Vapor Deposition Polymerization and Molecular Orientation of Polyimide Thin Films

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Abstract. Polyimide thin films were prepared by vapor deposition polymerization. Co-deposition of pyromellitic dianhydride and 1,12-diaminododecane spontaneously yielded a thin film of polyamic acid, which was imidized by annealing in nitrogen atmosphere at 200°C. It was observed that the polyimide thin film has preferential orientation to the (001) crystal plane with the molecular chain standing on the substrate. The orientation was enhanced by matching the ratio of monomer supply for vapor deposition. The molecular orientation was also influenced by modifying the substrate surface with self-assembled monolayers (SAMs). A SAM having anhydrous carboxy terminal was effective in enhancing the molecular orientation.

1. Introduction
Polyimide is a class of polymer material that has outstanding characteristics such as mechanical robustness and thermal stability. It is widely used as electrical insulator, and is an indispensable material for constructing flexible electronic circuits. In these days, polyimide insulating layers are introduced even inside the integrated circuits. Another important application of polyimide is the orientation layer for liquid crystals. For this application, the molecular orientation of polyimide is controlled by the rubbing method.

In spite of the unique properties, application of polyimide is not straightforward owing to its low processability that comes from its poor solubility and non-melting characteristics. Polyimide thin films are generally prepared by coating polyamic acid that can be dissolved in organic solvents, and then imidizing by annealing. However, residue of solvent in the film frequently causes problems. A method to overcome this limitation is the vapor-deposition polymerization, which produces polyimide thin films in high-vacuum environment without using a solvent [1, 2]. The vapor-deposition technique can alleviate the issues that originate in solvents, and is especially useful for such applications that require highly-controlled film deposition with low impurity. It is also reported that the vapor-deposition is capable of controlling the molecular orientation [3, 4]. In this paper, we report the film formation of polyimide by the vapor-deposition polymerization, and explore the molecular orientation in terms of the deposition condition. We also investigated a possibility of controlling the molecular orientation by using self-assembled monolayers (SAMs) that have reactive terminal units.
2. Experimental procedure

2.1. Vapor-deposition polymerization

Figure 1 shows the reaction scheme to form polyimide in this work. Monomers of 1,12-diaminododecane (DADD) and pyromellitic dianhydride (PMDA) were co-deposited from individual Knudsen cells in a high-vacuum chamber to form a thin film of polyamic acid. DADD was evaporated at a temperature of 80°C, and PMDA was evaporated at a temperature between 180 and 210°C. The deposition rate of each monomer was monitored by a quartz crystal microbalance, and the evaporation temperature of PMDA was adjusted to obtain a desired ratio of monomer supply. The films were deposited on glass slides coated with aluminum by vapor deposition. The substrate temperature was kept at 20°C.

The co-deposited film was exposed to the air, and annealed in nitrogen atmosphere at 100 to 250°C for 30 to 60 min to imidize by dehydration of polyamic acid. Infrared (IR) spectra of the film was measured by reflection-absorption method (HORIBA FT-730). The surface morphology was observed with an atomic force microscope (AFM: Keyence VN-8010). The crystallographic property was investigated with an X-ray diffractometer (Rigaku SmartLab, with Cu target) using the parallel beam configuration.

![Figure 1. Reaction scheme for polyimide formation.](image1)

2.2. SAM-modification of the substrate

It is known that the surface characteristics of the substrate gives a significant influence on the film growth of vapor-deposited films. As a consequence, the molecular orientation [5, 6] and electrical characteristics [7], as well as film morphology [8] of vapor-deposited organic thin films can be controlled by modifying the substrate surface with a SAM. It is interpreted that the modification of the surface energy is a primary role of the SAM [9]. On the other hand, the authors have investigated vapor deposition of polymers on the surface of SAMs that have reactive terminal units. The reactive SAMs can induce growth of polymer brush that is covalently tethered to the inorganic surface [10, 11]. It was revealed that the covalent tethering at the interface has remarkable effect in improving the morphology and stability of the vapor-deposited films [12, 13]. This technique was also effective for controlling the film/substrate interface of organic devices [14, 15]

![Figure 2. Structural formulae of SAMs used in this work.](image2)
In this work, four types of SAMs shown in Fig. 2 were prepared on the substrate surface to explore their influence on the molecular orientation of the vapor-deposited polyimide. The SAMs were prepared on aluminum surface that was oxidized by treating in a UV-ozone cleaner (Filgen UV253). The SAM having vinyl terminal (−C=C SAM) was prepared by immersing the substrate in 5 mM toluene solution of vinyltrimethoxysilane for 12 h. The SAM having amino terminal (−NH₂ SAM) was prepared by immersing the substrate in 1 wt% toluene solution of 3-aminopropyl trimethoxy silane for 1 h. The SAM having carboxy terminal (−COOH SAM) was prepared by oxidizing the −C=C SAM in an aqueous solution containing 0.5 mM KMnO₄, 19.5 mM NaIO₄, and 1.8 mM K₂CO₃ for 24 h. The SAM having anhydrous carboxy terminal (−SA SAM) was prepared by immersing the substrate in 3 mM toluene solution of 3-(trimethoxysilyl)propyl succinic anhydride for 3 h. All these solution processes were achieved at room temperature. After the immersing processes, the SAMs were finished by ultrasonic cleaning in toluene followed by annealing at 110°C for 1 h in nitrogen atmosphere. The SAM-modified surfaces were characterized by water contact angle measurement (First Ten Angstrom FTA-188). On these surfaces, vapor-deposition of polyimide was achieved in the aforementioned procedure.

3. Results and discussion

3.1. Formation of polyimide thin films

A film of about 300 nm thick was obtained by co-depositing DADD and PMDA for 20 min. Figure 3 shows IR spectra of PMDA monomer (a), DADD monomer (b), and a film obtained by co-depositing PMDA and DADD at an equimolar deposition rate (c). PMDA monomer is characterized by its terminal group of cyclic acid anhydride that gives C=O stretching bands in the region of 1750 to 1880 cm⁻¹ and C-O-C stretching band at 1246 cm⁻¹. DADD monomer has characteristic absorption by N-H stretching bands of amino terminal in the range of 3340 to 3150 cm⁻¹. These absorption bands of monomers were not observed in the co-deposited film. Instead, the co-deposited film showed C=O stretching band at 1643 cm⁻¹ and the combination band of C-N stretching and N-H bending at 1581 cm⁻¹ that are both attributed to amide bond. This result indicates that a film of polyamic acid was produced by the co-deposition of PMDA and DADD as shown by the first step of Fig. 1.

![Figure 3](image_url)

Figure 3. IR spectra of PMDA (a) and DADD (b) monomers, co-deposited film (c), and films annealed at 100°C for 1 h (d), additionally 200°C for 30 min (e), 200°C for 1 h (f), and 250°C for 1 h (g).
As the next step, the film of polyamic acid was annealed in nitrogen atmosphere to form polyimide. Figure 3 (d) shows the IR spectra after annealing the co-deposited film for 1 h at 100°C. After this heat treatment, a new peak appeared at 1724 cm\(^{-1}\). The IR spectra underwent further change after additional annealing at 200°C for 30 min as shown in Fig. 3 (e). The new bands at 1770 cm\(^{-1}\) and 1730 cm\(^{-1}\) can be assigned to symmetric and asymmetric stretching modes of imide C=O, and the band at 1404 cm\(^{-1}\) can be assigned as C-N stretching of cyclic imide. On the other hand, the absorption bands that originate in the amide bond disappeared after annealing at 200°C. This result indicates the formation of polyimide by cyclodehydration of polyamic acid as shown by the second step of Fig. 1. Further annealing at 200°C for 1 h did not result in significant change in IR spectra. An almost identical spectrum was obtained when the annealing was achieved at 250°C for 1 h. After the imidization, the film thickness was reduced to about 200 nm.

Figure 4 shows X-ray diffraction patterns of the co-deposited film (a) and the film after annealing under the different conditions (b–e). After the imidization, a prominent peak appeared at \(2\theta = 5.0^\circ\), which corresponds to a plane distance of 1.77 nm. This diffraction represents the (001) plane of monoclinic polyimide having alkyl chain in its backbone [16, 17]. The result of X-ray diffraction analysis indicates that the polyimide thin film prepared by the vapor-deposition polymerization has preferential crystal orientation with the molecular chain standing on the substrate surface. Figure 5 shows an optimized structure of the two repeating units of PMDA-DADD polyimide obtained by the semi empirical quantum chemical calculation (MOPAC PM3). This model gave the unit length of the PMDA-DADD imide as 2.21 nm. It suggests that the polymer backbone of the vapor-deposited polyimide is inclined by 37° from the substrate normal. When the annealing was performed at 250°C, the film lost its preferential orientation as shown by pattern (e) in Fig. 4. It is likely that the annealing temperature of 250°C was higher than the glass transition temperature of this polymer [18]. Therefore, the optimum temperature for imidization in this system is considered to be 200°C.

### 3.2. Effect of monomer supply ratio

The polymerization of polyimide proceeds by stepwise reaction of polyaddition process. With this type of reaction, the degree of polymerization is known to be largely influenced by the ratio

\[ \text{Ratio} = \frac{\text{Amount of A}}{\text{Amount of B}} \]

where A and B are the monomers. The ratio affects the molecular weight and the properties of the resulting polyimide film.
of monomer supply. Figure 6 shows IR spectra of polyimide films prepared with molar supply ratio of DADD:PMDA of 1:0.8 (a), 1:1 (b), 1:1.2 (c), and 1:1.5 (d). The films were annealed at 100°C for 1 h followed by 200°C for 1 h. All the films co-deposited in this range of supply ratio produced polyimide without appreciable residue of monomers or polyamic acid. DADD and PMDA monomers have low sticking coefficients by themselves, and surplus monomers tend to reevaporate spontaneously from the substrate surface. In other words, only those molecules that reacted to form the polymer accumulated stably on the substrate surface. For this reason, polyimide films were obtained without being crucially influenced by the monomer supply ratio.

On the other hand, a detailed inspection of Fig. 6 reveals that the monomer supply ratio influences the relative absorbance of the symmetric and asymmetric stretching bands of imide C=O at 1770 and 1730 cm⁻¹. It should be noted that the reflection absorption measurement employed in this work has preferential sensitivity to the transition dipole moment in the direction normal to the substrate surface, which means that the absorbance is influenced by the molecular orientation. The symmetric stretching mode of imide C=O has its transition dipole moment in parallel with the polymer backbone, while the transition dipole moment of the asymmetric stretching is in perpendicular to the backbone. Table 1 shows the ratio of symmetric/asymmetric absorption bands of imide C=O for the films deposited with different monomer supply ratio. The film deposited with equimolar monomer supply showed the most dominant absorption of the symmetric band, indicating that this film has the highest orientation with the molecular chain standing on the substrate surface.

The effect of monomer supply ratio was observed more explicitly in the X-ray diffraction patterns as shown in Fig. 7. The film deposited with equimolar monomer supply showed the most prominent orientation to the (001) plane. When the supply ratio deviated from the equimolar condition, the diffraction intensity of (001) plane was significantly reduced, while a new peak appeared at 2θ = 20°, which corresponds to either (011) or (101) plane of the monoclinic polyimide crystal. This result is in good accordance with the observation by the IR spectra. With
the stepwise polymerization, it is generally known that the degree of polymerization increases by properly matching the monomer supply. On the other hand, it is also known that vapor deposited rod-like molecules have a tendency to orient with their molecular axes standing on the substrate surface [19]. Therefore, it is considered that the proper balance of monomer supply results in polyimide of a longer chain, which has higher tendency to orient in normal direction.

Surface morphology of the polyimide films deposited with different ratio of monomer supply is shown in Fig. 8. The arithmetic average surface roughness $R_a$ of these films is listed in the last line of Table 1. The vapor-deposited polyimide films have excellent smoothness. However, $R_a$ increased slightly when there was surplus supply of PMDA. This is because PMDA monomer is less volatile than DADD, and has a higher possibility of affecting the film morphology when supplied in surplus amount.

3.3. Effect of SAM modification on the molecular orientation

The film growth morphology by the vapor deposition is primarily governed by the balance of surface energies and interface energy of the film and substrate materials. That is the main reason why SAMs are frequently employed to control the growth of organic thin films on inorganic substrates [20]. On the other hand, the authors have shown that covalent tethering at the film/substrate interface is an effective strategy to control the interfacial characteristics of organic
thin films. This was achieved by using SAMs that have reactive terminal units [21]. From this standpoint, the substrate surface was modified with different SAMs shown in Fig. 2, and the vapor-deposition polymerization was achieved on their surfaces.

Figure 9 shows X-ray diffraction patterns of polyimide thin films deposited on a bare aluminum (a) and on the aluminum modified with SAMs having −C=C (b), −NH₂ (c), −COOH (d), and −SA (e) terminal groups. All the films showed preferential crystal orientation to (001) plane as described in previous section. Above all, the film deposited on −SA SAM showed the strongest diffraction peak. It is frequently pointed out that the SAMs influence the film growth through modification of surface energy. Table 2 shows the water contact angles of the bare and the SAM-modified aluminum surfaces. The clean aluminum was hydrophobic and so was the surface modified with −C=C SAM. The reactive SAMs having −NH₂, −COOH, and −SA terminals were less hydrophobic than the bare aluminum, but there was no significant difference in water contact angles between these reactive SAMs. Therefore, the pronounced molecular orientation observed specifically on the −SA SAM cannot be explained only by the factor of surface energy.

From a chemical viewpoint, −SA group has higher reactivity than the −COOH group. The difference in reactivity can be an important factor to influence the molecular orientation. With a purpose to compare the chemical reactions of the SAMs, quantum chemical calculations were performed by the MOPAC (PM3) program for the reactions of −NH₂ SAM with PMDA (a), −COOH SAM with DADD (b), and −SA SAM with DADD (c). The optimized structures of these reaction products are shown in Fig. 10. The enthalpies for these reactions were calculated to be -52.0 kJ/mol for −NH₂ with PMDA, +32.3 kJ/mol for −COOH with DADD, and -34.3

Table 2. Water contact angles and surface roughness of bare and SAM-modified aluminum surfaces. Surface roughness of polyimide deposited on these surfaces are also listed in the last line.

| Substrate | Al | −C=C SAM | −NH₂ SAM | −COOH SAM | −SA SAM |
|-----------|----|----------|----------|----------|---------|
| Contact angle (deg) | 72.8 | 76.4 | 51.4 | 55.5 | 53.4 |
| Ra of substrate (nm) | 0.5 | 1.0 | 0.9 | 0.9 | 1.3 |
| Ra of polyimide (nm) | 0.5 | 0.9 | 0.6 | 0.7 | 1.1 |
Figure 10. Optimized structures by quantum chemical calculations for $\text{-NH}_2$ SAM reacted with PMDA (a), $\text{-COOH}$ SAM reacted with DADD (b), and $\text{-SA}$ SAM reacted with DADD (c).

kJ/mol for $\text{-SA}$ with DADD. It is considered that the $\text{-COOH}$ SAM is the least convenient of these three SAMs for causing the reaction. In general, the reaction of a carboxylic acid with an amine requires a dehydration reagent, although the vacuum environment is dehydrating itself. As far as the enthalpy change is concerned, the $\text{-NH}_2$ SAM appears to be the best of these three. However, the optimized structure shown in Fig. 10(a) implies that the reaction product of $\text{-NH}_2$ SAM and PMDA has a bent structure, which is not convenient for enhancing perpendicular molecular orientation of the polyimide chain. Therefore, it is considered that the $\text{-SA}$ SAM is appropriate both for tethering the interface and for enhancing the molecular orientation.

Figure 11 shows the surface morphology of the polyimide films deposited on the different surfaces. All the films had smooth surfaces. The surface roughness $R_a$ of these films are listed

Figure 11. AFM images of polyimide films deposited on bare aluminum (a), and on those modified with SAMs of $\text{-C=}=\text{C}$ (b), $\text{-NH}_2$ (c), $\text{-COOH}$ (d), and $\text{-SA}$ (e).
in Table 2 together with the \(R_a\) of the SAM-modified substrates. The film on -SA SAM seems to have slightly larger surface roughness, but it might originate in the roughness of the SAM itself. There was essentially no significant difference in film morphology by the SAM modification.

4. Conclusions
Polyimide thin films were obtained by the vapor-deposition polymerization method. Co-deposition of PMDA and DADD monomers yielded a film of polyamic acid in the as-deposited state, which was imidized by annealing at 200\(^\circ\)C in nitrogen atmosphere. The polyimide film had preferential crystal orientation with the (001) plane parallel to the substrate surface, which means that the polymer backbone is standing on the substrate. The ratio of monomer supply did not give a crucial influence on the reaction of polyimide formation. On the other hand, the molecular orientation was enhanced by matching the ratio of monomer supply to equimolar condition. It was also found that the SAM modification of the substrate surface is effective for controlling the molecular orientation. Above all, the SAM having an anhydrous carboxy terminal was effective in enhancing the molecular orientation. The major role of this SAM is considered to originate in the chemical reaction at the film/substrate interface rather than the simple difference in surface energy.

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