π-A Isotherms and Electrical Properties of Polyamic acid Alkylamine salts(PAAS) Langmuir-Blodgett Films

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Abstract

Deposition conditions, surface morphology, and electrical properties of polyamic acid alkylamine salts (PAAS) Langmuir-Blodgett(LB) films have been investigated through a study of surface pressure-area π-A isotherms, AFM (atomic force microscopy), and current-voltage characteristics. To obtain the optimum conditions of film deposition, the π-A isotherms were examined by varying temperature, barrier moving speed, dipping speed, spreading amount of solution etc. The Z-type LB films were made at the surface pressure of 5 mN m^{1} and 25 mN m^{-1} for the AFM study; the former surface pressure forms the gas phase and the latter one forms the solid phase. The LB film made in the gas phase show domains with a size of about 200 A diameter and 70 A height. However, the LB films made in the solid phase show a very smooth surface with 2 A surface roughness. In the current-voltage characteristics measured along the perpendicular direction of the films, ohmic conduction has been observed below $\cong 10^{5}$ V cm^{-1} and the calculated electrical conductivity is about 10^{-13} S cm^{-1}. Nonohmic conduction has been observed above = $10^{-1}1$ V cm ' and the conduction mechanism can be explained by the Schottky effect.

1. Introduction

Most semiconductor devices are normally based on inorganic materials such as silicon. A typical device size is the order of microns (10^{-6} m). This size is still large compared with that of the molecular level. It is being recognized as a limitation of miniaturization of the inorganic devices [1]. It is, however, expected in the near future that the size of device could be reduced to the molecular level. These devices are called the molecular-electronic devices. First of all, ultrathin films have to be manufactured for these devices to be developed. There are several ways of producing the ultrathin films. Among these methods, the Langmuir-Blodgett (LB) technique has recently received much attention. The basic concept of the LB method is to make the ultrathin films by transferring a monolayer which is formed at the air-water interface to a solid substrate. With this technique, we can easily control the thickness and orientation of the molecules. Optimum conditions of manufacturing the LB films were mostly determined by a study of surface pressure-area (π-A) isotherms, relating the surface pressure π to the effective area A occupied by one molecule on a subphase.

Polyimide is a well-known organic dielectric material, which has not only high chemical and thermal stability but also good electrical insulating and mechanical properties Suzuki and coworkers [2] reported a preparation of the pol-yimide LB films with a monolayer thickness of about 0.4 nm.

Tunnel junctions with metal-insulator-metal (MIM) structures were also fabricated using the ultrathin polyimide LB films by Kubota et al. [3].

In the past few years, we have synthesized a polyamic acid alkylamine salt (PAAS) molecule, which is a precursor of the polyimide. The PAAS molecule is composed of pyromellitic dianhydride (PMDA) and oxydianiline (ODA). An imidization of the PAAS molecule is performed by thermal or chemical treatment. In the point of view of fundamental study or application of the material, it is necessary to produce a fine quality of the LB films and to understand an electrical conduction mechanism. The surface quality was investigated by atomic force microscopy (AFM) because of its high spatial resolution and its capability of nondestructive observation. The electrical conduction mechanism was investigated by measuring the current-voltage characteristics.

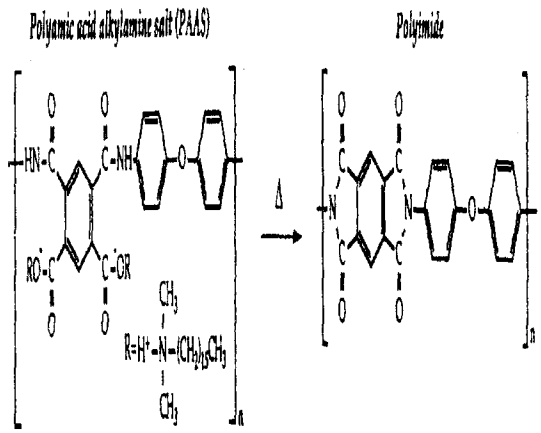

Fig. 1. A molecular structure of the PAAS (polyamic acid alkylamine salts), which is a precursor of the polyimide.

In this paper, we present some results on the deposition conditions, surface morphology and electrical properties of the PAAS LB films.

2. Experimental details

2.1. Preparation of specimen

Polyamic acid alkylamine salts were prepared as reported elsewhere [4] and purified by recrystallization from toluene, where PMDA was purified by sublimation method and ODA was used as purchased. The molecular structure of the PAAS, shown in Fig. 1, is composed of PMDA and ODA. The surface quality of a substrate is very important in manufacturing desired LB films. Several substrates were used depending on the type of experiments. Normal optical-microscope slide glass (76 mm × 26 mm × 1 mm) and mica (15mm × 20 mm) substrates were used for electrical measurements and for the AFM study, respectively. The glass substrate was cleaned ultrasonically more than 3 times for 20 min each in an ultrapure water (≈ 18 MΩ cm). To make the surface of substrate hydrophilic, it was dipped into a $K_2Cr_2O_3$-saturated solution of H_2SO_4 for more than 24 h. It was cleaned ultrasonically again more than 5 times for 30 min each, and then dried completely in an oven.

2.2. π-A isotherms and deposition

Since the π-A isotherm varies with change of environments, it was studied by giving different conditions of temperature, barrier moving speed, dipping speed, and spreading amount of solutions. A Kuhn type LB apparatus (KSV3000) was used, which has a trough size of 150 mm × 505 mm. Purified distilled water was used as a subphase, and a mixture of DMAc (N,N-dimethylacetamide) and benzene (1:1 volume ratio) was used as a solvent. After spreading solution (10^{-3} mol l^{-1} concentration) on the subphase, 30 min were allowed for the solvent to evaporate. The π-A isotherms were measured in the temperature range of 10~40℃. And the barrier moving speed was varied from 5 mm min^{-1} to 50 mm min^{-1}. The amount of spreading solution was used in the range of 10 μℓ to 100 μℓ. After investigating several properties of the π-A isotherms, we found that the proper surface pressure of the film deposition is in between 20 mN m^{-1} and 35 mN m^{-1}. Several X-, Y-, and Z-type LB films were deposited on the glass substrate at three different

surface pressures (25, 30, and 35 mN m^{-1}) and measured a transfer ratio.

2.3. AFM measurements

The surface morphology of the PAAS LB films was investigated by AFM, using an AutoProbe CP model from Park Scientific Instruments. AFM was conducted in a non-contact mode with a scanning rate of 2 Hz in order to avoid damage. A 0.6 ㎛ sharpened cantilever was used and typical amplitudes were of the order of 10 Å, using a 5 ㎛ scanner. The Z-type monolayer LB film was made at 5 mN m^{-1} and 25 mN m^{-1} surface pressure on the mica substrate. The former surface pressure forms the gas phase and the latter forms the solid phase. We tried to detect the difference in surface morphology of the films made at two different surface pressures.

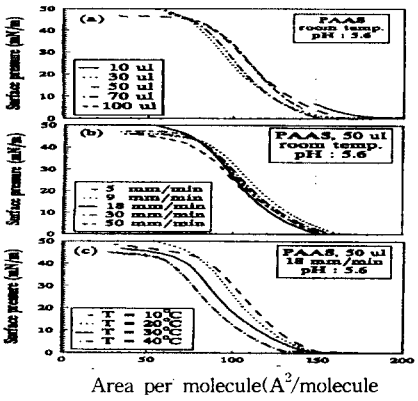

Fig. 2. π-A isotherms depending on (a) the spreading amount of solution, (b) the barrier moving speed, and (c) the temperature of the subphase.
The trough area is 150 mm × 505 mm

2.4. Electrical measurements

Electrical measurements were carried out to characterize the LB films with a conventional two-probe method. Aluminium electrodes were vacuum deposited at a pressure of 10^{-5} torr on both the top and the bottom of the specimen. The bottom electrode was used as a common one, and several electrodes were made on top of the film to increase the reliability of the electrical measurements. The area of the electrode (circular shape) is 20 mm^2. A thin metal wire (100 ㎛ diameter) was connected to the electrode with silver paste. A programmable Keithley 238 apparatus was used as a voltage source and as a current measuring device.

3. Results and discussion

3.1. A isotherms and deposition

Fig. 2 shows the π-A isotherm of the PAAS molecules depending on the several conditions of the environment. At first, we observed the π-A isotherms by varying the spreading amounts of solution from 10 ㎕ to 100 ㎕ on the subphase with the area of 150 mm × 505 mm. Fig. 2(a) displays the π-A isotherms depending on the spreading amounts of solution with a barrier moving speed of 18 mm min^{-1}. It shows that the π-A isotherm with 10 ㎕ solution does not reach the solid phase. On the other hand, the A isotherm with 100 ㎕ solution starts almost above the gas phase. The π-A isotherm with 50 ㎕ solution shows the typical behavior for transition from the gas phase to the solid phase. A limiting area of the molecule turned out to be around 138 $Å^2$. Fig. 2(b) shows the π-A isotherms measured by changing the moving speed of barrier from 5 mm min^{-1} to 50 mm min^{-1}. As is seen in the figure, there is little shift owing to the change of barrier moving speed. Fig.2(c) shows the π-A isotherms measured by varying the temperature from 10 to 40 °C with an increment of 10 °C. The whole curves show similar behavior except the limiting area. The limiting area decreases as the temperature increases. As the temperature increases from 10 to 40 °C, the limiting area decreases by around 20%. Fig. 3 (a) is a typical π-A isotherm of the PAAS molecules obtained at room temperature with 50 ㎕ spreading solution and 18 mm min- 1 barrier moving speed. Fig. 3(b) is a differentiation of the surface pressure with respect to the area A: $-d\pi/dA$. It has a maximum value at the surface pressure of about 25 mN m^{-1}, which indicates the formation of a

well-compacted monolayer on the subphase. Thus, we can safely say that the appropriate surface pressure for the film deposition is in between 20 mN m^{-1} and 35mNm^{-1}1.

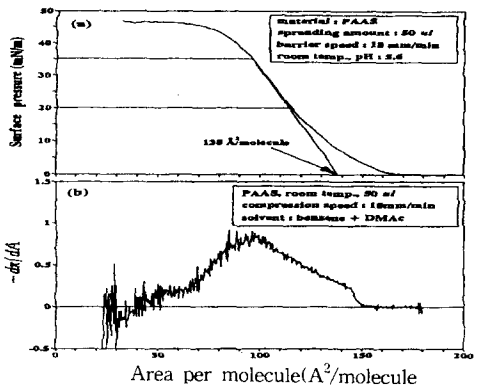

Fig. 3. (a) A typical π-A isotherm of the PAAS molecules and (b) a differentiation with respect to area A: $-d\pi/dA$.

Fig. 4 displays the transfer ratio as a function of number of layers depending on the type of stacking formation. Three different surface pressures (25, 30 and 35 mNm^{-1}) were chosen in this measurement. It is interesting to note that the appropriate surface pressure of film deposition varies slightly depending on the type of deposition. We obtained 35,35 and 25 mN m^{-1} for the appropriate surface pressure of the X, Y, and Z type, respectively.

3.2. AFM measurements

Fig. 5 shows typical AFM images of a single monolayer of the PAAS LB films made at 5 mN m^{-1} and 25 mN m^{-1} surface pressure. The area of Fig.5(a) and Fig. 5(b) is about 1 μm × 1 μm. Fig. 5(a) is the image of the LB film made at 5 mN m^{-1} (gas phase). We can see that there are white spots, which may be agglomerated granules. Fig. 5(c) is an expanded image of Fig. 5(a), and Fig. 5(e) is the height profile of the surface scanned along the line indicated in Fig. 5(c). Fig. 5(e) shows that the size of white spots is about 200 Å diameter, the height is about 70 Å and the

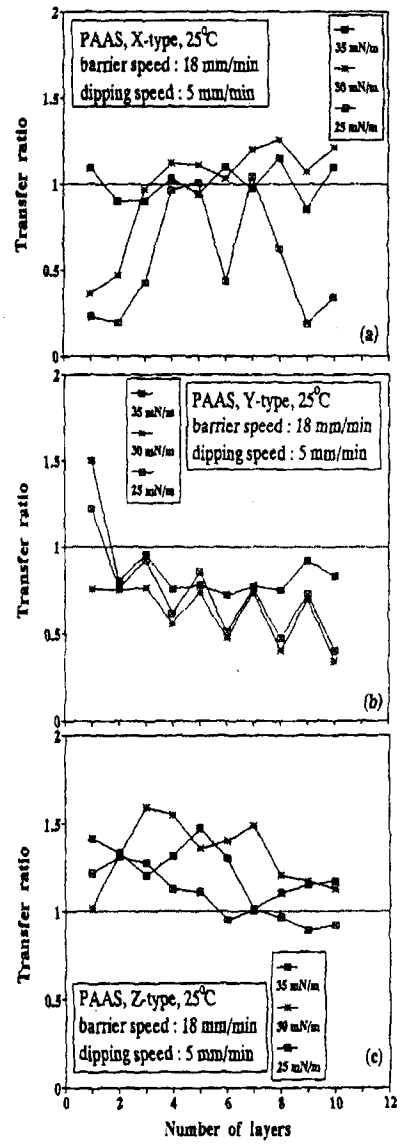

Fig. 4. A transfer ratio as a function of number of layer depending on the type of stacking formation: (a) X-type, (b) Y-type, and (c) Z-type.

surface has a roughness of about 10Å. On the other hand, Fig. 5(b) shows the LB films made at 25 mNm^{-1} (solid phase). It shows that the

molecules cover the substrate well, with some regularities. The expanded image and the height profile are shown in Fig. 5(d) and Fig. 5(f). Fig. 5(f) shows that the surface is very smooth with a roughness about 2 A. This indicates that the PAAS films formed at 25 mN m^{-1} are well packed compared with the PAAS films formed at 5 mN m^{-1}.

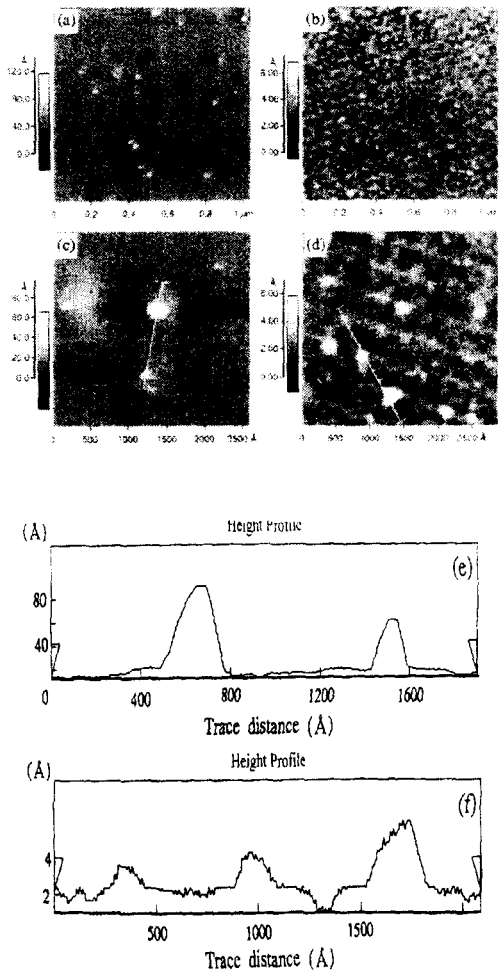

Fig. 5. AFM images of the single monolayer of the PAAS LB films made at 5 mN m^{-1} and 25 mN m^{-1} surface pressure.

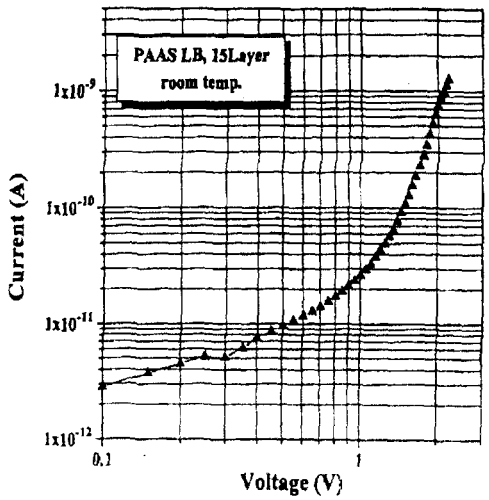

Fig. 6. Current-voltage characteristics of the PAAS LB films measured along the perpendicular direction.

3.3. Current—voltage characteristics

Fig. 6 shows the current-voltage (I-V) characteristic of the PAAS LB films measured along the perpendicular direction. The thickness of the LB films measured by spectroscopic ellipsometry is about 400 A. It shows an ohmic behavior below 1 V(≈ 10^5 V cm^{-1}). The electrical conductivity calculated in this ohmic range is about 10 - 13 S cm^{-1} 1. If we analyze these I-V characteristics further above 10 5 Vcm^{-1}, log I is proportional to $E^{1/2}$. This can explained by the Schottky effect, which is normally caused by a potential barrier generated between the metal electrode and the LB film. In this range the current increases b> than 2 orders of magnitude. If the current increases fi we have to worry about an associated Joule heating.

4. Conclusion

We have investigated the deposition conditions, surface morphology and the electrical properties of the PAA LB films. The following conclusion can be drawn.

1. The proper condition of the LB film deposition is in the following: room temperature,

spreading amount of solution 50 $\mu\ell$ (for a trough size of 150 mm × 505 mm) face pressure 25 mN m^{-1} .

2. In the AFM study, the surface morphology shows that the LB film made at the gas phase has a domain structure with a 200 Å diameter and a 70 Å height. However, the LB films made at the solid phase have a well-aligned structure with a surface roughness of 2 Å.

3. From the current-voltage characteristics, we have found that there is an ohmic conduction below 10 5 V cm^{-1}. The electrical conductivity calculated in the ohmic region is about 10^{-13} S cm^{-1}. The Schottky effect for occurs higher electric fields.

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< This paper was also published on Thin Solid Films, pp.500-504, 1996 >