Abstract: (Keywords: Phthalocyanine, Vacuum deposition, Gas sensor, Sensing temperature)

Copper phthalocyanine and copper tera-tert-butyl phthalocyanine were vacuum deposited on to alumina substrate. The surface morphology and crystalline structure of the films prepared were studied first. The effects of gas sensing temperature, as well as the NO2 concentration, on the sensing properties were studied. The experimental results show that both CuPc and CuTTBPC films exhibit fine-grain morphology and low crystalline structure. Due to the tera-tert-butyl substitution on the periphery of phthalocyanine, CuTTBPC film has a larger lattice spacing which is responsible for its rougher morphology, higher film resistance, and a higher recovery ratio in the NO2 sensing experiments. On the contrary, the response rate and the sensitivity of CuPc film are superior to that of CuTTBPC film. It was also found that elevation of sensing temperature has advantage of improving the response speed, recovery ratio, and the gas sensitivity of the sensing films.

1. Introduction

Many of the application of Pc compounds are based on their properties in the form of thin films. Due to the thermal/chemical stability of Pc compounds and their rather solubility in organic solvent, especially for the compounds without peripheral substitution, vacuum deposition technique are widely used to fabricate the phthalocyanine thin films [1-3]. Previous studies have shown that the sensing properties of a Pc film are affected by the film characteristics such as crystal structure [4], film morphology, and postdeposition annealing [3,4]. In addition to the film characteristics, the sensing temperature is another important parameter that affects the gas sensing properties[5,6].

Systematic studies on the film characteristics of CuPc and its application for NO2 gas sensing have been carried out in our laboratory [7,8]. In the previous studies, the reversibility of CuPc film was poor on exposing to 100 ppm of NO2 at the sensing temperature of 150°C. In the present work, we study the effects of sensing temperature, as well as the effects of NO2 concentration, on the reversibility and other sensing properties of the sensing films. The different features between films of CuPc and a derivative with tetra-tert-butyl (ttb) peripheral substitution (CuTTBPC) are also compared in this work.

2. Experimental section

The CuPc (purity >90%) and CuTTBPC (purity >97%) were purchased, respectively, from Fluka Chemika and Aldrich Chem. Co. and used without further purification. These compounds were vacuum-deposited on alumina substrate fitted with screen-printed interdigital gold electrodes. The electrode, with a dimension of 7mm x 9mm, contains 5 finger pairs of electrodes of 200 μm interelectrode spacing. Before deposition, the substrates were cleaned ultrasonically in succession with detergent, pure water, acetone, pure water, and then dried in nitrogen to get rid off possible contamination, if any.

The deposition was proceeded in a small coater of model ULVAC VPC-260 made by Sinku-Kiko Co. The base pressure of the vacuum charmer was controlled at 3x10^-3 torr. The substrates were kept at room temperature (ca. 25°C), and the deposition rate was controlled at
0.3 nm/sec by a temperature-controlled evaporation boat. In this work, the film thickness was controlled at 200 nm for the experiments of surface characterization and the gas sensing.

For gas sensing experiments, NO2 gas was diluted with high purity N2 to control the concentrations of 10, 50, or 100 ppm. The sensing experiments, the temperature of the sensing device was controlled at various values, 125, 150, 175, 200, and 225 °C by a PID controller.

Before the sensing temperature is established, only N2 of 400 ml/min is fed through the detection chamber. When the detection temperature is approaching a stable state, NO2 gas is added by controlling a constant total gas flow rate. For each specimen, three experimental cycles were carried out in succession with various NO2 concentrations of 10, 50, and 100 ppm. For each cycle, the NO2 concentration is maintained for 30 min and followed by a 90 min of recovering procedure in N2 atmosphere before the starting of next cycle.

3. Results and discussion
3.1 Morphologies and structures of films

When CuPc or CuTTBPc film of 200 nm in thickness was deposited on the substrate, the morphologies on both regions of alumina and gold were found to be nearly identical. Figure 2 shows the results of the two compounds.

For film of CuPc shown in Figure 1(a), fine-grain crystalline is found on the surface. This morphology is similar to that grown on SiO2 [1], and on glass [7] although the morphologies of SiO2 and glass substrates are much smoother than that of alumina used here. Comparing with CuPc film, the surface of CuTTBPc film exhibits a much larger grain-size and rougher structure as shown in Figure 1(b). This result is contrary to that reported by Lee et al. [24] which showed that CuTTBPc film has a smoother morphology than that of CuPc on glass surface. The different results of CuTTBPc on the two surfaces can only attributed to the distinction between the morphologies of the two substrates.

The results of X-ray diffraction for the two films were list in Table 1. In general, both of the two films have low crystalline structure. For CuPc film, the characteristic diffraction peaks (D=3.33 Å and D=12.76 Å) are similar to those reported in the previous paper [6,8], which represent various orientations of the packing structures. On the alumina surface, the two peaks have similar intensity, that is, the orientation of the film structure is more random. This is also a consequence of the rough surface morphologies of alumina.

For CuTTBPc film, the lattice spacing is larger than that of CuPc film which should be attributed to the tetra-tert-butyl substitution on the periphery of phthalocyanine ring. The difference in the lattice spacing between the two compounds is taken as the responsibility for their various surface morphologies and various gas sensing properties that will be discussed below.

3.2 Gas sensing properties to NO2

The films of CuTTBPc have higher resistance than that of CuPc films. Due to the larger lattice spacing of CuTTBPc (16.71 and 3.62 Å), comparing with CuPc (12.76 and 3.33 Å), the CuTTBPc molecules are supposed to be packed more loosely in the film structure. Consequently, the film resistance will be higher since the distance for the charge transfer is larger.

When CuPc and CuTTBPc films were exposed to NO2, the variation of the film resistance with the sensing time for various sensing temperatures and NO2 concentrations are shown in Fig. 2 and Fig.3, respectively. In general, the film resistance is higher for a higher sensing temperature after doping with NO2. Obviously, this is caused from the less adsorption amount of NO2 at elevated temperature.

The film resistance decreases rapidly and greatly at the initial stage of NO2 doping, but the decreasing rate slows down at the later sensing stage. The response rates of the films vary with the sensing temperature and the concentration of NO2. To compare the response speed, the response time t80 is defined as the time it takes to reach 80% of the final resistance (the resistance after sensing 30 min). According to this definition, a small value of the response time represents a quick response of the film to the detection gas. The estimated values of t80 for various sensing temperature and NO2 concentration are shown in Fig. 4. In general, elevation of the sensing temperature leads to a small value of t80 for both CuPc and CuTTBPc films. At low temperature, CuPc film exhibits a fast response than that of CuTTBPc film. However, at high temperature, the response times for the two films become identical.

To compare the recovery characteristic, the recovery ratio, defined as the ratio of film resistance after recovery step to that before NO2 doping, was estimated and was shown in Fig. 5. It is found that the recovery ratio increases with increasing sensing temperature. That is, by elevation of the sensing temperature, the
recovery characteristic can be improved. For the two materials studied here, CuTTBPc exhibits a better recovery property than CuPc does.

**Reference**


**Table 1.** X-ray diffraction peaks of CuPc and CuTTBPc films of 200 nm in thickness prepared on alumina surface

<table>
<thead>
<tr>
<th>material</th>
<th>XRD peaks</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2θ (deg)</td>
<td>D (Å)</td>
</tr>
<tr>
<td>CuPc</td>
<td>6.93</td>
<td>12.76</td>
</tr>
<tr>
<td>CuTTBPc</td>
<td>26.76</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>5.29</td>
<td>16.71</td>
</tr>
<tr>
<td></td>
<td>24.60</td>
<td>3.62</td>
</tr>
</tbody>
</table>

**Fig. 1** Surface morphologies of CuPc (a) and CuTTBPc (b) thin films of 200nm in thickness.
Fig. 2 Variation of film resistance of CuPc films with sensing time. The NO$_2$ concentrations for the sequentially sensing cycles are 10, 50, and 100 ppm, respectively.

Fig. 4 The effect of sensing temperature on the response time $t_{so}$ for various NO$_2$ concentrations.

Fig. 3 Variation of film resistance of CuTTBPe films with sensing time. The NO$_2$ concentrations for the sequentially sensing cycles are 10, 50, and 100 ppm, respectively.

Fig. 5 The recovery ratio of film resistance after 90 min of recovery time as a function of sensing temperature. The NO$_2$ concentration is 10 ppm.