論　文　内　容　要　旨

氏　　名	尚　　慧	提出年	平成 27　年
学位論文の題　　目	Exciton behavior in organic semiconducting crystals: Essential factor for realizing electrically driven lasers （有機半導体単結晶中の励起子の挙動：電流励起レーザーの実現に向けて）		

論　文　目　次

Abstract

Organic semiconductors recently attract considerable attention for new kind of lasers. They have plastic-like and favorable optoelectronic properties, with prospects for low energy consuming laser. Despite the optically pumped organic semiconductor lasers have been demonstrated since the early history of the laser, electrically driven laser has not been realized. It is still a challenge that sufficient exciton density must be created for population inversion. In organic electronics, two devise structure can provide light emission: organic light-emitting diode (OLED) and light-emitting field-effect transistor (LE-FET). Considering the fatal backwards in OLED devise structure that the generated exciton can be easily absorbed by electrodes, LE-FET is the most promising candidate for realizing laser.

Exciton density is generated from the recombination of electrons and holes which are determined the mean factor i.e. charge-carrier mobility in LE-FET. In particular, the organic field-effect transistors based on semiconducting crystals had demonstrated charge carrier mobility value more than 10 cm^2 V^{-1} s^{-1} and showed the intrinsic nature of the organic semiconductors. On the other hand, high luminescent efficiency is also a crucial factor for realizing lasers that they are capable to reduce the non-radiative losses caused by quenching and supplement the photo absorbed by electrodes. Optical properties, especially the luminescent efficiency, are related with molecular packing in organic crystals.

This doctor research had challenged several alternatives to pursuit the electrically driven organic lasers. To create sufficient current-induced exciton density for population inversion, which can be solved from the two aspects: one being decreasing the lasing threshold or the other being creating sufficient current density. And this thesis attempted on both of the aforementioned aspects, and mainly focus on the exciton behavior in organic crystals. For example, ASE behavior is due to interaction between photons and excitons; doping which can improve optical property is

determined by energy transfer (exciton migration); also, singlet fission and its reverse process i.e. triplet fusion make the exciton diffusion length to be in micro-scale.

To realize laser, investigating gain property is a necessary process because laser contains only a gain media with a resonator. In chapter 3, we focused on specific analysis of gain properties of BP2T, BP2F and BPFT single crystals. By comparing both the absorption and fluorescence spectra of these three co-oligomers in both single-crystalline and deposited thin-film forms, we assigned the dual gain-narrowed peaks corresponding to the vibronic transitions from $S_{1,0}$ to $S_{0,n}$ state. Combining the transient absorption spectra with ground-state absorption spectra, we finally determined that the number of gain-narrowed peaks corresponding vibronic transitions is affected by the re-absorption from both the ground/excited-state molecules, and energy distribution of this gain behavior is determined by transition probability from $S_{1,0}$ to $S_{0,n}$ and bleaching of the ground-state absorption. Furthermore, gain with the highest efficiency can be expected when only the vibronic transition with the highest transition probability is confined in the window of absorption at both ground state and singlet state. This research is not only the first report of the mechanism describing energy efficiency and its distribution but also a good guide to design high efficient materials for laser.

In chapter 4, tetracene-doped anthraene crystal is employed as a model for studying doping system based on RET theory. Both the fluorescent spectra and much more improved luminescent efficiency proved that there was an efficient energy transfer from the donor molecule to the acceptor molecule. Furthermore, we have successfully overcome the differences of molecular structures and their stacking modes, finally doped a certain quantity of CNDPASDB into *trans*-DPDSB by solution growth method, and maintained the original crystal structure of host crystal as proved by polarizing optical microscope analysis. Light emission color can be tuned by changing the doping ratio, due to intrinsically high QY of the host material and efficient energy transfer from *trans*-DPDSB molecules to CNDPASDB molecules. Therefore, emission spectra can cover both the emission region of the host (blue color) and that of the guest (orange color). With suitable balance of the ratio between host and guest, white light emission was successfully obtained. Moreover, superb high EQY (~80%) comparable with that in solution was obtained by doping, and it slightly decreased with increasing the doping ratio due to the singlet-singlet annihilation. Finally, carrier transport characteristic was also investigated in both pure *trans*-DPDSB and its doped crystals. It is concluded that dopant with smaller energy band gap may introduce carrier-traps, which means if the problem of carrier-trap is overcome in the doping system, electrically driven laser may be realized.

As described earlier, creating sufficient current density is also an important alternative for realizing laser. Considering the intrinsic confliction between carrier transport and luminescent efficiency in general materials, separation in functions of carrier-transport and light-emission is an intelligent strategy. In chapter 5 and 6, I further report a fabrication and characterization of a transistor with bilayer structure, which consists of a high field-effect mobility bottom layer and a high EQY top layer, and its emission mechanism in terms of exciton behavior in this new devise

structure was described.

Both pure and 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (DCM1)-doped tetracene crystals were prepared by a physical vapor transport method. After co-doping DCM1 in a tetracene crystal, the luminescent color was changed from green to somehow red, and EQYs were improved from 1% to 8%, yet the electron mobility decreased from 1.28 to 0.13 $cm^2V^{-1}s^{-1}$. Exciton diffusion length along the *c* axis in a tetracene crystal was obtained by characterization of polarization-dependent absorption coefficient and photocurrent. The absorption coefficient in a tetracene single crystal showed polarization dependent behavior, which results in a similar modulation of photocurrent. From the relationship between absorption coefficient and photocurrent, the exciton diffusion length along the *c* axis was calculated to be 1.87 μm. The diffusion length is longer than the thickness of the bottom layer (0.583 μm) of the bilayer transistor. For fabrication of a bilayer transistor, a DCM1-doped crystal was laminated on the center position of the tetracene crystal. Asymmetric Au and CsF/Ca electrodes were employed for injection of holes and electrons, respectively. The bilayer transistor showed red light emission from the top crystal, which is different from that of pure tetracene (green light emission). To further prove whether the top crystal can be excited by exciton transfer or photon absorption from the bottom layer, a TTC thin film insulator, which allows photon transport but blocks exciton migration, was inserted between them. Only green light emission was observed in the device, indicating that there is no light emission in the top layer. These results have proved our anticipation that excitons transferred from the high-mobility bottom crystal to the top crystal which has higher EQY. Furthermore, the current density in ambipolar region of this bilayer transistor was evaluated to be 14 kA/cm^2, which is 34 times higher than that in BP3T (412 A/cm^2, most promising material to date). This current density for providing exciton density for population inversion was dramatically increased and is surely promising for laser.

The pursuit for current-driven organic laser will remain a great challenge for several years to come, particularly from the viewpoint of the related fundamental physics. The field of easily processed organic semiconductor lasers is young at more than a decade old and advancing rapidly. As we look to the future, the realization of electrically driven lasers will be a breakthrough in the field of organic photonics. The development of device and material will help reduce threshold. Also the emerging technologies such as inject printing will pave the way for lasers to become practical sources, initially for use in a range of spectroscopic applications. From the applicational viewpoint, the organic semiconductor community expects current-driven organic laser can be available by the year 2030.

Publication lists

[1] H. Shang *et al*, submitted to *Adv. Funct. Mater.*

[2] H. Shang *et al*, to be submitted.

[3] H. Shang *et al*, *CrystEngComm*, **2012**, *14*, 869.

論文審査の結果の要旨

有機半導体は無機半導体と比較して、構造の柔軟性、デバイス作製の容易性、コストの低減などの観点から多くの注目を集めている。もう一つの特徴は、トランジスター構造においてゲート電圧の制御で同時に電子とホールを注入できる両極性キャリヤ制御が可能である事である。本研究は、両極性キャリヤ制御に着目して、有機半導体レーザーを実現する基礎として伝導キャリヤ制御と発光制御の役割を分離した二層有機単結晶電界効果トランジスター構造の作製と評価を目的として行われた。

有機半導体で電流励起レーザーを達成するためには、トランジスター内に注入された電子とホールの再結合により生成されるエキシトン状態を効率良く作り、多くの位相がそろったフォトンを発光として発生させる必要がある。しかし、従来のトランジスター構造では、このような閾値を達成するような状況を作る事は困難であった。本研究ではこの困難性を克服するために、電子およびホールの電極からの注入とエキシトンからのフォトン発光の機能異なる材料に担わせる新しい二層構造トランジスターを提案してその物性を詳細に検討した。高効率に電子とホールを電極から注入するために、テトラセン単結晶を下層に用いた。テトラセンは、高移動度を有し高効率で電子とホールの両極性注入が可能であると同時に三重項エキシトンを高効率に生成する事ができる。この特性を利用して三重項エキシトンを上層である DCM1 と呼ばれる発光物質をドープしたテトラセン単結晶に移動させて、高効率に発光を観測する事に成功した。この実験結果を解釈するために、詳細なトランジスター特性と光学測定からエキシトン拡散と発光機構に関して議論を行った。

本論文は、両極性伝導を利用した電流励起の有機半導体レーザーを実現に向けて、キャリヤ注入と発光現象の機能を分離した新しい二層有機単結晶電界効果トランジスター構造を提案して、その可能性を実験により明確にしたものである。この成果は、提出者が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって，尚　慧（Shang Hui）提出の博士論文は，博士（理学）の学位論文として合格と認める。