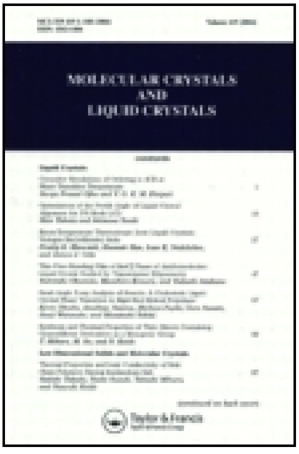

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Temperature-Dependent I-V Characteristics and Thermal Annealing Effects of C_{22}-Quinolium(TCNQ) Langmuir-Blodgett Films

Tae Wan Kim [a] , Dong-Myung Shin [b] , Il-Seok Song [b] , Dou-Yol Kang [b] & Young-Soo Kwon [c]
[a] Dept. of Physics, Hong-Ik Univ., 72-1 Mapogu, Seoul, KOREA
[b] Dept. of Electrical and Control Engineering, Hong-Ik Univ., Seoul, 121-791, KOREA
[c] Dept. of Electrical Eng., Dong-A Univ., Sahagu, Pusan, KOREA
Version of record first published: 04 Oct 2006.

Mol. Cryst. Liq. Cryst. 1994, Vol. 247, pp. 233–242
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

TEMPERATURE-DEPENDENT I-V CHARACTERISTICS AND THERMAL ANNEALING EFFECTS OF C_{22}-QUINOLIUM(TCNQ) LANGMUIR-BLODGETT FILMS

TAE WAN KIM
Dept. of Physics, Hong-Ik Univ., 72-1 Mapogu, Seoul, KOREA
DONG-MYUNG SHIN, IL-SEOK SONG and DOU-YOL KANG
Dept. of Electrical and Control Engineering, Hong-Ik Univ., Seoul, 121-791 KOREA
YOUNG-SOO KWON
Dept. of Electrical Eng., Dong-A Univ., Sahagu, Pusan, KOREA

Abstract Electrical properties and thermal annealing effects of C_{22}-quinolium(TCNQ) Langmuir-Blodgett(LB) films were studied. Typical current-voltage(I-V) characteristics along the perpendicular direction show an anomalous behavior of breakdown near the electric-field strength of 10^6 V/cm. From the study of I-V characteristics in the high-electric field region, it is found that there is a contribution of joule heating in addition to the electrical effect. To see the thermal influence of the specimen, current was measured as a function of temperature(20 ~ 180℃). It shows that the current increases about 4 orders of magnitude near 60 ~ 70℃, and remains constant for a while up to ~ 150℃ and then suddenly drops. Such increase of current near 60 ~ 70℃ seems to be related to a softness of alkyl chains. Besides the electrical measurements, UV/visible absorption(300 ~ 800nm) of the thermally annealed sample was measured to see the internal-structure change. It is found there are four characteristic peaks. At 494nm, the optical absorption of the thermally annealed specimen at 60℃ starts to increase and stays almost constant upto ~ 140℃. And eventually it disappears above 180℃.

INTRODUCTION

Memory capacity in a given volume has been tremendously increased with a remarkable progress of semiconductor technology. These devices are normally based on inorganic materials such as silicon, and a size is the order of micron(10^{-6}m). Near future it is expected that the geometrical size can be reduced to nanometer(10^{-9}m) by using molecular-electronic devices based on organic materials. For these devices to be more practical, we have to produce ultra-thin films. The Langmuir-Blodgett(LB) technique[1] has been proposed as a suitable method for a production of ultra-thin film of various organic materials. This technique has the advantage in controlling a thickness and orientation of the molecules.

TCNQ(tetracyanoquinodimethane) complexes have been attractive materials for a well-conducting system.[2] We have previously reported an anisotropic electrical conductivity of C_{22}-quinolium(TCNQ) LB films.[3] A measured conductivity along the lateral direction was higher than the perpendicular one by the order of 10^7 at room temperature. Current-voltage(I-V) characteristic curve in the perpendicular direction shows an ohmic behavior in the low-electric field region, and a nonlinear effect starts to occur in the high-electric field region. Its conduction mechanism seems to be space-charge limited current(or Child effect) and Schottky effect. Its mechanism is still controversial topic.[4] Due to these effects, there is a sharp increase of current in the high-electric field region. When the electric field exceeds further, there is an anomalous phenomena similar to breakdown. There is not many work done on this anomalous behavior occuring in the high-electric field.

In this work, we have studied (a)the anomalous phenomena in the high-electric field region through the I-V characteristics in the high-electric field region, and (b)the thermal annealing effects of C_{22}-quinolium(TCNQ) LB films through a UV/visible absorption by changing temperatures in the range of 20 ~ 220℃.

EXPERIMENTAL DETAILS

Preparation and π-A Isotherm

Synthesis, characterization, and purity of C_{22}-quinolium(TCNQ) molecules have been already published elsewhere[5] in our group. This molecule is composed of hydrophilic and hydrophobic part. Normal optical-microscope slide glass(76mm x 26mm x 1mm) was used as a substrate. The substrate was ultrasonically cleaned 3 times in an ultra-pure water and then dipped into a $K_2Cr_2O_7$ saturated solution of H_2SO_4 for 24 hours. It was thoroughly rinsed with distilled water and cleaned again in sonicator(Branson 2200) 5 times.

A Kuhn-type LB apparatus was used, which was manufactured by Kyowa Co. (Model:HBM-H). Purified-distilled water(~18MΩ·cm) and chloroform were used as a subphase and a solvent, respectively. After spreading the solution on the subphase, 30 minutes were waited for the solvent to evaporate. Since the π-A isotherm depends on the environments, it was studied by giving different conditions of temperature(12.5 ~ 50℃), pH(1.4 ~ 8.4), barrier moving speed, and spreading amount of solution.

A Z-type formation of the LB film has been deposited on the glass substrate within 16 layers of thickness under the surface pressure of 45mN/m. A vertical dipping method was employed with a dipping speed of 4mm/min.

Electrical Measurements

Current-voltage characteristics were measured by employing a conventional two-probe method. Aluminum electrodes were vacuum-deposited at a pressure of $\sim 10^{-5}$ Torr on both top and bottom side of the specimen. Area of the electrode is $7 \sim 9mm^2$. Silver paste was used to attach a thin wire(~50μm dia.) to the electrode. The specimen was kept inside a shield box.

Programmable Keithley 238 electrometer was used as a voltage source and a current measure, which supports step or pulse outputs. This electrometer was controlled by IBM 486-compatible computer. Temperature of the specimen was varied in the range of 20 ~ 220℃. Thermocouple was used as a temperature sensor.

Optical Measurements

UV/visible absorption of the LB film was measured in the range of 300 ~ 800nm using HP 8452A spectrophotometer. To see the thermal annealing effect, the absorption spectra of the specimen was measured after a heat treatment in a bath. Heat-treatment process is the following. After taking the absorption spectra at room temperature, specimen was put into the heat bath. It was heated upto a certain temperature with an increment ratio of 2℃/min. And then let it cool down to room temperature naturally and measure the absorption spectra.

EXPERIMENTAL RESULTS AND DISCUSSION

π-A Isotherm

From the measurements of π-A isotherm of C_{22}-quinolium(TCNQ) at different environments, the following optimum conditions were obtained for the film deposition: temperature 25℃, surface pressure 45mN/m, pH 5.6(pure water), spreading amount of solution $2.11 \times 10^{14} \sim 2.64 \times 10^{14}$ molecules/cm^2. Detailed information can be found in the reference 3. Figure 1 is a typical π-A isotherm obtained at the above conditions. As the area is compressed, the surface pressure increases monotonically.

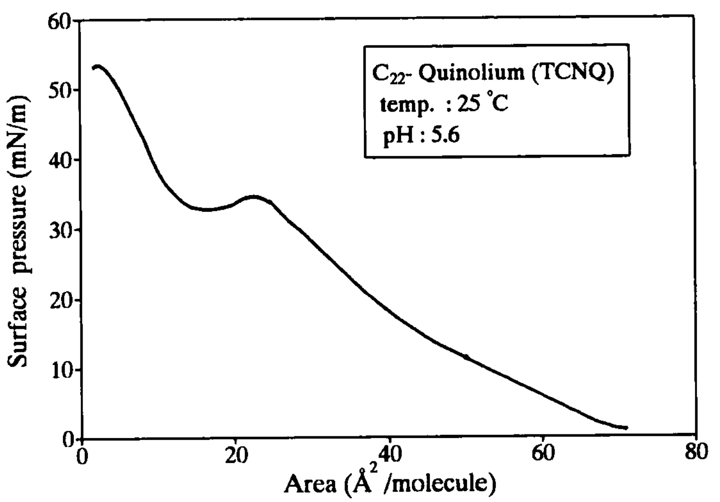

FIGURE 1 Typical π-A isotherm of C_{22}-quinolium(TCNQ) on the water subphase.

Current-Voltage Characteristics

We have investigated the I-V characteristics along the perpendicular direction. Figure 2 shows a difference of I-V characteristics measured at room temperature when the step or pulse voltage is applied. The duration time of each step is 4s and the off-time between the pulse is set to 4s. General feature of those two curves is similar. As the applied voltage increases, the current increases upto a certain value. Its characteristics have been already explained by conduction mechanisms of ohmic, space-charge limited current(or Child effect), and Schottky effect. Since our concern is the anomalous behavior in the high-electric field region, we are not going to discuss about the phenomena in low-electric field.

If the anomalous phenomena is due to an intrinsic effect only, it is expected that the breakdown voltage is independent of the type(step or pulse) of applied voltage. However, as is seen in Figure 2, the breakdown voltage is higher when the step voltage is applied. This implies that the anomalous behavior is partially associated to an internal thermal effect, possibly joule heating.

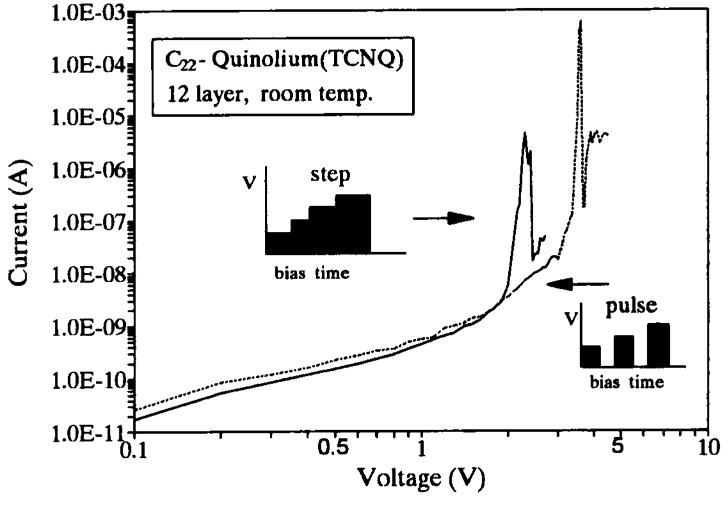

FIGURE 2 Current-voltage characteristics of the 12-layer C_{22}-quinolium(TCNQ) LB films at room temperature with the application of step and pulse voltage.

Next we have observed a difference in the I-V characteristics by varying a duration time of the pulse (2, 4, 8, and 16s) (See Figure 3). A time interval between the pulse (off time) is set to 4s in every measurement. It is found that the breakdown voltage shifts to the lower one as the duration time becomes longer even in the pulse voltage. This result says that the short duration time of pulse generates less joule heat in the high-electric field and, hence, is appropriate in the electrical characterization of the materials.

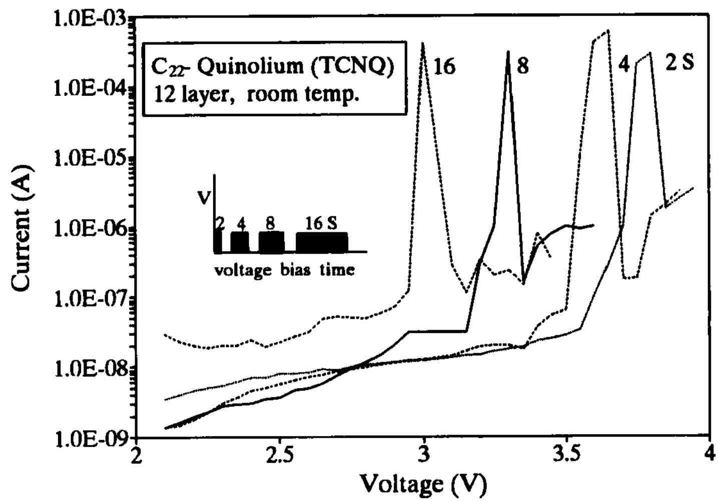

FIGURE 3 Current-voltage characteristics of the 12-layer C_{22}-quinolium(TCNQ) LB films at room temperature when the different duration time of pulse is applied.

Next, an external heating effect has been studied by measuring temperature-dependent I-V characteristics in the range of 20 ~ 180 ℃. Figure 4 displays a current-temperature (I-T) relation at 3 different bias voltages (0.5, 1, and 1.5V), which are lower than that of breakdown. Heating rate was 2℃/min. General feature of the I-T curve is similar to each other regardless of the bias voltage. In the measured range, current widely depends on the temperature. There is an increase of current about 4 orders of magnitude in the range of 60 ~ 70℃. Current stays almost constant in 80 ~ 150℃, and then suddenly drops more than 1 order of magnitude. The sharp rising of current near 60 ~ 70℃ seems to be related to a softness of alkyl chains. The sudden drop of current near 150℃ may be from a damage of the constituent components of the specimen, which are not clearly identified yet. To understand the internal-structure change of the film depending on the temperature, UV/visible absorption spectra of the thermally annealed specimen was studied.

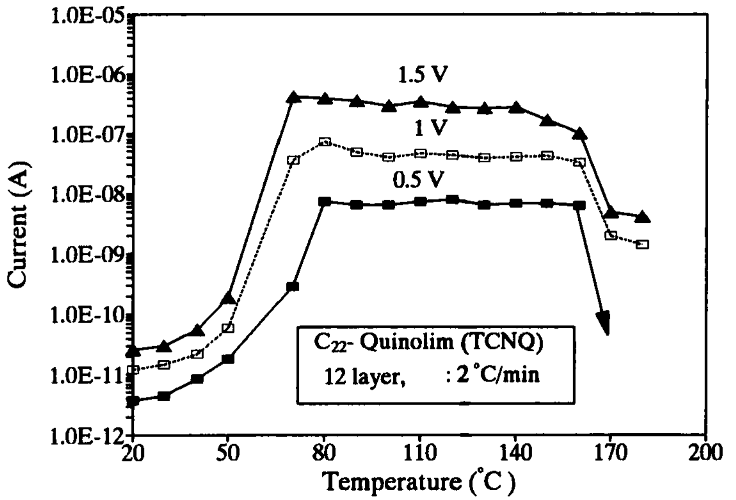

FIGURE 4 Current-temperature relation of C_{22}-quinolium(TCNQ) LB films at 3 different bias voltages (0.5, 1, and 1.5V).

Thermal Annealing Effects

Thermal annealing effects of the film were studied by UV/visible (300 ~ 800nm) absorption in the temperature range of 20 ~ 220℃. Figure 5 displays the absorption spectra of the 12-layer C_{22}-quinolium(TCNQ) LB films annealed at several temperatures. There are four characteristic peaks at 320, 380, 494, 678nm wavelengths.

A physical interpretation of each peak is not conclusive at present. If we trace the peak at 494nm which is supposed to be an intramolecular excitation of the TCNQ, it gradually increases with increasing temperature to ~ 100℃. The spectrum changes a little when the temperature increases further from 100℃ to 140℃. And then it starts to disappear as the temperature increases. The relative absorption intensity at 494nm is shown in Figure 6 as a

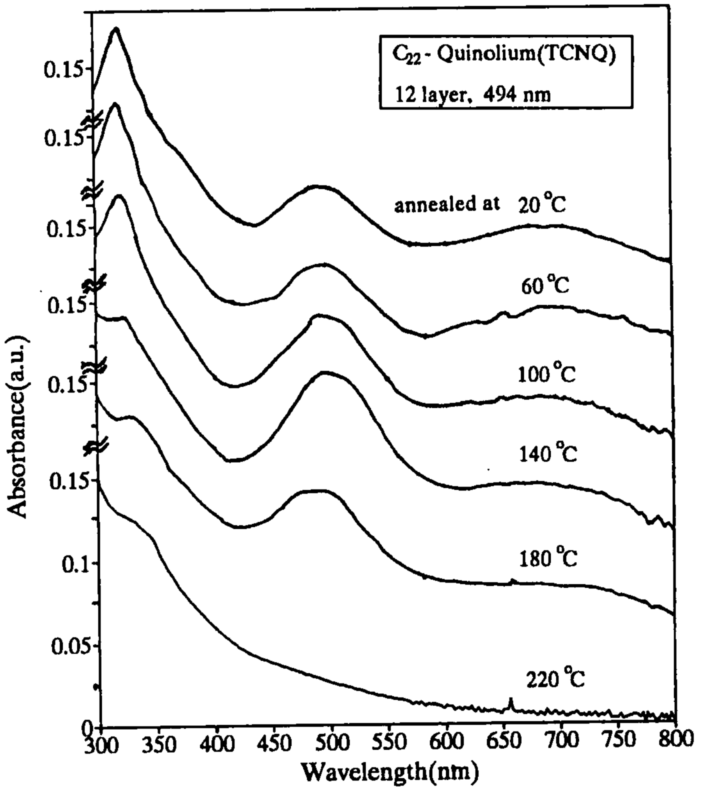

FIGURE 5 Absorption spectra of thermally annealed 12-layer C_{22}-quinolium(TCNQ) LB films.

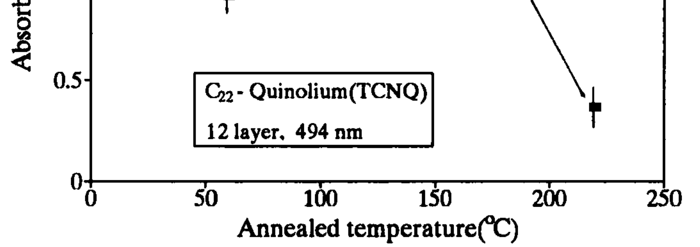

FIGURE 6 The relative absorption intensity as a function of annealed temperature at 494nm.

function of annealed temperature. The absorption intensities at the other peaks decrease with increasing temperatures. This fact demonstrates that the C_{22}-quinolium(TCNQ) LB film is sensitive to the temperature and the annealing affects the formation of aggregates.

CONCLUSIONS

We have investigated the electrical properties of the C_{22}-quinolium (TCNQ) LB films under the high-electric field along the perpendicular direction, and the thermal annealing effects of the films by UV/visible absorption. The following conclusions were able to be deduced.

(1) From the I-V characteristics under the high-electric field($\sim 10^6$V/cm), the LB film shows the anomalous behavior.

(2) The anomalous phenomena is partially associated to the joule heating effect on top of the electrical effect.

(3) The current-temperature characteristic shows that there is a sharp increase of current near 60 ~ 70℃, and stays almost constant from ~ 100℃ to ~ 140℃. Such increase of current seems to be from a softness of alkyl chains.

(4) The UV/visible absorption spectra of the thermally annealed LB films show that there are 4 characteristic peaks. These peaks are also sensitive to the temperature. The temperature dependence of the peak at 494nm is different from the other ones.

ACKNOWLEDGMENTS

This work was supported partially by a Grant-in-Aid from the Ministry of Science and Technology of Korea, and the Korea Electric Power Coorporation. We appreciate Sang-Kug Lee for UV/visible absorption measurements.

REFERENCES

1. K.B. Blodgett, J. Am. Chem. Soc., 57, 1007 (1935).
2. L.B. Coleman, M.J. Cohen, M.J. Sandmann, D.J. Yamagishi, A.F. Garito, and A.J. Heeger, Solid State Commun., 12, 1125(1973).
3. Tae Wan Kim, Seung-Kyu Park, Dou-Yol Kang, Eon-Sik Hong, and Chul Park, Mol. Cryst. Liq. Cryst., 227, 243 (1993).
4. G.G. Roberts, P.S. Vincett and W.A. Barlow, J. Phys. C; Solid State Phys., 11, 2077 (1978).
5. Dong-Myung Shin, Byung-Chung Sohn, Kang-Hoon Choi, Jung-Soo Kim, and Dou-Yol Kang, Trans. KIEE, 41, 753 (1992).