Electrical Properties of Junctions between Electrodeposited Magnesium Phthalocyanine and Aluminum

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(Received May 12, 1997)

ABSTRACT: 2,9,16,23-Tetracarboxyphthalocyaninatomagnesium(II) [Mg(II)-taPc] films were obtained on indium/tin oxide (ITO) coated glass electrodes by electrodeposition, using MgCl₂, CaCl₂, CoCl₂, or ZnCl₂ as a supporting electrolyte. The electrical properties of junctions between electrodeposited Mg(II)-taPc film and aluminum electrode were evaluated by current-voltage measurements. The diode based on Mg(II)-taPc film containing Mg²⁺ as a bridging metal ion exhibited Zener-type breakdown, while the diode based on Mg(II)-taPc film containing Ca²⁺ or Zn²⁺ as a bridging metal ion showed almost symmetrical I–V. The diode based on Mg(II)-taPc film containing Co²⁺ as a bridging metal ion was electrically unstable. The diode based on Mg(II)-taPc film containing Mg²⁺, Ca²⁺, or Zn²⁺ as a bridging metal ion exhibited a photocurrent on forward biased condition.

KEY WORDS Tetracarboxyphthalocyaninatomagnesium / Electrodeposition / Schottky Diodes / Zener-Type Breakdown / Photoconduction /

Metallophthalocyanines (Mt-Pc) attract considerable interest because of their high electrical conductivity,^{1,2} optical sensing properties,^{3,4} and *p*-type semiconduction.^{5–8} Early research on solar cells having a Pc film has focused on the Schottky junction.^{9–13} However, comparatively little has been done to investigate the fundamental aspects of junction interfaces between the film of phthalocyanine polymer doped with ion and metal electrode.

We reported a method for the preparation of 2,9,16,23-tetracarboxyphthalocyaninatocobalt(II) [Co(II)-taPc] films on indium/tin oxide coated (ITO) glass electrodes by electrodeposition.¹⁴ Recently we found that Mg(II)-taPc electrodeposited films can also be prepared on ITO electrode by similar method for Co(II)-taPc film. In this paper, we will report the fabrication of the Schottky-type diodes based on the junction interface between Mg(II)-taPc film containing bridging metal ions and aluminum electrode.^{15–17}

Since Mg-Pc shows strong fluorescence when exposed to ultraviolet or visible light,¹⁸ a device using a Mg-Pc film should be highly sensitive to light irradiation.⁴

An ITO electrode is used as material which enables holes to enter semiconductor film, whereas the counter electrode is aluminum which has a low work function and enables electrons to enter the conduction band of Pc.^{19,20}

This paper presents the electrical features of the junction interface between Mg-Pc film containing bridging metal ions and an aluminum electrode.

EXPERIMENTAL

Materials

Mg(II)-taPc was prepared according to the method for Co(II)-taPc.²¹ A reaction mixture consisting of 3.00 g (1.6×10^{-2} mol) of trimellitic anhydride, 0.37 g ($3.9 \times$

10^{-3} mol) of magnesium chloride, 10.0 g (1.7×10^{-1} mol) of urea, and 0.20 g (1.6×10^{-4} mol) of ammonium molybdate was poured into a separable flask and heated at 200°C for 20 min, stirring quickly the mixture. The residue was poured into 500 ml water and the solution was filtered off. After extraction in a Soxhlet for 24 h with water, the residue was poured into 150 ml 50 wt% KOH aqueous solution and the solution was refluxed at 80°C for 24 h. The precipitate was filtered off and extracted with water. A 6 M HCl aqueous solution was dropped into the alkaline solution until the pH of the solution changed into 2, and the resulting precipitate was filtered off. After extraction in a Soxhlet for 24 h with methanol, the product was dried *in vacuo* at room temperature: yield 0.42 g (16%); UV-Vis (*N,N*-dimethylformamide, DMF) $\lambda_{\max}$ 690 nm (Q-band for Pc); IR (KBr) 1698 cm⁻¹ ($\nu_{C=O}$). *Anal.* Calcd for Mg in Mg(II)-taPc: Mg, 3.51%. Found: Mg, 3.22%.

DMF was distilled under reduced pressure before use. Supporting electrolytes, acetone, and aluminum were of analytical grade from commercial origin.

Fabrication of Devices Based on Mg(II)-taPc Film Containing Bridging Metal Ions

Mg(II)-taPc films containing bridging metal ions on ITO electrodes were prepared by cathodic electrolytic deposition using a Hokuto-Denko HA-501 potentiostat/galvanostat. A mixture of Mg(II)-taPc (3×10^{-4} M) and MgCl₂, CaCl₂, CoCl₂, or ZnCl₂ (1×10^{-3} M) as supporting electrolyte in dry DMF was poured into the electrolytic cell containing an ITO working electrode and platinum counter electrode. Mg(II)-taPc films containing bridging metal ions on the ITO electrodes were prepared by cathodical polarization of the DMF solution containing Mg(II)-taPc and a supporting electrolyte with a constant current of $-35 \mu\text{A cm}^{-2}$ for 30 min. The deposited films were washed with acetone.

Aluminum electrodes were deposited on the Mg(II)-taPc modified ITO electrodes by sublimation at

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1.3×10^{-3} Pa.

MEASUREMENTS

IR spectrum for Mg(II)-taPc was measured with a JASCO FT-IR-7300 Fourier transform infrared Spectrometer using KBr disk. UV-Vis spectrum for Mg(II)-taPc was measured with a JASCO UVIDEK-505 UV-Vis Digital Spectrophotometer. Atomic absorption spectrometry for Mg in Mg(II)-taPc was carried out with a HITACHI 180-50 Atomic Absorption Spectrophotometer. Current-voltage characteristics were measured using an Advantest R8340 Ultra High Resistance Meter. Elemental analyses were carried out with a HORIBA energy-dispersive X-ray microanalyzer, EMAX-5770W. Photoconduction of devices was measured under irradiation of white light from a 300 W slide projector lamp. Surface structures and thickness of the electrodeposited Mg(II)-taPc films containing bridging metal ions were examined with a HITACHI S-2380N scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Green thin films were obtained on ITO electrodes by constant current electrodeposition from DMF solutions containing Mg(II)-taPc and MgCl_2 , CaCl_2 , CoCl_2 , or ZnCl_2 as a supporting electrolyte. When PbCl_2 was used as a supporting electrolyte, heterogeneous Mg(II)-taPc film containing Pb^{2+} as bridging metal ion was deposited on the ITO electrode. Films failed to form when FeCl_2 or CuCl_2 was used. These results suggest that the chemical stability of bridging metal ion is an important factor for the electrodeposition of Mg(II)-taPc film. Since Mg^{2+} , Ca^{2+} , and Zn^{2+} have closed shells of electron configurations, these bivalent ions are chemically stable.^{22,23} Since Fe^{2+} , Co^{2+} , and Cu^{2+} have electron configurations whose d orbitals are not filled by electrons and Pb^{2+} has electron configuration whose p orbital is not filled by electrons, the valences of these metal ions can be changed. The electron configurations of these metals are listed in Table I.

The chemical structure of Mg(II)-taPc film containing bridging metal ions is shown in Figure 1. The monomer of M(II)-taPc is polymerized by bridge formation with bivalent metal ion in the electrodeposited M(II)-taPc film.¹⁴

The Schottky-type diodes were prepared by the formation of aluminum electrode on the Mg(II)-taPc film containing bridging metal ions. Since Pc derivatives are *p*-type semiconductors, Schottky-type or Mott-type barriers are formed by contact with low work function metal such as aluminum.¹⁵ Mott-type barriers are likely to be formed because low work function metals are easily oxidized and a resistive thin layer is formed at the junction interface between semiconductor film and metal electrode. The device structure is shown in Figure 2.

The diode based on Mg(II)-taPc film containing Mg^{2+} as a bridging metal ion exhibited Zener-type breakdown generated by other molecules in the neighborhood of rectifying barriers. This would be due to the existence of bridging metal ions in Mg(II)-taPc film. Actually, the existence of bridging metal ions was confirmed for each

Table I. Diode performance

Bridging metal (Electron configuration)	Aspect of film	I—V characteristic	Photocurrent /dark current
Mg ([Ne]3s ²)	Homogeneous	Zener-type	8
Ca ([Ar]4s ²)	Homogeneous	Symmetrical	118
Fe ([Ar]3d ⁶ 4s ²)	Not deposit	—	—
Co ([Ar]3d ⁷ 4s ²)	Homogeneous	Unstable	1
Cu ([Ar]3d ¹⁰ 4s)	Not deposit	—	—
Zn ([Ar]3d ¹⁰ 4s ²)	Homogeneous	Symmetrical	2
Pb ([Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²)	Heterogeneous	—	—

Figure 1. Molecular structure of Mg(II)-taPc film containing bridging metal ion.

Figure 2. Schematic representation of the diode.

device by X-ray microanalyzer. It seems that the existence of the bridging metals causes the present devices to generate Zener-type breakdown. In fact, many investigators report that devices using the semiconductors with other molecules showed breakdown under the reverse biased condition,²⁰ while the devices without other molecules did not.¹⁶ It is thought that tunneling effect is generated at the interface of the Mg(II)-taPc film containing Mg^{2+} as a bridging metal ion and aluminum electrode under the reverse biased condition because of the decrease of gap between LUMO and HOMO.^{15,24}

For previous Schottky-type diodes made by vacuum-deposition of organic semiconductors, high resistance of organic semiconductors decreased electric conductivity.¹⁶ The high conductivity of the present device is attributed to bridging metal ions in Mg(II)-taPc films, since the electrodeposited films with ions have metallic high conductivity.²⁵ The dark current-voltage of the diode based on Mg(II)-taPc film containing Mg^{2+} as

Figure 3. Dark current-voltage characteristic for diode based on Mg(II)-taPc film containing Mg^{2+} as bridging metal ion.

bridging metal ion is shown in Figure 3.

The low breakdown voltage of the device is due to the great number of bridging metal ions. In conventional Zener-type diodes constructed by an inorganic semiconductors, breakdown voltage is comparatively high since the number of dopants is easily controlled.¹⁵ However, in the present devices, control of the number of metal ions is difficult because Mg(II)-taPc films are prepared by bridge formation with metal ions originating from supporting electrolytes in electrodeposition.

I-V of the diode based on Mg(II)-taPc film containing Ca^{2+} or Zn^{2+} as bridging metal ion was almost symmetrical. The magnitude of applied voltage for turn-on of forward biased current was almost equal to that for breakdown of reverse biased current. The electrical properties of the devices of Mg(II)-taPc film containing Mg^{2+} , Ca^{2+} , or Zn^{2+} as bridging metal ion were reproducible. The results can be explained by the chemical stability of these metal ions which have closed shells of electron configurations.^{22,23}

The diode based on Mg(II)-taPc film containing Co^{2+} as bridging metal ion was electrically unstable. The reproducible values of current of the device were not obtained in any measurement. The electrical instability is due to the various oxidation states of cobalt ions.^{22,23}

The diode based on Mg(II)-taPc film containing Mg^{2+} , Ca^{2+} , or Zn^{2+} as bridging metal ion exhibited photocurrent under the forward biased condition. The current after light irradiation was larger than that before light irradiation under the forward biased condition. Photocurrent/dark current, the ratio of photocurrent to dark current, of the present devices at applied voltage of +0.8 V is summarized in Table I. The diode based on Mg(II)-taPc film containing Ca^{2+} as bridging metal ion showed the largest photocurrent/dark current, which indicates the efficiency of photogeneration of charge carriers. The Mg(II)-taPc film containing Ca^{2+} as bridging metal ion (350 μm) was thicker than the film containing Mg^{2+} or Zn^{2+} as bridging metal ion (250 μm). It is thought that the number of charge carriers in the film containing Ca^{2+} as bridging metal ion drastically increases by light irradiation because of the large absorbance of this thick film. UV-Vis spectra of Mg(II)-taPc film containing Mg^{2+} as bridging metal ion and that of Mg(II)-taPc film containing Ca^{2+} as bridging

Figure 4. UV-Vis spectra of Mg(II)-taPc film containing (a) Mg^{2+} and (b) Ca^{2+} as bridging metal ion.

metal ion are shown in Figure 4. The absorbance of Mg(II)-taPc film containing Ca^{2+} as bridging metal ion was about 12 times that of Mg(II)-taPc film containing Mg^{2+} as bridging metal ion. The spectra show that these films especially take up light in the short wavelength region or high energy region.

The turn-on voltage of the diode based on Mg(II)-taPc film containing Mg^{2+} as bridging metal ion was high, while the breakdown voltage was very low (Figure 3). In the present devices in Table I, more than 0.8 V applied voltage was necessary for the generation of photoconduction under the forward biased condition. These results suggest that Mott-type barriers, which would prevent the rising of forward biased current because of a thin resistive layer, are formed at the interface of semiconductor and aluminum.^{17,20} It is thought that applying high voltage is necessary for charge carrier transfer at the interface of the Mg(II)-taPc film containing bridging metal ions and aluminum electrode under the forward biased condition, while charge carriers are transferred by tunneling effect under the reverse biased condition.

It was confirmed by SEM observation that the film containing Mg^{2+} as bridging metal ion had a comparatively flat surface while the film containing Ca^{2+} as bridging metal ion and one containing Zn^{2+} as bridging metal ion had rough surfaces. The flatness of surface of film containing Mg^{2+} as bridging metal ion may promote effective tunneling of valence electrons at the junction between Mg(II)-taPc film containing Mg^{2+} as bridging metal ion and aluminum electrode under the reverse biased condition, since it can be expected that the barrier layer is thin enough for the tunneling effect.

CONCLUSION

Mg(II)-taPc films containing bridging metal ions were obtained from DMF solutions containing MgCl_2 , CaCl_2 , CoCl_2 , or ZnCl_2 as supporting electrolyte. The present devices based on these Mg(II)-taPc films have potentially

useful features for Zener-type diodes or photoelectric tubes. In particular, the diode based on Mg(II)-taPc film containing Mg^{2+} , Ca^{2+} , or Zn^{2+} as bridging metal ion exhibited reproducible electrical properties and photocurrent. The diode based on Mg(II)-taPc film containing Mg^{2+} as bridging metal ion exhibited a Zener-type breakdown on dark condition. This would be due to bridging metal ions in electrodeposited Mg(II)-taPc film. The diode based on Mg(II)-taPc film containing Ca^{2+} as bridging metal ion showed the largest photocurrent/dark current. These results suggest that the bridging metal ion in the Mg(II)-taPc film is an important factor for deposition of Mg(II)-taPc film and the diode performance.

Acknowledgments. We are grateful to Mr. T. Sakaguchi (Technical Research Laboratories, Ishihara Sangyo Co., Inc.) for help in the setting and operation of the electrometer and high vacuum evaporator and Dr. T. Yamazaki (Nagano Prefectural Institute of Technology) for kind help in the operation of the SEM machine.

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