Electrical and Photoelectrical Conduction of VDP Polypyromellite-imide Films

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ABSTRACT

The electrical and photoelectrical currents are measured for the pyromelliteimide films prepared by vapor deposition polymerization. The temperature dependence of " dark " currents in the range of 20 - 200℃ gave two kinde of apparent activation energies, viz., ΔE_h = 28.3kcal/mol at T ≧ ca. 120℃ and ΔE_l = 9.1kcal/mol at T ≦ ca. 120 ℃. The photocurrents showed a peak at 500nm, being about 100-fold larger than that for the conventional Kapton film.

INTRODUCTION

Vapor deposition polymerization (VDP) is a dry process advatageous for strictly avoiding the effect of solvents or contaminations. Recently, polyimide (PI) films were made successfuly by vapor deposition polymerization[1, 2]. The VDP can provide thin films pin-hole free at least in the few hundreds angstrom scale[3].

There have been some investigations of the electrical and photoelectrical conduction for conventional polypyromelliteimide, PI(PMDA/ODA), films, but very few for VDP-PI(PMDA/ODA) films[4]. Photoconductivity of thermally stable aromatic polyimides arouses interest of possible use as a photoreceptor in electrophotographic and energy conversion applications.

In this study, both VDP-PI(PMDA/ODA) films and Kapton films were used to understand on a molecular level the mechanism of electrical and photoelectrical conduction for this material.

EXPERIMENTAL

Samples: For the preparation of VDP-PI(PMDA/ODA) film, both PMDA and ODA were evaporated at a stoichiometric molar ratio by heating at 230 ℃ and 190 ℃, respectively, under a pressure of 2 x 10^{-5} Torr. The film was deposited on an qurtz glass substrate at 200 ℃ in a reaction chamber. The polyimide film was prepared by heating the deosited film (thickness, ca. 20 μ m) at 250 ℃ for 2 h and at 350 ℃ for 2 h.

Commercialy-available Kapton H films of thickness 50 μ m were employed for comparison.

Electrical Current Measurments: Al was evaporated on both surfaces of films. The electric current was measured under the applied voltage of 500V for Kapton films and 300V for VDP films, respectively, using a vibrating reed electrometer (Advantest Co., TR8411). The temperature was changed in 20 degree steps over the range of 20-200 ℃ in a vacuum of 10^{-2} Torr.

Photocurrent Measurments: Au semitransparent electrode was prepared as the illuminated electrode and Al electrode was used for the back electrode by evaporation. Steady-state d.c. photocurrent measurements were made also with the TR8411 electrometer at room temperature in a vacuum, using monochromatic light from a xenon lamp (200V/1kW).

RESULTS AND DISCUSSIONS

Electrical Conduction: Figure 1 shows the electrical resistivity, ρ, as a function of reciprocal temperature for VDP-PIfilm at an applied voltage of ca. 150kV/cm. In this range of applied voltage the resistivity at room temperature was almost ohmic. As it can been seen from Figure 1, different apparent activation energies are obtained as ΔE_h = 28.3kcal/mol at T ≧ ca. 120 ℃ and ΔE_l = 9.1kcal/mol at T ≦ ca. 120 ℃. For the Kapton film two kinds of apparent activation energies were also obtained, that is, ΔE_h = 32.9kcal/mol at T ≧ ca. 100 ℃ and ΔE_l = 13.2kcal/mol at T ≦ ca. 100 ℃. Voishchev et al.[5] has reported that the electrical conductivity at T ≦ ca. 100 ℃ for convetional PI(PMDA/ODA) films is mainly contributed by contaminants. Sacher[6] has shown that the conductivity at temperature at 65 - 125 ℃ is ionic, due to protons ionized from residual polyamic acid in dry samples and due to residual impurity ions in wet samples.

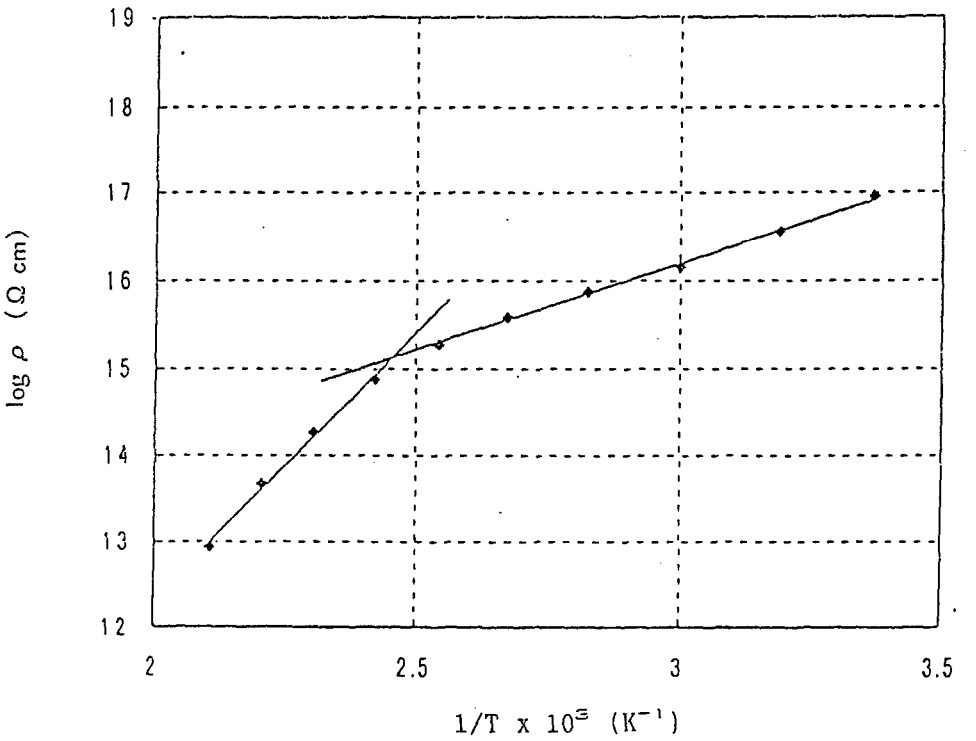

Figure 1. Electrical resistivity as a function of reciprocal temperature for VDP-PI(PMDA/ODA) film

Photoconduction: Figure 2 indicates the variation of the spectral responses of photocurrents for the VDP-PI(PMDA/ODA) film. The photocurrents show an apparent peak at 500nm, while the photocurrent Ip(+) with the illuminated electrode positive is slightly greater than the photocurrent Ip(-) with the same electrode negative around the peak. The photocurrents for the Kapton film also showed a similar peak at 500nm but little polarity effect of the applied field. The photocurrent Ip(+) at the peak for the VDP-PI(PMDA/ODA) film is about 100-fold larger than that for the Kapton film. It was also about 100-fold larger than the dark current for the same VDP film.

The process of photoconductivity can be divided into three indivisual steps: (1)excitation;(2) charge carrier generation; (3)free charge transport. The first two steps for PI(PMDA/ODA) may explained mainly in terms of the intermolecular charge-transfer complex[7, 8] formed between the diphenyl ether portion, electoron donor, and the imide portion, electron acceptor, of the polymer backbone. The carrier transport in PI(PMDA/ODA) has been analyzed by phenomenological models[9, 10]. The effect of change in morphology of photoconductivity of Kapton films has been discussed in some detail[11, 12].

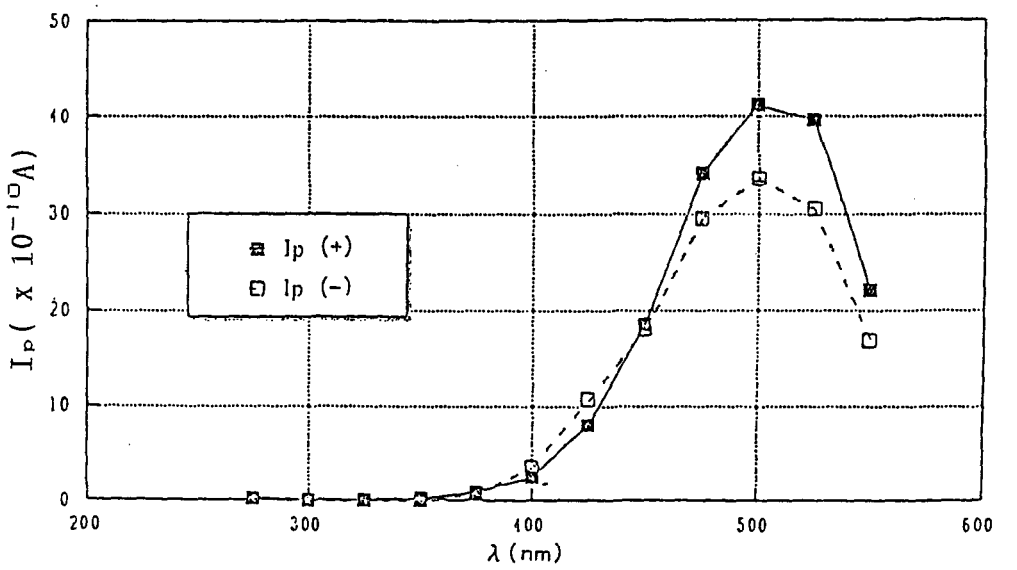

Figure 2. Photocurrent spectra for VDP-PI(PMDA/ODA) film,
I_p(+): positive electrode illuminated,
I_p(-): negative electrode illuminated.

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