OUKA
The University of Osaka
Institutional Knowledge Archive

| | |
|---|---|
| Title | Molecular orientation analysis in organic transistor devices by polarization dependent and low-frequency Raman spectroscopy |
| Author(s) | Bhardwaj, Bishwajeet Singh |
| Citation | 大阪大学, 2020, 博士論文 |
| Version Type | VoR |
| URL | https://doi.org/10.18910/76527 |
| rights | |
| Note | |

*The University of Osaka Institutional Knowledge Archive : OUKA*

https://ir.library.osaka-u.ac.jp/

The University of Osaka

# Abstract of Thesis

Name ( Bishwajeet Singh Bhardwaj )

| | |
|---|---|
| Title | Molecular orientation analysis in organic transistor devices by polarization dependent and low-frequency Raman spectroscopy<br>(偏光ラマン分光及び低周波ラマン分光を用いた有機トランジスタデバイスの分子配向分析) |


## Abstract of Thesis

Nowadays, organic semiconducting materials are used in several electronic devices such as electronic skin, plastic circuits, non-volatile plastic memories, sensors, and flexible displays. These applications are possible due to the lightweight and flexible properties of the organic materials. Among various organic materials, the application of pentacene and dinaphthothienothiophene (DNTT) has recently increased due to their high charge carrier mobility in an organic field-effect transistor (OFET) device. The structural properties of these materials, such as molecular orientations and the molecular density distribution, significantly affect their charge carrier mobility in transistor devices, therefore investigating these properties is essential. Raman spectroscopy has been recognized as a promising technique that can investigate the structural properties of organic molecules with a high spatial resolution.

In this dissertation, I investigated the orientation distribution of pentacene molecules in real transistor devices by polarization-dependent Raman spectroscopy. The presence of impurities changes alignments of pentacene in transistor devices and hence, affects the flow of charge carriers in the device. Sublimation is a well-known process to remove impurities. In my research, I mapped the variation of molecular orientation between neighboring positions that are separated by a distance of a few hundred nanometers in devices fabricated using non-sublimated and sublimated pentacene. The variation of the tilt orientation can be directly correlated to the device performance and can be utilized to improve the performance of the device.

I also investigated Raman spectroscopic studies on DNTT in a transistor device for the first time. I found that a typical Raman spectrum of DNTT molecules shows various vibrational modes. I investigated the spatial density distribution of DNTT molecules through Raman imaging. Further, in order to identify the measured vibrational modes, density functional theory (DFT) calculation was performed that helped me to describe the nature of vibrations of the atoms in all observed vibrational modes. I also investigated the orientations of DNTT molecules within a transistor device using Raman spectroscopy.

Further, I investigated the intermolecular interactions of DNTT molecules in the transistor device using the low-frequency Raman spectroscopy. I used several Bragg notch filters in the optical path to detect low-frequency Raman signals. I found out that DNTT molecules clearly show a few low-frequency Raman modes for the first time. I further investigated the spatial variation of intermolecular interactions, i.e., the molecular packing of DNTT molecules in the device using a low-frequency Raman imaging. This work helped me to identify the regions of the device that could have high carrier mobility with a high spatial resolution. This information could be used in designing high performing transistor devices.

様式 7

# 論文審査の結果の要旨及び担当者

| 氏　名 | ( Bhardwaj Bishwajeet Singh ) | | |
|---|---|---|---|
| | | (職) | 氏　名 |
| 論文審査担当者 | 主 査 | 教授 | バルマ　プラブハット |
| | 副 査 | 教授 | 民谷　栄一 |
| | 副 査 | 教授 | 井上　康志（生命機能研究科） |
| | 副 査 | 教授 | 尾崎　幸洋（関西学院大学理工学部） |

## 論文審査の結果の要旨

This dissertation is focused on investigating the molecular orientation and molecular arrangements of organic semiconductor molecules, particularly, dinaphthothioenothiophene (DNTT) and pentacene, in the active layer of an organic field effect transistor (OFET) device. OFETs are becoming very popular due to their attractive electronic and physical properties, such as high charge carrier mobilities and flexibility. Although researchers have observed good electronic properties, there is no tool available to understand the molecular arrangements of these organic molecules in the active layers of OFET devices, so that these devices could be further improved. A nondestructive technique that works at high spatial resolution is required. This dissertation takes this challenge and studies OFET devices with DNTT and pentacene as active layers though polarization-dependent Raman spectroscopy, which is a nondestructive optical technique with a spatial resolution of a few hundreds of nanometers. Main points of the research in this dissertation are described below.

- Charge carrier mobility and hence the electronic properties of an OFET device depend on efficient overlap of the $\pi$-electrons of neighboring molecules. In order to have better overlap of the $\pi$-electrons, neighboring molecules should be in close proximity and must be well-aligned. Thus, the local variation in molecular orientation and proximity would affect the electronic properties of the device. Both DNTT and pentacene, which are long organic molecules, may stand tilted on the substrate and/or may have slight twist along their molecular axis, which can vary from position to position within the device. Also, the fabrication process that involves deposition of these organic molecules, may result in non-uniform molecular density in the active layer. Therefore, investigation and surface mapping of molecular orientation as well as their proximity within a transistor device at sufficiently high spatial resolution is of great importance.
- Raman scattering probes the molecular vibrations with a spatial resolution equivalent to the diffraction limit of light, which is about 200-250 nm for the green light used in this dissertation. Some vibrations of these molecules are polarization dependent, which show enhanced vibrational intensities when incident light is polarized in a particular direction, and weak intensities for a perpendicular polarization. The change in intensity of this mode depends on the relative orientation of the molecule. This can be effectively utilized to determine the tilt and twist of molecules within the active layer of a device, because the intensity ratio for two mutually perpendicular polarizations would depend on the molecular tilt and twist. This dissertation takes advantage of this to map the molecular tilt/twist along the device as well as the relative twist between neighboring molecules.
- Next, in order to understand the variation in molecular proximity, low-frequency Raman spectroscopy is used. When neighboring molecules are in close proximity, they induce van der Waals interactions between the molecules, resulting in new low energy vibrational modes. These modes with weak oscillation energies are observed in the low-frequency range of Raman spectrum. Therefore, an observation of these low-frequency Raman modes confirms the proximity of neighboring molecules, and at the same time the intensity of these modes depends on the closeness of the molecules. Therefore, a low-frequency Raman mapping shows the distribution of molecular proximity, which is directly related to the charge carrier mobility, within the device. This dissertation studies this phenomenon in details and suggests where the device has a possibility for further improvement.

Overall, this dissertation shows great potential of Raman spectroscopy, both with polarization-dependent Raman scattering and low-frequency Raman scattering, for the purpose of realizing the molecular orientation and proximity for the future improvement of OFET devices. The referees found consistent consideration and strategy to demonstrate the not-so-well-explored strength of Raman spectroscopy to characterize OFET devices. Therefore, the referees have accepted that this dissertation has remarkable achievements and it deserves a doctoral degree.