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Electrical Properties of Tetrakis(alkylthio)tetrathiafulvalene Thin Film

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1. Introduction

In the past several years, extensive studies on organic thin film transistor (TFT) have been carried out. Carrier mobility of organic TFT using pentacene as an active layer is comparable to amorphous Si TFT[1]. To expand the bandwidth of organic crystals by a large overlap of π electrons between neighboring molecules, we have to reduce the intermolecular distance. However compressed materials inside of the high pressure cell is not suitable for device application. Fastener effect [2] is one of the chemical pressure effects which is developed using tetrakis(alkylthio)tetrathiafulvalene (TTC_n-TTF) derivatives, whose molecular structure is shown in Fig.1. In this abbreviation n denotes the number of carbon atoms in an alkyl-chain, which is used as an index of alkyl-chain length. TTC_n-TTF molecules form aggregates by van der Waals force between alkyl-chain. Then van der Waals force becomes stronger for large number of n. Many studies on the fastener effect had been carried out in 1980s. The melting point of TTC_n-TTF steeply drop from n=1 to 4 and gradually arise from 5 to 18[3]. The rise of melting point in n>5 indicate the enhancement of van der Waals force. Also, the electric resistivity[4] and inter-TTF-ring distance[5] between neighboring molecule decrease with increase of alkyl-chain length.

In this work, we have fabricated thin film transistors of TTC_n-TTF by solution casting method, and revealed n dependence of the electric conductivity and field effect mobility.

2. Experimental details

TTC_n-TTF films were fabricated on a 300nm thick SiO_2 which was thermally grown on a heavyly doped n-type Si wafer. Parallel source / drain electrodes with 20μm spacing were deposited on the SiO_2/Si wafer by a standard evaporation method. TTC_n-TTF (n:1,2,5,18) were purchased from Tokyo Kasei Kogyo Co., Ltd. High purity grade chloroform were purchased from Wako Chemical Industries, Ltd. TTC_n-TTF were dissolved in chloroform in the glove box which was filled with dry N_2 and saturated vapor of chloroform at room temperature. Several drops of the solution were dropped on the SiO_2/Si substrate. The solution was slowly vaporized and crystals of TTC_n-TTF were grown in the solution. Sample were stored in a vacuum desiccator for a month to remove residual chloroform incorporated in the crystals.

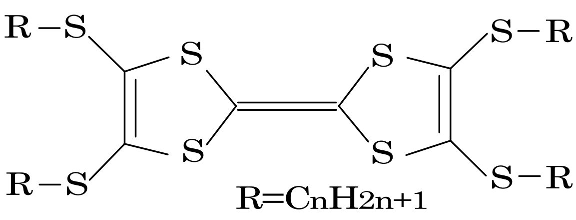

Fig.1 Molecular structure of TTC_n-TTF.

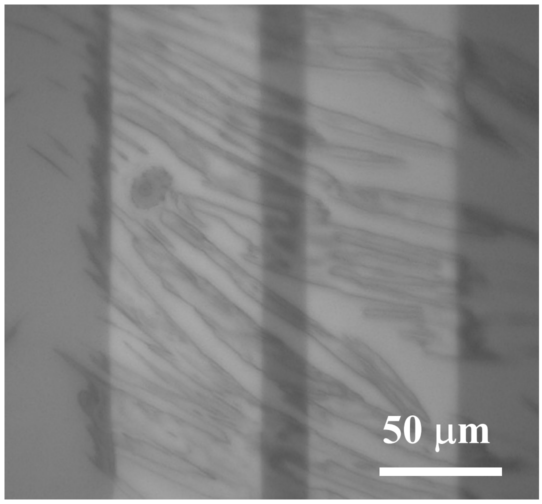

Fig.2 Optical microscope image of TTC_5-TTF grown from chloroform solution at room temperature.

3. Results and discussion

TTC_1-TTF and TTC_2-TTF are the most and second simple molecule of the derivatives. Crystals of TTC_1-TTF and TTC_2-TTF grown from chloroform solution on the SiO_2 surface looked like water drops. TTC_1-TTF and TTC_2-TTF are hydrophobic and condense themselves on the SiO_2 surface. But on the Au/Cr electrode, TTC_1-TTF and TTC_2-TTF grow to be an aggregate. Estimated electric conductivity of TTC_1-TTF and TTC_2-TTF are approximately 10^{-11}S/cm. Field effect mobilities of TTC_1-TTF and TTC_2-TTF are approximately 10^{-9} - $10^{-8}cm^2/V\cdot s$ estimated from their p-channel FET characteristics. Low electric conductivity and field effect mobility are reasonable for their crystal structure and short alkyl-chain.

TTC_5-TTF has the lowest melting point of the derivatives. Figure 2 is the optical microscope image of

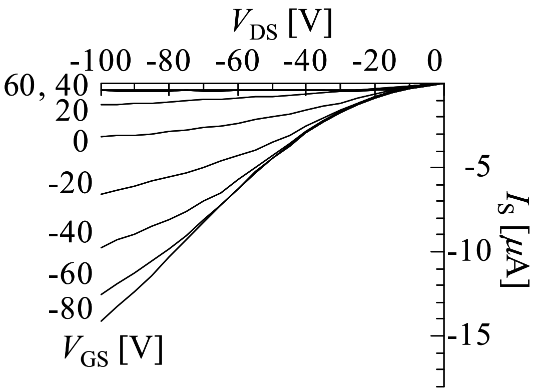

Fig.3 FET characteristic of TTC_5-TTF film.

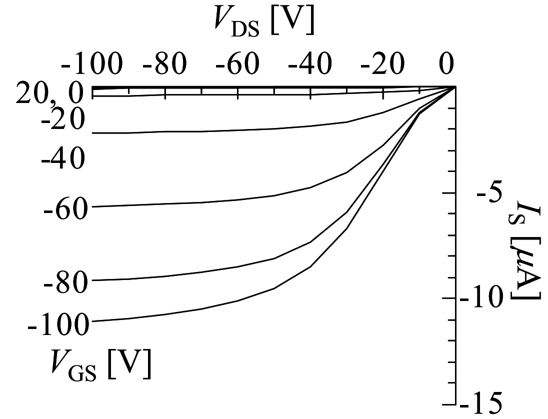

Fig.5 FET characteristic of TTC_{18}-TTF film.

TTC_5-TTF crystals grown from chloroform solution. Two parallel Au/Cr electrodes are seen in the center of image. TTC_5-TTF crystals cover approximately 60% of SiO_2 surface to bridge two electrodes. In contrast to the TTC_1-TTF and TTC_2-TTF, growth of TTC_5-TTF on SiO_2 surface was similar to that on Au/Cr surface.

FET characteristic of TTC_5-TTF is shown in Fig.3, which indicates p-channel FET characteristics due to the donor nature of TTF ring. Unlike the typical FET characteristics, obvious saturation region is not seen in Fig.3. The estimated carrier mobility is 1.7×10^{-4}cm^2/V·s in linear region. Electric conductivity of TTC_5-TTF is approximately 10^{-5}S/cm, which is higher than that reported by *Imaeda et al*[4]. The higher electric conductivity is due to the effect of contamination of oxygen. Air exposure is unavoidable to transport the sample from glove box to the electric measurement chamber. The unusual FET characteristic will be affected by oxygen and water vapor in air.

TTC_{18}-TTF is the largest molecule among commercial TTC_n-TTF derivatives. The melting point of TTC_{18}-TTF is the highest among the derivatives due to the strongest intermolecular force. Figure 4 shows the TTC_{18}-TTF crystals grown from chloroform solution. Different from other TTC_n-TTFs (n=1,2,5), needle-like crystals are randomly grown on the SiO_2 surface and make bridges between parallel Au/Cr electrodes. FET characteristic of TTC_{18}-TTF is shown in Fig.5, which indicates p-channel characteristic with on/off ratio of 330. Different from other TTC_n-TTFs, FET characteristic show saturation region. Threshold behavior is seen in the low drain voltage region. The estimated field effect mobility is 7.5×10^{-4}cm^2/V·s, which is four times higher than that of TTC_5-TTF. Electric conductivity of TTC_{18}-TTF is approximately 10^{-6}S/cm. The effective cross section of conductive channel of TTC_{18}-TTF crystals is obviously narrower than that of TTC_5-TTF because of large occupancy of long alkyl chain. The electric conductivity of TTC_{18}-TTF is lower than that of TTC_5-TTF because of wide band gap of 0.48eV compared to TTC_5-TTF (0.29eV)[4]. In addition, the penetration of oxygen depends on the alkyl-chain length, which affect the difference of dielectric conductivity of TTC_{18}-TTF and TTC_5-TTF.

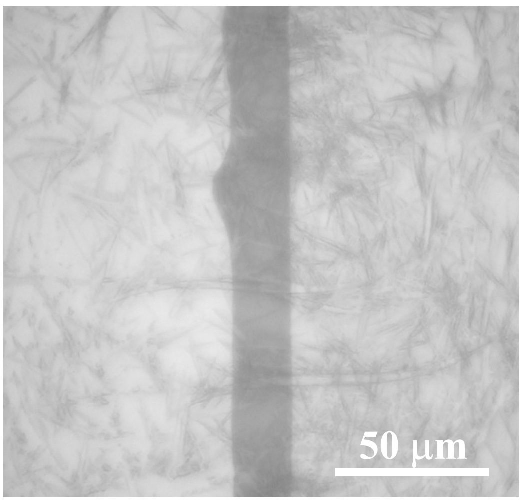

Fig.4 Optical microscope image of TTC_{18}-TTF crystals.

3. Conclusions

We have carried out the fabrication of TTC_n-TTF thin film transistor using solution casting. Different types of aggregates are formed with respect to the length of alkyl chain. The field effect mobility increases with increasing the length of alkyl chain.

References

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