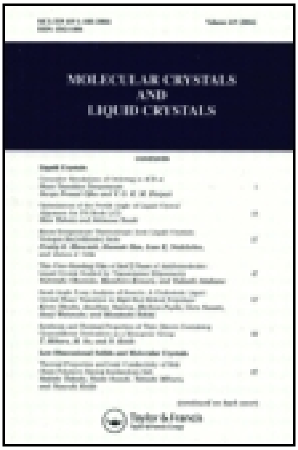

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Nonlinear Electrical Properties of Evaporated Lead Phthalocyanine Films

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NONLINEAR ELECTRICAL PROPERTIES OF EVAPORATED LEAD PHTHALOCYANINE FILMS

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Abstract Current-voltage characteristics of Au/evaporated lead phthalocyanine film/Au sandwich-type cells showed nonlinear electrical properties with asymmetric barriers. From analyses of crystal structures of PbPc films, these barriers were found to be attributable to nonuniformity of crystal structure and orientation along the film thickness.

INTRODUCTION

Recently, optical and electrical properties of phthalocyanines have intensively been investigated. Lead phthalocyanine (PbPc) has been expected to be a one-dimensional electronic conductor because non-planar molecules of PbPc co-facially stack to form a molecular column parallel to the c axis in a monoclinic form[1,2]. Metal/PbPc/metal sandwich-type cells have displayed an electrical switching phenomenon[3,4]. The conductivities of lead phthalocyanines has also been known to be sensitive to atmosphere or adsorbed gases. Dark conductivity is affected by diffusion of oxygen[5,6] and NO_2[6] molecules and rectifying properties of an Al/PbPc/Au structure are quite different for air and vacuum atmospheres[7].

We found that evaporated PbPc films showed a new type of switching phenomenon[8], in which the conductivity changed between a high resistance (OFF) state and a low resistance (ON) state by applying an electrical field normal to the film surface. In this paper, we report on current-voltage (I-V) characteristics of evaporated PbPc films and discuss the effects of atmosphere and crystal structure on the nonlinear electrical properties.

EXPERIMENTAL

PbPc used in this study was commercially supplied and purified by repeated vacuum sublimations. Quartz glass was used as a substrate and a PbPc film of 0.1 to 1 μm thick was evaporated at pressures around 10^{-4} Pa. The temperature of the crucible was controlled at 410 to 480 °C for a deposition rate of PbPc in a range between 0.4 and 2.0 A s^{-1}. The film thickness and deposition rate were controlled using a quartz oscillation thin film deposition controller. A sandwich-type cell of an Au/PbPc/Au structure (the surface area of 1 x 1 mm^2) was prepared through Au evaporation. In I-V characteristic measurements, the top electrode was grounded and the voltage was applied to the bottom electrode and a 20 kΩ load resister was serially connected in the circuit. Scanning rate of the applied voltage was varied from 0.04 to 4.0 V s^{-1}.

RESULTS AND DISCUSSION

I-V Characteristics in Dry Air

Figure 1 shows I-V characteristic of an evaporated PbPc film measured in dry air with a scanning rate of applied voltage of 4.0 V s^{-1}. The conductivity changes from an OFF state to an ON state when positive voltage is applied, and from an ON state to an OFF state when negative voltage is applied. The ON state was memorized after the applied voltage was removed, but it gradually recovered to the OFF state as time passed[9]. The speed of conductivity change was very slow and profiles of I-V characteristics varied depending on the scanning rate. It should be noted that the I-V characteristic is asymmetric in spite of the apparently symmetric cell structure and it exhibits considerably higher barriers in spite of the use of Au electrodes.

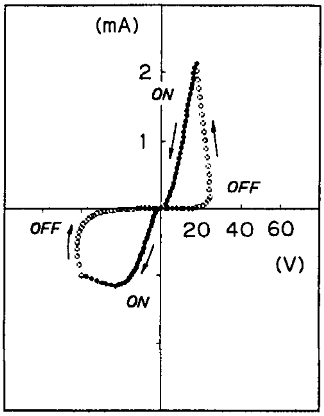

FIGURE 1 I-V characteristic of PbPc film.

The positive barrier height increased when the bottom electrode material was substituted with Al, while the negative barrier height increased when the top electrode material was substituted with Al. This implies that the barrier in the positive polarity exists at the bottom electrode interface and that the barrier in the negative polarity exists near the top electrode.

An X-ray diffraction pattern of the film which was deposited at a rate of 0.4 A s^{-1} to 1 μm thickness is shown in Fig. 2. Diffraction peaks are observed at d values of 12.78, 11.82, 7.27, 7.02 and 3.63 A. The peaks at d values of 12.78, 7.02 and 3.63 Å were assigned to monoclinic (200), (320) and (111) peaks, respectively[1]. The peaks at 11.82 and 7.27 Å were assigned to triclinic (100) and (020) peaks, respectively[10]. Thus, this film consists of both monoclinic and triclinic modifications.

I-V Characteristics in Vacuum

To investigate changes of I-V characteristics in vacuum, we let the films in a chamber evacuated with a turbo molecular pump to 10^{-3} Pa and measured the I-V characteristics at intervals. As time passed, the hysteresis loop became smaller and the I-V characteristics became close to the ON state in the positive voltage polarity and to the OFF state in the negative voltage polarity. Figure 3 shows an I-V characteristic of the film held in vacuum for 4 days, which has no hysteresis loop but displays a

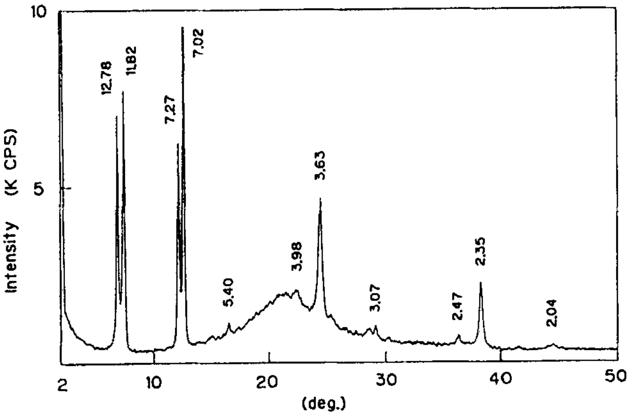

FIGURE 2 X-ray diffraction pattern of PbPc film.

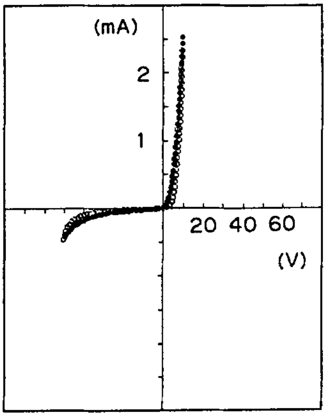

FIGURE 3 I-V characteristic of PbPc film held in vacuum for 4 days.

rectifying property. The change was irreversible and the original I-V characteristic could not be recovered even though dry air was reintroduced. Some impurities may have been removed from the film to the vacuum atmosphere and this is thought to be the intrinsic I-V characteristic to the sandwich-type cell of a pure PbPc film.

I-V Characteristics of Triclinic and Monoclinic Films

When the substrate temperature was held at 100 °C during deposition, the X-ray diffraction pattern of this film showed an intense triclinic (100) peak at a d value of 11.82Å and its higher-order peaks as shown in Fig. 4. This result suggests that this film has good crystallinity and high orientation of the triclinic form. The I-V characteristic of the triclinic film shown in Fig. 5 indicates that there is no barrier in both polarities and no conductivity change.

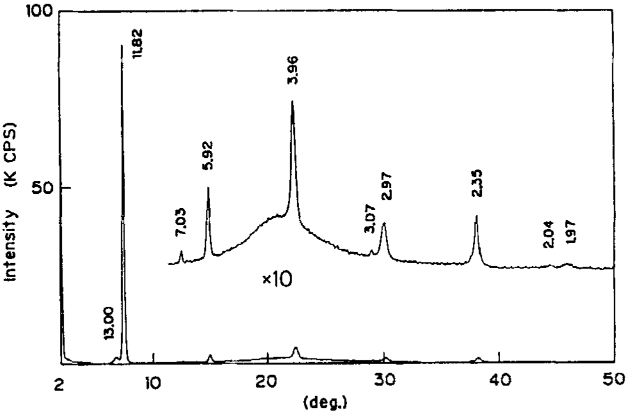

FIGURE 4 X-ray diffraction pattern of PbPc film deposited on the substrate of 100°C.

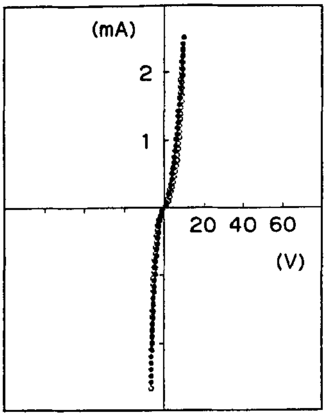

FIGURE 5 I-V characteristic of PbPc film deposited on the substrate of 100°C.

When the substrates were cleaned by glow discharge of -1 kV and 1 mA in a 6 Pa N_2 atmosphere before PbPc evaporation, the X-ray diffraction pattern of the film had only monoclinic (320) peaks mainly at a d value of 7.03Å as shown in Fig. 6. After acetone dipping of this film to remove impurities, an I-V characteristic having a 10

V barrier in the positive polarity and a 30 V barrier in negative polarity was obtained (Fig. 7).

X-ray diffraction measurement was made with PbPc films of various thicknesses. The ratio of peak heights of monoclinic (320) to (200) reflections remarkably increased as the thickness increased. From this result, the portion near the film surface consists of crystals with monoclinic (320) orientation and the initially growing layer of the film has preferred monoclinic (200) orientation. The asymmetric barriers of I-V characteristic of Fig. 7 are attributable to this nonuniformity of film structure. As for the perfectly rectifying properties shown in Fig. 3, the bottom electrode is thought to be covered with a very thin layer of PbPc of triclinic or other modification.

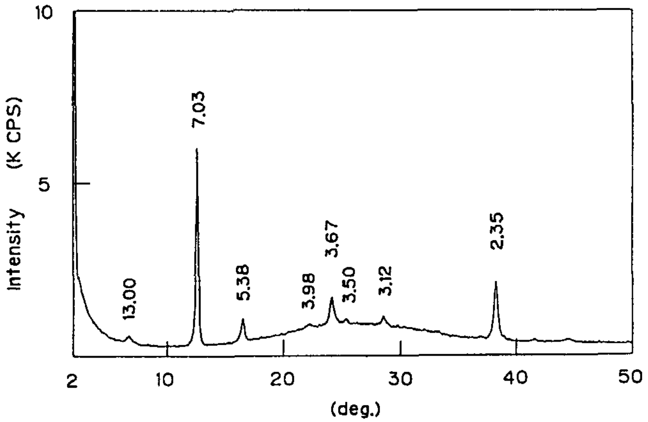

FIGURE 6 X-ray diffraction pattern of PbPc film deposited on precleaned substrate by glow discharge.

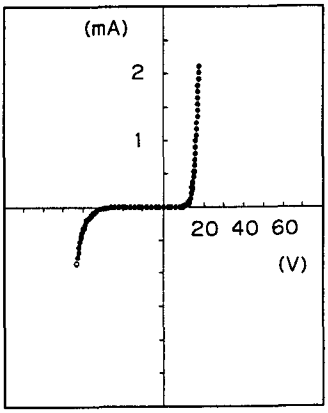

FIGURE 7 I-V characteristic after acetone dipping of PbPc film deposited on precleaned substrate by glow discharge.

CONCLUSION

The I-V characteristics of Au/PbPc/Au sandwich-type cells showed nonlinear electrical properties with asymmetric barriers. The rectifying property in vacuum is attributable to nonuniformity in the film structure along to the film thickness. The monoclinic modification of PbPc was found to form a considerably higher barrier between Au electrode.

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