Development of compact CW-IR laser deposition system for high-throughput growth of organic single crystals

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Abstract

We developed a compact continuous-wave infrared (CW-IR) laser deposition system for the high-throughput growth of organic single crystals. In this system, two CW-IR lasers are used for the sample heating and thermal evaporation of materials. The CW-IR laser heating is simple and allows good control of the deposition rate and growth temperature, in response to the on/off laser switching. Six samples can be loaded simultaneously in a chamber, which allows one-by-one sequential deposition for high-throughput experiments, without breaking the vacuum. Using this setup, we studied the effect of ionic liquids on the growth of C$_{60}$ crystals in vacuum.

Keywords: CW-IR laser deposition, organic single crystal, liquid flux, ionic liquids

1. Introduction

Precise control of the growth temperature and deposition rate is a key in the organic vapor deposition of high-quality organic crystals and thin films, for example, of pentacene, rubrene and fullerene, which are often used as active materials in organic semiconductor devices [1]. Because of the difficulties in controlling the temperatures of the sample and thermal evaporator, a long time is often needed to reach steady-state conditions. These difficulties originate from the large heat capacities of conventional resistive heaters. The accurate measurement of the sample temperature in high-vacuum chambers is often impeded by the presence of a sample transfer system, which hinders the direct attachment of a thermocouple to the sample. As to thermal evaporators, the conventional systems such as a Knudsen cell do not allow quick and precise evaporation control, which could be synchronized with a modulation of the sample temperature, as discussed below.

To overcome these problems, we have developed a new organic-material deposition system using two continuous-wave infrared (CW-IR) lasers of 808 nm wavelength for heating the sample holder and evaporating the target cell. For sample heating, the laser beam is introduced to the chamber through a silica window to the backside of the sample holder [2]. Laser heating of the sample holder is well established in high-temperature oxide epitaxy, but not in low-temperature growth of organic thin films and crystals. As to laser-induced evaporation, CW-IR laser deposition was first reported by Yaginuma et al in 2007 [3, 4]. Pulsed laser deposition (PLD) using a UV laser is a more popular method of producing inorganic materials with high melting points such as metal oxides. However, the energy of a single UV photon is too high for evaporating organic materials without decomposing their molecules [5]. In contrast, a CW-IR laser can evaporate organic materials through gentle heating rather than ablation by PLD. CW-IR laser deposition can be applied to various organic materials. Even if they do not absorb IR light, as is the case of ionic liquids (ILs), the heat can be provided through the addition of an IR absorbent such as Si powder [6].

In this paper, we report the development of a compact CW-IR laser deposition system, which is suitable for the precise control of the sample temperature and deposition rate. Using this system, we carried out high-throughput experiments on the ionic liquid (IL)-assisted
vacuum deposition of C₆₀. This advanced version of vapor–liquid–solid growth can provide single-crystal quality of organic thin films and crystals, as demonstrated for oxide epitaxy [7] and organic crystal growth [8, 9] using oxide melt or low-vapor-pressure solvent. ILs have attracted much attention owing to their stability in high vacuum and have already been used as a solvent in crystal growth by solution methods [10, 11]. ILs functioned well even in a vacuum process, as a solvent for the dispersion of nanoparticles by metal sputtering [12]. However, the crystal growth in ILs by vacuum deposition is still not explored. We have reported the validity of the IL-assisted vacuum deposition for the epitaxial growth of alkali halide nanocrystals [13] and the growth of pentacene single crystals in IL droplets [14]. Here, we report the application of this technique to the growth of highly oriented C₆₀ crystallites on a substrate rather than in the IL droplet and discuss the effects of process parameters on the growth.

2. Development of a compact CW-IR laser deposition system

Figure 1 shows a photograph and a schematic of the compact CW-IR laser deposition system. In this system, two CW-IR lasers (wavelength 808 nm) are used for heating the sample holder (figure 1(a)) and evaporating the target cell (figure 1(b)). Their beams are guided by optical fibers and then introduced to the vacuum chamber through a silica window. Instead of using a sample-transfer system, we designed a holder supporting up to six samples. The holder is rotated so that only one sample at a time is selected for deposition using a mask as shown in figure 1(c). This design saves time for reloading the samples into the chamber and reduces the variations in the deposition conditions from sample to sample, as was verified in our previous work [15]. The chamber has a liquid N₂ trap (figure 1(d)) in order to improve the vacuum quickly and protect organic thin films from water vapor. Since the chamber lacks a sample-transfer system, the temperature can be directly measured by attaching a thermocouple to each sample (figure 1(e)). To reduce the temperature gradients, the sample holder is made of copper (figure 1(f)) and is cooled by streaming water (figure 1(g)). Each target to be evaporated is mounted on a holder, which is rotated to achieve uniform evaporation and one of the four source materials is selected (figure 1(h)). The deposition rate is monitored using a quartz crystal microbalance (QCM) sensor placed on the shutter (figure 1(i)).

As shown in figure 2 for the example of pentacene, the sample temperature and deposition did follow the on/off laser switching and could be well controlled between 25 and 75 °C. For efficient cooling, the water temperature was set to 10 °C. Heating at a rate of 10 °C min⁻¹ resulted in an overshoot by less than 4 °C, followed by return to the set temperature within 1.5 min as shown in figure 2. Then, the set temperature could be kept constant within ±0.2 °C. The deposition rate was stable and followed the on/off laser switching, as monitored using the QCM sensor.

3. High-throughput experiments in organic single-crystal growth

3.1. Experimental details

C₆₀ (99.9% purity, sublimed) was purchased from Aldrich Co. and used as received. We used the following ILs, all without purification: 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([Omin][TFSA], 99% purity, Iolitech Co.), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([Bmim][TFSA], Tokyo Chemical Industry Co. Ltd) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄], Tokyo Chemical Industry Co. Ltd). The substrates were made of sapphire single crystals (α-Al₂O₃ (0001)). After ultrasonic cleaning in ethanol and acetone and annealing at 1000 °C for 5 h in air, they exhibited atomically flat surfaces [16]. The ILs were dropped with a micropipette (1 μl per droplet) on the substrates and no treatment was applied to spread them. Then six substrates were placed in the sample holder and
Figure 2. Temperature modulation, synchronized with deposition of pentacene by on/off laser switching. The black line is the temperature measured at the sample, the red dotted line is the set temperature, and the blue line is the thickness of the deposited pentacene monitored using the QCM sensor. The inset magnifies the sample temperature curve in the 57–64 min range.

The chamber was evacuated to below $3 \times 10^{-7}$ Torr. The six substrates were in turn heated to 90, 100, 110, 120, 130 and 140 °C, respectively, and C$_{60}$ were deposited on each substrate at a rate of 8 nm min$^{-1}$. The substrate temperature was kept constant within ±0.2 °C during the deposition. The deposition rate was controlled by independently changing the laser power and illumination time.

The morphology of C$_{60}$ crystallites was observed with a confocal scanning laser microscope (LM; VK-9700, Keyence Corporation) after rinsing them in acetone to remove the ILs. Their crystal structures were characterized by conventional powder x-ray diffraction (XRD). Before measuring the C$_{60}$ concentrations in ILs, the ILs were agitated in an ultrasonic bath for 2 h at 50 °C. The solutions were then aged for 24 h and their optical absorptions were compared with that of the o-dichlorobenzene standard.

3.2. Results and discussion

Figure 3 shows a set of LM images of C$_{60}$ crystallites obtained by one-by-one sequential deposition in the [Omm][TFSA] IL at different temperatures. Higher temperatures promoted the formation of aggregated bulk-like crystals. At 90 °C, the crystals looked like 2D dendrites with flat and nonfaceted surfaces. When the sample temperature was increased to 120 °C, the crystals became more three-dimensional and faceted, but still resembled dendrites. Note that this IL evaporated at temperatures above 130 °C, which complicated the growth mechanism, the amount of IL decreased during the deposition resulting in needle-like crystals.

C$_{60}$ solid grown at 100 °C was studied by XRD. When deposited on α-Al$_2$O$_3$ without ILs, it formed an amorphous film exhibiting no XRD peaks (figure 4(a)). In contrast, for growth in IL, other peaks were observed besides those of the α-Al$_2$O$_3$ substrate. They were assigned to (001) hcp and (hhh) fcc C$_{60}$ peaks [17–19]. It is difficult to distinguish the hcp and fcc C$_{60}$ structures from the XRD patterns alone because of the similarities in the spacing $d$ between the crystal planes. For example, $d$(002) = 8.18 Å in hcp [20] and $d$(111) = 8.1596 Å in fcc C$_{60}$ (JCPDS No. 44-558). Nevertheless, these
Figure 5. Results of particle analysis of C$_{60}$ crystals grown in ILs at different temperatures (a) and deposition rates (b). Open circles: number of particles; solid triangles: average size.

Figure 6. LM images of C$_{60}$ crystallites grown in different ILs at 100 $^\circ$C at a deposition rate of 8 nm min$^{-1}$: (a) [Omim][TFSA], (b) [Bmim][TFSA] and (c) [Bmim][BF$_4$].

XRD results demonstrate that the C$_{60}$ crystallinity was much improved by growing C$_{60}$ in an IL.

Particle analysis was applied to the C$_{60}$ crystals grown in ILs. The number of particles and their size distributions are plotted as functions of the growth temperature and rate in figures 5(a) and (b), respectively. The data for 130 and 140 $^\circ$C were excluded because of the growth instabilities mentioned above. The crystals are larger and less numerous when grown at higher temperatures or lower deposition rates. Both tendencies can be naturally explained using the standard models of crystal growth kinetics and thermodynamics in solution in terms of the diffusion length, solubility and supersaturation.

We also examined the effect of IL on the C$_{60}$ growth using [Omin][TFSA], [Bmim][TFSA] and [Bmim][BF$_4$]; the solubility of C$_{60}$ was the highest in the first IL as reflected in table 1, and the growth results are shown in figure 6. A clear difference was observed for [Bmim][BF$_4$]: fine particles were formed instead of large crystals, which can be explained as follows. The low solubility of C$_{60}$ resulted in multiple nucleation sites that aggregated before growing in size. Secondary C$_{60}$ crystallites exhibited a more dendritic shape in [Bmim][TFSA] than in [Omin][TFSA]. This was a dominant consequence of the low solubility, although the diffusion rate should also be taken into account as the dendritic crystals generally form under the diffusion-limited condition. These results illustrate the importance of solubility in the growth of organic crystals in ILs.

Table 1. IL properties: solubility of C$_{60}$ and viscosity at 30 $^\circ$C [21].

| Ionic liquid                        | Solubility (µg ml$^{-1}$) | Viscosity (Pa s) |
|------------------------------------|---------------------------|-----------------|
| 1-Octyl-3-methylimidazolium        | 4                         | 0.071           |
| bis(trifluoromethanesulfonyl)amide |                           |                 |
| [Omin][TFSA]                       |                           |                 |
| 1-Butyl-3-methylimidazolium        | 1                         | 0.040           |
| bis(trifluoromethanesulfonyl)amide |                           |                 |
| [Bmim][TFSA]                       |                           |                 |
| 1-Butyl-3-methylimidazolium        | –                         | 0.075           |
| tetrafluoroborate [Bmim][BF$_4$]   |                           |                 |

* Below the detection limit of absorption spectroscopy.

It should be emphasized that all the growth experiments were performed in the sample setup. Each experiment type took about 40 min, including 5 min for heating and 5 min for cooling to room temperature. Thus, a high throughput was achieved and systematic results were obtained on the growth of C$_{60}$ at different growth temperatures and rates and in different ILs.

4. Conclusions

We developed a compact CW-IR laser deposition system for high-throughput experiments on organic single-crystal growth. The system allows precise control of the growth temperature and rate, with the growth synchronized to the on/off laser switching. Using this system, we studied the
growth of C$_{60}$ in ILs. The C$_{60}$ crystallinity was higher for ILs with a higher C$_{60}$ solubility. The one-by-one sequential depositions of C$_{60}$ at different growth conditions provided a set of systematic data in a short time.

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References

[1] Dimitrakopoulos C D and Malenfant P R L 2002 Adv. Mater. 14 99
[2] Ohashi S, Lippmaa M, Nakagawa N, Nagasawa H, Koinuma H and Kawasaki M 1999 Rev. Sci. Instrum. 70 178
[3] Yaginuma S, Yamaguchi J, Haemori M, Itaka K, Matsumoto Y, Kondo M and Koinuma H 2007 J. Phys.: Conf. Ser. 59 S20
[4] Yaginuma S, Itaka K, Haemori M, Katayama M, Ueno K, Ohnishi T, Lippmaa M, Matsumoto Y and Koinuma H 2008 Appl. Phys. Express 1 015005
[5] Yamaguchi J, Itaka K, Hayakawa T, Arai K, Yamashiro M, Yaginuma S and Koinuma H 2004 Macromol. Rapid Commun. 25 334
[6] Maruyama S, Takeyama Y, Taniguchi H, Fukumoto H, Itoh M, Kumigashira H, Oshima M, Yamamoto T and Matsumoto Y 2010 ACS Nano 4 5946
[7] Yun K S, Choi B D, Matsumoto Y, Song J H, Kanda N, Itoh T, Kawasaki M, Chikyow T, Ahmet P and Koinuma H 2002 Appl. Phys. Lett. 80 61
[8] Voigt M, Dorsfeld S, Volz A and Sokolowski M 2003 Phys. Rev. Lett. 91 026103
[9] Ishii Y, Shimada T, Okazaki N and Hasegawa T 2007 Langmuir 23 6864
[10] Pusey M L, Paley M S, Turner M B and Rogers R D 2007 Cryst. Growth Design 7 787
[11] Reichert W M, Holbrey J D, Vigour K B, Morgan T D, Broker G A and Rogers R D 2006 Chem. Commun. 4767
[12] Torimoto T, Okazaki K, Kiyama T, Hirahara K, Tanaka N and Kawabata S 2006 Appl. Phys. Lett. 89 243117
[13] Kato S, Takeyama Y, Maruyama S and Matsumoto Y 2010 Cryst. Growth Design 10 3608
[14] Takeyama Y, Maruyama S and Matsumoto Y 2011 Cryst. Growth Design. 11 2273
[15] Takahashi R, Matsumoto Y, Koinuma H, Lippmaa M and Kawasaki M 2002 Appl. Surf. Sci. 197–198 532
[16] Yoshimoto M, Maeda T, Ohnishi T, Koinuma H, Ishiyama O, Shinohara M, Kubo M, Miura R and Miyamoto A 1995 Appl. Phys. Lett. 67 2615
[17] Itaka K, Yamashiro M, Yamaguchi J, Haemori M, Yaginuma S, Matsumoto Y, Kondo M and Koinuma H 2006 Adv. Mater. 18 1713
[18] Snyder E J, Anderson M S, Tong W M, Williams R S, Anz S J, Alvarez M M, Rubin Y, Diederich F N and Whetten R L 1991 Science 253 171
[19] Richter A, Ries R, Szulzewsky K, Pietrzak B and Smith R 1997 Surf. Sci. 394 201
[20] Krätschmer W, Lamb L D, Fostiropoulos K and Huffman D R 1990 Nature 347 354
[21] Tokuda H, Tsuzuki S, Susan M A B H, Hayamizu K and Watanabe M 2006 J. Phys. Chem. B 110 19593