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NO_2 sensing characteristics of copper phthalocyanine films: Effects of low temperature annealing and doping time

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Abstract

Low temperature annealing was performed on CuPc films to evaluate the possible structure transformation of the sensing films during the gas sensing period. The effects of heat annealing, as well as the doping time of NO_2, on the sensing characteristics of CuPc films were investigated. The result shows that the structure transformation cannot be avoided even at a temperature as low as 100 °C. The structure transformation causes a decrease in film resistance and sensitivity to NO_2, but an increase in response rate. After the NO_2 doping period, the CuPc films cannot recover completely to the original resistance before doping due to the possible structure transformation and the deep diffusion of NO_2 into the bulk crystal. The incomplete recovery problem of CuPc films can be solved by using responsivity instead of film resistance. The doping curves for the succeeding sensing cycles are nearly coincident, indicating that the change in film characteristics, resulted from the irreversible doping or structure transformation, can be eliminated by the present treatment. The experiments on the NO_2 doping time show that a longer doing period causes a higher responsivity but a slower recovery rate.

Keywords: Phthalocyanine; Gas sensor; Heat annealing; Sensitivity

1. Introduction

Metal phthalocyanine (MPc) and their derivatives are semiconductive organic materials that has been used in various applications including chemical sensor, photo-conductive agents, non-linear optics, electrocatalysis and other photoelectronic devices [1,2]. The conductivity of MPc are known to be sensitive to the presence of oxidizing or reducing gases, being caused by the change in the charge-carrier concentration due to the donor–acceptor state arising from the adsorption of gases. Such property has led to a considerable interest in their use as gas sensors [3–5].

The MPc materials are always prepared in thin film form to increase the surface area to be used as gas sensors [6–11]. Among the various techniques employed to prepare MPc films, vacuum deposition is the most common method adopted in the literature [12–18]. The application of thermal deposition is based on the thermal/chemical stability of MPc materials and their rather small solubility in organic solvents, especially for the compounds without peripheral substitution. Previous studies showed that the sensing properties of MPc films were affected by the film structure and film morphology determined by the film preparing procedure. In addition, the sensing temperature [19–23], film thickness [23–25] and post-deposition annealing [18,26,27] are also important parameters that affect the gas sensing properties.

PbPc and CuPc are the most interesting MPc materials studied in the literature. PbPc has been reported to be superior to other MPc materials in terms of sensitivity, recovery, reproducibility and response rate in the detection of oxidization gases [12,13,21,24,26]. However, by considering the selectivity, it is impossible to use only one material in a gas sensor and thus, other MPc materials have also been studied in the literature [14–17,25]. Systemic studies on the film characteristics of CuPc and the related NO_2 sensing properties have been performed in our laboratory [22,23,27–29]. The reversibility of a CuPc film was found to be poor, especially when the sensing was operated at low temperature. The poor reversibility can be improved by elevating the sensing temperature [22] or by decreasing the film thickness [23]. How-

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ever, heat annealing occurs during the high-temperature sensing stage, which leads to a structure reorganization or phase transformation [27]. As a result, the stability and reproducibility of the sensing film decreases due to the change in film characteristics. We have also found that satisfactory reversibility can be obtained at a moderate sensing temperature (100 °C) by decreasing the film thickness (to ca. 100 nm) and shorting the doping time (3 min) [23]. However, under the consideration of long-term utilization of a sensor, it is required to study the annealing effect and stability of the CuPc films at moderate temperatures.

Low temperature annealing was performed on CuPc films to evaluate the structure transformation during the sensing period. We will demonstrate here that the structure transformation cannot be avoided at a temperature as low as 100 °C but the incomplete recovery of film resistance can be overcome by using responsivity instead of film resistance.

2. Experimental

CuPc was purchased from Fluka Chemika (purity >90%) and used as received. Glass plates fitted with interdigital gold electrodes were used as electrode for gas sensing. The electrode, with a dimension of 39 mm × 12 mm, contained 10 finger pairs of electrodes of 500 μm interelectrode spacing. Such gold electrode was prepared by vacuum deposition of Ti (10 nm) and Au (110 nm) in succession on pre-treated glass plates. The finger-pairs electrode was patterned directly during the deposition by using of a stainless mask positioned in front of the substrate. The titanium layer used here acted as an intermediate layer to enhance the adhesion of gold to the glass surface.

The deposition was carried out under a base pressure of 3×10^{-5} Torr in a small coater made by Sinku-Kiko Co. (model ULVAC VPC-260). The substrate temperature and the deposition rate were controlled at 100 °C and 0.3 nm/s, respectively. The deposition rate and the film thickness were monitored by the frequency shifts of a quartz oscillator. In this work, the film thickness was controlled at 100 nm for the experiments of surface characterization and gas sensing. The as-deposited films were also heat-treated at 100 °C for various time (4 and 6 h) to evaluate the heat annealing effect during the sensing period.

Crystalline structure of the film was determined by X-ray diffraction with Cu Kα monochromatic radiation and the surface morphology was observed by scanning electron microscopy.

For gas sensing experiments, NO_2 gas was diluted with high purity N_2 to control a concentration of 25 ppm. The total gas flow rate was controlled at 400 ml/min by a mass flow controller. To measure the film resistance (R_s), a multimeter made by Yokagawa Co. (Yokagawa 7552) was used directly to record the variation of resistance during the sensing period. For each specimen, three sensing cycles of various doping time (5, 10 and 30 min) were performed. Following each doping period, the film was recovered in nitrogen to approach a steady film resistance before initiation of the succeeding doping process. The gas sensing was operated at 100 °C.

3. Results and discussion

3.1. Morphology and structures of films

The surface morphology of 100 nm CuPc film prepared at 100 °C is shown in Fig. 1(A). Fine-grain crystallites are found on the CuPc film surface, which resembles the results reported

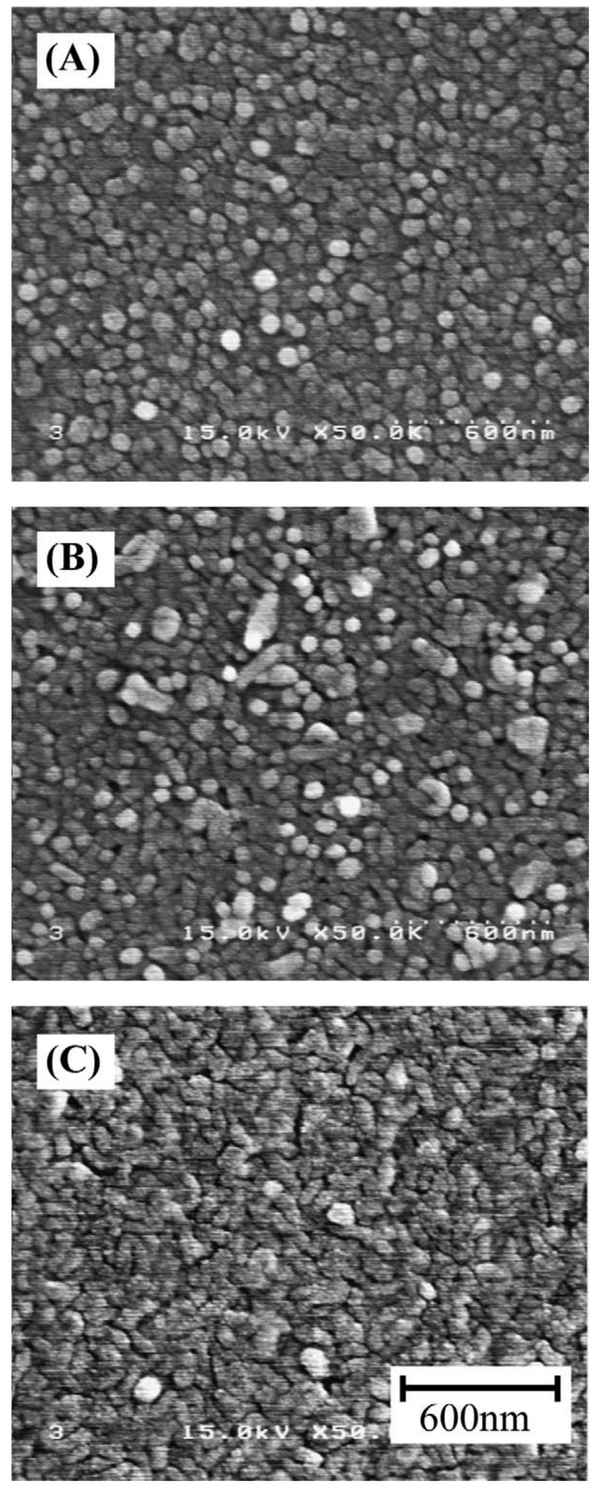

Fig. 1. Surface morphology of 100 nm CuPc films as-deposited (A) and after annealing at 100 °C for 4 h (B) and 6 h (C).