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Continuous wave infrared laser deposition of organic thin films

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Abstract. We developed a continuous-wave infrared laser molecular beam epitaxy (CW-IR-LMBE) optimized for the fabrication of organic semiconductor films. The crystal quality of these organic thin films deposited by CW-IR-LMBE was substantially the same as those deposited by thermal evaporation. Due to the possibility of quick switching of evaporation sources, CW-IR-LMBE is especially advantageous for rapid screening of composition, thickness, and fabrication parameters in materials and device optimization based on combinatorial technology.

1. Introduction

π -conjugated organic semiconductors show potential as flexible electronic device applications such as paper-like displays and smart cards [1]. As a result of developments of organic devices in recent years, organic materials and device structures are becoming complicated, and mixing and layer structures are already used for organic devices such as field effect transistors [2], diodes [3] and solar cells [4]. For rapid screening of such complex materials and device structures, combinatorial technology is very effective way [5]. The combinatorial synthesis of thin film devices requires control of a precise film deposition rate, and quick-switching for the material source. Besides, the same requirements are indispensable for fabrication of superlattice structure, which can control the band structures.

There are mainly two methods as the way to gasify solid organic materials under high vacuum conditions: one is use of a heat source such as in the case of thermal evaporation (TE) with a Knudsen cell (K-cell) [6], and the other is use of a light source such as in the case of pulsed laser deposition (PLD) [7, 8]. However, both these methods listed above can not satisfy to the requirement in combinatorial synthesis. TE is good film fabrication method to avoid the destruction of molecular structure because of its low energy excitation. Although organic thin film grown by TE shows high crystallinity and keeps original molecular structures, the controllability of film deposition (stability of deposition rate and quick-switching of material source) is insufficient for synthesis of combinatorial library and superlattice. In the case of inorganic compounds, PLD is now powerful method for the fabrication of the combinatorial library or superlattice structure, whereas in the case of fabrication of organic compounds, PLD

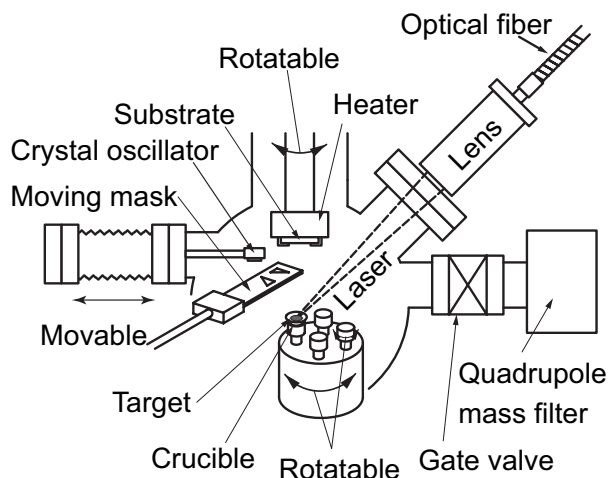


Figure 1. Schematic illustration of the continuous-wave infrared laser MBE system. Organic source materials are placed in a crucible made of metals, carbon or ceramics. The focus of infrared laser onto the crucible is controlled by lens.

has some problems in comparison with TE as follows: (1) in the case of nano sec or micro sec pulsed laser, too large energy density (typically 5 MW/cm^2 during the laser irradiation) is required for the ablation, which energy is enough to break chemical bonds in organic molecules. (2) The photon energy (for example, 4.7 eV, fourth harmonic generation (FHG) of Nd:YAG laser) of ultraviolet laser is quite larger than the energy of π - π bonds in organic molecules and causes ring opening process and the change from π -bonds to sigma bonds. Therefore, since thin films deposited by PLD contained many molecules that changed from the source molecules [7, 8], the PLD film is unsuitable for the usage as the active layer in organic semiconductor devices.

In this paper, we report on the development of continuous-wave infrared laser molecular beam epitaxy (CW-IR-LMBE) system for organic thin films devices, which equips a fiber-guided continuous-wave infrared laser (wave length = 808 nm). The thin films deposited by CW-IR-LMBE showed equivalent quality to that fabricated by TE, and CW-IR-LMBE has the similar controllability to PLD. These results indicate that CW-IR-LMBE satisfies the requirement in synthesis of combinatorial library and superlattices.

2. Experimental

Figure 1 shows a schematic illustration of the CW-IR-LMBE chamber. Organic powder sources in crucibles are ablated by a semiconductor laser (wave length = 808 nm) focused on the source by a quartz lens. Each crucible is mounted on the stage with rotation and revolution mechanisms for the uniform ablation and the selection of 4 source materials. There was no substantial differences for deposition among crucible made of metal, carbon, and ceramics. A moving mask of this system enables us to fabricate thickness-gradient and composition-spread films for combinatorial library. The amount of vaporized molecules into the chamber and the film deposition rate were monitored by a quadrupole mass spectrometer (QMS) and a crystal oscillator in order to investigate the response of the deposition against the laser switching.

The ionization room of QMS cracks the wafting molecules in the chamber to lower-mass products, for example, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2^*$ in the case of pentacene. The relative increase of wafting molecules in the chamber by the laser ablation was evaluated from the mass spectrum. The monitored thickness is corrected for the temperature change of the quartz oscillator caused by the thermal radiation of irradiated laser.

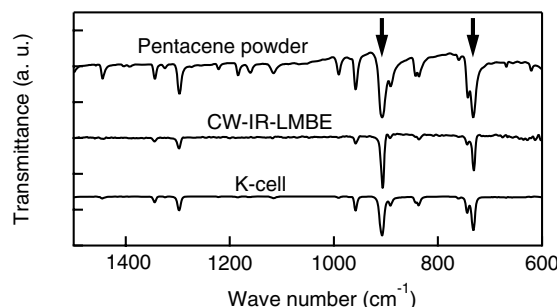


Figure 2. Fourier transform infrared spectra of source powder, thin film deposited by CW-IR-LMBE and thin film by a Knudsen cell in the case of pentacene. Typical absorption peaks of pentacene at 908 cm^{-1} and 733 cm^{-1} are marked in graph. Because of the orientation of deposited thin films on substrates, only the peaks corresponding to the in-plane vibrations were observed in the thin film spectra.

Pentacene thin films were deposited on silicon or sapphire (0001) substrates having atomically flat surface [9] at room temperature using CW-IR-LMBE and MBE with a K-cell. The crystallinity and surface morphology of the films on sapphire substrates were measured by an X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. The modification of molecular structure by the deposition was checked by fourier transform infrared (FT-IR) spectra of the thin films on silicon substrates. The film thickness was measured by a stylus profiler (Veeco; Dektak3 ST).

3. Results and discussion

Figure 2 shows FT-IR spectra of source powder, thin film deposited by CW-IR-LMBE and thin film by MBE with a K-cell in the case of pentacene. The thickness of pentacene thin films was 400 nm. Only the peaks corresponding to the in-plane vibrations were observed in the thin film spectra because of the orientation of deposited thin films on substrates. In the finger-print region, two typical peaks at 908 cm^{-1} and 733 cm^{-1} that should be related to a pentacene molecule were observed in the spectra of the source powder and both of thin films. The spectrum of the film deposited by CW-IR-LMBE was substantially the same to that of films by the K-cell. This FT-IR spectrum shows that molecular structure is not destroyed by laser ablation.

Figure 3 (a) and (b) show AFM images of pentacene films grown on sapphire (0001) substrates with a thickness of approximately 150 nm by CW-IR-LMBE and TE with a K-cell. The similar dendritic morphology with a grain size of approximately $1.5\mu\text{m}$ in both thin films was observed. The pentacene film deposited by CW-IR-LMBE has rather larger grain size than that by K-cell. This implies that pentacene molecules sublimated by CW-IR-laser have larger kinetic energy than the molecules, that is, rapid heating by laser may promote migration.

We measured $\theta-2\theta$ X-ray diffraction patterns along surface normal direction of the pentacene films to compare crystallinity, and only diffraction peaks along the c^* -axis were observed. The c -axis length of each film is evaluated to be $15.5\text{ \AA}$ from the peak position. From out-of-plane X-ray rocking curves of pentacene (001) peak in both films, the full-width at half maximum (FWHM) of both films were 0.03 degree. These XRD data means the pentacene films deposited are high crystallinity and c -axis oriented. These AFM and XRD results indicate that there is no substantial difference between thin films grown by CW-IR-LMBE and by TE with a K-cell. Therefore, we demonstrated that CW-IR-LMBE can deposit high crystal quality organic thin films without molecular structure change.

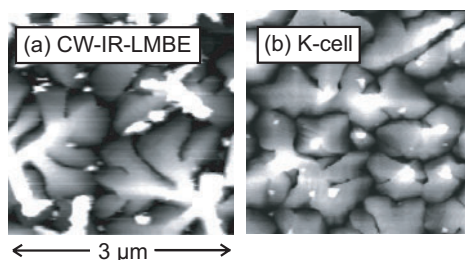


Figure 3. AFM images of pentacene thin films deposited by (a) CW-IR-LMBE and (b) thermal evaporation with a Knudsen cell. Each image size is $3 \times 3 \mu\text{m}^2$.

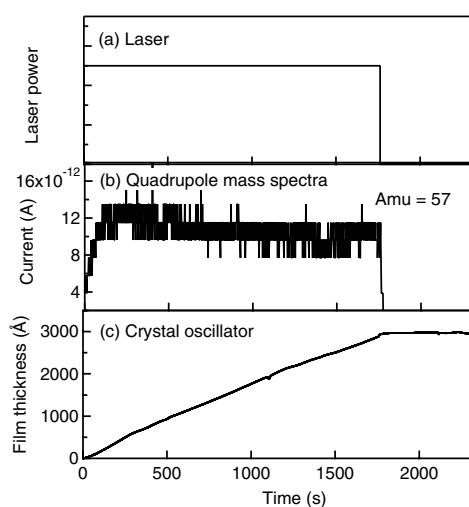


Figure 4. The responses to (a) laser switching of CW-IR-LMBE during the ablation of pentacene powder. Time dependences of (b) peak intensity with an atomic mass of 57 in the quadrupole mass spectra and (c) thickness monitored by a crystal oscillator.

In order to clarify the controllability and stability of the deposition, deposition rate of CW-IR-LMBE was investigated. Figure 4 shows pentacene deposition monitoring at successive irradiation condition of CW-IR laser: (a) laser switching of CW-IR-LMBE during the ablation of pentacene powder, and time dependence of (b) peak intensity with an atomic mass of 57 in the quadrupole mass spectra and (c) thickness monitored by a crystal oscillator. The film thickness was clearly responded CW-IR laser on/off and long time stable deposition was realized. The standard deviation of film thickness was 300 ± 14 nm. Therefore we understand that CW-IR laser sublimates the molecule itself directly and crucible is not heated. As the results of pentacene deposition at quasi pulsed laser condition (see figure 5), deposition could repeat many times stably. Standard deviation of film thickness was 930 ± 19 nm. CW-IR-LMBE is first technique to realize precise deposition control of organic molecular crystal thin films. This method is more likely to be appreciable to alternate atomic layer growth of various kinds of organic molecules than conventional thermal evaporation.

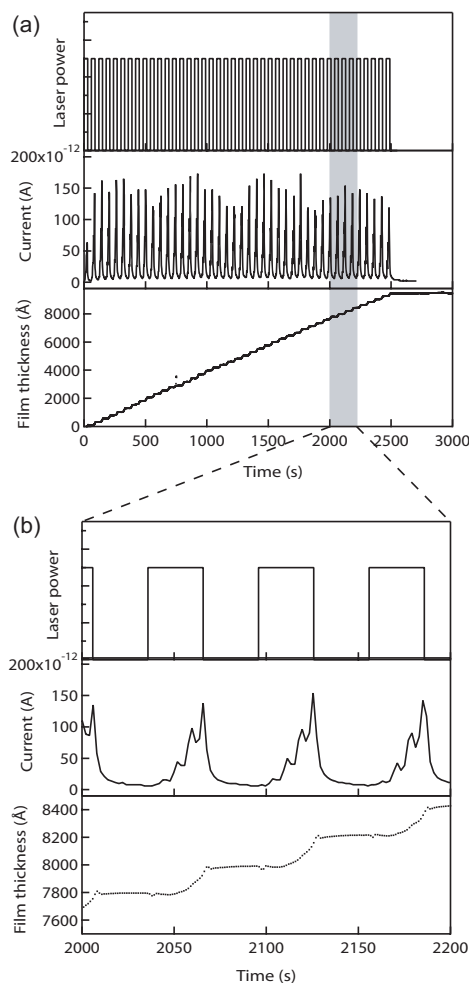


Figure 5. (a) The repeatability test to quasi-pulsed laser during the pentacene ablation. Time dependences of peak intensity with an atomic mass of 57 in the quadrupole mass spectra and thickness monitored by a crystal oscillator. (b) Magnified graph of (a).

4. Conclusions

We have developed continuous-wave infrared laser molecular beam epitaxy (CW-IR-LMBE) of organic semiconductor thin films. Using CW-Infrared laser, the merits of pulsed laser deposition and thermal evaporation are combined, rapid response and digital, stable and repeatable deposition with conservation of their molecular structure. Although pulsed ultraviolet laser deposition is frequently used for inorganic solid thin films, infrared laser is expected to be more relevant for organic thin films in view of preservation of original chemical bonds in the source materials. Because crystallinity and surface morphology of the pentacene films grown by CW-IR-LMBE are similar to the films deposited using Knudsen cell (K-cell), CW-IR-LMBE is as suitable methods as MBE using K-cell for organic films. Therefore, CW-IR-LMBE has great advantage for rapid screening of condition parameters based on combinatorial synthesis of organic thin films.

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