Preparation of Superconducting Edge Junctions Using Polymeric Langmuir–Blodgett Films as Barrier Layers

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SYNOPSIS

Aromatic polyamic acid alkyl ammonium salt exhibits very good transfer behavior under suitable deposition conditions. A superconducting thin film of $YBa_2Cu_3O_X$ (YBCO) on Langmuir–Blodgett film (LB) has been obtained when the substrate temperature is higher than 500°C. Superconducting edge junctions of (Pb—In)/LB/(Pb—In) and YBCO/LB/YBCO incorporated with polyimide LB films were fabricated. Their current-voltage characteristics are discussed in terms of the temperature stability of polyimde LB films.

INTRODUCTION

Langmuir–Blodgett (LB) films have been studied as an insulating layer in metal–insulator–metal (MIM) devices,[1] metal–insulator–semiconductor (MIS) diodes,[2,3] field effect transistors (FETs),[4] and low transition temperature (T_c) Josephson junctions.[5,6] Since the discovery of high-temperature superconductors, interest in the superconducting devices has grown considerably during recent years due to their potential application in electronics. For example, superconductor–insulator–superconductor (SIS) devices have been investigated by a few research groups with the insulating layers of $PrBa_2Cu_3O_X$ (Ref. 7) and $SrTiO_3$ (Ref. 8). The physical properties required of any insulating layer are rather significant and include at least the following: (1) high-temperature stability, higher than 550°C; (2) superthin, thickness of 50 Å or less; (3) high resistivity at temperatures below the T_c of the $YBa_2Cu_3O_X$ (YBCO); and (4) pinhole-free. The polyimide (PI) LB films[9] with a monolayer thickness of about 0.4 nm and a small number of conducting defects, high resistivity, and high-temperature stability common to all imide polymers make them one of the most promising materials for SIS research. In this article, we describe the physical properties of LB films of PI and the preparation of SIS edge junction incorporating with such LB films. Preliminary electrical results are also discussed.

EXPERIMENTAL

Fabrication of LB films of PI

The synthesis of aromatic polyamic acid alkyl ammonium salt (PAA) (Fig. 1) was performed by referring to the method of Imai et al.[10,11] The preparation of LB film was carried out on a KSV-5000 computer-controlled instrument (Finland). A solution of aromatic polyamide acid (PA, inherent viscosity ca. 1.2) in a mixture of *N,N*-dimethylacetamide and benzene (1 : 1) at a concentration of 1 mmol/mL and a solution of *N,N*-dimethylhexadecylamine in the same mixed solvent at a concentration of 2 mmol/mL were prepared. These solutions were combined in equal volumes to produce the ammonium salt before spreading on double-distilled water (18 ± 2°C). The surface pressure–area (π–A) isotherm was measured at a compression speed for the barrier of 20 mm/min. The multilayers were deposited as Z-type films at the surface pressure of 20 mN/m with a dipping speed of 5 mm/min. Using the step-heating method, the LB films were

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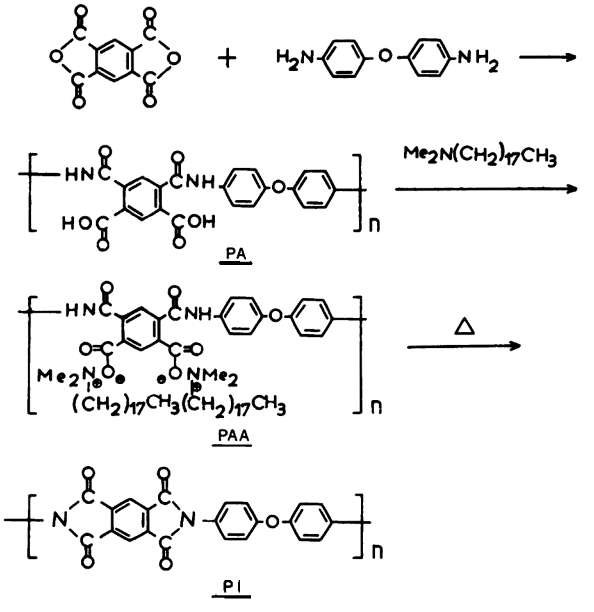

Figure 1 Synthetic scheme of PI.

treated with heat up to 300°C, converting the PA ammonium salt into a PI.

Sample Description

The (Pb—In)/LB/(Pb—In) edge junction was prepared as follows: Figure 2 shows its fabrication procedure. First, a Pb—In alloy (8 wt % In) band, 2 mm in width, with a thickness of about 1000 Å was vacuum-evaporated on a quartz substrate to form a bottom electrode. Then, a MgO layer with a thickness of about 2000 Å was applied by using the radio-frequency (rf) sputtering method. A fresh cross section on the Pb—In alloy band was cut by a sharp knife just before the LB films were deposited. After proper heat treatment, a Pb—In alloy electrode of about 3000 Å thick was evaporated on top. Finally, a Ag electrode and an In pellet with wire were formed. The resulting (Pb—In)/LB/(Pb—In) edge junctions were used for the low-temperature measurement.

Table I Sputtering Conditions

	Bottom Electrode YBCO Film	Top Electrode YBCO Film
Substrate temp (°C)	670	550-560
Anode voltage (V)	115	115
Anode current (mA)	500	500
Ar gas pressure (Torr)	0.2	0.2
O_2 gas pressure (Torr)	0.1	0.1
Sputtering rate (Å/s)	0.3	0.3
Sputtering time (h)	1	1

In the case of YBCO/LB/YBCO edge junctions (Fig. 2), a $SrTiO_3$ (110) single-crystal substrate and a direct current (dc) magnetron-controlled sputtering method were employed. The experimental conditions for sputtering are listed in Table I. A standard four-probe method was used in the current-voltage (I-V) measurement.

RESULTS AND DISCUSSION

Characterization of PAA LB films

The surface pressure area isotherm of a monolayer of PAA is presented in Figure 3. From the isotherm,

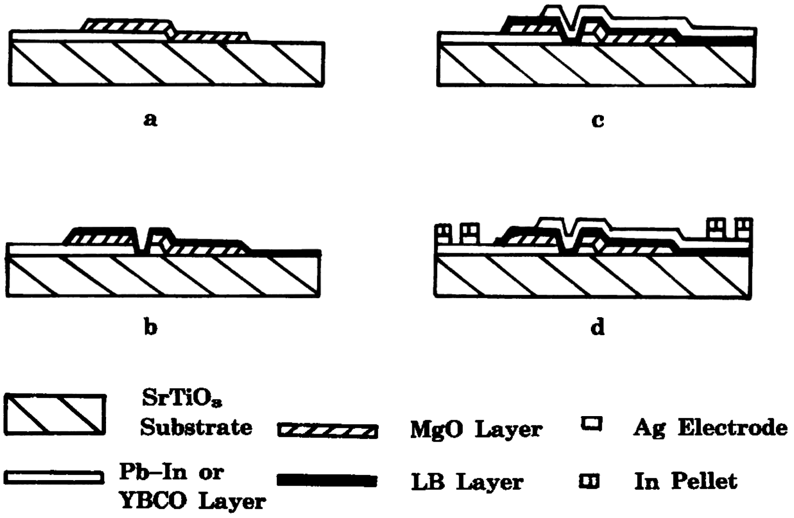

Figure 2 Cross-section view of fabrication procedure.

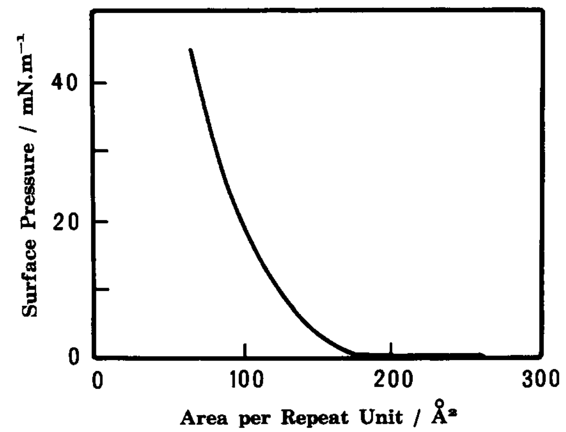

Figure 3 Surface pressure–area isotherm of PAA.

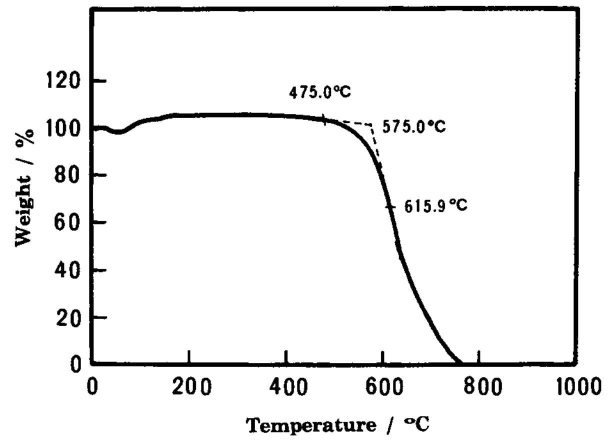

Figure 5 TGA curve of PI.

a limiting surface area of 140 Å^2 of a repeat unit of an aromatic PA ammonium salt was obtained, which was in good agreement with the value calculated by a CPK model.[7] This fact indicates that this salt forms a stable monolayer on the air–water interface and its aromatic rings lie flat on the water surface.

Figure 4 shows transfer behavior of PAA. The dynamic transfer ratio (DTR) was calculated by computer automatically every 5 s. During the deposition, the surface pressure was maintained at a constant pressure (~ 20 mN/m) and the fluctuation of DTR was less than ±0.2. This does not always happen even in the case of the typical LB film materials, e.g., arachidic acid or stearic acid, demonstrating that such a modified polymer exhibits very good transfer behavior.

Temperature Stability of Polyimide (PI) Cast Films

It is well known that wholly aromatic PI is a typical thermally stable insulating material and has been used in microelectronics.[12] Due to the requirement of the LB technique, in normal cases, amphiphilic molecules can form a stable monolayer. As mentioned above (see Fabrication of LB Films of PI), the addition of long-chain alkyl amine before the film-forming is based on this consideration. Without such a long alkyl chain, the PA stable monolayer cannot be formed. However, the ammonium salt produced exerts a negative influence both on temperature stability and on insulating behavior, so that a chemical method or a heat treatment were used to eliminate the long alkyl amine and to imidize the PA into PI. Because of the sensitivity of the thermogravimetric analysis (TGA) instrument, cast film of PI was used in the present study instead of LB films. The TGA curve (Fig. 5) shows that initial decomposition temperature, flection temperature, and maximum decomposition temperature are 475, 575, and 615.9°C, respectively. In our experiment for preparation of the YBCO/LB/YBCO edge junction, the temperature of the substrate was between 550 and 560°C, which was at the upper-limit

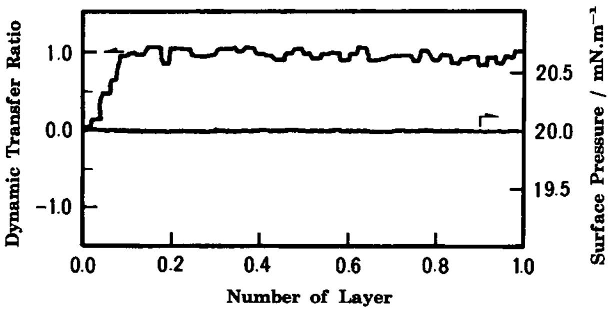

Figure 4 Transfer behavior of PAA.

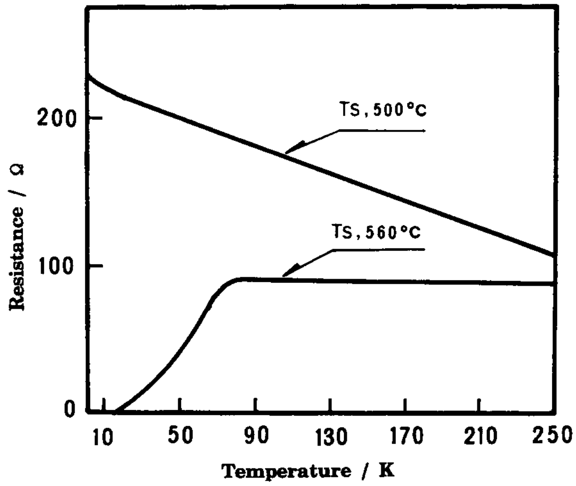

Figure 6 The temperature dependence of resistance for YBCO films on LB(n)/SrTiO$_3$, n = 9.

temperature of this material. This will be further discussed in the following section.

Influence of Substrate Temperature (T_s) on the Resistance of YBCO Films on LB/SrTiO$_3$

In our previous work,[13] the YBCO superconducting thin films on single-crystal SrTiO$_3$ could be prepared using either the rf or dc magnetron sputtering method with the T_s at about 640–670°C. Obviously, this temperature is too high for the LB films of PI to withstand when the top YBCO film was sputtered. Figure 6 indicates the influence of T_s on resistance of the thin films, whereas other deposition conditions were approximately the same. No superconducting phenomenon was observed until the T_s is up to 500°C. When T_s is 560°C, the T_c is 15 K. This is the reason why we chose the sputtering conditions as listed in Table I despite the fact that the temperature is near the flection decomposition temperature of the PI films.

Characterization of I–V Curves

Multilayer films of PAA on the bottom electrodes were either immersed overnight in a mixture of acetic anhydride–pyridine–benzene (1 : 1 : 3) or heated up to 300°C to afford PI films. In the former cases, all the bottom electrodes became nonsuperconductors at 4.2 K, although the causes are unknown at the present stage, possibly due to the deterioration of the chemicals toward the electrodes. The following results were all obtained by using heat treatment.

Typical I–V characteristics for the (Pb—In)/LB/(Pb—In) junction measured at the liquid helium temperature are shown in Figure 7. Here, the number of deposited LB films was nine layers, and the thickness was about 36 Å. A supercurrent at zero voltage of ca. 2 mA, which was sensitive to microwave radiation and the magnetic field, was observed. A tendency for the quasi-particle current to increase at the voltage of ±2.4 mV was also seen, corresponding to the existence of a gap structure.

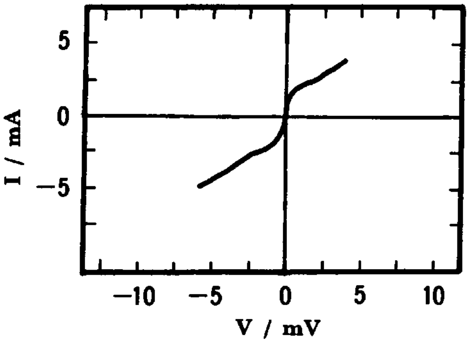

Figure 7 I–V curve for (Pb—In)/LB/(Pb—In) junction at 5 K.

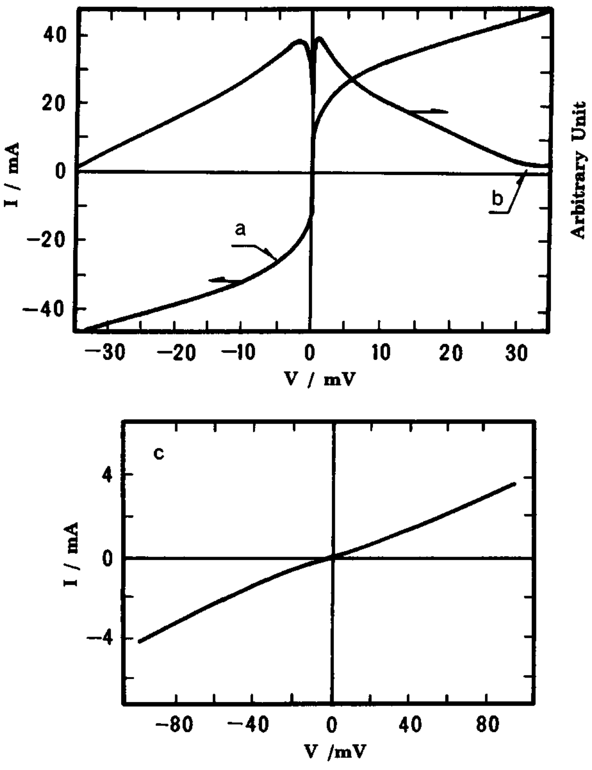

Figure 8 (a,c) I–V characteristics and (b) dV/dI–V curve for YBCO/LB/YBCO junction at 5 K.

In the case of YBCO/LB/YBCO junctions, two kinds of I–V curves were obtained. One possessed the supercurrent at zero voltage [Fig. 8 (a,b)] but no gap structure. The other one [Fig. 8 (c)], without the supercurrent at zero voltage but a nonlinear change at ±32–40 mV, was observed, depicting a slight increase of quasi-particle current.

In our experiment for preparation of the YBCO/LB/YBCO edge junction, the temperature of the substrate was between 550 and 560°C, which was at the upper-limit temperature of PI. In addition, during the imidization of PAA, water and hydrocarbon molecules were released, which makes the densely stacked LB films produce pinholes. This may be the reason that the micro short circuit observed in our experiment existed in the LB films. We believe that the characteristics for both low T_c and high T_c SIS junctions could be improved if a PI polymer with even higher thermal stability and a multi-heat-treatment method for the deposited LB films are employed.

CONCLUSION

The modified aromatic PA is a very good LB film material. Superconducting edge junctions can be prepared by using polymeric LB films as barrier layers. A supercurrent at zero voltage and a gap structure were observed both for (Pb—In)/LB/(Pb—In) and YBCO/LB/YBCO edge junctions.

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