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Self-assembled submicron-height terrace structures of pentacene single crystals formed in liquid crystal cells

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A flat-surface single crystal structure of pentacene organic semiconductor was formed, with a submicron-height terrace structure, in liquid crystal solvent cells; the formation mechanism is discussed. By cooling the pentacene solution in a heated cell until supersaturated, a variety of segregated crystal morphology was observed, including dendrite, lozenge and needle-like crystals. Segregation of lozenge crystals was promoted by the appropriate pentacene concentration combined with the rubbing process of polyimide alignment layers, and the crystal morphology was examined in detailed. As a result, based on terrace-structural growth, low-profile flat-surface crystal morphology was found in addition to conventional pyramidal morphology. The molecular alignment of the flat pentacene crystal was confirmed by anisotropy of the microscopic Raman scattering intensity of the polarized incident light used for excitation. The self-assembly of flat thin single crystal plates, whose maximum size reach 150 μm approximately, may be applicable to practical electronic devices such as organic transistors.

1. Introduction

Flexible plastic electronics based on organic semiconductors are of great interest for future use in field effect transistors [1, 2] such as thin film transistors in flexible screen displays [3]. A pentacene molecule with a skeleton of linear benzene-ring condensate is anticipated as a next-generation semiconductor material in many types of organic semiconductor. This is because its hole-carrier charge mobility reaches that of amorphous silicon inorganic semiconductor. For progress in pentacene semiconductors, single crystal growth is desired with a molecular alignment like that of rod-like liquid crystal (LC) molecules, because the overlapping of π-electron orbitals (due to C=C chemical double bonding) between molecules aligned in a certain direction increases their charge mobility. The overlapping of numerous pentacene molecules is desirable for obtaining high charge mobility, and a flat thin single crystal film with perfect molecular alignment would be ideal for coating metal electrodes and driving charge in organic thin film transistors.

However, it is well known that liquid phase crystal growth of pentacene is difficult, because there are few organic solvents to match the strong intermolecular bonding force of pentacene. The pentacene organic semiconductor features a skeleton with a large π-electron conjugate system, and the rigid molecule is similar to a segment of a LC molecule. Pentacene does not have such long flexible skeletons (including alkyl chains) as LC materials, therefore solid pentacene semiconductor exhibits little solubility in most organic solvents.

Although a precursor in the synthesis of a pentacene component has been reported in an other fabrication process [4], it is thought that high purity film formation is difficult because of non-reacted chemical components. As a result, thin film deposition by vacuum evaporation of pentacene is now used in the fabrication of field effect transistors. This vapor phase growth process generates multiple crystal grains due to different molecular alignment directions [5, 6], and grain boundies reduce the carrier mobility because of alignment defects with charge traps.

It is expected that LC features such as a rod-like molecular shape and fluidity can contribute to organic electronics with alignment control. We have proposed the use of LC solvents for obtaining liquid phase growth of pentacene single crystal. In previous research, it was recognized that a large amount of pentacene powder can be dissolved in heated terphenyl or biphenyl LC materials in the isotropic phase [7]. This may be caused

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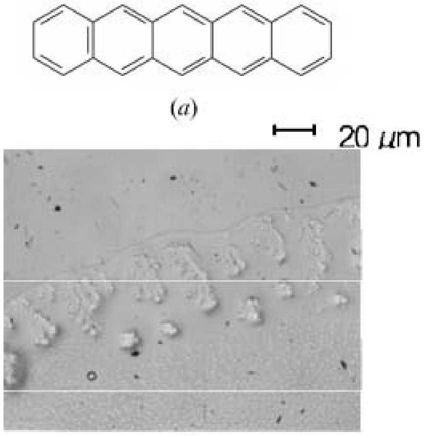


Figure 1. (*a*) Molecular structure of pentacene. (*b*) Scanning electron microscope photograph of pentacene segregated by benzene solvent evaporation.

by the transformation of pentacene/LC molecular packing states to solution or crystal. By using this phenomenon we demonstrated that alignment-controlled large pentacene single crystals can be grown on a rubbed polyimide layer. Thus orientation-controlled pentacene single crystal growth with pyramidal lozenge morphology is obtained in cooling the pentacene/LC solution.

To apply the single crystal to practical electronic devices, morphological control of the pentacene crystal is needed. In particular, thin flat-surface crystal formation [8] is essential in the organic transistor field. In this report, we in detail describe a flat-surface single crystal plate with self-assembled terrace-structured morphology, which is suitable for electronic device applications. The detailed crystal formation process is reported, and the crystallization mechanism of the terrace structure is discussed in terms of molecular stacking and alignment.

2. Experimental

The pentacene material shown in figure 1 (*a*) is soluble in few organic solvents. As experimental reference, commercially available pentacene powder was dissolved in benzene to crystallize it. As shown in the photomicrograph of figure 1 (*b*), a small amount of pentacene was segregated as dendrite or foliated small crystals when the benzene solvent was evaporated from the solution (pentacene concentration: 0.005 wt %). In the last-to-evaporate area pentacene crystallization was recognized. However, neither regularly shaped crystal morphology, nor uniform molecular alignment was obtained. The irregular and local pentacene crystals obtained cannot be applied to practical electronics use.

On the other hand, our crystallization method using an LC solvent is as shown in figure 2. The same pentacene powder was dissolved in cyanobiphenyl or terphenyl LC mixtures (E 7 or MJ 911421, Merck, respectively), where the pentacene and LC were heated at over 180°C. The solution was then filled into a glass substrate cell (cell gap 50 μm) with polyimide alignment layers (AL-1254, JSR). The surface of the polyimide layer was rubbed in advance with a spinning roll with nylon micro-fibres, so that the molecular chains of the

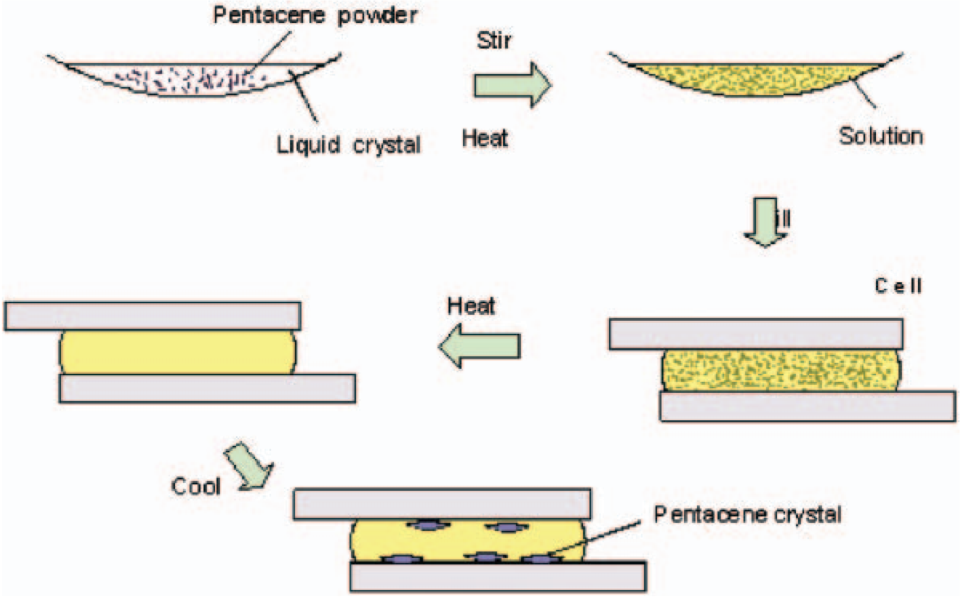


Figure 2. Formation process of pentacene single crystals using a pentacene/LC solution cell.

polyimide surface could orient to the rubbing direction. The solution cell was finally cooled to room temperature.

In the cooling process of the solution cell, segregation and growth of pentacene single crystal were possible in the supersaturated state. Crystal segregation was observed in both the isotropic and nematic phases (with molecular alignment) of the cooling solution. We considered that both rod-like molecules of LC and pentacene form molecular stacking or aggregates in the solution, because the light absorption spectrum [7] (yellow) of the solution is greatly changed from that (blue or violet) of the original pentancene material. We infer that the large spectral change in the molecular aggregate is caused by considerable deformation of the pentacene π-electron orbitals due to short distance packing of a part (the π-electron conjugate system) of the LC molecule.

3. Morphological control

The solution conditions control the morphology of the segregated pentacene crystal. Dependence of crystallization on pentacene concentration was examined in detail first, using an optical microscope (Optiphoto 2-POL, Nikon) with a temperature-controlled bath (WT-STC200, Toyo). The observation form of crystals segregated from solution in cyanobiphenyl LC material is shown in figure 3. From a low concentration solution of 1 wt%, blue lozenge single crystals appeared. A typical lozenge crystal is shown in the small circle of figure 3 (*a*). On increasing the ratio to 3 wt%, black radial dendrite crystals were seen, having no macroscopic order morphology, figure 3 (*b*).

It is thought that both the blue lozenge and black dendrite crystals are composed of pentacene material, and the light absorption difference is due to the thickness difference, i.e the lozenge crystal is thinner than the dendrite crystal. We consider that the crystal polymorph is caused by different pentacene-component feed rate (or quantity supplied) from the solution and due to different solubilities of the crystals formed.

When the pentacene concentration of the solution was increased to 5 wt%, large yellow needle-like crystals appeared, as shown in figure 3 (*c*). These may be crystals of pentacene/LC molecular aggregate or stacking, because its light absorption spectrum is extremely similar to that of the yellow LC/pentacene solution.

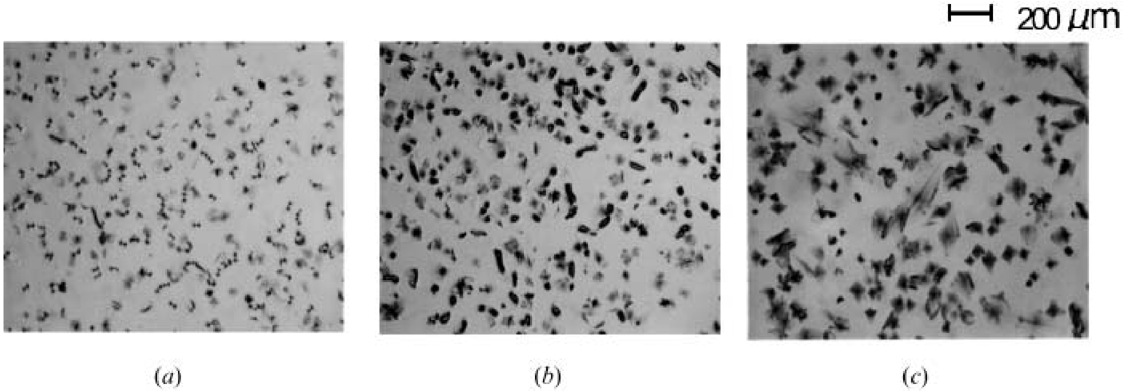
The thin lozenge crystals shown figure 3 (*a*) are preferable for electronic device applications, because of their ordered thin morphology. We then changed the rubbing process time for polyimide alignment layers of the solution cell, using a pentacene concentration of 1 wt%. Figure 4 shows the form of segregated pentacene crystals. By increasing the rubbing time, the size of lozenge crystals was clearly increased. The rubbing process of the polyimide alignment layer thus promotes the growth of large lozenge single crystals. This indicates that crystal nucleation of lozenge pentacene occurs on the polyimide surface with molecular chain alignment.

4. Terrace structure

While the rubbing of alignment layers promoted generation of large lozenge crystals, we observed two different behaviors of the single crystals: stationary, or drifting in thermal convection of the solution. The former crystals adhere to the alignment layer surface, and the latter are removed from the alignment layer. To examine lozenge crystal morphology in detail, one glass substrate was removed from a solution cell using the terphenyl LC, and the solution and drifting crystals were washed off with ethanol. The lozenge crystals remaining on the substrate surface were observed by a confocal laser microscope (VK-8510, Keyence).

(*a*) (*b*) (*c*)

Figure 3. Photomicrographs of pentancene crystals segregated in solution cells with different pentacene concentrations: (*a*) 1, (*b*) 3, (*c*) 5 wt%.



(a) (b) (c)

Figure 4. Photomicrographs of pentancene crystals segregated in the cells having alignment layers with different rubbing times: (a) no rubbing, (b) single rubbing, (c) 30 times rubbing.

While high profile pyramidal morphology [7] was already confirmed in our previous studies, we have now recognized that lozenge crystallization consists of submicron-height terraces. Moreover, for the first time we found growth of a flat-surface single crystal plate comprising a single terrace (thickness approximately 0.2 μm), figuer 5 (a), among pyramidal crystals formed with several terraces, figure 5 (b). While the pyramidal morphology progresses and enlarges with the growth of thin terrace structures, a terrace extension perpendicular to the substrate surface is suppressed in the flat-surface crystals. The terrace height corresponds to more than several hundred times the size of a pentacene molecule; the terrace edge features a slope structure.

Scanning electron microscope (VE-7800 of Keyence) observation of a flat-surface lozenge crystal is shown in figure 6. The figures almost express the real area/height aspect of the terrace shapes, while the height (thickness) axis is extended in figure 5. The maximum length of flat crystals obtained in our experiment reached 150 μm, as shown in figure 5 (a). The length is sufficient for a gate gap in thin film transistors. The thin large-area flat pentacene crystal plate is suitable for electronic device applications such as transistors, because its flat surface and constant thickness are beneficial for charge carrier movement.

We have already confirmed by Raman scattering studies that segregated blue pyramidal crystals are composed of pentancene [7]. The obtained single-terrace pentacene crystals with uniform molecular alignment must have considerable anisotropy of Raman scattering behaviour due to the long molecular structure shown in figure 1 (a). In this experiment, we used an optical microscopy method [9] to study Raman scattering, based on polarized exciting light. In practice, various wavelength-shifted Raman scattered radiation from a lozenge single-terrace plate pentacene crystal adhereing to the substrate were observed using a polarizing microscope (JRS-System TEM-200, Renishaw). It is already known that pentacene has Stokes line wavelength shifts [7] of 1375 cm^{-1} for ring-skeleton vibration. The pentacene molecule also shows 1162 and 1181 cm^{-1} Raman shifts for the C–H bond angle vibration. In the results shown in figure 7, the polarization angle of incident exciting laser light of wavelength 633 nm is changed with respect to the rubbing direction.

The Raman scattering peaks of wavelength shifts for incident light polarized parallel to the rubbing direction are larger than those for light polarized perpendicular to the rubbing direction. This observed Raman scattering anisotropy confirmed that the long rigid molecules of pentacene in the lozenge single crystal align parallel to the rubbing direction.

5. Formation mechanism

From the experimental results of morphological observation and molecular-alignment evaluation, we consider a model for the formation of pentacene terrace morphology as shown in figure 8. The LC and pentacene molecules align in parallel or form a molecular aggregate in a heated solution cell, where the rigid long plate-like π-electron conjugate segment of the LC skeleton may be laminated with a rigid long plate-shaped pentacene molecule (in case of terphenyl LC, the length of the LC π-electron conjugate is close to that of pentacene). The molecules including pentacene can thermally move and flow in the solution because of the flexible alkyl chain segment of the LC molecule, without crystallization or segregation. During cooling of the heated solution, thermal molecular movement is weakened, and flexible alkyl chains with weakened

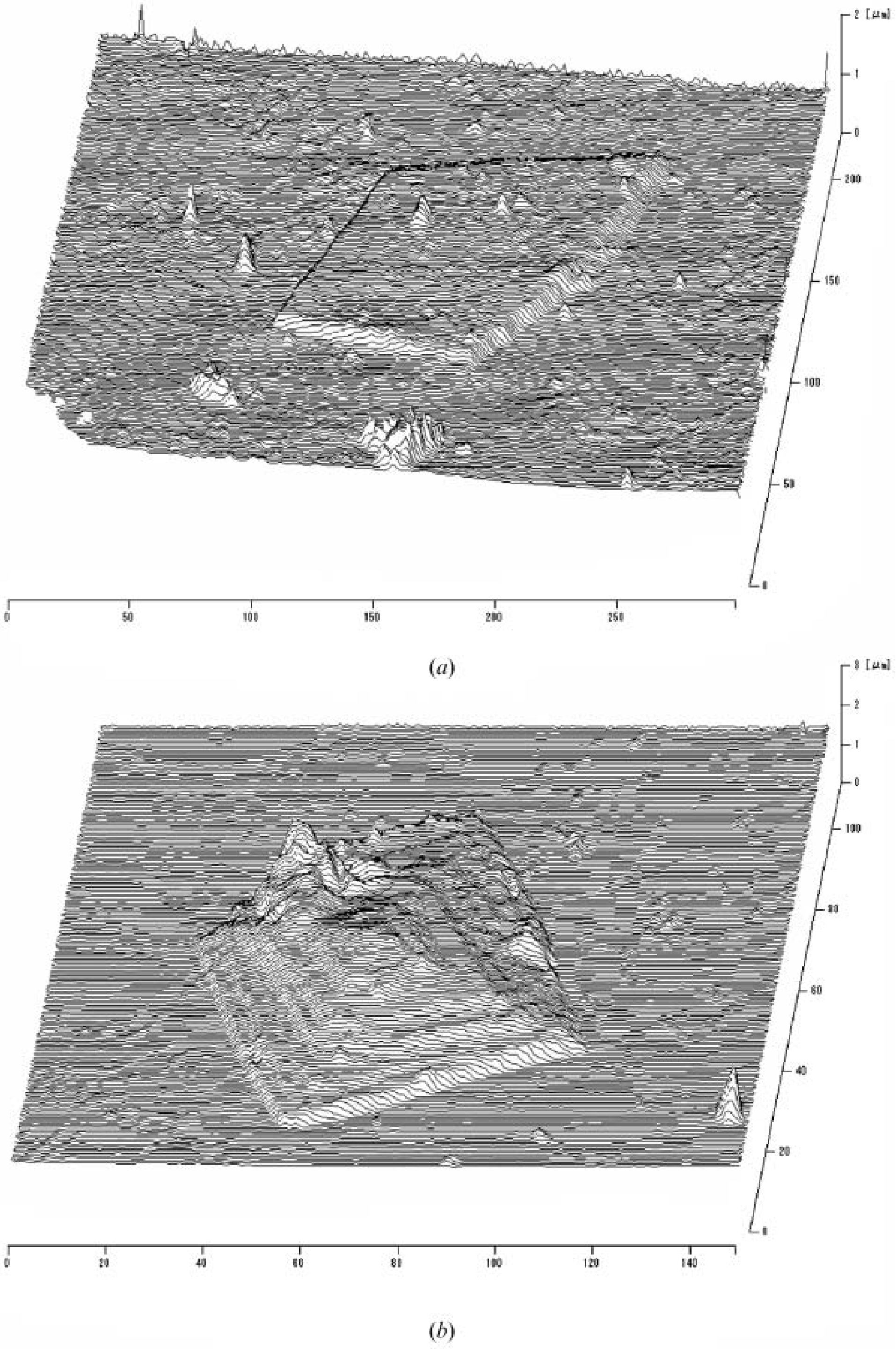


Figure 5. Confocal photomicrographs of lozenge pentacene crystals: (*a*) thin flat-surface plate, (*b*) pyramidal morphology with terrace structure.

thermal movement no longer have a sufficient effect to intercept the pentancene–pentacene molecular packing. As a result, pentacene molecules are separated from LC molecules, and crystal growth nuclei are then generated on a polymer chain-aligned surface of the rubbed alignment layer. This is because there is anisotropic interaction between the long pentacene molecule (or long pentacene/LC molecular aggregate) and the

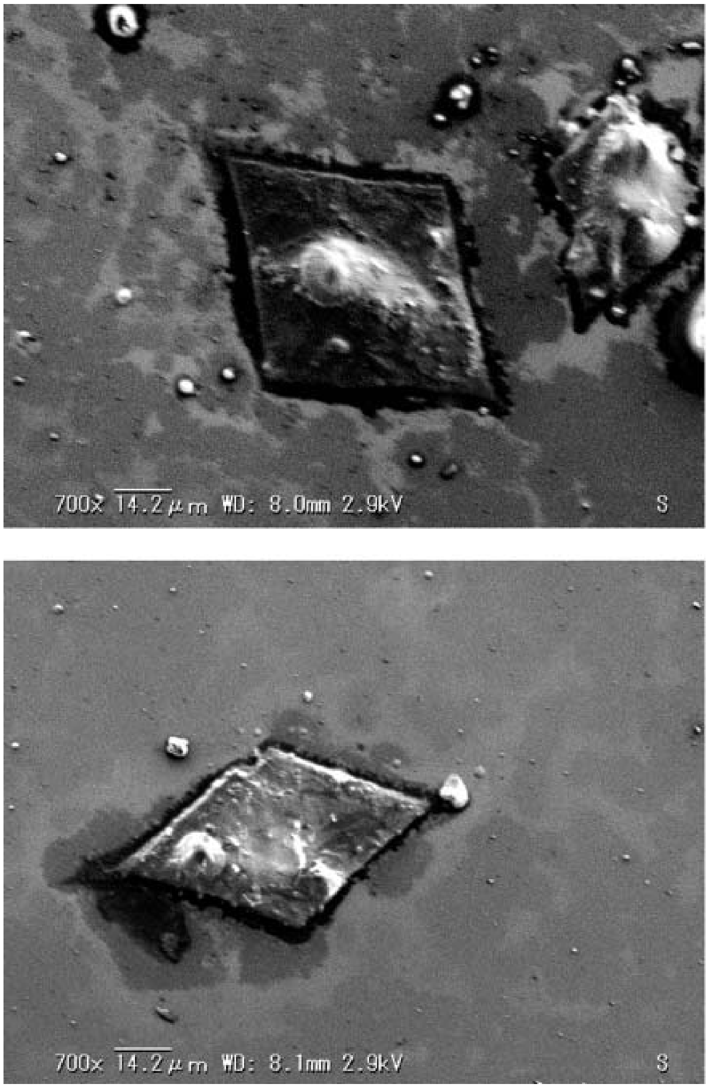


Figure 6. Scanning electron microscope photomicrographs of segregated single-terrace pentacene crystal.

aligned polyimide chains even in the isotropic phase of the solution cell.

Subsequently, crystal growth progresses through pentacene molecular lamination based on anisotropic interaction (interaction in the molecular short axis direction is larger) between aligned pentacene molecules. As a result, large single crystals of pentacene, molecularly aligned parallel to the rubbing direction, are obtained on the substrate surface. The low-profile single-terrace formation is induced by faster growth parallel to the substrate surface plane. The terrace height must be determined by intrinsic anisotropic surface energy of the pentacene crystal and interfacial energy with the substrate surface. The order degree of terrace formation is also influenced by the feed rate of pentacene from the solution, which is induced by thermal solution convection in the cell. The height of terraces appears modulated as shown in figure 5 (*b*).

The difference in formation mechanism of the single-terrace and multi-terrace structures is not clarified in detail. It may be related to slight differences in molecular orientation direction or molecular packing in the initial fine growth nucleus formed on the alignment layer surface.

6. Conclusions

We have shown that the formation of single-terrace pentacene crystal morphology is possible in a pentacene/LC solution by use of appropriate pentacene concentration and rubbing conditions. It was also confirmed that a flat thin single crystal plate, suitable for electronic devices, can be achieved with molecular

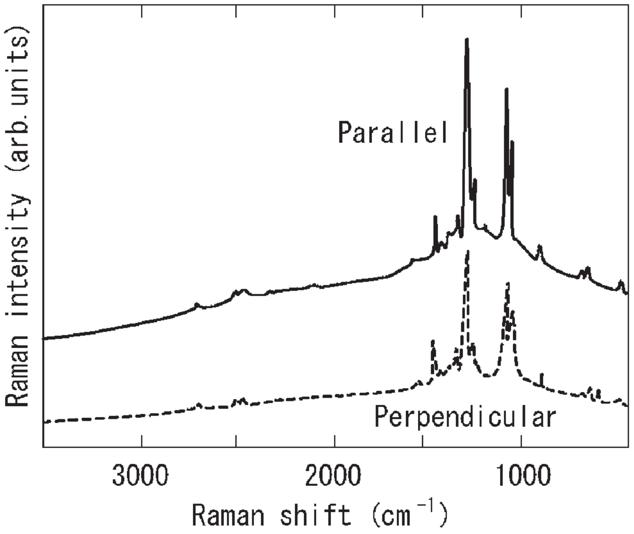


Figure 7. Anisotropic microscopic Raman scattering spectra of a segregated lozenge single-terrace pentacene crystal for two orthogonally-polarized incident excitiation beams.

alignment. We also discussed pentacene crytalization mechanism in terms of molecular stacking and packing models. In the next stage of research, a more detailed self-assembled terrace segregation mechanism, and charge mobility anisotropy of the obtained pentacene crystals, must be investigated. The controlled molecular alignment of a single crystal will enhance various organic electronic performances in future.

Spatial control of segregation and molecular alignment of pentacene crystals is also affected by local surface processing of a substrate. The spatial crystallization control of various organic semiconductors has a great potential to open up a new application field for LC materials as functional solvents.

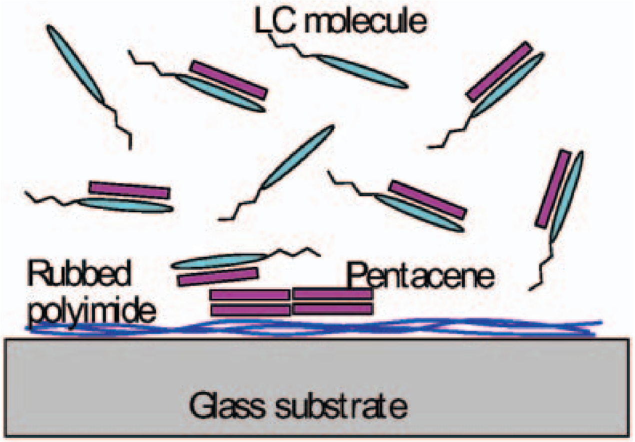


Figure 8. Formation model of single-terrace pentacene crystals in a pentacene/LC isotropic phase solution cell with rubbed alignment layers.

References

[1] C.D. Dimitrakopoulos, A.R. Brown, A. Pomp. *J. appl. Phys.*, **80**, 2501 (1996).
[2] G.H. Gelinck, T.C.T. Geuns, D.M. de Leeuw. *Appl. Phys. Lett.*, **77**, 1487 (2001).
[3] H. Fujikake, H. Sato, T. Murashige. *Displays*, **25**, 3 (2004).
[4] A. Afzali, C.D. Dimitrakopoulos, T.L. Breen. *J. Am. chem. Soc.*, **124**, 8812 (2002).
[5] F.J.M. Heringdorf, M.C. zu, Reuter, R.M. Trimp. *Nature*, **412**, 517 (2001).
[6] M.L. Swiggers, G. Xia, J.D. Slinker, A.A. Gorodetsky, G.G. Mallaras, R.L. Headrick, B.T. Weslowsky, R.N. Shasidhar, C.S. Dulcey. *Appl. Phys. Lett.*, **79**, 1300 (2001).
[7] H. Fujikake, T. Suzuki, F. Isaka, F. Sato. *Jpn. J. appl. Phys.*, **43**, L536 (2004).
[8] H. Fujikake, T. Suzuki, Y. Fujisaki, T. Murashige, H. Sato, H. Kikuchi, T. Kurita. *Proc. int. Display Workshops, LCTp1-3*, 109 (2004).
[9] H. Fujikake, T. Murashige, H. Sato, M. Kawakita, H. Kikuchi. *Appl. Phys.Lett.*, **82**, 1622 (2003).