell by means of a NF FG100D function generator, and recording the corresponding displacement current vs applied voltage curve at various temperature using a Keithley 617 electrometer and an X-Y recorder. An amplitude of applied voltage is 0.15 V and frequency is varied from 0.025 Hz to 0.5 Hz. Figure 6(a) shows exeperimental C-T curves for undoped-MC sample. In this figure, a capacitance step occurs at approximately 230 K, and the step position shifts to upward with increasing frequency of triangular wave voltage. In the C-T curves for TCNQ-doped-MC sample (figure 6(b)), a new step occurs at aproximately 150 K, but no new step occurs in the C-T curves for TTF-doped-MC sample. The activation energy of these steps can be evaluated from the step shift.[6] The activation energies are 0.5 eV and 0.27 eV for the step at 150 K and 230 K respectively.

From these results, it is suggested that the TSC peak at 130 K and the capacitance step at 150 K are due to the same relaxation process and the TSC peak at 170 K corresponds to the capacitance step at 250 K, however their activation energies are not agreement with each other. The disagreement between activation energies of TSC and C-T may be due to the Pool-Frenkel effect, because the amount of space charge in the sample during TSC measurement is greater than that during C-T measurement.

CONCLUSION

In this study, we have measured the I-V, TSC and C-T characteristics of MC evaporated films containing TCNQ and TTF, and compared the data with the undoped-merocyanine sample. For the TCNQ-doped-MC sample, the bulk conductivity increased with doping, and a new TSC peak and capacitance step appeared at low temperature. However the bulk conductivity decreased for TTF-doped-MC sample, and no new TSC peak appeared at low temperature. These results suggest that shallow acceptor and donor (compensation) centers are introduced in merocyanine evaporated films by doping of TCNQ and TTF, and the electrical properties of merocyanine films is controlled by those centers.

REFERENCES

1. H. Meier, Organic Semiconductors, Verlag Chemie, Weinheim (1974).
2. H. Meier, W. Albrecht and U. Tschirwitz, Photogr. Sci. Eng., 18, 276 (1974).
3. K. Kudo and T. Moriizumi, Jpn. J. Appl. Phys., 20, L-553 (1981).
4. K. Kudo and T. Moriizumi, Appl. Phys. Lett., 39, 609 (1981).
5. D. L. Morel, A. K. Ghosh, T. Feng, E. L. Stogryn, P. E. Purwin, R. F. Shaw and C. Fishman, Appl. Phys. Lett., 32, 495 (1978).
6. A. J. Twarowski, J. Chem. Phys., 77, 4698 (1982).