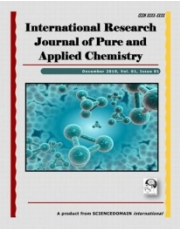

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Micrometer–Range Pattern Formation of Crystal Films from Liquid Thin Films of Maleimide Methanol Solution

Janice B. Rabor[1], Toshifumi Yoshidome[1*], Keigo Tamaki[1], Yuki Tsurumura[1], Brian J. Sarno[1] and Morihide Higo[1]

[1]Graduate School of Science and Engineering, Kagoshima University, Korimoto 1–21–40, Kagoshima City, Kagoshima Prefecture, Japan 890-0065.

Authors' contributions

This work was carried out in collaboration between all authors. JBR performed experiments, managed the literature searches, wrote the first draft and revised the manuscript. TY designed the study, revised the manuscript and headed the group discussions. KT designed the study, performed experiments and managed the literature searches. YT wrote the first draft of the manuscript. BJS and MH participated in group discussions. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Crystal films of maleimide were produced from methanol solution liquid thin film climbing a vertical glass substrate. Optical microscopy and infrared (IR) spectroscopy were used to evaluate the crystal films. Maleimide methanol solution produced four banded crystal films with different thickness appearing alongside each other in horizontal position. Each band of crystal films had a uniform pattern different from the other bands. The differences of pattern among the banded crystal films were attributed to fluid dynamics, temperature and liquid film thickness as consequence of a particular experimental condition. Each band of crystal films also exhibited different sublimation nature and variations in IR spectra.

**Corresponding author: Email: tome@apc.kagoshima-u.ac.jp;*

Keywords: Liquid thin films; pattern formation; fluid dynamics; morphology; maleimide; crystal growth.

1. INTRODUCTION

Pattern formation of crystal film deposited on a substrate from its solution after drying of solvent is one of the self–organizations resulting from a nonequilibrium process accompanied by free energy loss (Okubo, 2006, 2008; Okubo et al., 2007a, 2007b, 2007c, 2008, 2009a, 2009b, 2010). Research in this area arises from general interest in understanding nonequilibrium dynamics, crystal growth and also from requirements of industrial technologies such as film formation of semiconductors. In the recent years, controlled drying process is used for the production of film made from functional materials such as organic semiconductors (Hu et al., 2004; Maenosono et al., 1999; Yase et al., 1998) and organic light–emitting devices (Forrest, 2004; Ikegawa and Azuma, 2004) and its application to a production of large–scale nanostructure film with flatter and more homogeneous surface is desired. However, pattern formation of deposited crystal film is influenced by many chemical and physical factors such as transports of solutes and heat, interaction between molecules, convection, evaporation of liquid, etc. (Wie–Jie et al., 2007). Furthermore, crystal film formation for pattern studies is usually carried out by drying the bulk solution in a glass dish or a watch glass and hence pattern of crystal film formed is sometimes dependent on the location in such a vessel as usually observed. These make a comprehensive understanding of the phenomenon difficult.

Liquid thin film is always formed on an upper wall of glass test tube containing methanol in the bottom. We found out that gradual evaporation of the liquid thin film of a methanol solution led to the formation of a uniform crystal thin film that was highly dependent on experimentally controlled conditions. The formation of uniform crystal thin film that the experimental condition completely determined is an excellent characteristic of this system, which is advantageous for studying the pattern of crystal film on its formation mechanism, properties and structures. Actually, spectroscopic technique was applied to the structure analysis in this research, and brought useful information about the structures of the crystal film. Another significant characteristic of this system is that the liquid film formed, which produced the crystal film after the evaporation of methanol, was very thin. Liquid thin film is expected to be different from a bulk liquid in a glass dish or a watch glass in chemical and physical phenomena such as transports of solutes and heat, and fluid dynamics, which can lead to appearance of new patterns. This system, namely liquid thin film system, is first used for the studies on the drying pattern of crystal films as reported in this paper by the authors. These studies will bring new information about patterns and will also contribute to more ideal film technology in industrial fields. New pattern formation will make a new functional crystal film.

In this paper, we report the formation of crystal films of maleimide from methanol solution climbing a vertical glass substrate under certain controlled experimental conditions. Maleimide has a character of sublimation which gives interesting and useful characteristic to analyze the crystal film formed. Infrared (IR) spectroscopy was used to evaluate the crystal films together with the observations of patterns formed using optical microscopy in the micrometer range. The experimentally controlled conditions each produced only one corresponding unique pattern, that is, crystal films with unique properties were formed under different experimental conditions. Physical and chemical states of the system producing the patterns such as transports of solute and heat, fluid dynamics, temperature, liquid film thickness, and molecular interaction were estimated by considering the patterns formed and

spectra obtained together with conditions applied, and formation processes of patterns were discussed based on these estimated states.

2. MATERIALS AND METHODS

Methanol (Wako Pure Chemical Industries Ltd.) and maleimide (Tokyo Chemical Industry Co. Ltd.) were all purchased in high purity. Maleimide methanol solution (0.33, 0.11 M) was prepared from corresponding solid without further purification. The substrate, a micro slide glass (76mm x 26mm x 1.2mm, Matsunami Glass Industries Ltd.) was cleaned ultrasonically with methanol, then acetone for 20 min each prior to the actual experiment. Maleimide methanol solution (10 mL) was poured into a 50–mL beaker. A rubber sheet with opening (10.1mm x 21.6mm) covered the beaker. This set up was placed inside a glove box. The glass substrate was vertically inserted into the beaker through its opening in which the excess upper part of the substrate (17 mm) was stuck out (Fig. 1).

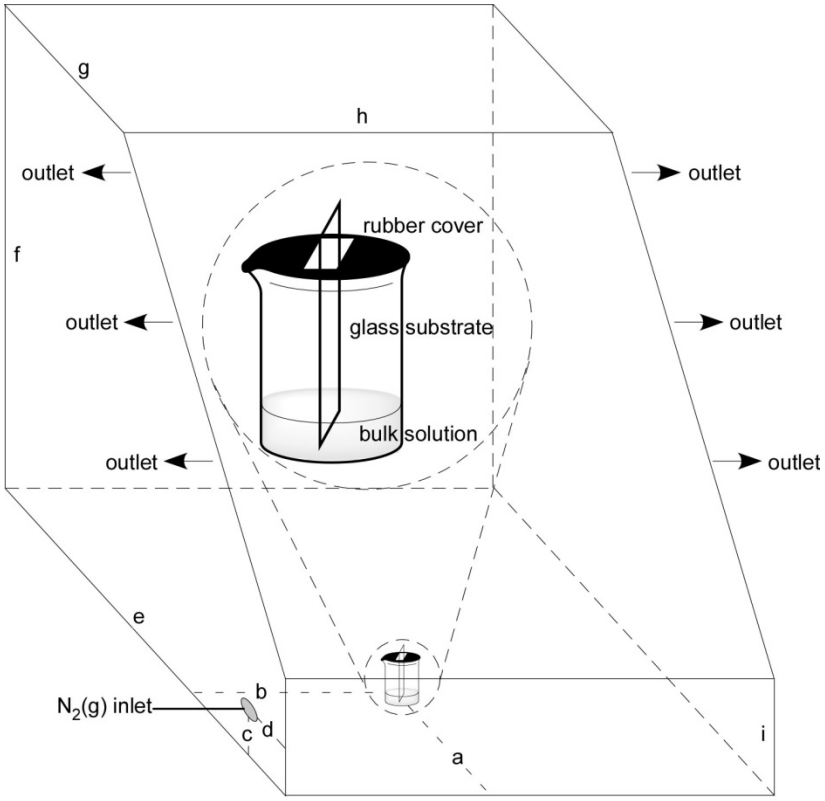

Fig. 1. The liquid thin film system consists of a beaker (inset) placed inside a glove box with the following dimensions in cm: 15.5 (a), 25 (b), 5 (c), 5.5 (d), 55.1 (e), 63.8 (f), 23.3 (g), 64.7 (h), 15.5 (i)

The solution was allowed to rise/climb onto the glass substrate for 5 min and then N_2 inflow (0.25, 1.0 kg/cm^2) was applied into the glove box for another 5 min. The N_2 flow rate near the glass substrate was about 0.05 and 0.2 m/s for 0.25 and 1.0 kg/cm^2 of N_2 inflow pressure, respectively, as measured by an anemometer (SK–73D, Sato Keiryoki Mfg. Co. Ltd.). The glass substrate was taken out from the beaker and was vertically put on a paper to remove

an excess solution on the glass substrate while still continuing the N_2 inflow. Microscope observation or IR measurement was performed immediately after the glass substrate containing the crystal film formed was taken out from the glove box.

Observations of the macroscopic and microscopic patterns were performed in an air–conditioned room at 20ºC and below 40% humidity. The macroscopic drying patterns were observed on a desk covered with a black paper. A Nikon D5000 digital camera with a macro–lens (AF–S Micro NIKKOR 60mm f/2.8G ED) was used for taking pictures of macroscopic patterns. Microscopic drying patterns were observed with an optical microscope (Model CS, Carton Valley Microscope Scientific Instruments) accessorized with digital microscope camera (Moticam 1000 1.3 MP).

The FT–IR spectra were recorded at a resolution of 8 cm^{-1} on a Perkin Elmer Spectrum One spectrometer equipped with a lithium tantalate ($LiTaO_3$) detector and 200 scans were accumulated. The glass substrate was mounted in the sample shuttle. The FT–IR spectrum of pre–cleaned glass substrate was measured and used as a reference spectrum. The same glass substrate was used in the pattern formation experiment and the FT–IR spectra of subsequently formed maleimide crystal thin films were measured immediately. The measurements were performed in an air–conditioned room at 20ºC and below 40% humidity.

For comparative purposes, 50 µL of 0.33 M maleimide methanol solution was dropped on the center of a horizontal glass substrate placed on top of a desk. The methanol solution was allowed to evaporate naturally under the atmosphere and followed by macroscopic and microscopic observations. We call this system as the dropped solution system.

3. RESULTS AND DISCUSSION

When 50 µL of 0.33 M maleimide methanol solution was dropped onto a horizontal glass substrate, the solution spread out in all directions and dried up within 90 s. Some of the drying patterns of separate trials under same experimental conditions are shown in Fig. 2. The macroscopic pictures showed mosaic patterns (A and C) and a grainy pattern (B). The microscopic pictures (a – c), corresponding to upper macroscopic pictures each, showed a common branching feature resulting from diffusion of solute, anisotropy of interfacial tension and fluctuation (Wang et al., 2009), but also showed different patterns in detail depending on uncontrollable fine condition difference. The angles between branches, for example, were 60º (b) and 45º (c). Thus, both the macroscopic and microscopic pictures revealed that the patterns formed were different even though the experimental conditions set were the same.

In the liquid thin film system, maleimide crystal film was formed on the glass substrate after the procedures described in the experimental section. As can be seen in Fig. 3a, banded crystal films divided into four regions (from the top, Regions 1 – 4) appeared alongside each other in a horizontal position depending on the experimental condition. The crystal films in Regions 1 and 2 were generated from the liquid thin film connected to the bulk solution in the beaker before and during N_2 inflow, respectively, as explained below. When the glass substrate was inserted vertically into the methanol solution, the solution climbed along surface of the glass substrate to wet them in the same manner as capillary rise does. A liquid thin film of maleimide methanol solution covered the surface of the glass substrate. As the liquid thin film reached higher positions on the glass substrate, the concentration of maleimide methanol solution became higher and higher due to methanol evaporation resulting in the formation of the crystal film in Region 1. When N_2 inflow was introduced while the substrate was still submerged in the bulk solution, crystal film in Region 2 was

generated. When the substrate was removed from the bulk solution with continuing N_2 inflow, crystal film in Region 3 was generated from the liquid thin film, while crystal film in Region 4 was generated from the residual solution left at the immersed region. The formation of the four different regions was a result of sequential experimental procedures. Each procedure can't produce a specific region alone. For example, Region 2 can't be formed without forming Region 1 since the rise/climb of the solution on the substrate is necessary before applying the conditions for the formation of Region 2. The four crystal films were visually white and homogeneous in each region. Region 3 had the darkest hue while Region 4 had the lightest hue. The liquid film thickness, whose measurement was difficult, was approximately 5 μm in the case of liquid film formed on the wall of test tube without N_2 inflow using spectroscopic technique (manuscript in progress). The liquid film on a glass substrate under N_2 inflow could be thinner than 5 μm due to rapid evaporation of methanol. We have plans for complete determination of film thickness and further studies of thinner liquid films.

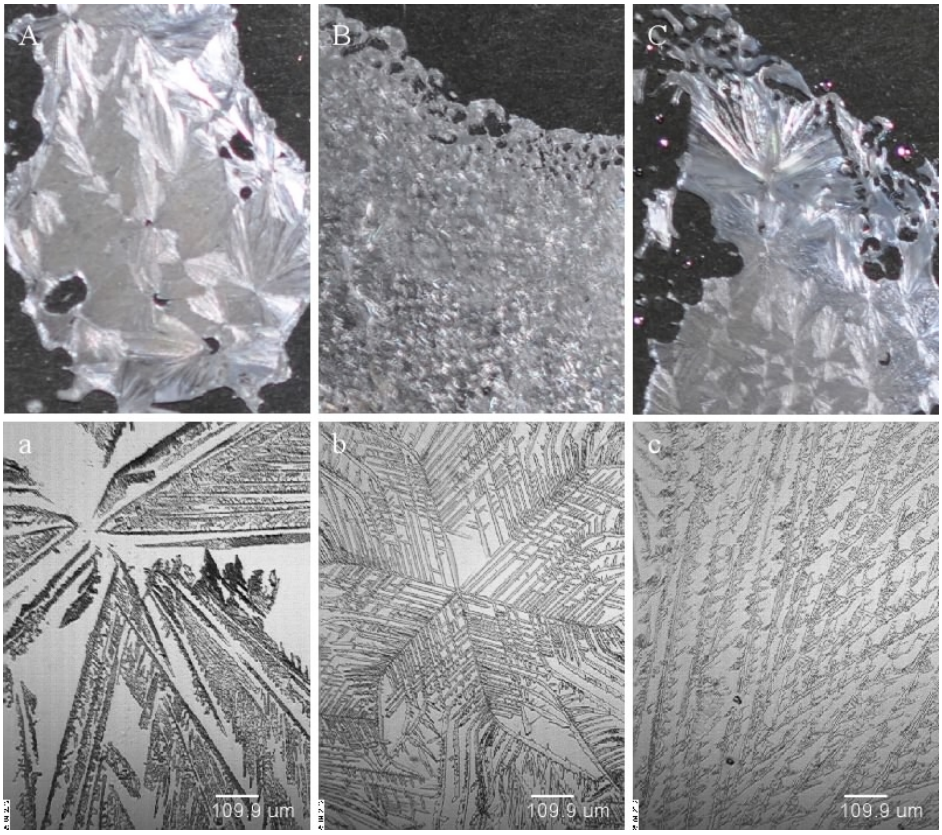

Fig. 2. Macroscopic (A – C) with its corresponding microscopic (a – c) drying patterns of maleimide crystal films produced from the dropped solution system

Under an optical microscope (10x magnification), the crystal films, as shown in Fig. 4, gave a meshlike, a dendritic, a curved–radial and a needlelike pattern from top of the glass substrate (Region 1) to bottom (Region 4). The pattern was uniform over each region, and furthermore, was unique to each region. The meshlike pattern was spread over Region 1, and less remarkable smaller structures could be observed, which was different from Regions

2 and 3. The evaporation of methanol is slow because of the absence of N_2 inflow. Taking this into account together with the pattern formed, in Region 1, the solution in the liquid thin film is thought to flow in nearly–stationary state from the bulk solution in the beaker, and the temperature decrease due to loss of heat of vaporization must be small because of the slow evaporation of methanol and adequate inflow of the solution from the bulk solution in the beaker. Homogeneous phase under equilibrium usually generates compact crystal with less significant pattern (Buckley, 1951) which is similar to Region 1. Thus, this meshlike pattern was formed under the physical state closer to stationary and equilibrium than the other regions.

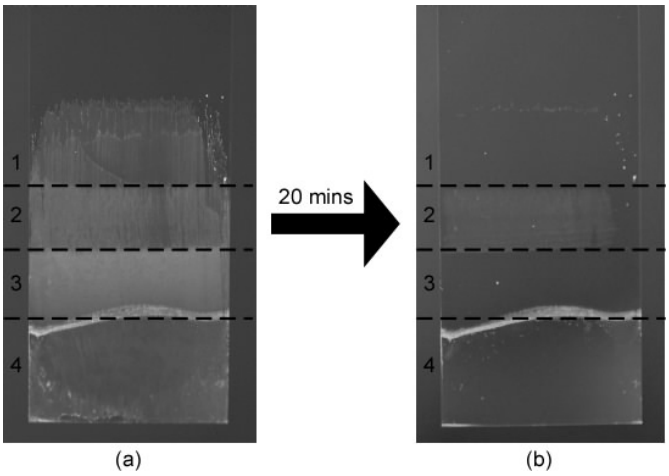

Fig. 3. Macroscopic drying patterns of the different regions of maleimide crystal film produced from the liquid thin film system: (a) immediately after N_2 inflow, (b) after 20 min

The dendritic pattern of Region 2 consisted of smaller structures of longitudinal lines (trunks) with two kinds of branches. The branches were highly localized in direction: the left branch was 43º ± 5º while the right branch was 49º ± 4º with respect to the vertical direction, which was similar to one of the angles (45º) observed in dropped solution system in Fig. 2c. Only the presence of N_2 inflow resulted in the change of pattern from meshlike in Region 1 to this dendritic one. The physical states in Region 2 of this system, however, must be different from that in Region 1 because of more rapid evaporation of methanol by N_2 inflow. In Region 2, directional evaporation of methanol must have occurred from top to bottom, the solution in the liquid thin film is thought to flow in non–stationary state from the bulk solution, and the temperature decrease must be larger than that in Region 1. Under these inhomogeneous circumstances, the side branches are generated by the fluctuation of the crystal interface in a similar manner as usual cases (Buckley, 1951). The longitudinal trunk crystals were expected to be parallel to the solution flow but were on the slant by about 3º, which is thought to be due to the fluctuation of the front of solution interface going down. Thus, these physical states of the system, aside from the chemical properties of maleimide, produced the dendritic pattern and determined the features such as the angles. Among the four regions of maleimide crystal film in this liquid thin film system, the dendritic pattern was most similar to the patterns formed from the solution dropped on a horizontal glass substrate shown in Fig. 2 (especially c). This indicates the pattern formations in the dropped solution system shown in Fig. 2 were caused by the nonstational flow of solution similar to Region 2.

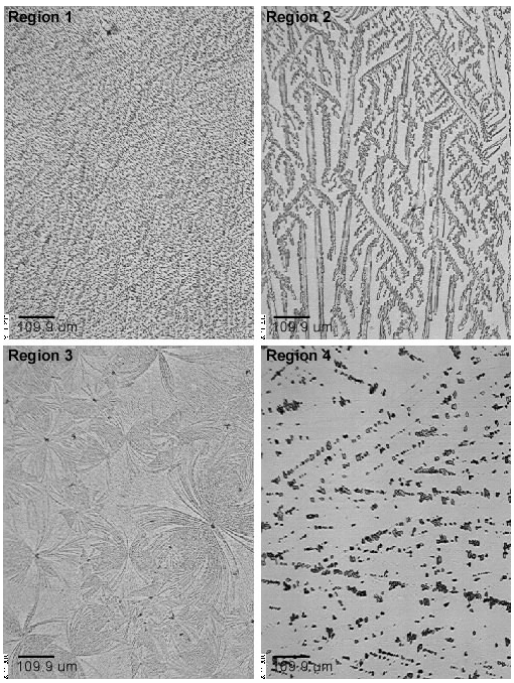

Fig. 4. Microscopic drying patterns of the different regions of maleimide crystal films produced from the liquid thin film system

In Region 3, an isotropic curved–radial pattern served as a unit structure that was uniformly repeated within the region. Isotropic nature suggests the vertical set up of the substrate did not largely influence this pattern formation. The constituent curved line crystals in each isotropic curved–radial pattern had no branches, which was different from the dendritic pattern shown in Fig. 2 and Region 2 and appeared to be self–assembled. This self–assembly nature is thought to generate the curved–line feature. These constituent self–assembled curved–lines are characteristic of Region 3 and were not observed in any other regions and in the dropped solution system shown in Fig 2. Nucleations were observed at the centers of some of the isotropic radial patterns. In Region 3, the liquid thin film was isolated from the bulk solution, causing only the uniform occurrence of rapid evaporation of methanol from all over Region 3 by N_2 inflow without any solution inflow, which suggests that the temperature decrease was larger than in Region 2. This isotropic curved–radial pattern was formed from such a physical state with high nonstationary and nonequilibrium over the region. The direction of crystal growth is usually determined by interfacial tension (Buckley, 1951), which result in dendritic pattern like those in Fig. 2 and Region 2. In Region 3, the liquid film was thin, less than 5 μm, which means the crystal formed on the substrate, occupied larger volume compared to the solution in the liquid film and was also close to the surface of the liquid thin film. Large obstacles can change the features of fluid dynamics including diffusion of solute and heat in the liquid thin film, which may lead to the formation of such a self–assembled pattern. Under faster diffusion of maleimide than evaporation of methanol in the liquid thin film, the following scenario is possible. When a trunk crystal is formed by diffusion of maleimide, the maleimide concentration of the immediate surrounding will decrease more largely than that far from the trunk crystal. Smaller concentration of the immediate surrounding should change the surface tension causing differences in fluid

dynamics such as Marangoni effect. Thus, fluid dynamics is modulated largely by generation of crystal formed, leading to the formation of such a self–assembled pattern. Further, large temperature decrease must have affected the fluid dynamics such as convection flow and Marangoni effect (Okubo et al., 2007c; Wie–Jie et al., 2007), which should influence this curved–radial crystal growth. Actually, Marangoni effect happens on the surface of volatile liquid (Linde et al., 1979) and the radial structures neighboring each other resemble honeycomb pattern of convection flow of liquid (Ball, 1999). Curved lines were observed in a flower–like pattern of 7–hydroxylcumarine crystal deposited on a horizontal slide glass (Okubo et al., 2007c). This pattern was not as radial as that in Region 3 of our system, but also might be affected by dynamical fluid motions. In the dropped solution system, the authors have not yet observed this self–assembled isotropic curved–radial pattern, which implies that this isotropic curved–radial pattern can be characteristic of the liquid thin film system.

The crystal film in Region 4 consisted of small aggregation in shape of islands. These exhibited a certain fixed directivity that made it look needlelike as a whole. In Region 4, the liquid film was isolated from the bulk leading to a large temperature decrease similar to that in Region 3, but was a thicker film as a result of its previous immersion in the bulk solution. The difference in liquid film thickness must be one of the reasons of the difference in pattern between Regions 3 and 4. Thicker liquid film must have changed the fluid dynamics in it; actually, characteristic size of convection is reported to be as large as the depth of solution prepared in vessel (Linde et al., 1979).

The influences of maleimide concentration and N_2 inflow pressure on the pattern formation were investigated in our liquid thin film system. Only the pattern in Region 3 is shown here since it was the most characteristic of the liquid thin film among the four regions. On decreasing the concentration from 0.33 to 0.11 M, the 0.11 M maleimide methanol solution appeared to be a thinner film than that of 0.33 M maleimide methanol solution, but both exhibited similar features in pattern, size and number of constituents as shown in Fig. 5. The number of constituent pattern per mm^2 and radii are summarized in Table 1 for each combination of N_2 inflow pressure and maleimide concentration. The general feature of pattern formed was not affected by concentration in this range because the concentration change by 1/3 is not thought to have caused the change in fluid dynamics. However, when the N_2 inflow pressure was increased from 0.25 kg/cm^2 to 1.0 kg/cm^2, bigger radial pattern was formed and nucleation further lessened as shown in Fig. 5 and Table 1. The increase of N_2 inflow pressure leads to an increase of evaporation rate and more turbulent airflow. The fluid dynamics such as Marangoni effect is expected to have changed due to larger decrease of temperature caused by the increase of evaporation rate, which can lead to dynamical change in pattern formation. The increase of N_2 inflow pressure to 1.0 kg/cm^2, however, merely accelerated the pattern formation (crystal growth) rate, resulted in larger size of constituent and decrease of nucleation number. If higher pressure is applied, a very different pattern formation can be expected. For example, faster solvent evaporation and a more turbulent airflow may induce maleimide molecules to pack in a disordered manner since they don't have enough time to move into ordered equilibrium positions. Thus, changes of N_2 inflow pressure and maleimide concentration caused the changes in number and size of constituent, and film thickness, but kept pattern feature.

The pattern formations were discussed above in terms of fluid dynamics of liquid thin film and evaporation of solvent. Though the dynamics of N_2 inflow such as turbulence and convection may affect the pattern formations, its influence is thought to be small on our present system prepared because the N_2 flow rate near the glass substrate was as small as

about 0.05 m/s for 0.25 kg/cm^2 N_2 inflow pressure. By modulating N_2 flow rate near the glass substrate, however, more unique pattern could be expected. Therefore, in the system of liquid thin film climbing onto the glass substrate wall, constructed by the authors for these studies, significant pattern characteristic of each region was established. This condition–determining formation of uniform crystal film over each region is much different from the crystal film formation in the dropped solution system. Owing to the characteristic of this climbing liquid thin film system, the physical and chemical states were estimated in each region by taking account the pattern formed together with experimental conditions, which made it possible to discuss the pattern formation processes.

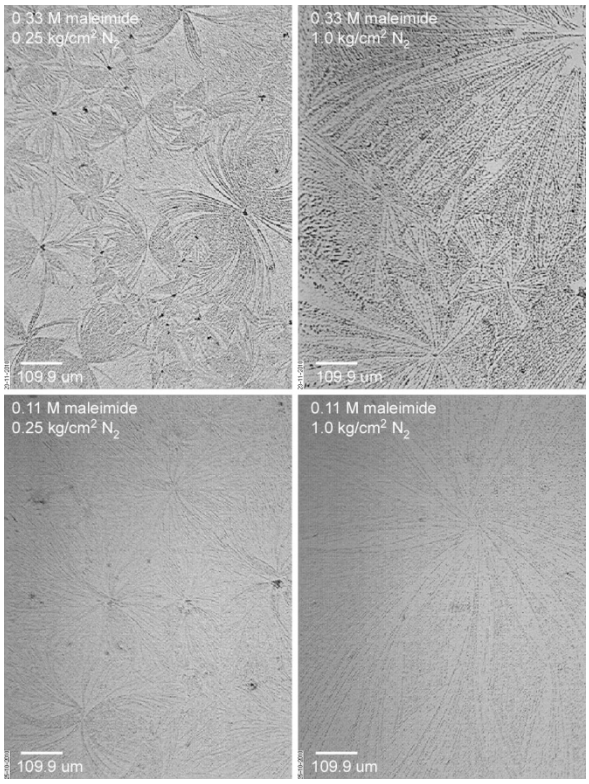

Fig. 5. Microscopic drying patterns of Region 3 of maleimide crystal films produced from the liquid thin film system as a function of maleimide methanol concentration and N_2 inflow pressure

Table 1. Radius (top) of the radial pattern and number of constituents (bottom) of the crystal thin films found in Region 3

N_2 inflow (kg/cm^2) / **[Maleimide] (M)**	**0.25**	**1.0**
0.33	66 – 266 μm 10.5 constituents	113 – 576 μm 2.2 constituents
0.11	126 – 209 μm 9.8 constituents	696 μm 1 constituent

When the glass substrate containing the crystal film formed was left unattended for 20 min, Regions 1 and 3 were lost to sublimation (Fig. 3b). The difference in film thickness between regions is thought to be one of its reasons. Regions 2 and 4, as seen in Fig. 4, had structures made up of larger size aggregations that can lead to longer sublimation time. The difference in crystal structure of maleimide between regions is also thought to be another reason, that is, the crystal films in Regions 2 and 4 may have stronger intermolecular interactions than those in Regions 1 and 3.

IR spectrum was measured for each region. Since the glass substrate absorbs light at 3000 – 450 cm^{-1}, the IR spectra were obtained at 3400 – 2800 cm^{-1}, where ν(NH) and ν(CH) vibrations were observed as shown in Fig. 6. The ν(NH) varied in peak position among regions as stated below. Both Regions 1 and 3, containing easily sublimable crystal films, had ν(NH) at 3196 cm^{-1}. Regions 2 and 4, on the other hand, had ν(NH) at 3184 cm^{-1} and 3181 cm^{-1}, respectively. This blueshift results from, for example, weakening of intermolecular hydrogen bonding. In this case, the sublimation nature will increase as a result, which is consistent with the experimental facts. In the IR spectrum, however, a shoulder was exhibited at the higher side of 3196 cm^{-1}, this shoulder appeared strong in the spectra of Regions 1 and 3 but appeared weak in Regions 2 and 4. The increase of the shoulder in Regions 1 and 3 can shift the band peak higher. One of the possible reasons for this increase of the shoulder is lowering of crystal symmetry caused by the distortion of crystal structure based on group theory (Powell, 2010). If the crystal structure is distorted, the sublimation nature will become high, and this is also consistent with the experimental fact. The clear difference seen in the IR spectra shows that crystal film in each region is not only different in thickness but in crystal structure as well. The spectral measurements are desired in lower wavenumber region using IR–transparent substrate. Furthermore, X–ray diffraction technique can strongly support these results, but the sublimation nature of the maleimide together with the experimental apparatus for pattern formation pose a problem in using this technique.

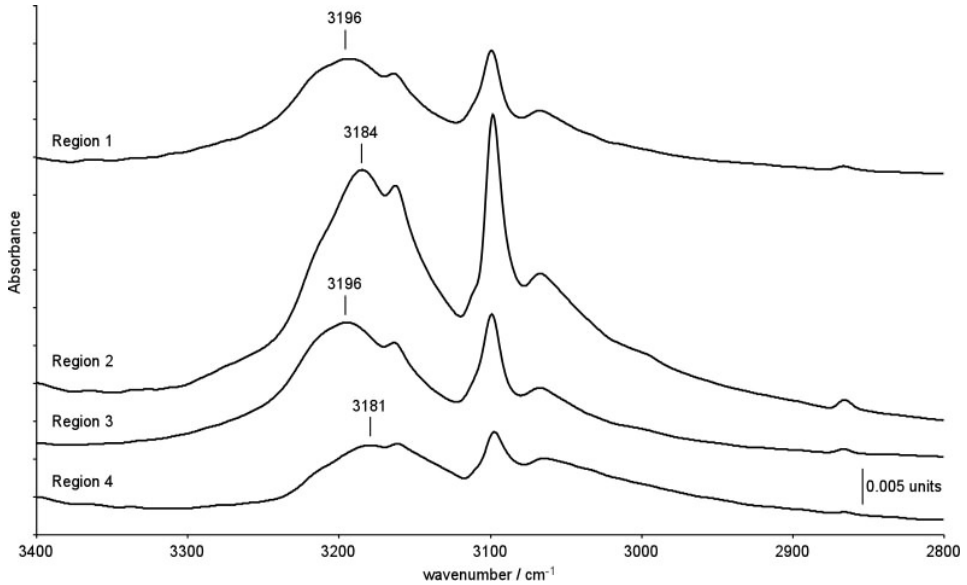

Fig. 6. IR spectra of the different regions of maleimide crystal film produced from the liquid thin film system

The thickness of the crystal film formed is an important characteristic, but its measurement is difficult due to sublimation of maleimide. When the crystal film is thick, multilayer with different properties is possible. Our present experimental set–up, however, does not make this multilayer film based on the following results. In our liquid thin film system, maleimide was deposited on front and back of glass substrate. We removed the crystal film deposited on the back of the glass substrate leaving the crystal film on the front. We took microscopic drying patterns (Fig. 7) of the crystal film from the front and through the back of the glass substrate and found that the patterns were similar. We also took microscopic pictures of the crystal film at time intervals.

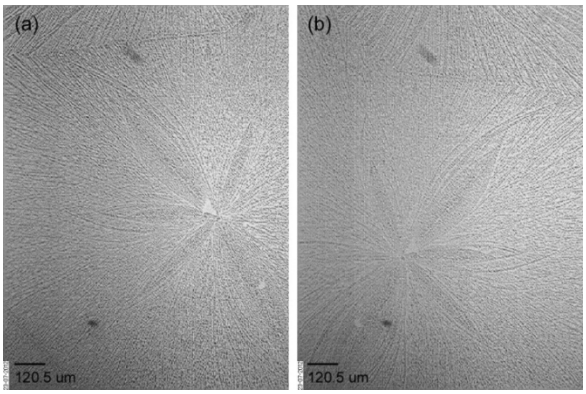

Fig. 7. Microscopic drying pattern of Region 3 of maleimide crystal film produced from the liquid thin film system taken (a) through back and (b) from front of the glass substrate

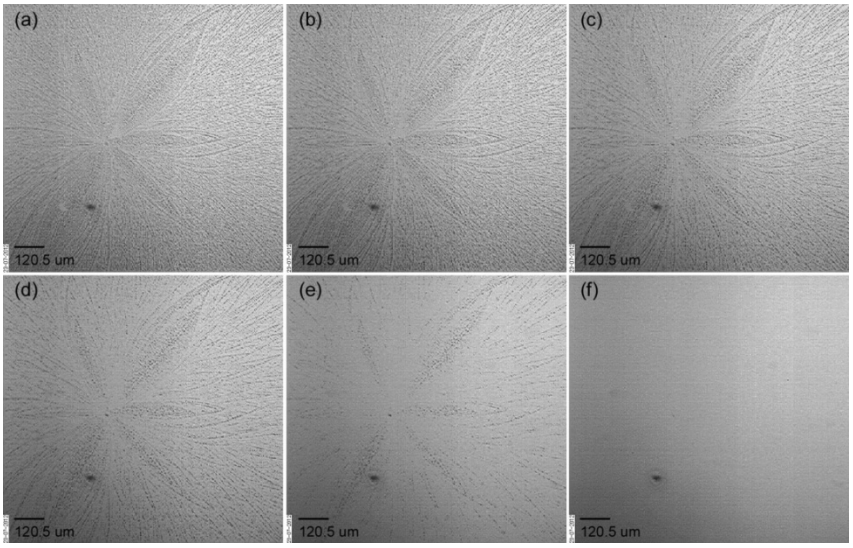

Fig. 8. Microscopic drying pattern of Region 3 of maleimide crystal film produced from the liquid thin film system as a function of time: (a) 0 min, (b) 2 min, (c) 4 min, (d) 6 min, (e) 8 min and (f) 10 min

As shown in Fig. 8, the thickness of the film was reduced over time but the general features of the drying pattern remained the same. This means that the crystal film formed was not multilayer, but unilayer. It may be possible to realize multilayer crystal film with different structures and/or patterns, which is an interesting research theme. For more complete and detail analyses of the crystal structure, the authors are preparing experimental apparatus and procedures.

4. CONCLUSION

The present study reported the formation of crystal thin films from climbing liquid thin films of maleimide methanol solutions using a vertical glass substrate. Macroscopic and microscopic investigations have shown that maleimide methanol solution produced four regions of uniform crystal films with different thickness and patterns of a meshlike, a dendritic, a radial and a needlike depending on the experimental conditions employed. The pattern formations were discussed in terms of fluid dynamics of liquid thin film and evaporation of solvent and significant pattern characteristics of each region was established. Especially, the pattern in one of the regions was characteristic of the liquid thin film system: isotropic curved–radial pattern was formed in Region 3, which has not yet been observed in usual dropped solution system. This condition–determining formation of uniform crystal film over each region is different from the crystal film formation in the usual dropped solution system. Furthermore, differences in IR spectrum has shown that the crystal film of each region was not only different in thickness but in crystal structure as well. In the case of Region 3, the changes of N_2 inflow pressure and maleimide concentration caused changes in number and size of constituent, and film thickness, but kept pattern feature. Therefore, unique pattern formation from liquid thin film system is expected to serve as basic information for new functional crystal film.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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