

# Electrical conduction of polyimide films prepared from polyamic acid (PAA) and pre-imidized polyimide (PI) solution

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**Abstract.** Electrical conduction characteristics in two different polyimide films prepared by the imidization of polyamic acid (PAA) and pre-imidized polyimide (PI) solution were investigated. It is found that the current density of the polyimide film from PAA was higher than that of the polyimide film from PI at the same electric field, even though the conduction mechanism in both polyimide films follows the ionic hopping model. The hopping distance was calculated to be 2.8 nm for PAA type and 3.2 nm for PI type polyimide film. It is also found that the decay rate of the residual electrostatic charges on the polyimide films becomes faster in the PAA type than in the PI type polyimide film.

**Keywords:** *thermosetting resins, polyimide, electric conductivity, static charge dissipation*

## 1. Introduction

Thin films of polymeric materials have been used widely in the field of microelectronics for insulation, isolation and passivation. Particularly, polyimides are growing important especially in various applications because of their excellent thermal and electrical properties [1–4]. One of the most important applications of polyimide films is used as alignment layers in liquid crystal display (LCD) device, which enable liquid crystal to orient along its designated direction [5, 6]. For this application, polyimide films can be simply prepared by coating either polyamic acid or pre-imidized polyimide solution onto glass substrates where thin film transistor (TFT) and color filter (CF) patterns are already prepared. With the thermal curing process at a high temperature thin films of polyimides are formed on the glass substrate and are subjected to

the rubbing process for creating an alignment path [1–6].

However, since polyimides are one of the typical polymers having high electrical resistance, the electrostatic charges can be easily created on the surface by rubbing it with polyester cloth. Once electrostatic charges are formed on the polyimide layers, they last for some time during the manufacturing process, creating their own electric field between the two alignment layers. Then, liquid crystal director responds to the electric field from the electrostatic charges on the polyimide films, and this leads to unwanted light-transmission modulation of the liquid crystal that can be recognized as ghost images on the LCD panel [6, 7].

Even though this phenomenon is one of the major problems frequently occurring in the LCD manufacturing process, its mechanism has not been well understood. Since this phenomenon is believed to be related to the electrostatic charge-retention prop-

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erties of polyimide films, the measurement of the electrical properties for polyimide films prepared from different precursors become necessary.

Here, we present the comparison of the electrical properties in polyimide films which were separately prepared from polyamic acid and pre-imidized polyimide solution. The electrostatic charge susceptibilities of the two polyimide films are discussed in terms of their charge transport behavior.

## 2. Experimental details

The experiments reported here were performed on polyimide films which were separately prepared from two different types of precursors, namely polyamic acid (PAA) and pre-polymerized polyimide (PI) solution.

The polyimide films were prepared on a glass substrate by a solvent casting method and pre-baked at 80°C on a heating plate, then subjected to a thermal curing in a vacuum oven at 180°C for 90 min. Then, the polyimide films were taken as free standing films and compression molded using a hot press at 200°C. The film thickness was controlled by the concentration of precursor solution and pressure to be 100  $\mu\text{m}$ . Silver was vacuum evaporated through a mask to the surface of the polyimide films to form electrodes.

The apparatus used to measure the conduction currents was composed of a power supply (Keithley 247), electrometer (Keithley 617), and test cell. The test cell contained a measuring electrode, the counter electrode, and a guard ring. The contact

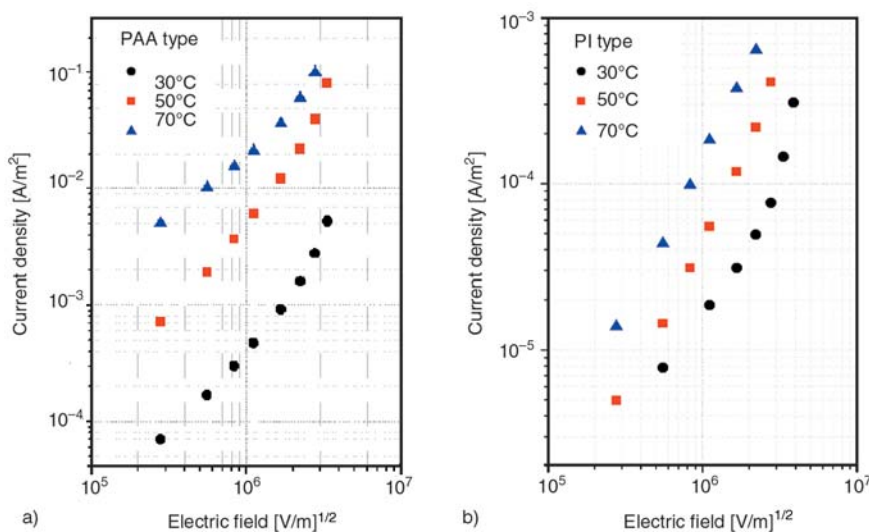
area of measuring electrode was 6.202  $\text{cm}^2$ . The temperature of 50–100°C was controlled in an air convection oven. All experiments were continued for a time period long enough to reach a steady-state current.

For the evaluation of electrostatic charge susceptibility, two sets of normally dark mode LCD panels were fabricated using PAA type and PI type polyimide films as an alignment layer. Then, 1 kV of DC voltages were applied across the LCD panels and the brightness of light through LCD panel was measured by luminance calorimeter (BM-7, Topcon) on the voltage switching-off.

## 3. Results and discussion

Figure 1 shows a typical  $J$ - $E$  plot of two different polyimide films prepared by the imidization of polyamic acid and pre-imidized polyimide solutions. A classical way to identify the conduction mechanism is to examine linearity in  $J$ - $E$  curves.

The plot consists of two regions, in the lower region of the applied electric field, the slope is around 1, and in the higher region, the slope is around 2. This means that both of polyimide films follow the ohmic conduction in the lower range of electric field, whereas non-ohmic conduction mechanisms are involved in higher range of electric field. There are three different types of electronic conduction mechanisms, namely, space charge limited conduction (SCLC), Shottky conduction, Poole-Frenkel conduction, and one of these mechanisms would be dominant in higher range of electric field [8, 9].



**Figure 1.**  $J$ - $E$  curves of polyimide films: a) polyamic acid type and b) pre-imidized polyimide type

When  $J$  is proportional to  $E^n$ , one can say that the sample obeys the SCLC mechanism. In this case, the slope of 2 represents the trap free SCLC, whereas the slope of 2–6 represents the trap modulated SCLC [8–12]. In Figure 1, the slope of 2 in higher field could be an indication that the samples follow the trap-free SCLC mechanism. However, for SCLC mechanism, the thickness dependence of the space charge limited current follows the relation of  $J \propto d^{-n}$ , where  $n$  is a parameter which depends on the trap distribution and is equal to or greater than 3 [8, 9].

Figure 2 shows the thickness dependence of the current density and the slopes of PAA- and PI-type polyimide samples are found to be 0.41 and –0.04, respectively. These values are much less than that required for space charge limited conduction so that SCLC conduction mechanism is ruled out.

The conduction mechanisms of the polyimide films were further examined in terms of Schottky and Poole-Frenkel mechanisms which can be expressed by the Equation (1) [10–13]:

$$J = AT^2 \exp\left(\frac{\beta E^2 - \phi}{kT}\right) \quad (1)$$

where  $J$ ,  $E$ ,  $\phi$ ,  $k$ , and  $\beta$  are the current density, the electric field, the barrier height between the interfaces, the Boltzmann constant, and coefficient, respectively. The  $\beta$  coefficient is also given by the Equation (2):

$$\beta = \left(\frac{e^3}{a\pi\epsilon\epsilon_0}\right)^{\frac{1}{2}} \quad (2)$$

where  $a = 1$  for Poole-Frenkel effect and  $a = 4$  for Schottky emission,  $\epsilon$  is the dielectric constant and  $\epsilon_0$  is the permittivity of free space.

According to Equation (1), a plot of  $\log J$  versus  $E^{1/2}$  should yield a straight line if either of the above mentioned two mechanisms is dominant in polyimide films. The  $\beta$  coefficients are first calculated from the slope of  $\log J$  vs  $E^{1/2}$  plots, and the dielectric constants are then estimated from these coefficients using Equation (2). If these dielectric constants agree with the values cited in the literature, it can be said that the samples follows the corresponding conduction mechanism.

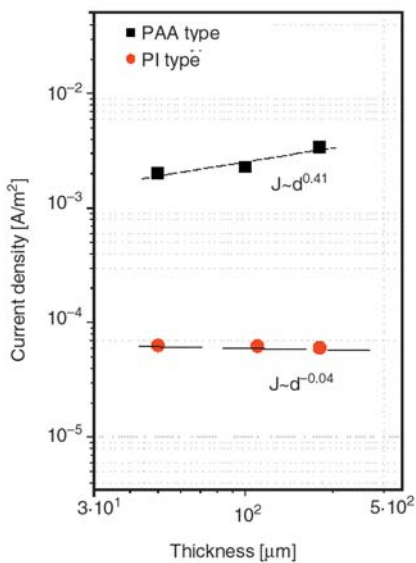
The dielectric constants derived from the slope in Figure 3a and 3b range from 0.6 to 0.9 in the case of Schottky mechanism, whereas those from literatures range from 3.9 to 4.0 [14, 15]. A comparison of these values indicates that Schottky conduction mechanism is not the case for the polyimide films because dielectric constant of less than 1.0 is not conceivable. Since the dielectric constants by a Poole-Frenkel mechanism is twice of those by a Schottky mechanism, the Poole-Frenkel mechanism can be automatically excluded.

Measurement of complex impedance is one of the ways to determine whether the conduction mechanism is electronic or not. The measurement of complex impedance in the frequency range of 1 kHz–5 MHz showed a semicircle for both types of polyimide samples, which implies that the dominant charge carriers are rather ions than electrons. When the ions existing in the polyimide samples are thermally activated and participate in the conduction process, the current density  $J$  is expressed in terms of ionic hopping conduction model as Equation (3) [16, 17]:

$$J = n\alpha v \exp\left(-\frac{U}{kT}\right) \exp\left(\frac{eE\alpha}{2kT}\right) \quad (3)$$

where  $e$ ,  $n$ ,  $\alpha$ ,  $v$ ,  $U$ ,  $k$ , and  $T$  are the charge of electron, carrier density, hopping distance, attempt to escape frequency, activation energy, Boltzmann constant, and absolute temperature.

Based on the ionic hopping model, Figure 4 compares the current density of two different types of polyimide films with respect to the applied electric



**Figure 2.** Thickness dependence of current density at 300 V in polyimide films

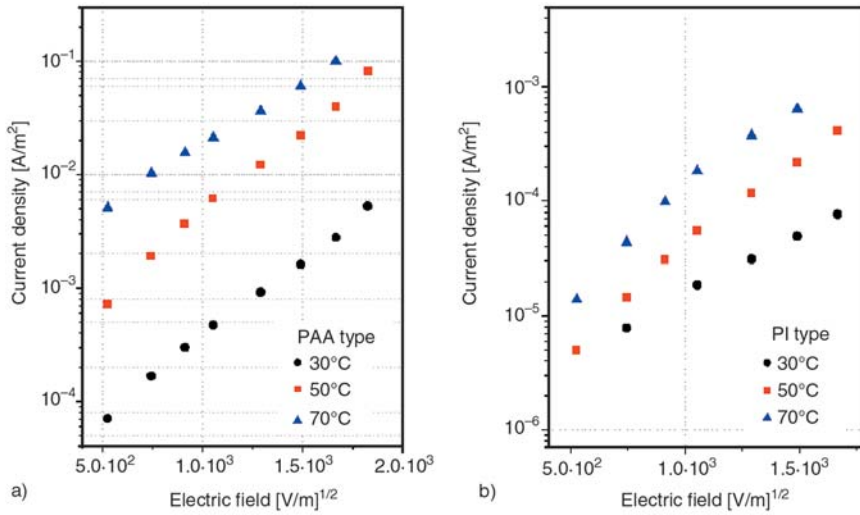


Figure 3. Plot of  $\log J$  vs  $E^{1/2}$ : a) polyamic acid type and b) pre-oxidized polyimide type

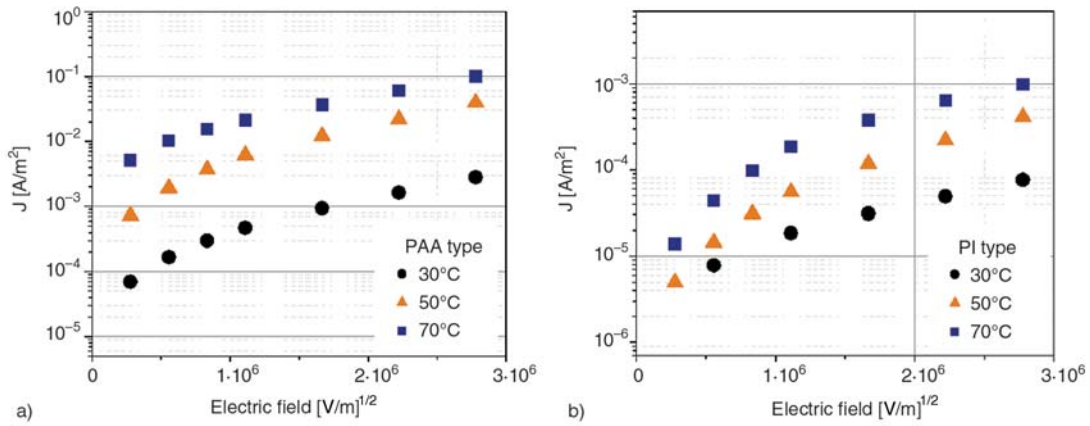


Figure 4. Plots of  $\log J$  vs  $E$ : a) polyamic acid type and b) pre-oxidized polyimide type

field. It is clearly seen that the PAA type polyimide has the higher current density than PI type polyimide sample at the same electric field. In addition, since  $\exp(-U/kT)$  term in Equation (3) is independent of the electric field and can be treated as a constant with respect to electric field, the hopping distance  $\alpha$  can be estimated from the slope of  $\log J$  vs  $E$  plot and the hopping distances for the PAA type and PI type polyimide were found to be 2.8 and 3.2 nm for 50°C, respectively. This is an indication that the ionic hopping motion is facilitated rather in PAA type than in PI type sample.

In order to verify that ionic hopping is more favorable in PAA type than in PI type sample, the activation energies of the two different samples were calculated from the slope of the  $\ln[J/\sinh(eE\alpha/2kT)]$  vs  $1/T$  plot in Figure 5. A linear relationship was observed in this figure, which further confirms that the conduction mechanism did not change over the corresponding temperature ranges. The activation

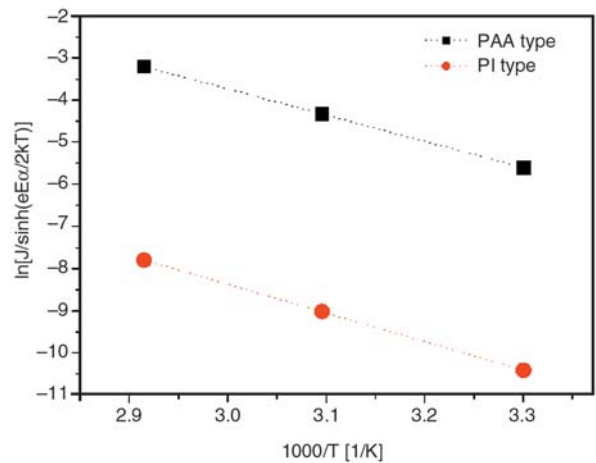


Figure 5. Temperature dependence of current densities in polyimide films

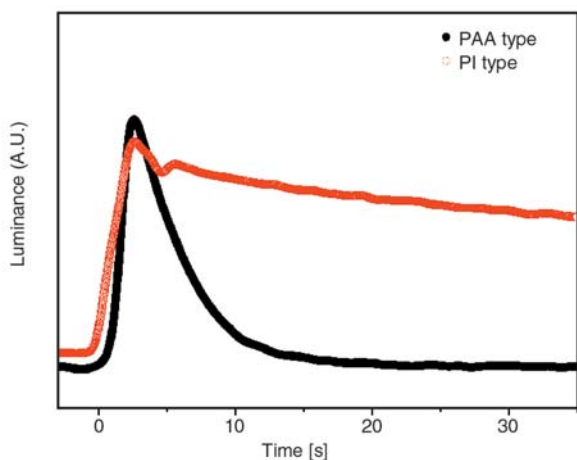
energy were found to be 0.16 eV for PAA type polyimide and 0.19 eV for PI type polyimide and this corresponds with the results that the ionic conduction is much more favorable in PAA type polyimide.



Since ionic hopping conduction is known to originate from the ionic impurities such as polar and partially dissociable molecules, it is speculated that there are more impurities that contribute to the ionic conduction in PAA type sample [18, 19]. However, the sources of ionic conduction in PAA type polyimide are not identified at this moment.

In order to examine whether the ionic conductivity of polyimide films affects the electrostatic susceptibility of the LCD panel, two different sets of LCD panels were fabricated using PAA type and PI type polyimide films as an alignment layers and a DC voltage of 1 kV was applied across the LCD panels. When a voltage is applied across the normally dark LCD panels, the liquid crystal molecules respond instantaneously with an electric field, so that optical transmission increases. When the applied voltage is switched off, the optical transmission decreases as the liquid crystal molecules are restored to their original state. When charge accumulates on the alignment film, liquid crystal molecules are exposed to a residual voltage after the applied voltage is switched off. The slow decay of this residual voltage is expected to cause a slow change in the alignment of the liquid crystal molecules, and thus a slow change in the optical transmission.

Figure 6 compares the luminance of two LCD panels as a function of time. For the LCD panel with an alignment layer of PAA type polyimide film, the luminance decrease sharply on the removal of voltage application, whereas the slow change was observed in the case of the LCD panel with PI type



**Figure 6.** Comparison of the luminance with respect to time for LCD panels with PAA type and PI type polyimide films

polyimide film. This means that the residual charges remain for a longer period of time for PI type alignment film and these residual charges keep the liquid crystal light switch with a long relaxation time. In such case, the displayed image is retained after the applied voltage is switched off and recognized as a sticking image that is highly undesirable in the LCD manufacturing process. On the other hand, PAA type polyimide film shows higher ionic conductivity so that the residual charges can dissipate along or through the film or the charges can be neutralized by the mobile ions in PAA type polyimide film, enabling the liquid crystal molecule to be restored to its original state with a less probability of causing a sticking image.

#### 4. Conclusions

Polyimide films prepared from two different types of precursors are studied in terms of electrical conduction and electrostatic susceptibility. Although both polyimide films prepared from polyamic acid (PAA type) and pre-imidized polyimide (PI type) solution were governed by the thermally activated ionic hopping process, the polyimide film from PAA showed the current density higher than that from PI type solution at the same electric field. It is also found that the hopping distance and activation energy for PAA type sample was calculated to be 2.8 nm and 0.16 eV, while 3.2 nm and 0.19 eV for PI type sample.

Experiments for evaluating electrostatic susceptibility of the LCD panels incorporating two different polyimide alignment layers revealed that the residual charges on the PI type polyimide film remained over a time period of greater than 30 s, whereas the residual charges on the PAA type polyimide films decays rapidly. This implies that the charge accumulation is reduced for PAA type polyimide films so that image sticking problem can be minimized.

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