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A Study on the Electric Conduction Mechanism of Polyimide Ultra-Thin Films

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Abstract: : 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. In this research, the electric conduction mechanism of PI Ultra-Thin Films was investigated at room temperature. At low electric field, ohmic conduction ($I \propto V$) was observed and the calculated electrical conductivity was about $4.23\times10^{-15} \sim 9.81\times10^{-15}$ S/cm. At high electric field, nonohmic conduction ($I \propto V^2$) was observed and the conduction mechanism was explained by space charge limited region effect. The dielectric constant of PI Ultra-Thin Films was about 7.0.

Keywords : polyimide, dielectric material, electric field, conduction mecahnism, conductivity.

1. Introduction

Polyimides have been widely used in microelectronic industries because of their outstanding characteristics such as high tensile strength and modulus, low thermal expansion and dielectric constant, and good resistivity against organic solvent[1-3]. Also, polyimide(PI) is well-known as a good electrical insulating material. They are therefore used in microelectronic devices, in aircraft and in space applications. Especially for microelectronic application, the preparation of Ultra-Thin Films of PI is required to obtain high performance materials[4]. One of the well-known methods for the preparation of organic Ultra-Thin Films is the Langmuir-Blodgett(LB) technique[4-9]. A lot of attentions have been paid on this LB technique since about twenty years ago because it can provide the desired control on the order at the molecular level. In these days, the investigations of PI Ultra-Thin Films were mainly for pyromellitic dianhydride(PMDA) and 4,4-diaminodiphenylether(DDE) system. But, we have been studying PI Ultra-Thin Films of PMDA and benzidine system, which was superior to PMDA and DDE system in terms of thermal stability. The preparation of PI Ultra-Thin Films was previously reported[10,11]. In these studies, PI

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Ultra-Thin Films composed of the PMDA and benzidine with a thickness from ten monolayers to forty monolayers were formed on substrates by using LB technique.

In this research, to find out electric conduction mechanism of PI Ultra-Thin Films of pyromellitic dianhydride (PMDA)-benzidine system, we tried to examine electrical conduction mechanisms of PI Ultra-Thin Films by measuring the properties of electrical currents and voltage after imidization of manufactured Metal/PI Ultra-Thin films (insulator)/Metal(MIM) form samples where Al electrode was deposited on the top and bottom of PAAS LB films[1].

2. Experimental

2.1. Reagent and Equipment

611D/2B LB trough manufactured by NIMA technology was used in making LB films, and Milli-Q reagent water system manufactured by Millipore was used in making ultra pure water which was used as subphase. Also, in washing a substrate, UV-O_3 Cleaner of Nippon Laser & Electronics Lab. was used, while in measuring UV/vis. absorption for checking the cumulative condition of LB films, UV2-300 spectrometer of ATI UNICAM was used. Besides, to measure capacitance, EDC-1630 Digital LCR meter made by ED Lab. was used. In manufacturing electrode, a vacuum evaporator (SWMC-320A, evaporation of JBS international) was used, and in measuring characteristics of electric currents and voltage, 236 source measure unit produced by Keithley was used. Fig. 1 shows the structure of PAAS which is film material used in this experiment.

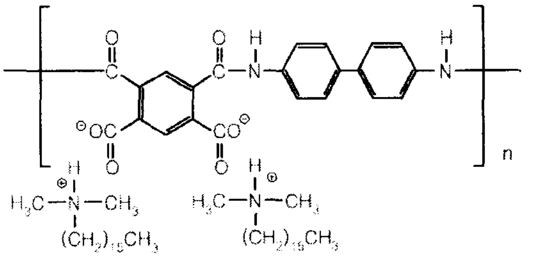

Fig. 1. Molecular structure of PAAS.

2.2. Preparation of PI Ultra-Thin Films

The LB films were deposited at the surface pressure of 27 mN/m, dipping speed of 5 mm/min after spreading PAAS solutions on deionized water at 20℃. The LB films were deposited as Z-type, where the transfer ratio constant was almost 1, only at the up-ward stroke[12].

2.3. Electrical Properties of PI Ultra-Thin Films

To measure the electrical properties of PI Ultra-Thin Films, specimens having the structure of vertical electrode (MIM) were made as shown in Fig. 2.

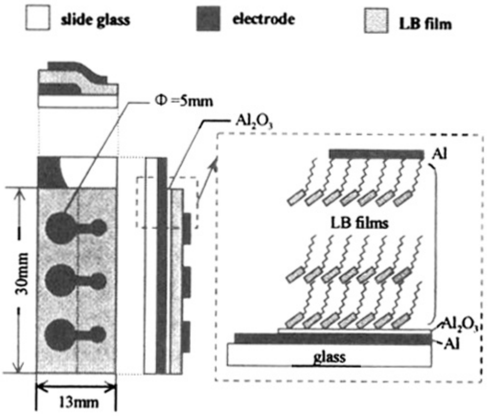

Fig. 2. Structure of electrode for an electrical measurement.

Bottom electrode was made by depositing Al on the glass substrate under vacuum, and PAAS LB films were cumulated on it, followed by making several top electrodes by depositing Al under vacuum. The samples produced in this process was treated with imidization at 250℃ for 30 minutes, and then PI Ultra-Thin Films were made[11]. After that, by measuring capacitance and properties of electrical currents and voltage, the dielectric constant and electrical conductivity of PI Ultra-Thin Films and the electrical conduction mechanism was examined.

3. Results and Discussion

3.1. Measuring the Dielectric Constant of PI Ultra-Thin Films

In Fig. 3, the value of reciprocal number(1/C) of PI Ultra-Thin Films by the number of layers of cumulation was plotted.

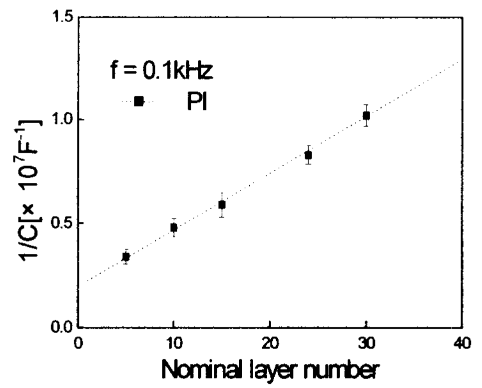

Fig. 3. Number of layers vs. reciprocal capacitance of PI Ultra-Thin Films.

As shown in Fig. 3, considering that the value of l/C showed a good linear relationship by the number of cumulative layers, the thickness of films was well controlled. At that time, the dielectric constant of PI Ultra-Thin Films was calculated, using the calculated value of gradient. The thickness of oxide films was about 33Å, which was almost in accord with the value which other researchers had presented, and the dielectric constant of PI Ultra-Thin Films of PMDA-benzidine system was about 7.0. This value was higher than that of Kapton-type PI, so it seems that continuous studies are needed.

3.2. Electrical Properties of LB Films

I-V characteristics of PI Ultra-Thin Films (30 layers) in the vertical direction were shown in Fig. 4. As shown in Fig. 4, ohmic properties were shown in about 1.2V or less, while in about 1.2V or over nonohmic properties were shown. Thus it could be confirmed that the relationship between electrical currents and voltage was ohmic in low electric field whose voltage was relatively low. The electrical conductivity measured in the vertical direction in the ohmic region shows good insulating properties: about 4.23×10^{-15} ~ 9.81×10^{-15}[S/cm].

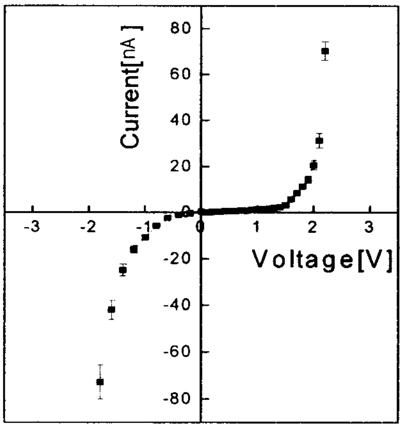

Fig. 4. I-V characteristics of PI Ultra-Thin Films.

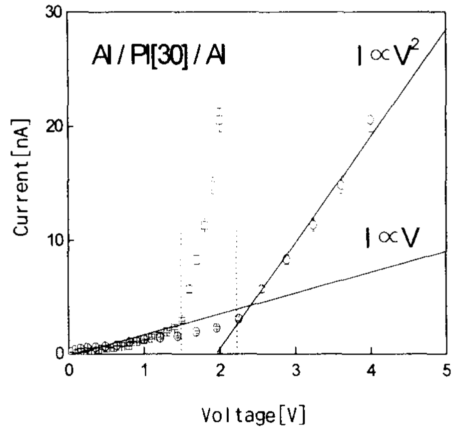

Fig. 5. I-V characteristics of PI Ultra-Thin Films; $I \propto V$, $I \propto V^2$.

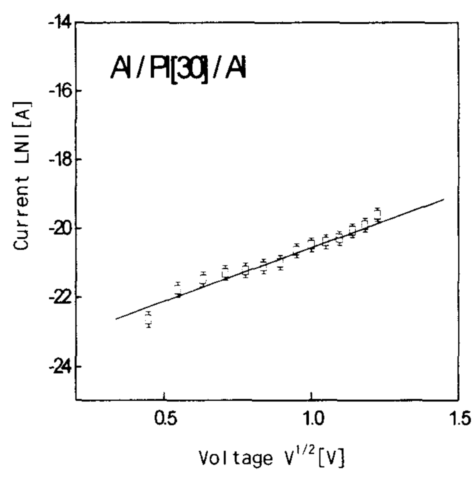

Fig. 6. Schottky plot for I-V characteristics.

Fig. 5 showed the properties of electrical currents and voltage of PI Ultra-Thin Films in the vertical direction in both low and high field regions. If the applied voltage increases and reaches high field region, the electrical current may increase nonlinearly. This region, in this experiment, was shown after ohmic region, and space charge limited current could be observed in about 1.8V. In Fig. 6, Schottky electrical currents are caused by electrical potential barriers which are formed in the interface of metal and dielectrics, and the electrical current ln I increases in proportion to voltage $V^{1/2}$. Accordingly, it could be known that electrical conduction was produced by Schottky effect in 0.3~1.0V.

4. Conclusions

The results of the measurement of electrical properties by manufacturing PI Ultra-Thin Films of PMDA-benzidine system, using LB technique, are as followings. The measured dielectric constant of imidizated PI Ultra-Thin Films which was 7.0, which was relatively high. In terms of properties of electrical currents and voltage measured in the vertical direction, ohmic properties were shown for the voltage range less than 1.2V, while nonohmic properties were shown for the voltage range larger than 1.2V. Thus in low electric field that was formed in relatively low applied voltage, the relationship between electrical currents and voltage was ohmic, and electrical conductivity was about 4.23×10^{-15}~9.81×10^{-15} S/cm, showing good insulating property. In addition, in high electric field of around 1.8V, space-charge-limited current was observed, and electrical conductivity by Schottky effect took place in 0.3~1.0V.

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