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Alignment Control of Organic Thin Films by Recrystalization under Laser Heating

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We propose a new approach to make uniform area of organic thin films from a few μm to a few hundreds μm using heat injection by laser irradiation. A conventional visible laser diode is applicable to the laser heating. Alignment control of the molecules is also possible by laser sweeping. Our method is composed of melting the organic thin films by laser heating and recrystalization by cooling. The large difference of growth rate with respect to crystal orientation enables growth of a large crystal with preferred orientation from numerous small crystals with random orientation.
Key words: alignment control, thin film, laser, heat

1. INTRODUCTION

Development of organic thin film devices (electro luminescence, light emitting diodes and displays, thin film transistors, etc.) becomes prosperous in recent years [1-4]. In particular, transistors require high charge mobility, since the channel length is much longer than those of other devices. In order to obtain higher mobility, appropriate molecular alignment in large area is essential.

In most cases, organic thin films consist of polycrystals with grain size of less than a few μm. Domain boundaries between them deteriorate charge mobility. These thin films do not show intrinsic mobility. Therefore, a method to grow large grain is required. The growth size should be at least a few tens of μm in case of organic thin film transistors, since typical channel length between the source and drain electrodes is 10～50μm. The method also needs alignment control of the molecules, because the charge hops through π-π stacking of the molecules.

Alignment control of molecules using light is an effective method. Ichimura *et. al.* reported a UV-vis photoalignment of nematic and discotic liquid crystals on an azobenzenene monolayer film[5,6]. Trans-cis photoisomerization of the azobenzene molecule is the driving force of the alignment control. Shimizu *et. al.* proposed the alignment control of discotic liquid crystals using infrared polarized laser [7,8]. Vibrational exitation of the discotic molecules and molecular dichroism are the driving force of the alignment control.

In this paper, we present a new approach to grow grains of a few hundreds of μm in size using heat injection by laser irradiation. A conventional visible laser diode is applicable to the laser heating. Alignment control of the molecules is also possible by laser sweeping. Our method is composed of melting the organic thin films by laser heating and recrystalization by cooling. The large difference of growth rate with respect to crystal orientation enables growth of a large crystal with preferred orientation from numerous small crystals with random orientation.

2. EXPERIMENT

2.1 SAMPLE PREPARATION

Copper (II) 1,4,8,11,15,18,22,25 -octabutoxy-29H, 31H-phthalocyanine (PC mp: 228℃) used in this study was obtained from SIGMA-ALDRICH, Inc.. Molecular structure of PC is shown in Fig. 1. This molecular has a discotic structure and forms a columner crystal in which π-orbitals of the molecules stack. The PC was dissolved in

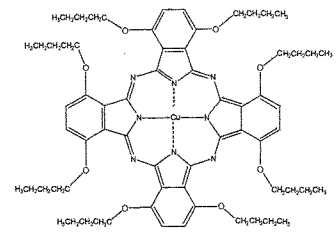

Fig.1 Structure of copper (II) 1,4,8,11,15,18,22,25-octabutoxy-29H, 31H-phthalocyanine (PC)

dimethylcyclohexane (DMCH) at a concentration of 20g/L, and filtered through a 0.20μm pore size PTFE membrane syringe filter. The solution was dropped onto polyimide (PI) film (drop-casting process) and heated at 90℃ for 1 hour to evaporate the solvent. The thickness of the PC layer was 2μm.

Figure 2(a) shows X-ray diffraction pattern of the PC film. A longitudinal arrangement of the

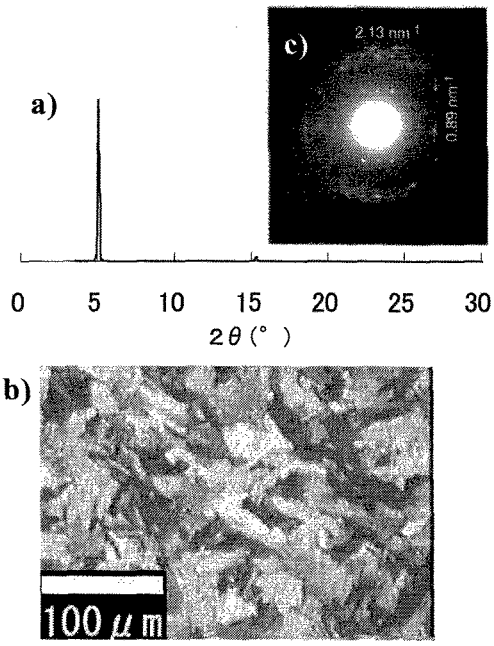

Fig.2 X-ray diffraction pattern of the PC film (a). Microscope picture of the PC film (b) and TED pattern of the film (c).

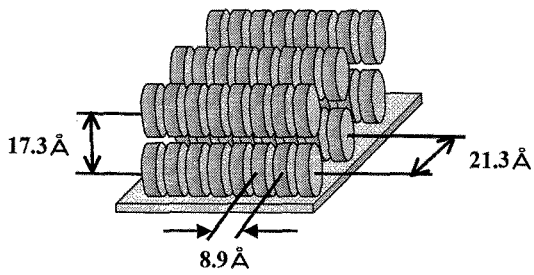

Fig.3 Model structure of a monodomain in the PC film by XRD and TED results.

PC is supposed from the spectrum. The PC columns stack paralell to the underlying PI layer and the longitudinal distance between the columns is 17.3 Å . Figure 2 (b) shows a microscope picture of the PC film under cross Nicol configuration. The film had grain structure and the average size of each small grain was from several to several tens of μm. Lateral direction of the column in the PC film was random. Figure 2 (c) is a transmission electron diffraction (TED) pattern of a small grain. Clear spots were observed at 8.9 Å and 21.3 Å. Spots at 8.9 Å correspond to distance of intracolumner π-π stacking. Spots at 21.3 Å mean the lateral distance between the columns. The structure of the grain derived from the X-ray diffraction and the TED patterns is shown in Fig. 3. The longitudinal distance between columns was 17.3 Å , and the lateral one was 21.3 Å . The intermolecular distance in the PC column was 8.9 Å.

We used visible laser diode (TOSHIBA co. TOLD9150 30mW) to heat the PC films. The wavelength of the laser diode was 689nm. Figure 4 shows the absorption spectrum of the PC film and the wavelength of the laser used in this experiment. The beam of the laser diode was focused on the PC surface and size of the beam spot was about 100μm. Beam power of the laser on the sample surface was about 20mW.

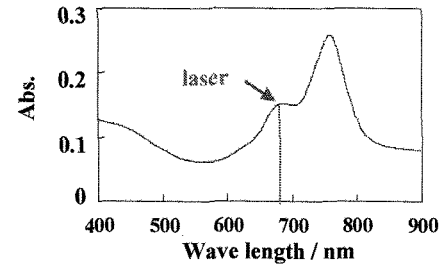

Fig.4 Absorption spectrum of the PC film and the wavelength of the laser used in this experiment.

2.2 GROWTH OF ALIGNMENT AREA BY LASER HEATING

Process of growth from small grain by laser heating is shown in Fig. 5. Before the laser heating, the PC film had a grain structure. During the laser heating, liquid phase is observed in Fig. 5b, and its diameter was about 140μm. When the laser stopped, the liquid phase started to recrystlize from the edge of the melted area toward the center and growth of grain is observed (Fig. 5c). The size of the grains after the laser heating was about 100~200 μm, which is much larger than that of the original ones.

2.3 GROWTH OF ALIGNMENT AREA AND ALIGNMENT CONTROL BY LASER SWEEPING

Experimental results about growth of grain and alignment control by laser sweeping are shown in Fig. 6. Grain structure of the PC film before the laser irradiation is shown in Fig. 6a. The laser beam was irradiated and was swept in a line from lower right to upper left of Fig. 6b with 12.5μm/s. The direction of the sweeping and the polarization axis A were parallel. The growth of grain from the lower right of the figure was observed. After the sweeping, a large (over 200μm) grain is observed in Fig. 6c. The area showed a single color of dark tone. When we rotate the film counterclockwise by 45° , the dark area becomes bright as shown in Fig. 6d.

3 DISCUSSION

To explain the results, we made calculation about temperature distribution in the PC film caused by laser irradiation using a Fourier series method [9]. The size of the laser beam was 100μm. The results are shown in Fig. 7. The

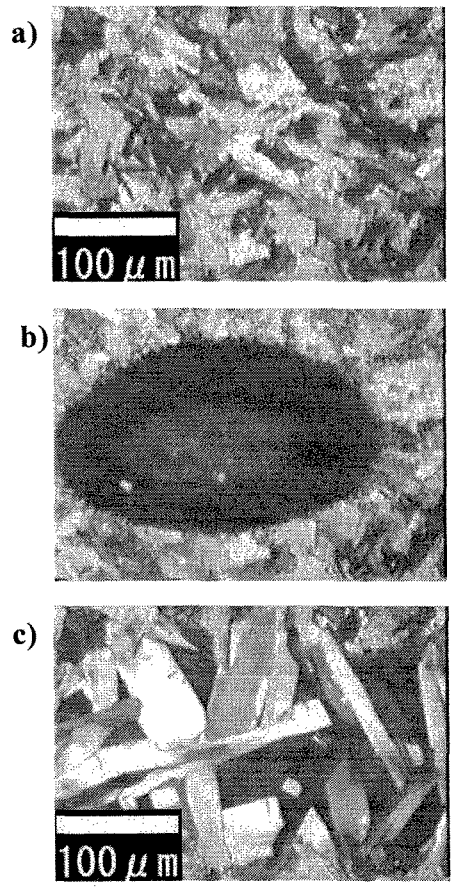

Fig.5 Domain growth by laser heating. (a) Microscope picture of the PC film before the laser irradiation, (b) during the irradiation , (c) after the irradiation.

temperature distribution shows 2-dimentional gaussian distribution along the surface, and thermal gradient in the depth direction is negligibly small. The diameter of the melted area is estimated to be approximately 140μm, which coincides with the observed value (about 120μm).

Next, we made calculation about the influence of laser sweeping on the temperature distribution. The calculated results (not shown) demonstrated that there was no dynamical effect of laser sweeping on the temperature distribution up to speed of several hundreds of mm/s. From these results, we conclude that the statical one-dimentional model can be used to describe the recrystalization and the domain growth by laser sweeping.

In the one-dimentional model, the velocity of recrystalization from liquid phase is given as follows [10];

$$V_n = K_T \cdot \Delta T / T_{MO}$$

$$K_T = \frac{\Delta h}{\pi a^2 \eta} e^{-\Delta s / k_B}$$

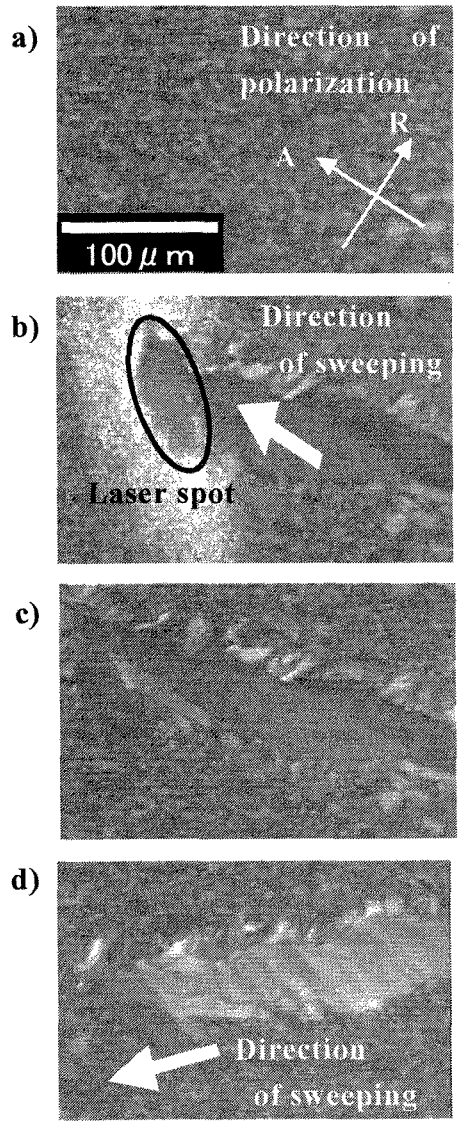

Fig.6 Pictures of the PC film under cross Nicol. (a) Multidomain structure before the laser heating. Two directions of polarization axis are shown by arrows (A and R). (b) Laser beam was being swept in a line. The direction of the laser was parallel to the polarization axis A. (c) After the sweeping. (d) The 45 ° rotated PC film.

where T_{MO} means the melting point of the interface between the crystal phase and the liquid phase. ΔT is the degree of supercooling of the liquid phase. Δh is latent heat of a molecule. Δs is difference of entropy between the crystal and the liquid phase. a is the lattice constant of the crystal. η is viscosity. k_B is Boltzmann constant. The velocity of recrystalization is inversely proportional to the lattice constant. Crystal axis with the least lattice distance shows the fastest growth.

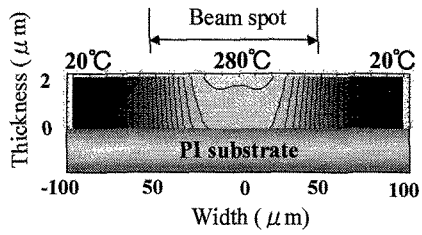

Fig.7 Calculated temperature distribution of a PC film under illumination by laser diode. Spot size of the laser beam was 100um. Thermal conductivity of air , PC and PI was 0.026, 0.3 and 0.29J/mKs, respectively.

Schematic explanation of the crystal growth by laser sweeping is shown in Fig. 8a. Crystal grows in any directions at the starting point of the recrystalization (the interface between the liquid phase and crystal phase), but the direction of the least lattice distance overwhelms all the other directions at last. In the PC column, the intracolumner $\pi-\pi$ stacking has the least lattice constant. Therefore, we can expect that the direction of the column is parallel to the direction of the laser sweeping. The schematic image of the concept is shown in Fig. 8b.

4.CONCLUSION

We propose a new method to grow grains of a few hundreds of μm in organic thin films using heat injection by laser irradiation. A conventional visible laser diode is applicable to the laser heating. Alignment control of the molecules is also possible by laser sweeping. The direction of the PC columns was parallel to the direction of the laser sweeping. Our method is composed of melting the organic thin films by laser heating and recrystalization by cooling. The large difference of growth rate with respect to crystal orientation enables growth of a large crystal with preferred orientation from numerous small crystals with random orientation. This method is expected to be useful in improving mobility in organic transistors. The method has position selectivity, which is suitable for highly-integrated organic devices.

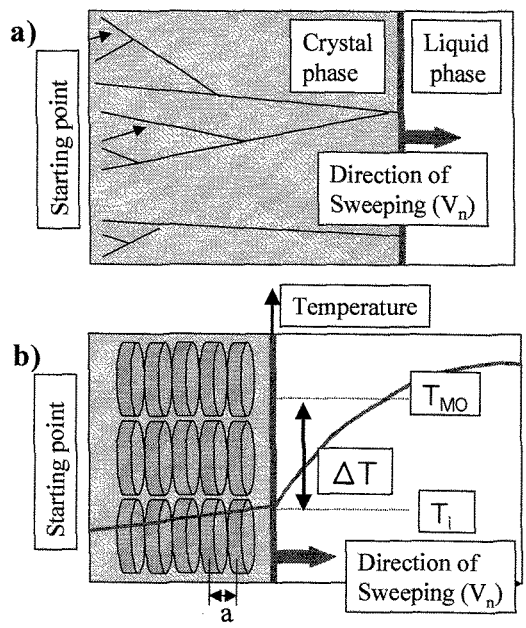

Fig.8 (a) Schematic explanation of crystal growth. (b) Schematic image of the alignment control by laser sweeping. T_i means the temperature of the interface between the liquid phase and the crystal phase.

5. REFERENCES

[1] A. Dodabalapur, Z. Bao, A. Makhija, J. G. Laquindanum, V. R. Raju, Y. Feng, H. E. Katz and J. Rogers, *Appl. Phys. Lett.* **73**, 142 (1998).

[2] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Loeglund and W. R. Salaneck, *Nature* **397**, 121 (1999).

[3] H. E. A. Huitema, G. H. Gelinck, J. B. P. H. van der Putten, K. E. Kujik, C. M. Hart, E. Cantatore, P. T. Herwig, A. J. J. M. van Breeman and D. M. de Leeuw, *Nature* **414**, 599 (1999).

[4] H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbaserkaran, W. Wu and E. P. Woo, *Science* **290**, 2123 (2000).

[5] K. Ichimura, Y. Hayashi, Y. Kawanishi, T. Seki, T. Tamaki and N. Ishizuki, *Langmuir* **9**, 857 (1993)

[6] K. Ichimura, *Chem. Rev.* **100**, 1847 (2000).

[7] Y. Shimizu, K. Awazu and H. Monobe, *Thin Solid Films*, **393**, 66-72 (2001).

[8] H. Monobe, K. Awazu and Y. Shimizu, *Adv. Mater.* **12**, 1495-1499 (2000).

[9] W. B. Joyce and R. W. Dixon, *J. Appl. Phys.* **46**, 855-862 (1975).

[10] S. Saito, "Kessyo Seicho", Shokabo, 2002 (in Japanese)

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