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AN APPLICATION OF PLASMA-POLYMERIZED YbPc$_2$ FILM: HUMIDITY SENSOR

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ABSTRACT

Humidity sensing cheracterisrics of vacuum deposited plasma poly merized YbPc$_2$ films were evaluated. In both films, humidity caused an increase of pro-ton conduction. Polymerised film shows a threshold fo humidity increase and its sensitivity diminishes more than 38℃ of relative humidity. Furthermore, for the polymerized film, two min. of ressponse time and 1 min. of recovery time are also obtained. The sensitivity between 10% and 85% of relative hum-idities is found to be one hundred higher than that of the vacuum deposited film.

INTRODUCTION

Many of metal phthalocy anines(MPc's) show high thermal stability, low conductivity and semiconductivity sensitive to gas adsorption and desorption, and then have attracted as gas sensors for toxic species such as NO$_2$, NH3, and HC1$^{1-4)}$ In general, MPc's exhivit p-type semiconductivity : the conductance is increased by exposure of electron acceptor gases and decreased by exposure of electron donor gases.

In the case of water, however, changes in the condustion depend on the procedure of film preparation, that is, the surface states of films. The vacuum eaporated CuPc and CoPc films exhibit semiconductive behaviors : the conductance of the films is decreased in the presence of water vapor which acts as an electron donor on the Pc film surface$^{5)}$. On the other hand, the conductance is increased for a Langmuir-Blodgett CuPc film$^{6)}$. This result may be attributed to protonic conduction in the presence of water vapor. Since the change in conductance is very sensitive to high humidity, a strong chemical adsorption is expected between water molecules and the film surface.

Lanthanide di-phthalocy anines(LnPc$_2$'s) have a structure in which a lanthanideion is sandwiched with two Pc ligands and are susceptible to redox reactions in electrolytes compared with the MPc's. It leads that LnPc$_2$ films are expected to be gas sensors$^{7-10)}$. In fact, LnPc$_2$ films prepared by vacuum depodition have properites of p-type semiconductor. These films exhibit hole conduction for NO$_2$ and HN$_3$ adsorption and desorption. Contrary to the MPc films mentioned above, however, protonic conduction is shown at the presence of water vap or. Furthermore, a plasma-polymerized YbPc$_2$ film is found to exibit high er sensitivity and longer life time to water vapor than those of the vacuum deposited filmes.

In this paper, we propose a humidity sensor using a plasma-polymerized YbPc$_2$ film as one of plasma applications.

EXPERIMENTAL

The YbPc$_2$ compound was synthesized according to Moskalev and Kirin's method11). A mixture of o-phthalonitrile and ytterbium chloride in a molar ratio of 16 : 1 was heated to 270℃ in an open tube reacter with flowing argon. The crude product was washed twice with 0.1N HC1 aqueous solution. Afterward, some impurities were extracted by immersion in methanol for 150h. Finally, the product was heated at 460℃ in a vacuum to remove the remaining impurities.

The humidity sensors were fabricated as followed : a gold film was vacuum deposited on a quartz glass with a pair of interdigitated electrodes having a gap of 0.6㎜. Then, a YbPc$_2$ film was deposited on the gold electrode by either vacuum or plasma-polymerization methods.

The vacuum depsited YbPc$_2$(vd-YbPc$_2$) films were prepared by subilmation method. The YbPc$_2$ was deposited by thermal evaporation in vacuum at a pressure of 1×10^{-3} Pa. The thickmess was about 200nm. The plasma-polymerized YbPc$_2$(vd-YbPc^2) films were prepared in a plasma reacter with two horizontal parallel plate electrodes. The bottom, grounded electrode is equipped with an alumina-coated tungsten boat for sublimation of YbPc$_2$ powder supply. Argon was used as the carrier gas. The film preparation was carried out as followed : the argon plasma was generated in 10.6Pa after the chamber was evacuated to 1×10^{-3} Pa. The quartz substrate was then bombarded with the plasma for 5 min. Next, YbPc$_2$ was sublimated from the tungasten boat to the Ar plasma where the YbPc$_2$ underwent poly-merization reactions. Then, the pp-YbPc$_2$ was deposited on the substrate. Finally, the humidity sensor which was fabricated by the procedure mentioned above is shown in Fig. 1.

The sensor was attached in the box in which the relative humidity was varied over 10-85% by using saturated salt solutions, and ther-mostated at a given temperature. The characteristics of the sensors were evaluated by mea-suring the condauctance. The response and recovery times were determined by rapidly changing the relative humidities between 10% and 85%, and cycling life was estimated by repeating the above humidity test.

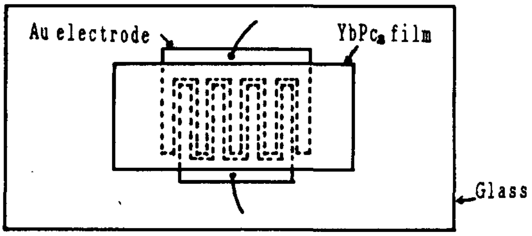

Fig. 1 Humidity sensor structure.

RESULTS AND DISCUSSION

Figure 2 shows comparison of visible absorp-tion spectra between the vd-YbPc$_2$ and $_{pp}$- Yb$_P$c$_2$ films. The pp-YbPc$_2$ film shows the broadening of the absorption peak

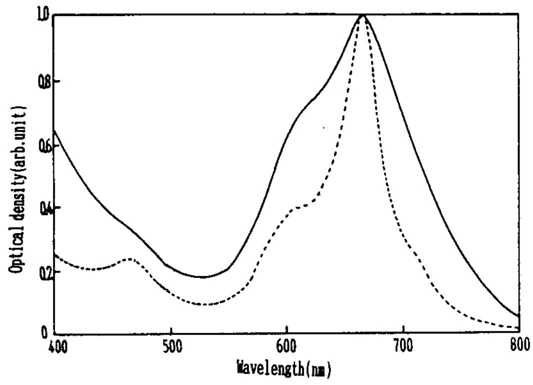

Fig. 2 Visible absorption spectra of vd-YbPc (---) and pp-YbPc$_2$ (---) films. The absorbance is normalized at absorption peaks.

at 670 nm which is char-actristic of YbPc$_2$ molecules. It can be concluded that YbPc$_2$ molecules are ploymerized without serious destrustion of the original ring structure. In general, LnPc$_2$'s are apt to dissolve in a strong polar solvents such as dimethylformamide(DMF), contrary to divalent metal phthlocy anines such as CuPc, but are insoluble in weak polar solvents like methanol (MeOH). Using these properties, plasma-plymerised CuPc has been prepared for sensing organic gases[12, 13].

The pp-YbPc$_2$ film is, however, insoluble even in a mixture of DMF and MeOH at a ratio of 5.5(v/v). This result suggests a possibility of organic gas sensing by the pp-YbPc$_2$ sensor

The temperature dependence of conductance is illustrated for the vd-YbPc$_2$ and pp-YbPc$_2$ films in Fig. 3. Semiconductive characteristics are obtained for both films, resulting in activation energies : 0.20 eV for the vd-YbPc$_2$ film and almost zero for the pp-YbPc$_2$ film. The conductance of the pp-YbPc$_2$ film is lower by about two orders than that of vd-YbPc$_2$ film. This conductance decreast is lead to high sensitibity for humidity sensing.

Fig. 4 shows the surface morphology of the pp-YbPc$_2$ film by scanning electron micro-

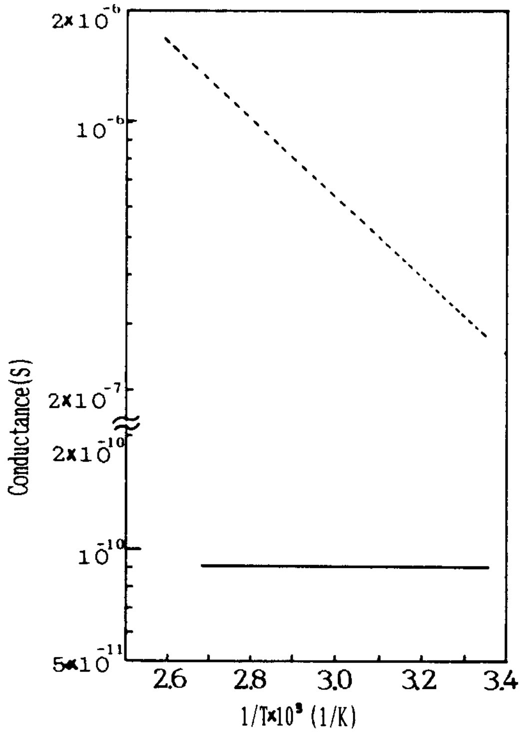

Fig. 3 Temperature dependences of conductance in vacuum for vd-YbPc$_2$(----)and pp-YbPc$_2$ (----) film.

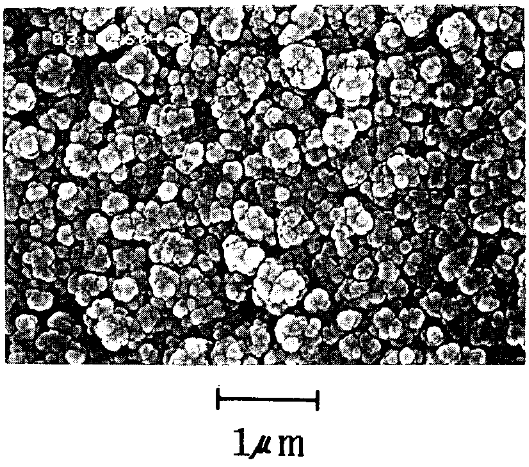

Fig. 4 Electron microscopy photogragh of pp-YbPc$_2$ film.

gragh. There are clumps of particulate matter resulting from plasma irradiation. In general, boundaries give rise to gas adsorption sites for semiconductor semsors. So, the boundaries of clumps may offer adsorption sites for water vapor. It is found that the size and the demsity of particulate matter are cotrolled by plasma conditions which are the RF power, the gas pressure and the rate of depodition. Since the film with large clumps and adhesion to the substrate may be suited for the humidity sensor, in this study, the poly meric film was prepared with an RF power of 20W and a rate of deposition of about 60 nm/min.

Figure 5(a) and (b) show the dependence of sensor conductance on relative humities for vd-$YbPc_2$ and pp-$YbPc_2$ films, respectively. The characteristic curves are illustrated at various temperatures of the sensor substrate. In both cases, the condustance increast with the increase in relative humidity. For the vacuum deposited film, increment with relative himidity is small and the conductance is increased with the substrate temperature, as shown in Fig. 3. On the other hand, the increase of the conductance for the pp-$YbPc_2$ film has a humidity threshold. In fact, a threshold of 56% for 28℃ of the sensor substrate and the threshold is shifted toward high teperature region with increase of the sensor temperature. At 40℃ of the substrate, the sensitivity for humidity is drastically decreased. Since the conductance is increased with humindity increasing in spite of p type semiconductive characteristics of $YbPc_2$ film, the origin of carriers is attributed to protons derived from water dissociation on the film surface. The threshold property of the conductance increase may support the proton conduction.

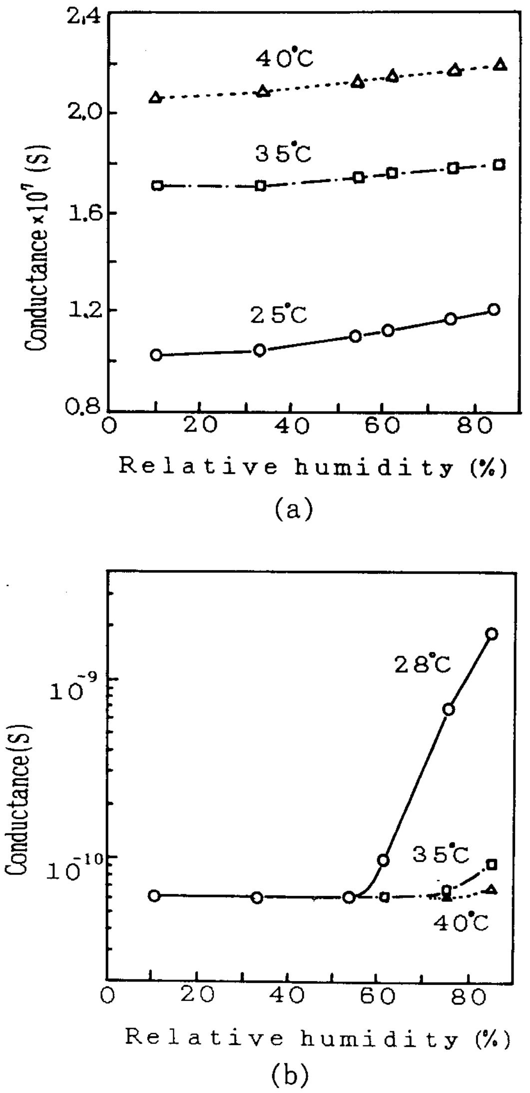

Fig. 5 Dependence of sensor conductance on relative humidities for (a)vd-$YbPc_2$ sensor and (b) pp-$YbPc_2$ sensor. The figures in the Fig. are the sensor temperatures.

From Fig. 5(b), the relationship between the conductance and the sensor temperature is illustrated in Fig. 6. In spite of the values of relative humidities, the sensitivity diminishes more than 38℃ of the sensor temperature, resulting in detachment of water melecules from the surface of the pp-$YbPc_2$ film.

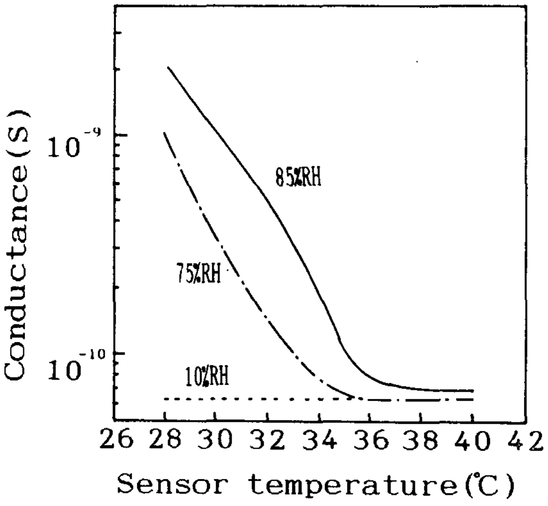

Fig. 6 Relationship between conductance and sensor temperature for pp-YbPc$_2$ sensor at 10 %, 75% and 85% relative humidities.

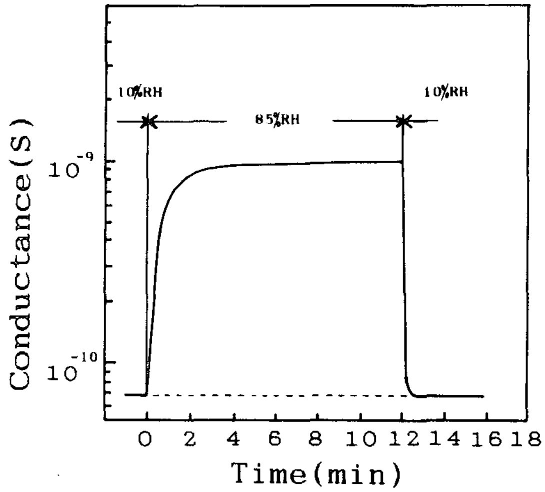

Fig. 7 Conductance response of pp-YbPc$_2$ sensor to a change between 10% and 85% relative humidities. Sensor temperature is 28℃.

Figure 7 shows the conductance response of pp-YbPc$_2$ sensor to a rapid change between 10% and 85% relative humidities at a 28℃ of the substrate. In this case, the sensitivity is defined as follow : the ratio of the conductance change for a change from 10% to 85% of relative humidity to the conductance at a 10% of relative humidity. The sensitivity is found to be 15 from Fig. 7, which is higher by one hundred times than that for the vacuum deposited film under the same conditions. The response and recovery tines are determines to be ca. 2 min. and less than 1 min, respectively. Cycling the relative humidity between 10% and 85% gives the same curve regardless of the diection of humidity chnage, so the reversibility for humidity change is found to be adequate for applications. In the cast of the vacuum deposited film, perfect reversibility is nor obtained. Furthermore, the conductance drift for 30 times cycling test was not measured.

CONCLUSIONS

The humidity cheracteristics have been compared between vd-YbPc$_2$ and pp-YbPc$_2$ films. As a result, the pp-YbPc$_2$ film illustrates high sensitivity, short response and resovery times, an reversibility adequate for cycling operation with almost superimposible response curves. It is found that the pp-YbPc$_2$ film may be a candidate for humidity sensor. Gas adsorption is controlled by the properties of surface adsorption sites. So, to improve the cheracter-istics, the control of the plasma poly merization for the film preparation, such as RF power and despossition rate as well as substrate are needed for application.

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