The Korean Journal of Ceramics, 6[3] 296-299 (2000)

Phthalocyanine Organic Semiconductor for NO_X Gas Sensor

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(Received September 23, 1998)

The electrical properties of various metal phthalocyanine(MPc) thin film sensors were tested in the presence of NO_X gas. Among the Phthalocyanine(Pc) thin films, lead phthalocyanine(PbPc) thin film showed the best results and its sensitivity was over 80% at 5 ppm of NO_X gas. Optimal operating conditions including response time and cyclic treatment of NO_X were tested and discussed.

Key words: Phthalocyanine, Sensor, Response time, Cyclic treatment

I. Introduction

Gas sensors using organic semiconductors,[1] especially metal phthalocyanine(MPc)[2] as host materials have been extensively investigated for their high sensitivities to the oxidizing gases (such as NO_X, SO_X and Cl_2) and their easy processing like vacuum sublimation[3] to make thin films. Compared the conventional NO_X gas sensors,[4-8] the sensors have very simple structures and they are convenient in gathering and monitoring the samples continuously. But the difficulties in applications like high resistance in air and unstability in the operating temperature must be solved in the future.

In this paper the gas sensors using a various metal Pc's were prepared to investigate their properties for NO_X gas.

II. Experimental

The structure of the planar phthalocyanine molecule consists of four isoindole units linked by aza nitrogen atom and two hydrogen atoms. In the simple metal Pc's, such as ZnPc, FeNc, PbPc and NiPc, the two central hydrogen atoms are replaced by a single metal atom. All the Pc molecule are thermally stable and can be sublimated in vacuum without decomposition even at high temperature.

ZnPc and NiPc are commercially available reagents made by Aldrich Co.(USA). FePc was sythesized in the lab. And two kinds of PbPc's were used, one of which named TCI PbPc with 90% purity was made by TCI Co.(Japan) and other named Syn PbPc with 99% purity was synthesized in the lab.

Vacuum evaporation, spin coating and L-B method[9] can be used to make thin films on the substrate.

Because of low solubility to solvent of the most Pc's used, vacuum evaporation technique was used in this experiment.

Fig. 1 shows the sensing device used in this experiment. Interdigitated platinum electrode arrays were preprinted onto alumina substrate. On the back side, platinum heater were printed to control the temperature of the device. The effective area of sensing membrane was about 10×5 mm^2 and the gap between electrodes was 0.5 mm. PbPc powders

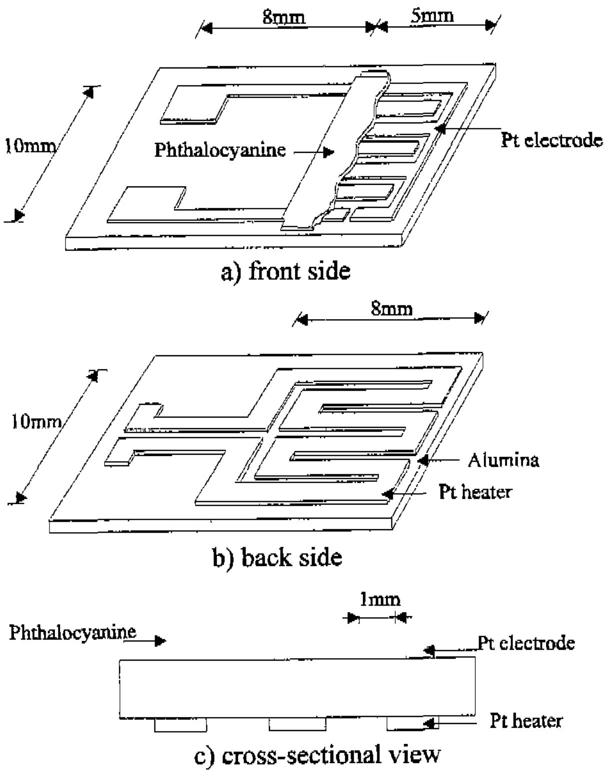

Fig. 1. Structure of the sensing device. a) front side, b)back side and c)cross-sectional view.

were evaporated at 390°C and 350°C by using a molybdenum boat located in the vacuum chamber with base pressure of about 2×10^{-5} torr. The distance between substrate and boat was 4 cm and the substrate temperature was 25°C. A flow system with mass flow controller and mixer was prepared to control humidity and gas concentration.

The operating temperature of device was controlled by the applied voltage from power supply and the spot thermometer(Minolta, R-0506C) was used to measure the temperature. To measure the gas sensitivities of the sensors, D.C.10V(V_{CC}) was allowed and then output voltage(V_L) in a variable load resistance(R_L) was measured by using Keithley 2001 multimeter.[10]

The sensor resistance(R_S) was calculated as follows ;

$$R_s = R_L \times \left(\frac{V_{cc}}{V_L} - 1\right)$$

From the data of sensor resistance, sensitivity of the sensor was defined as follows ;

$$S(\%) = \frac{R_{Air} - R_s}{R_{Air}} \times 100$$

Where, R_{Air}: sensor resistance in air
R_S: sensor resistance after NO_X is injected

III. Results and Discussion

3.1. ZnPc, NiPc, FeNc, PbPc thin films

To detect low concentration of NO_X gas, 0.01 g of various metal Pc's were evaporated on the alumina substrate. The resistance of each thin film as a function of temperature is shown in Fig. 2. The resistance tends to be decreased with increasing temperature. The resistances of ZnPc, NiPc and FeNc were higher than hundreds of megaohm, but that of PbPc was decreased from 19.5 to 4.7 MΩ when the temperature was increased from 80° to 160°C. The small difference and low resistance of PbPc could be regarded as a characteristics of the most suitable Pc for sensor.

The sensitivities of the thin films for 5 ppm of NO_X were

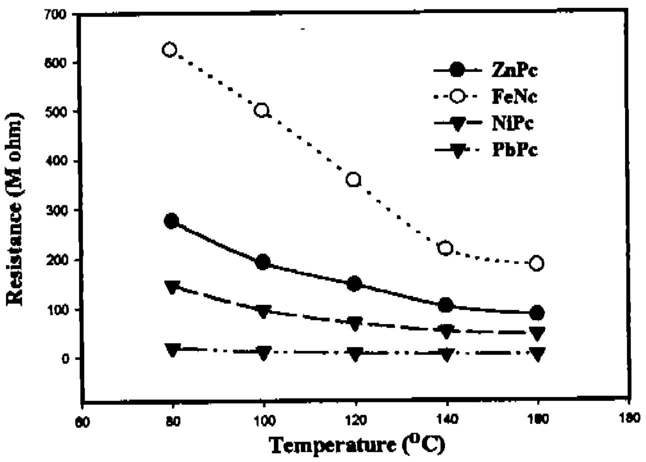

Fig. 2. Resistance of the various Pc films.

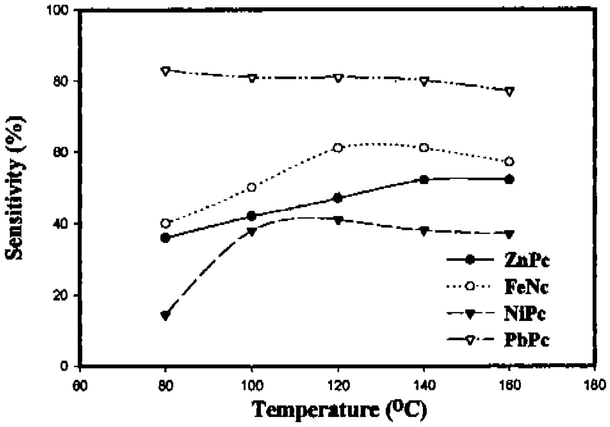

Fig. 3. Sensitivity of the various Pc films.

shown in Fig. 3. The sensitivity of PbPc is much higher than that of ZnPc, NiPc and FeNc at all the temperatures. The highest sensitivity was 61% and 41% at 120°C for FeNc and NiPc, respectively. The value was 52% at 140°C for the ZnPc.

The sensitivity of each sensor was stabilized above 120°C.

3.2. XRD data PbPc

XRD data of the PbPc films prepared at 390°C and 350°C was shown in Fig. 4. Depending on the preparation temper-

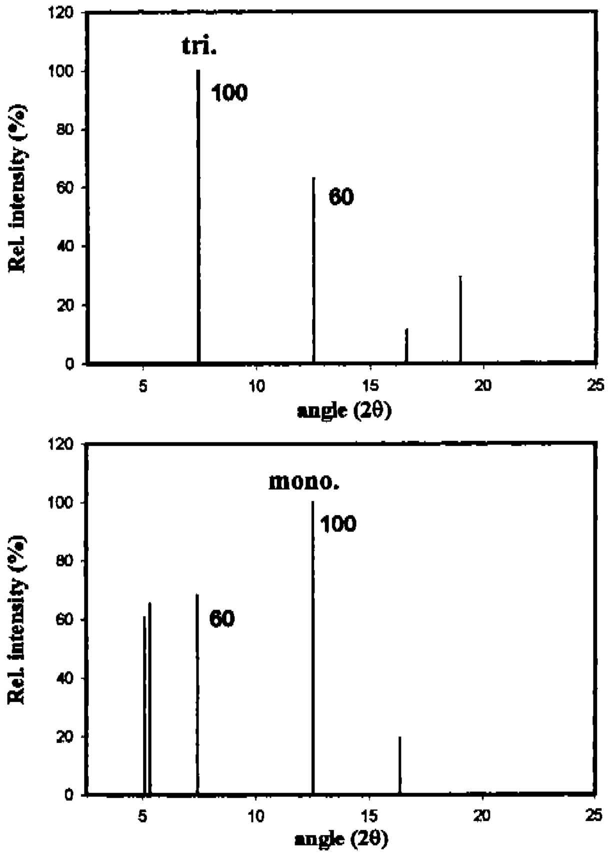

Fig. 4. XRD data of PbPc films on alumina. a) 390°C and b) 350°C.

ature, crystal structure was varied much. At 390°C, mixed crystal structure with 100 : 60 of triclinic: monoclinic ratio was obtained whereas the 60 : 100 ratio of crystal was obtained at 350°C.[11]

It was reported by A. Miyamoto that monoclinic PbPc film having only (320) orientation was obtained at a substrate temperature 20°C, with a deposition rate higher than 1.0nm/s and that monoclinic film composed of (200) and (320) orientations was obtained at a substrate temperature 20°C, with a deposition rate of 0.8 to 0.2 nm/s. But the monoclinic PbPc was known to be converted to the triclinic form by anealing in 10^{-4} Pa at 100°C or treating at high temperature.[12]

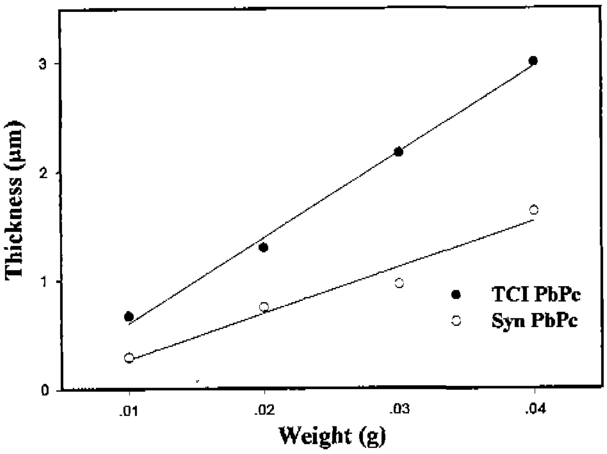

Fig. 5. Film thickness of TCI and Syn PbPc.

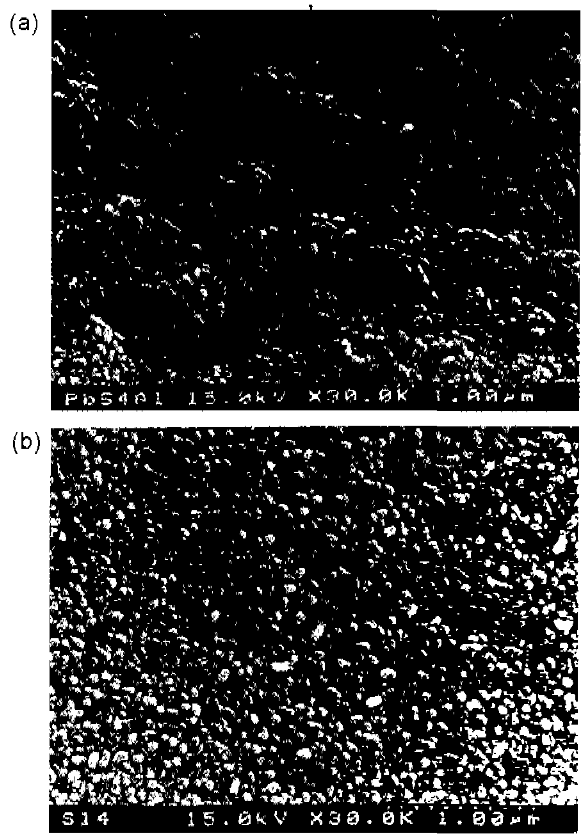

Fig. 6. Surface morphology of TCI and Syn PbPc. a) TCI PbPc and b)Syn PbPc.

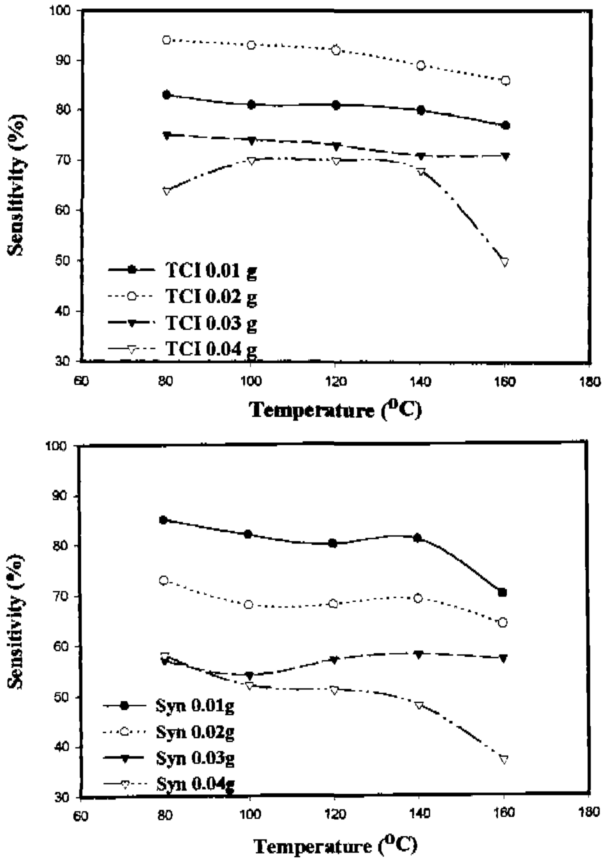

Fig. 7. The effects of film thickness on the sensitivity of PbPc. a) TCI PbPc and b) Syn PbPc.

3.3. The effects of film thickness on the sensitivities of TCI and Syn PbPc devices

Fig. 5 shows the dependency of film thickness of TCI and Syn PbPc on the loading. For all samples, film thickness increased linearly when the loading used increased. As shown in Fig. 6, a grouping particles were shown for TCI PbPc whereas the particles were homogeneous and dense for the Syn PbPc. As film thickness is increased, the resistance of PbPc is decreased. Even though the difference in film thickness and morphology between TCI PbPc(90% purity) and Syn PbPc(99% purity) could not be explained now, the sensitivity is thought to be inversely proportional to the film thickness as shown in Fig. 7. The maximum sensitivity of TCI PbPc was found in the sensor with 0.02 g of TCI PbPc, indicating that there is an optimal thickness.

3.4. Adsorption and desorption property

Fig. 8 and 9 show the time response curve of TCI PbPc at different temperature and the signal output after repeated adsorption and desorption of 5 ppm of NO_X gas. Because all the experiments were carried out in the flow reactor sys-

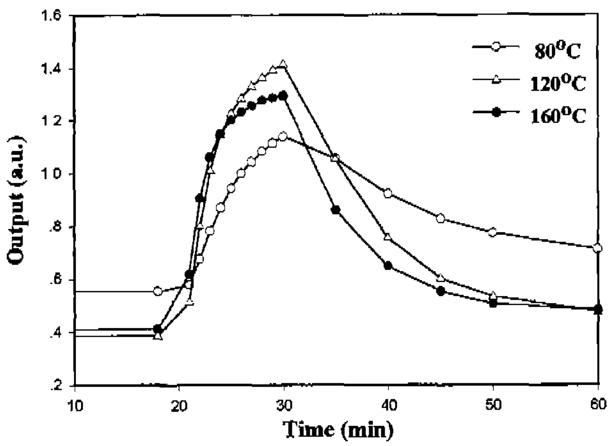

Fig. 8. Response curves at different operating temperatures.

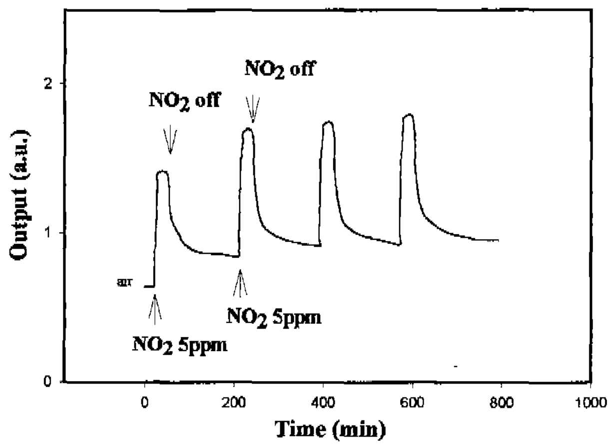

Fig. 9. Adsorption and desorption cycle.

tem , the delay of time was observed. But these results confirmed that the PbPc could be used for the rapid detection of NO_X gas.

4. Conclusions

Gas sensors using organic reagents were prepared to study their properties for NO_X gas. The results are summarized as follow.

1. PbPc sensor has higher sensitivity and lower resistance than ZnPc, FeNc, NiPc
2. Thin film deposited at 390°C shows mixed tri and monoclinic crystals
3. As film thickness is decreased, the sensitivity and the resistance of PbPc is increased
4. Optimal operating temperature of the sensor is 120°C and NO_X gas is reversibly adsorbed.

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