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SURFACE CHARACTERIZATION OF ULTRA-THIN POLYIMIDE FILMS FORMED BY USING LANGMUIR-BLODGETT METHOD

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Abstract The polyimide films were prepared by imidizing the polyamic acid long-chain alkylamine (dimethylhexadecylamine) salt films with a thermal treatment up to 300℃ for 30 minutes, where the polyamic acid alkylamine salt films were formed on various substrates by using Langmuir-Blodgett (LB) method. The imidization of polyamic alkylamine salt films with various thickness were identified with FT-IR and UV-visible absorption spectroscopies. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) have been used to investigate the surface morphology of polyamic acid alkylamine salt and imidized films with a thickness from one monolayer to ten monolayers. It was found that the imidization of the polyamic acid alkylamine salt films with a thermal treatment significantly increases the surface microroughness of those films by forming sub-micron order of polyimide grains on substrates and no defects such as pin holes were observed by SEM analysis.

INTRODUCTION

Polyimides are very important dielectric materials for microelectronic and electronic packaging applications because of their excellent thermal and chemical stability, good mechanical properties, low dielectric constant and their processability.[1, 2] Especially for microelectronic application, the preparation of ultra-thin films of polyimide is required to obtain high performance materials.[2] One of the well-known methods for the preparation of organic thin films is the LB technique. A lot of attentions have been paid on this LB technique only about ten years ago because it can provide the desired control on the order at the molecular level.

Recently, the polyimide films with a monolayer thickness of about 0.4nm have been successfully prepared by LB technique.[3] Tunnel junctions with MIM structures were also fabricated using ultra-thin polyimide films formed by LB technique.[4, 5] In such a case, the surface morphology of thin films, in other words, the quality of those films becomes so critical for the effective control of device performance as the

minimum dimension of devices are diminished. Some research activities on surface morphology and the molecular structure of polyimides has been done recently by AFM and X-Ray scattering experiments with a theoretical modeling, respectively.[6, 7]

In this paper, ultra-thin polyimide films composed of the pyrometillic dianhydride (PMDA) and oxydianiline (ODA) with a thickness from one monolayer to ten monolayers were formed on various substrates by using LB technique and the surface morphology and molecular structure of those films were investigated by using AFM and SEM.

EXPERIMENTALS

Materials

Polyamic acid dimethylhexadecylamine salt was prepared as reported in elsewhere[8] and purified by recrystallization from toluene, where PMDA was purified by sublimation method and ODA was used as purchased.

Preparation of LB films

LB films were deposited by using computer-controlled Kuhn type KSV 3000. Distilled water as a subphase was purified by a Milli-Q Reagent Water System. For UV and IR absorption spectroscopic analysis, polished quartz plates and one side polished p-type silicon wafers (100) were used as a substrate, respectively, and cleaned prior to deposition . For AFM analysis, on the other hand, mica were used as a substrate. Polyamic acid alkylamine salt powder were dissolved in a mixture of N,N-dimethylacetamide (DMAC) and benzene (1:1) to a concentration of 1mmol/ℓ just before deposited. The LB films were deposited at the surface pressure of 35mN/m, compression speed of 1mN/m/min and dipping speed of 5mm/min after spreading polyamic acid salt solutions on deionized water at 20℃. The LB films were deposited as y-type, where the transfer ratio constant was almost 1. The obtained LB films of polyamic acid alkylamine salt were imidized with a thermal treatment up to 300℃ for 30min.

Measurements

For the identification of imidization of polyamic acid salt films, IR spectra were recorded on BIO-RAD FTS-10 spectrometer and UV-visible spectra were recorded on HP 8452A diode array type spectrometer, respectively. The surface morphology of LB films before and after imidization was investigated by using AFM, model AutoProbe LS from PSI and SEM from JEOL. For the AFM analysis, polyamic acid alkylamine salt films were deposited and imidized at the same condition as mentioned before, where AFM was operated in the constant force imaging mode.

RESULTS AND DISCUSSION

UV-visible spectra of polyamic acid alkylamine salt films with a various thickness of

monolayers are shown in Fig. 1. Plots of absorbance at 206 and 260nm of polyamic acid alkylamine salt films for each layers are also shown in Fig. 1, which gives a good linear relationship between the number of layers and the absorbances at two different peaks. This suggests that the layer by layer deposition of polyamic acid alkylamine salt films at molecular level were successfully controlled.

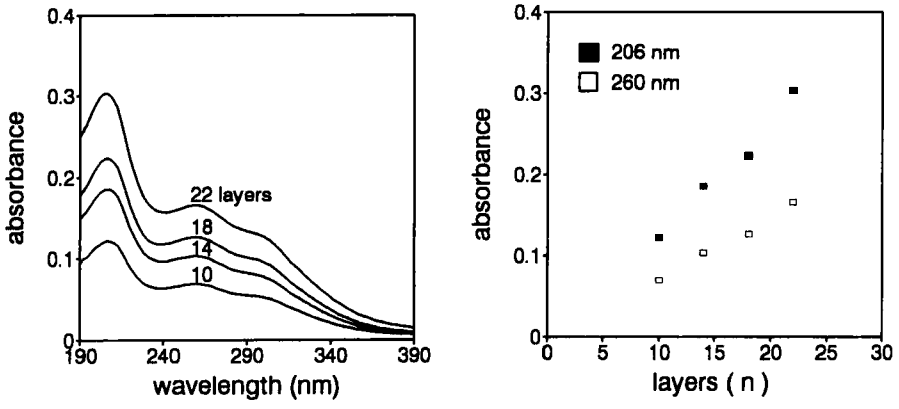

Fig. 1. UV-visible absorption spectra of polyamic acid alkylamine salt film with a various layers. Plots of UV-visible absorbance against the number of layers of polyamic acid alkylamine salt films at 206 and 260nm are also shown in this figure.

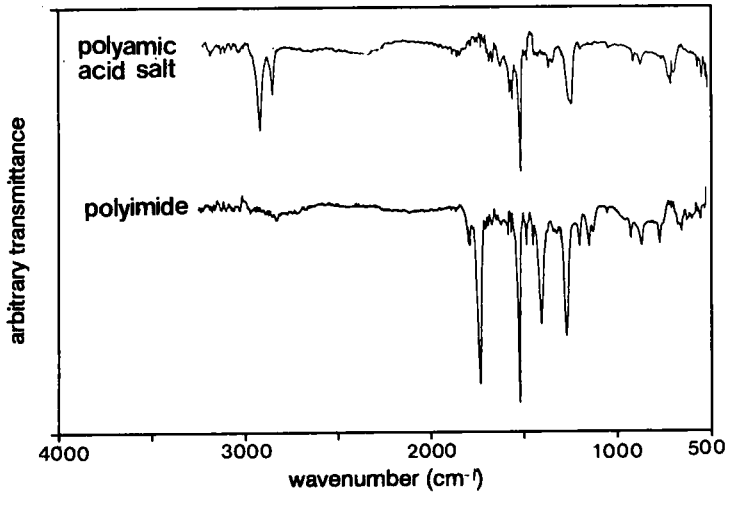

Fig. 2. FT-IR spectra of the polyamic acid alkylamine salt film and imidized film, deposited 102 monolayers, with 4-cm^{-1} resolution.

Fig. 2 shows IR spectra of polyamic acid alkylamine salt film and imidized film, deposited 102 layers. Disappearance of the double peaks due to hydrocarbon group of dimethylhexadecylamine at 2875 and 2930cm^{-1} and appearance of the peaks due to carbonyl group of polyimide at 1780 and 1720cm^{-1} imply that the imidization of polyamic acid alkylamine salt film was completed with the removal of long-chain alkylamine.

The surface morphology of polyamic acid alkylamine salt films and imidized films were also studied by SEM. The imidized film was as flat as that of polyamic acid salt film, but only one defect as shown in Fig. 3 was observed on the whole imidized films with an area of 1.5cm×3cm. Thus the defect seems to be due to the agglomerated contaminants contained in polyamic acid alkylamine salt solution itself not by LB deposition method.

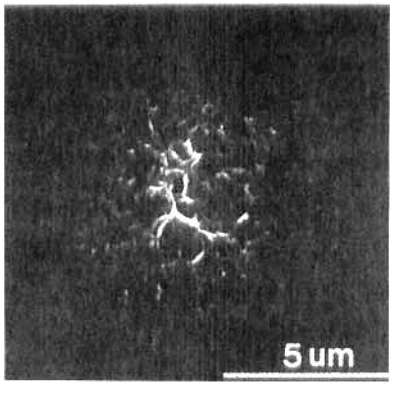

Fig. 3. Scanning Electron Micrograph of the defect found on imidized film with a thermal treatment.

AFM has been widely used to investigate the surface structure of insulating materials because of its high spatial resolution and its capability of nondestructive observation. Fig. 4 shows typical AFM images of one monolayer of polyamic acid alkylamine salt film and also imidized film on mica plates, respectively, with an area of about 0.2μm×0.2μm and also shows the height profiles of the lines, as marked on each film. It was found in Fig. 4 that there are apparent changes of surface morphology before and after the imidization of polyamic acid alkylamine salt, where the surface microroughness of polyamic acid alkylamine salt film was 0.25Å and that of imidized film was increased to 2.6Å. It can be understood in terms of the formation of polyimide grain during imidization that the average surface microroughness of imidized film is much higher than that of polyamic acid alkylamine

salt film. As shown in height profiles of two different films in Fig. 4, the peak to valley height for polyamic acid salt film was almost less than 1.0Å, but that for imidized film was more than 4.0Å and the distance between the valleys was sub-micron order level. This indicates that the flat polyamic acid salt film changed into the polyimide grains with a size of less than 0.1μm by cyclization of polyamic acid salt into polyimide with a thermal treatment.

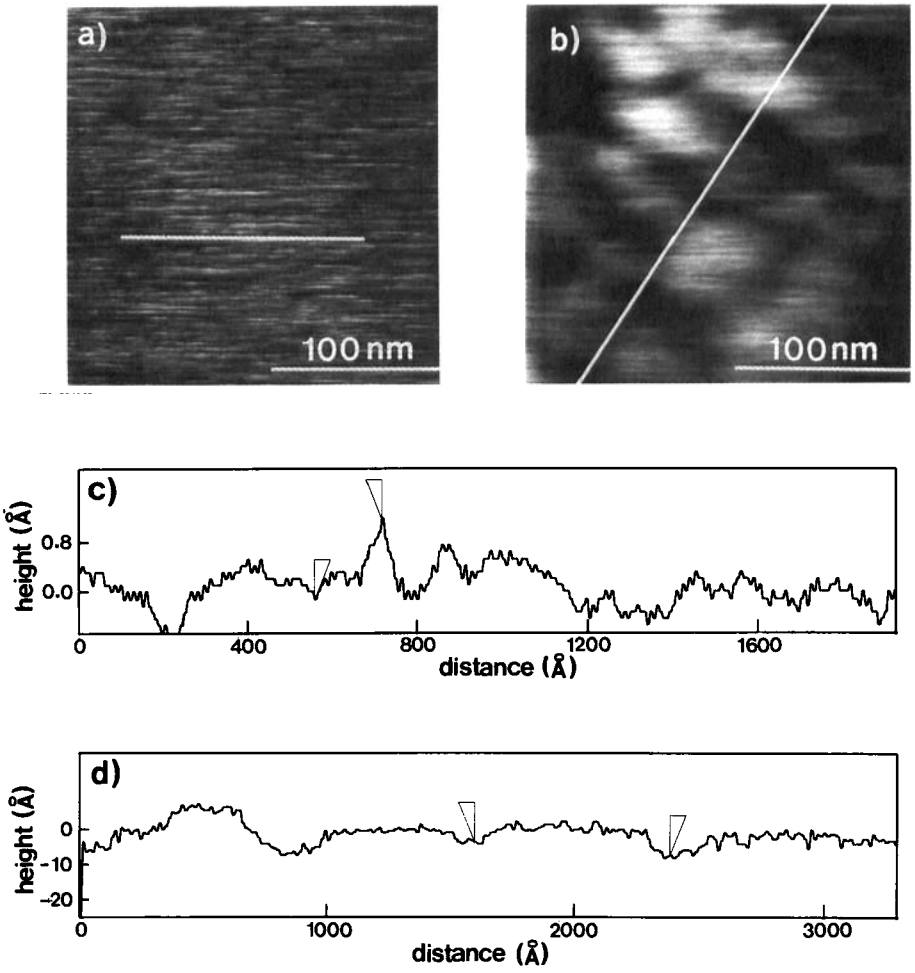

Fig. 4. AFM images of one monolayer of (a) polyamic acid alkylamine salt film and (b) imidized film on mica plates with an scanning area of 0.2μm×0.2μm. Height profiles of (c) polyamic acid alkylamine salt film and (d) imidized films are also shown in this figure.

Fig. 5 shows also the AFM images of ten monolayers of polyamic acid salt film and imidized film on mica plates, respectively, with a scanning area of 0.8μm×0.8 μm. The average microroughness of polyamic acid salt film with ten monolayers was 3.0Å, which is much higher than that of polyamic acid salt film with one monolayer. On the other hand, the average microroughness of imidized film was about 21Å, which is about an order of magnitude higher than that of one monolayer of imidized film and there was no difference in shape and size of polyimide grains between one monolayer and ten monolayers of imidized films except the thickness of the grains. This seems to be
due to the reduction of volume of polyamic acid salt during the imidization process, in which the elimination of H_2O due to cyclization of polyamic acid salt to polyimide and the removal of long dimethylhexadecylamine with a thermal treatment occur simultaneously.

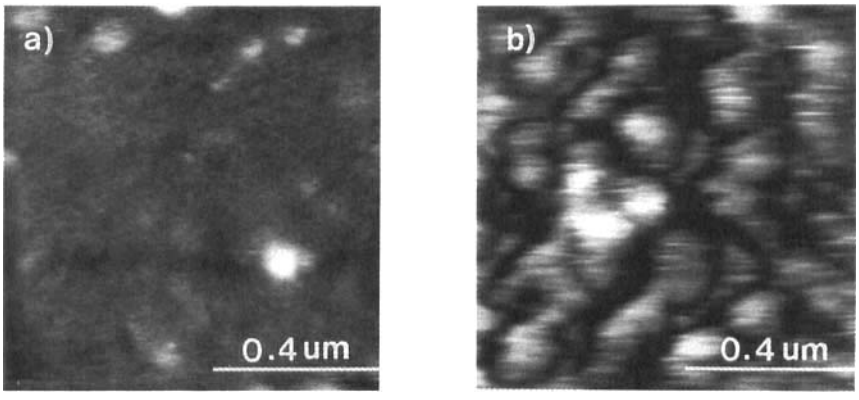

Fig. 5. AFM images of ten monolayers of (a) polyamic acid alkylamine salt film and (b) imidized film on mica plates with an scanning area of 0.8μm×0.8μm.

In order to investigate the imidized film at molecular level, the imidized film on mica plate with a thickness of one monolayer were scanned over an area of 10nm× 10nm with AFM, which is shown in Fig. 6. Unprocessed image and high- frequency noise filtered image of the imidized film are shown in Fig. 6 (a) and (b), respectively. The filtered AFM image as shown in Fig. 6 (b) gives the more clear molecular structure of the imidized film than the unprocessed AFM image in Fig. 5 (a). According to the molecular modeling with wide-angle X-ray scattering experiments, the optimized PMDA-ODA polyimide should reveal a planar zigzag structure.[7, 9] The edge-on separation, the separation between the centers of two

adjacent planar units in a direction perpendicular to the stacking direction, is approximately 6Å. Both grains (white region) and grain boundary (black region) can be distinguished in Fig. 6 (b). While the grain region tends to show regular zigzag structures, the grain boundary region does not show zigzag structures, but straight broken line features. This suggests that complete imidization seems to be achieved in the grain region, but imidization seems to be incompletely achieved in the grain boundary region. The distance between the polyimide chains was estimated about 6Å as shown in Fig. 6 (b), which is in a good agreement with the results of X-Ray scattering experiments.

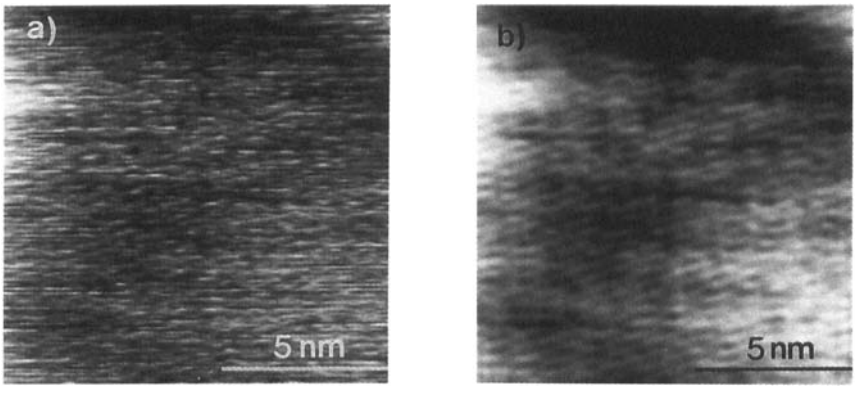

Fig. 6. AFM images of one monolayer of imidized film on mica plates. (a) unprocessed image and (b) high-frequency filtered image.

CONCLUSION

Polyamic acid salt films were successfully deposited on various plates at molecular level by LB technique. It was found that the imidization with a thermal treatment changed polyamic acid salt films into polyimide films forming grain boundaries even at monolayer level, where the grain size of polyimide films was sub-micron order level. It was also found that grain region shows the crystalline feature such as zigzag structure, but grain boundary region does not. More details on the preparation and molecular structure properties of the imidized multilayer films will be presented elsewhere.

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